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Carbon, nitrogen, and phosphorus in headwater streams of boreal catchments:

Long term data analysis, consequences of anthropogenic management and ways to mitigate disturbances

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Carbon, nitrogen, and phosphorus in headwater streams of boreal catchments: long term data analysis, consequences of anthropogenic management and ways to mitigate disturbances.

Abstract

The relative supply of carbon (C), nitrogen (N), and phosphorus (P) to freshwater ecosystems is of fundamental importance to aquatic productivity, nutrient cycling, and food web dynamics, which can ultimately influence ecosystem services, recreational values and the provision of drinking water. Using over ten years of water quality data and field experiments, this thesis focuses in understanding the simultaneous supply of C, N and P from boreal catchments to freshwater ecosystems, how this natural supply is disrupted by forest management activities and evaluating a way to mitigate disturbances. Our findings show that catchment characteristics directly influenced the opposing mobilization response of inorganic N and P and organic C and N to increases in flow. Conversely, regardless of catchment characteristics, we found a widespread decline for inorganic P and N in streams over time, co-occurring with an increase in DOC concentration and revealing changes in the ratio of energy to nutrient supply. Alongside, catchments with forest operations, specifically clear cut, showed an increase in the exports of organic C and N and inorganic N and P, yet if followed by ditch cleaning, organic and inorganic nutrient concentration decreased. Finally, we found that the disturbance in C and N concentration could be mitigated using a biochar filter, if the nutrient concentration is high enough. Given the critical interplay between the supply of resources from catchments and their demand in aquatic ecosystems, understanding the spatial-temporal variability of C, N, and P concentrations and their ratios is key to predicting how northern rivers and downstream lakes may respond to ongoing and future environmental changes.

Keywords: carbon, nitrogen, phosphorus, boreal catchments, water quality.

Kol, kväve och fosfor i rinnande vatten: förändring över tid, konsekvenser av skogsskötsel och möjliga sätt att mildra påverkan.

Sammanfattning

Kol (C), kväve (N) och fosfor (P) i rinnande vatten har grundläggande betydelse för produktivitet och födovävsdynamik, vilket i slutändan kan påverka en mängd rad olika ekosystemtjänster, rekreationsvärden och vattenkvalité. Med hjälp av över tio års vattenkemiskdata och fältexperiment fokuserar denna avhandling på att förstå tillförseln av C, N och P från avrinningsområden till rinnande vatten, hur den naturliga dynamiken påverkas av olika skogsskötselåtgärder samt utvärdera sätt att mildra påverkan. Mina resultat visar att avrinningsegenskaper och flödesförändringar direkt påverkade dynamiken av oorganiskt N och P och organiskt C och N i vattendrag. Omvänt, oavsett avrinningsegenskaper, fann vi en utbredd minskning av oorganiskt P och N i vattendrag över tid, vilket inträffade samtidigt med en ökning av DOC-koncentrationen och avslöjade viktiga förändringar i förhållandet mellan energi och näringstillförsel. Utöver detta visade mitt arbete att avrinningsområden med olika skogsskötselmetoder, speciellt kalhyggesbruk, en markant ökning av exporten av organiskt C och N samt oorganiskt N och P, men också att om de åtföljdes av dikesrensning så kan koncentrationen av organiska och oorganiska näringsämnen minska. Slutligen fann vi att påverkan på C- och N-koncentrationen kunde mildras med ett biokolfilter, om koncentrationerna från början var tillräckligt höga. Med tanke på det kritiska samspelet mellan tillgången på resurser från avrinningsområden och deras efterfrågan i akvatiska ekosystem, är förståelsen av den rumsliga-temporala variationen av C-, N- och P-koncentrationer och deras förhållanden en nyckel till att bättre kunna förutsäga hur nordliga vattendrag och nedströms sjöar kan reagera på pågående och framtida miljöförändringar.

Keywords: kol, kväve, fosfor, boreala avrinningsområden, vattenkvalitet.

Photo: Alejandro Gándara

Photo: Virginia Mosquera

Dedication

To Nicolás, who taught me that everything is possible.

> “Science is mind applied to nature.”
> –Alexander Von Humboldt

Photo: Alejandro Gándara

Contents

List of publications

This thesis is based on the work contained in the following papers, referred to in the text with the respective Roman numeral:

I. **Mosquera, V*.** Laudon, H., Blackburn, M., Hasselquist & E. Sponseller. (2023) Concentration-Discharge Patterns Reveal Catchment Controls Over the Stoichiometry of Carbon and Nutrient Supply to Boreal Streams. Journal of Geophysical Research: Biogeosciences 128 (1-18). https://agupubs.onlinelibrary.wiley.com/doi/10.1029/2022JG007179

II. **Mosquera, V*.** Hasselquist, E.M., Sponseller, R.A. and Laudon, H. (2022), Co-occurrence of browning and oligotrophication in a boreal stream network. Limnology Oceanography, 67: 2325-2339. https://aslopubs.onlinelibrary.wiley.com/doi/10.1002/lno.12205

III. **Mosquera, V*.** Laudon, H., Karimi, S., Sponseller, R. & Hasselquist, E. (2024). Cumulative and discrete effects of forest harvest and drainage on the hydrological regime and nutrient dynamics in boreal catchments. (submitted)

IV. **Mosquera, V*.** Gundale, M. J., Palviainen, M., Laurén, A., Laudon, H., & Hasselquist, E. M. (2024). Biochar as a potential tool to mitigate nutrient exports from managed boreal forest: A laboratory and field experiment. GCB Bioenergy, 16, e13131. https://onlinelibrary.wiley.com/doi/10.1111/gcbb.13131

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1. Introduction

The world´s freshwater resources are currently threatened by increasing surface and groundwater pollution, global climatic changes, and the destruction and degradation of aquatic ecosystems with direct repercussions on societal well-being, economic stability, and ecosystem health (Gleick, Singh, & Shi, 2001). Even in sparsely populated regions at high latitudes, freshwater ecosystems are being affected by long-range transport and deposition of pollutants, climate change, and land use change, such as forest management (Laudon et al., 2011; Teutschbein et al., 2017). Addressing these challenges, however, requires improved understanding of how, when, and where changes in water quantity and quality occur within river networks. To reach these goals, we need to recognize how different catchment features are organized to regulate surface chemistry at multiple scales and under different hydrological conditions (Laudon & Sponseller, 2018). However, while understanding hydrological functioning is critical, this must be combined with efforts that explicitly address how anthropogenic activities directly impact water resources for human consumption, as well as the transport of nutrients and contaminants to downstream receiving water bodies. Overall, despite significant progress in recent decades, substantial knowledge gaps still exist that need to be address to enhance our ability to predict and protect water quality.

1.1 Boreal landscapes

The boreal biome makes up only 8% of the global land area, but constitutes one third of the world’s forests and contains an estimated of one third of the terrestrial carbon pool (Bradshaw & Warkentin, 2015). The boreal landscape comprises a mosaic of terrestrial and aquatic patches, including forests, lakes and mires, all drained by a network of streams and rivers. The drainage area, often called catchment, commonly contains a mixture of soil types, vegetation, geology, topography and consequently hydrological regimes. Topography influences the persistence of these three features, as mires form in areas where water flow accumulates and saturates the soil surface, whereas drier upland areas are predominantly covered by forests, and water-filled basins are occupied by lakes (Ivanov, 1981). Generally speaking, such features have different hydrological and biogeochemical characteristics, for instance, the boreal forest soils consist of a thin layer of organic soils overlaying mineral soils with a terrestrial-aquatic interface dominated by organic matter rich riparian zones (Ledesma et al., 2018), whereas mires are dominated by a deep waterlogged peat layer (Mulqueen, 1986). The organization of these landscape units gives rise to a complex and dynamic hydrology that can vary depending on stream size and season (Troch et al., 2009). In northern latitudes, annual hydrological regimes are dominated by long winters, intermittent soil frost, and large snow melt events during spring and early summers, often making up to 40-60% of the total annual water yield (Laudon, Hasselquist, et al., 2021). Here, input as snowmelt or rainfall can become runoff as overland flow during spring or percolate into soils where it is partitioned into shallow or deep groundwater flow paths, making it seasonally available to plants or runoff to streams. In the soil matrix, water interacts with organic and minerogenic materials while moving through flow paths influencing the subsurface water chemistry depending on the residence time and vertical storage of solutes in the subsurface (Bishop, Seibert, Köhler, & Laudon, 2004). Consequently, the distinct chemical signature downstream of each catchment conveys the products of terrestrial productivity, mineral weathering, hydrologic flow paths and atmospheric deposition. As such, these integrated catchment features exert first-order controls over stream water quality, influencing the magnitude and timing of different element fluxes (Laudon & Sponseller, 2018).

In this thesis, I focused on carbon (C), nitrogen (N) and phosphorus (P) dissolved in water, as they are the major elements that compose all organisms and are essential for growth and reproduction both in terrestrial and aquatic ecosystems. Particularly, boreal catchments are characterized by high amounts of organic carbon available for transport to water bodies (Kritzberg et al., 2020), N-poor boreal soils with strong N retention and therefore N limitation (Högberg, Näsholm, Franklin, & Högberg, 2017) and P that weakly adsorbs to peat and therefore is easily transferred to the receiving water by runoff (Rodgers et al., 2010). The dissolved organic carbon (DOC) flux to headwater streams is largely determined by the quantity and quality of soil organic matter (SOM) in peatlands (I. F. Creed, Beall, Clair, Dillon, & Hesslein, 2008) and organic-rich riparian forest soils (Ledesma, Futter, Laudon, Evans, & Köhler, 2016), while N fluxes are highly variable due to a multitude of abiotic and biotic processes influencing N storage, transformations, and transport; these are nevertheless influenced by forest type, hydrogeology and topography (I. F. Creed & Beall, 2009). For example, headwater mires constitute an important source of reactive N to receiving streams, by vertically separating N supply from biotic demand (Sponseller, Blackburn, Nilsson, & Laudon, 2018). Finally, similar to other landscapes, P loading from catchments to streams, is controlled by chemical characteristics of soil and presence of P-adsorption elements such as Al, Fe, Ca and Mg (Hartikainen, 1979).

1.2 Water quality in boreal landscapes

The quality of stream water reflects the interaction between hydrological and biogeochemical characteristics of the distinct landscapes. As such, stream water quality is comprised of a multitude of dissolved and suspended materials, all of which varies, sometimes independently, depending on the landscape types and seasonal timing (A. M. Ågren et al., 2014). Among these exported elements, dissolved C, N and P are mobilized from catchment soils and exported to streams, downstream lakes and eventually the sea. In freshwater ecosystems, the concentration and stoichiometry of naturally occurring C, N and P in water can regulate productivity, nutrient cycling, secondary production, aquatic community composition, and food web dynamics. (Eimers, Watmough, Paterson, Dillon, & Yao, 2009; J. J. Elser et al., 2000). Specifically, DOC plays an important role in the biogeochemistry and ecology of surface waters (Schelker, Eklöf, Bishop, & Laudon, 2012). DOC exerts control over acid-base chemistry (Buffam, Laudon, Temnerud, Mörth, & Bishop, 2007), affects the transport of organic pollutants (De Paolis & Kukkonen, 1997), and influences metal export in streams and rivers (Bishop et al., 2020). Similarly, N and P are the most important limiting nutrients in both terrestrial and aquatic environments, and in freshwater ecosystems the concentration of these elements are regarded as the most important determinant of aquatic productivity (i.e., growth and abundance of aquatic organisms) and water quality (Schindler, 1974). Specifically, the supply of inorganic N and P can directly and indirectly limit the metabolic activity of heterotrophic microorganisms, increase primary producer biomass and consequently influence aquatic food webs.

Changes in supply of DOC, N and P from catchments to freshwater ecosystems thus have important ecological consequences (Cloern, 2001; Irena F. Creed et al., 2018), which can ultimately influence ecosystem services such as fish biomass production and other recreational values (Smith & Schindler, 2009; van Dorst et al., 2019), but also the provision of drinking water (Lavonen, Gonsior, Tranvik, Schmitt-Kopplin, & Köhler, 2013; Smith, Joye, & Howarth, 2006). For example, increases in DOC concentration and water color plays an important role in the so-called “brownification” of water bodies, while the enrichment of N and P, beyond the natural capacity of receiving water bodies, leads to eutrophication of lakes and streams. Some of the largest and most dramatic “brownification” trends have been recorded in boreal regions (De Wit et al., 2021), which is likely due to the high amounts of organic carbon available for transport to water bodies (de Wit, Austnes, Hylen, & Dalsgaard, 2015). Likewise, receiving water bodies in northern regions, such as the Baltic sea, have been classified as affected by eutrophication due to nutrient inputs from human activity (Andersen et al., 2017). However, in some northern streams, ‘oligotrophication’ trends, or decreasing concentration of N and P dissolved in stream and lake water, has also been reported (Huser, Futter, Wang, & Fölster, 2018; Lucas et al., 2016).

In northern boreal landscapes, there is increasing evidence that catchment exports of C, N and P to lakes and streams are changing in response to multiple environmental drivers (De Wit et al., 2020; Deininger, Kaste, Frigstad, & Austnes, 2020; Fork, Sponseller, & Laudon, 2020). For example, DOC concentrations in surface waters have increased throughout northern Europe and North America, as a result of recovery from acid deposition (Clark et al., 2010; Chris D. Evans et al., 2012; Monteith et al., 2007), but also from changes in climate and land use (De Wit et al., 2016; Kritzberg et al., 2020). At the same time, inorganic N and P appear to be declining, reflecting a reduction in atmospheric deposition, tightening of biogeochemical cycles on land in response to climate warming and elevated CO_2 (Lucas et al., 2016; Mason et al., 2022), as well as emergent geochemical sinks (Huser & Rydin, 2005). Moreover, most of the expected changes in the concentration and balance of C, N and P will co-occur with biogeochemical changes driven directly by land use changes, including forest management. Here, different forest operations have been shown to impact DOC, N and P exports to surface water (Shah et al., 2022) due to the highly mechanized and intensive operations followed during the forestry rotation (Kuglerová et al., 2021). In this regard, the combined effects of these changes in surface water chemistry have the potential to alter energy and nutrient supply to aquatic ecosystems (Stetler, Knoll, Driscoll, & Rose, 2021) with important ecological and chemical consequences in streams and lakes (e.g. the Baltic Sea) as well as impacts on drinking water (M. Bieroza, Baker, & Bridgeman, 2009; Conley et al., 2009) and agricultural water supplies (Gleick et al., 2001). Therefore, understanding the controls over C, N, and P exports in the face of multiple direct and indirect drivers is central to predicting the water-quality consequences of changing environmental conditions, including increases in anthropogenic nutrient loading (e.g., Wachholz et al., 2023), various land management activities (Shousha, Maranger, & Lapierre, 2021), and ongoing climate change (e.g., Teutschbein et al., 2017).

1.3 Management of boreal catchments

Forestry is the dominant land-use in many forested regions of the world and constitutes an important economic base for numerous regions and countries (Birdsey & Pan, 2015). For example, in boreal regions, specifically in Sweden and Finland, more than 50% of the land area is covered by forests, and over 70% of their forested area is classified as productive forest land that experiences some forestry operations (Kuglerová et al., 2021). Due to the recent efforts to shift to a more bio-based economy, global forest biomass demand is increasing and in boreal regions a significant proportion of this increasing demand is met by the biomass harvest from the peatlands historically drained for forestry (Nieminen, Piirainen, et al., 2018). The drainage of peatlands, started after extensive forest logging in the early mid-1800s where most of low productive peatlands in the boreal regions were drained to enhance forest production (Norstedt, Hasselquist, & Laudon, 2021) even though prior to the 1900´s peatlands constituted an important resource for farmers. Just in Fennoscandia, about 15 million ha of peatlands and wet mineral soils, of which nearly 60% is located within the Baltic Sea basin, were drained in the last century to increase forest production (Paavilainen & Päivänen, 2013; Sikström, Jansson, & Pettersson, 2020), resulting in a total of approximately 1 million km of a century old artificial drainage channels (Laudon et al., 2022). Today, boreal forests are subject to a range of management interventions in a relatively long rotation cycle (i.e., 60-100 years) with highly mechanized and intensive operations. In Sweden, the typical forest management rotation cycle includes a series of operations including mechanized site preparation by disk trenching or mounding before planting conifer seedlings (Esseen, Ehnström, Ericson, & Sjöberg, 1997), pre-commercial and commercial thinning, harvest by clear cutting of the even-aged, single-story stand, and finally ditch maintenance by clearing the old ditches (a process called ditch cleaning) that have lost their drainage capacity because of sediment infilling and establishment of vegetation (Nieminen, Piirainen, et al., 2018).

Water draining managed forests is generally classified as of high quality (Kauffman and Belden, 2010), with forests having a positive effect on water quality (Duffy et al., 2020), mainly as a result of low runoff volumes and low sediment yield due to the protective function of forests as nutrient sinks rather than source due to nutrient uptake by fast growing trees (Koivusalo et al., 2006). However forests subject to different management operations have the potential to impact catchment hydrological processes and impair water quality (Shah et al., 2022). In boreal catchments, forest management interventions have been found to increase loads and the concentration of C, N and P in runoff water, becoming one of the main concerns connected to the impact on water quality and freshwater ecosystem health (Shah et al., 2022). Specifically, harvest by clear cutting, has been shown to increase DOC, N and P exports to surface water for several years (Kaila et al., 2014; Schelker et al., 2012, 2016) and ditch cleaning may account for over 60-70% of the total sediment and nutrient loads from forests, resulting in long-term increased levels of DOC (Asmala, Carstensen, & Raike, 2019; Kuglerová et al., 2021). The magnitude and duration of such changes in nutrient loads during and after forest management interventions is dependent on several factors, including catchment topography, soil properties, hydrology, harvest intensity, and climate, among others (Kreutzweiser, Hazlett, & Gunn, 2008). In a boreal context, such extensive and intensive forest management operations could have large ecological consequences for both terrestrial and aquatic ecosystems, despite the small magnitude and limited duration compared with other land uses such as agriculture or urban landscapes (Deval et al., 2021; Loehle et al., 2014). Furthermore, several studies reveal that the response in water quality and quantity to different forest management operations could be connected and have potentially cumulative effects, including short and long-term effects on hydrological processes (Koivusalo et al., 2008) and on the storage, availability and export of nutrients and other pollutants (Kļaviņa et al., 2021). It is therefore imperative to further improve our understanding of the nutrient load dynamics occurring individually in each forest management operation as well as the cumulative effect of the forestry rotation. Similarly, understanding the relationships among forest management, ongoing environmental change, and ecosystem functioning is critical to managing boreal forests in ways that promote sustainability and protects surface water resources.

1.4 Ways to mitigate the effect of forestry on water quality

Leaching of C, N and P from catchments with forest management in drained peatlands imposes a threat to quality of surface waters in boreal landscapes (Nieminen, Ahti, Nousiainen, Joensuu, & Vuollekoski, 2005). Developing and implementing management strategies, with concrete water protection methods is recognized as a major challenge in maintaining the sustainability of forest management in boreal landscapes (Laudon et al., 2011). Nevertheless, a large variety of different potential mitigation measures have been used or proposed to mitigate nutrient export load to boreal watercourses. Currently, efforts focus on tree retention strategies such as implementing forested riparian buffers or operation-free zones adjacent to small streams, with the most common approach being thin fixed width, conifer-dominated buffers (Kuglerová, Muotka, Chellaiah, Jyväsjärvi, & Richardson, 2024; Richardson, Naiman, & Bisson, 2012). However, these thin buffers do not always provide the protection or the desired subsidies, in terms of leaf litter quality, needed to maintain water quality and robust aquatic communities (Hasselquist et al., 2021). Kritzberg et al. (2020) similarly proposes altering vegetation type in highly hydrological connected areas by managing spruce trees via thinning and actively planting broadleaf tree species. Other conventional methods to mitigate nutrient export are sedimentation ponds, which typically maintain a permanent pool of water to improve water quality by settling of settleable or suspended solids and sediment-bound pollutants. The sedimentation ponds have been shown to decrease dissolved nutrient export loads but are rather ineffective outside the growing season (Väänänen et al., 2008). On the other hand, many scientist are proposing a change in silviculture practices, changing from clear cut harvesting to continuous-cover forestry and therefore improving water quality, biodiversity and carbon sequestration (Laudon & Hasselquist, 2023). Yet, the development of management plans through continuous cover forestry requires a holistic ecosystem approach within a broader landscape perspective (Laudon et al., 2011).

At present, this wide range of technologies and methods for safeguarding water resources are either expensive, require large areas, or are inefficient in reducing dissolved nutrients export loads, especially outside the growing season (Hynninen, Sarkkola, Laurén, Koivusalo, & Nieminen, 2011; Liljaniemi et al., 2003). Consequently, new scalable tools are needed to counteract the negative effects of forest management on water quality. Biochar has been proposed as a promising solution to reduce nutrient exports with adsorption- based purification of runoff water (Saarela, Kakaei Lafdani, Laurén, Pumpanen, & Palviainen, 2020). Biochar is a carbon- rich product made from any type of organic material (feedstock) by pyrolysis where the organic matter is heated at 300–800°C under low oxygen concentrations (Lehmann & Joseph, 2012). Biochar has been shown to be an effective nutrient adsorbent (Laird, Fleming, Wang, Horton, & Karlen, 2010) due to its porous structure, large specific surface area, and high cation and anion exchange capacity (Ahmad et al., 2014; Gwenzi, Chaukura, Noubactep, & Mukome, 2017). Furthermore, it is also well established that the application of biochar to soils can promote soil fertility, which ultimately may enhance plant growth (Barrow, 2012; Jeffery et al., 2011). Hence, suggesting a potential circular system where nutrients successfully captured by biochar could then be applied back to forests, adding to the soil carbon stocks, and serving as a source of nutrition to trees that enhances growth (Palviainen et al., 2020). However few studies have addressed the use of biochar in water protection in peatland forests (Kakaei Lafdani et al., 2021; Kakaei Lafdani, Saarela, Laurén, Pumpanen, & Palviainen, 2020; Saarela et al., 2020), and to our knowledge, there are no studies that have tested the biochar adsorption capacity in on- site field conditions. Therefore, in order to upscale this technology it is important to understand the effectiveness and limitations of this method in a field context.

Photo: Virginia Mosquera

2. Knowledge gap and research objectives

Long-term and seasonal variation in the supply and stoichiometry of C, N and P can influence a wide range of ecological and biogeochemical processes in streams, rivers, and lakes (Sardans, Rivas-Ubach, & Peñuelas, 2012). While the supply of DOC to boreal streams have been widely studied, for example, establishing that during high flows DOC is exported (Bishop et al., 2004; Fork, Sponseller, et al., 2020) or that DOC concentrations have increased in many high latitude streams (Evans, Monteith, & Cooper, 2005), the simultaneous response to high flows or the long-term trends for N and P and therefore the appearing ratios among these resources, are not well documented. Furthermore, while the large scale anthropogenic drivers, such as climate change and recovery from acidification are suspected to be the major contributing forces on the DOC trends (De Wit et al., 2016; Lawrence & Roy, 2021), it is still not certain how these drivers can affect N and P. Likewise, the effect of local scale anthropogenic drivers, such as forest management, simultaneously on C, N and P has not been studied in detail. The overall aim of this thesis is to understand the natural and anthropogenic-driven change in the supply of C, N and P to freshwater ecosystems from catchments with different characteristics and anthropogenic intervention in a boreal landscape. This thesis is based on four studies and the objective of each study was to:

I. Understand the variability and controls over C, N, and P exports from diverse catchments in a boreal landscape using concentration-discharge (c-Q) relationships. The specific objectives were to study (i) how the dynamics of C, N, and P supply to a boreal stream network are regulated by hydrology, (ii) how catchment characteristics influence this supply, and (iii) how c-Q and ratio-discharge (ratio-Q) relationships vary at seasonal, annual, and decadal time scales (Paper I).

II. Determine how C, N, and P concentration in surface waters of a boreal stream network has changed over the last decade in catchments with different characteristics. The specific objectives were to evaluate (i) trends of inorganic N and P, (ii) seasons when the directional change in nutrient chemistry is particularly strong or weak, (iii) how the different catchment characteristics influenced these trends, and (iv) influence in the stoichiometric balance of dissolved resources (Paper II).

III. Examine the discrete and cumulative effect of two forest management operations on total export loads of C, N and P to water bodies in a boreal landscape. The specific objectives were to assess (i) the change in nutrient concentration in outflow water after each individual forest operation, and (ii) the additive or reversible effects on nutrient concentration and exports of both the forest operations together.

IV. Investigate the water purification capacity of biochar filters to alleviate the impact of forest management operations on C, N and P in streams. The specific objectives was to (i) test for different initial nutrient concentrations exported from different forest management operations.

3. Methods

3.1 Study sites

Papers I and II were based on the Krycklan Catchment Study (KCS), a northern boreal catchment composed of different sub catchments with variable land-cover properties, but with limited anthropogenic activities. Papers III and IV were carried out in the Trollberget Experimental Area (TEA), a managed boreal forest catchment located less than 1 km from the KCS. In paper III, the forested KCS sub catchments (i.e., C1 and C2) were used as controls to evaluate the effect of clear cutting and ditch cleaning on carbon and nutrient exports to surface waters in the TEA.

3.1.1 The Krycklan Catchment Study (Paper I-IV)

The Krycklan Catchment Study (KCS) is a long-term research and monitoring watershed located in the boreal zone of northern Sweden (64° 14′ N, 19° 46′ E) approximately 60 km from the Baltic Sea coast. The 68-km^2 catchment is composed of 14 intensively monitored sub catchments ranging over three orders of magnitude in size, from 12 to over 1900 ha (Figure 1). Like other boreal regions, the KCS consists of a mosaic of land covers; dominated by forests with 87% of the total area while mires occupy 9% and lakes 1% of the catchment area (Laudon et al., 2013). Forests are dominated by Scots Pine (*Pinus sylvestris*; 63% cover) found mostly on the dry uplands, Norway Spruce (*Picea abies*; 26%) in wetter low-lying areas, and deciduous trees (~10%), primarily birch (*Betula* spp.) with an understory of ericaceous shrubs, mostly bilberry (*Vaccinium myrtillus*) and lingonberry (*Vaccinium vitis-idaea*) on moss-mats dominated by *Hylocomium splendens* and *Pleurozium schreberi*. When divided by sub catchments, the KCS presents a land cover gradient ranging from 100% forest cover (i.e., C2) to up to 44% of open peatlands, with two monitoring stations located in outlets of a *Sphagnum*-dominated mire (acid, oligotrophic, and minerogenic mire; C4), and a small humic lake (C5). This landscape is underlain by quaternary deposits dominated by till (51%) that vary in thickness from a few centimeters to tens of meters, and sorted sediments (30%) (Laudon et al., 2013).

The climate is typical of the northern boreal zone, characterized as a cold temperate humid type with short and cool summers followed by long dark winters. The 30-year mean annual air temperature (1986– 2015) is 2.1°C with the highest mean monthly temperature occurring in July and the lowest in January (+14.6 and -8.6°C, respectively; Kozii et al., 2020). The area is affected by general warming as mean annual temperature has increased by 2.5°C in the last 40 years, most rapidly during late autumn and winter months (Laudon, Hasselquist, et al., 2021). The average snow cover is 167 d yr^{-1}, typically from late October to early May, but has been declining at a rate of ~0.5 d yr^{-1} (Laudon & Löfvenius, 2016). Total annual precipitation averages around 614 mm yr^{-1} of which approximately 35–50% falls as snow and 311 mm becomes runoff (Laudon et al., 2013). The hydrologic regime is characterized by high flow during the spring snowmelt (April–May), which accounts for 40–60% of the annual discharge. In addition, hydrologic inputs to KSC streams are dominated by shallow groundwater flow paths (Bishop et al., 2004), although this can vary across the channel network. More specifically, in smaller sub catchments, lateral subsurface flow paths contribute ~80% of stream baseflow due to a compact layer of basal till with substantially lower hydraulic conductivity (Jutebring Sterte, Lidman, Lindborg, Sjöberg, & Laudon, 2021). By comparison, for sub catchments larger than 10 km^2 (i.e., C15 and the KCS outlet C16), deeper groundwater sources can contribute 70%–80% of surface water during baseflow periods (Peralta-Tapia et al., 2015).

Approximately 25% of the KCS has been protected for research since 1922, whereas the ownership of the remaining area is divided among private individuals and forest companies (Laudon, Hasselquist, et al., 2021). Historically, prior to the early 1900's, up to 22% of the original peatland area in the KCS was used for hay harvest on mire meadows whereas only 3% were drained for more modern agriculture. Afterwards, beginning around 1900, mires were drained to enhance forest wood production and as a consequence about 40% of the original peatland area is currently forested (Norstedt et al., 2021). Consequently, within the KCS, there are approximately 162 km of forest ditches (E. M. Hasselquist, Mancheva, Eckerberg, & Laudon, 2020) and approximately 180 km of natural, permanent streams (A. Ågren, Lidberg, & Ring, 2015).

3.1.2 The Trollberget Experimental Area (Paper III and IV)

The Trollberget Experimental Area (TEA; 64° 10′ N, 19° 51′ E), is located approximately 50 km northwest of the city of Umeå in northern Sweden (Figure 1) and is part of the KCS which provides long-term study sites in upland catchments and serves as references. The TEA is built around replicated and controlled experimental catchments based on a BACI (before-after control-impact) approach, consisting of four side-by-side catchments (Figure 1b and a) with two forestry management intervention treatments (clear-cut with or without ditch cleaning) and two unharvested, but drained catchments in the KCS. The climate is similar to that of KCS, being characterized as a cold temperate humid type with relatively short and cool summers followed by long dark winters. The forested catchments are covered by Scots pine (*Pinus sylvestris L.*) trees and Norway spruce (*Picea abies L.*) primarily with an understory of ericaceous shrubs. Here, the underlying soils have an average organic soil depth of 140mm and are dominated by Humic Podzol, with some Humo-Ferric Podzol in drier areas and Histosols in wet areas. The TEA experimental catchments have a drainage area ranging from 4 to 10 ha, an average tree volume prior to clear-cut of 270 m^3 ha^{-1} and a ditch density of 166±40 m ha^{-1}. Comparably, the reference KCS catchments have an average tree volume of 200 m^3 ha^{-1} and a ditch density of 252 m ha^{-1} (Laudon, Hasselquist, et al., 2021; Zannella et al., 2023).

In summer 2020, all four TEA catchments were clear cut harvested using standard forestry practice and tree stems and branches were removed from the site (i.e., DC1, DC2, DC3 and DC4; Figure 1 and Figure 2). Approximately one year after, in September 2021, two of the four catchments were ditch cleaned using a 20-ton crawling excavator in DC1 and DC3, whereas the ditches were left uncleaned in DC2 and DC4 as controls. Further, as a forested reference catchments, I used C1 and C2 of the KCS, which are 98 and 100% forested, respectively and similar in terms of soil types and forest composition (Laudon, Hasselquist, et al., 2021). C1 is larger in comparison, with an area of 48 ha. Both the treated and reference catchments have been affected by historical ditching activity that occurred in the early 20th century to improve drainage and increase forest production (Päivänen & Hånell, 2012). Typical ditch dimensions before cleaning at TEA were similar across the ditch cleaning catchments, on average 500 mm (± 150) deep and 1470 mm (± 360) wide at the top. This is comparable to ditches at KCS unharvested forest reference sites, which are on average 500 mm (± 210) deep and 860 mm (± 530) wide.

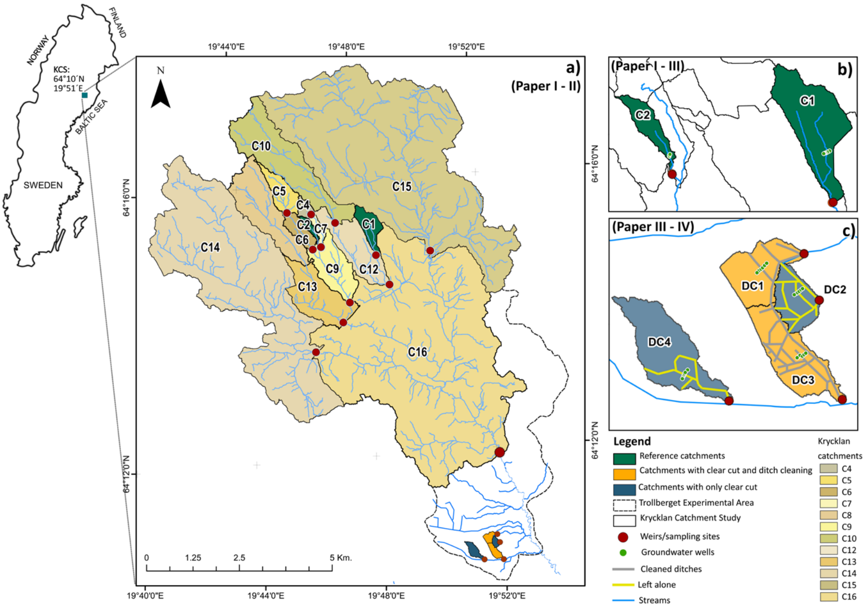

Figure 1. Location of the study sites within Sweden (left). The (a) Krycklan Catchment Study (KCS) shown with sub catchments including the Trollberget Experimental Area (TEA) and a close up of the (b) KCS reference and (c) TEA treated sub catchments. Red circles are the locations of water quality monitoring weirs in the KCS and TEA. Blue and mustard shaded areas delineate the different forest management treatment catchments (DC1-DC4); green areas are the reference catchments in the KCS (C1 and C2). C1-C16 are the permanent KCS monitored sub catchments. The bold grey and yellow lines denote the cleaned and left alone ditches, respectively; blue lines are natural or naturalized perennial streams.

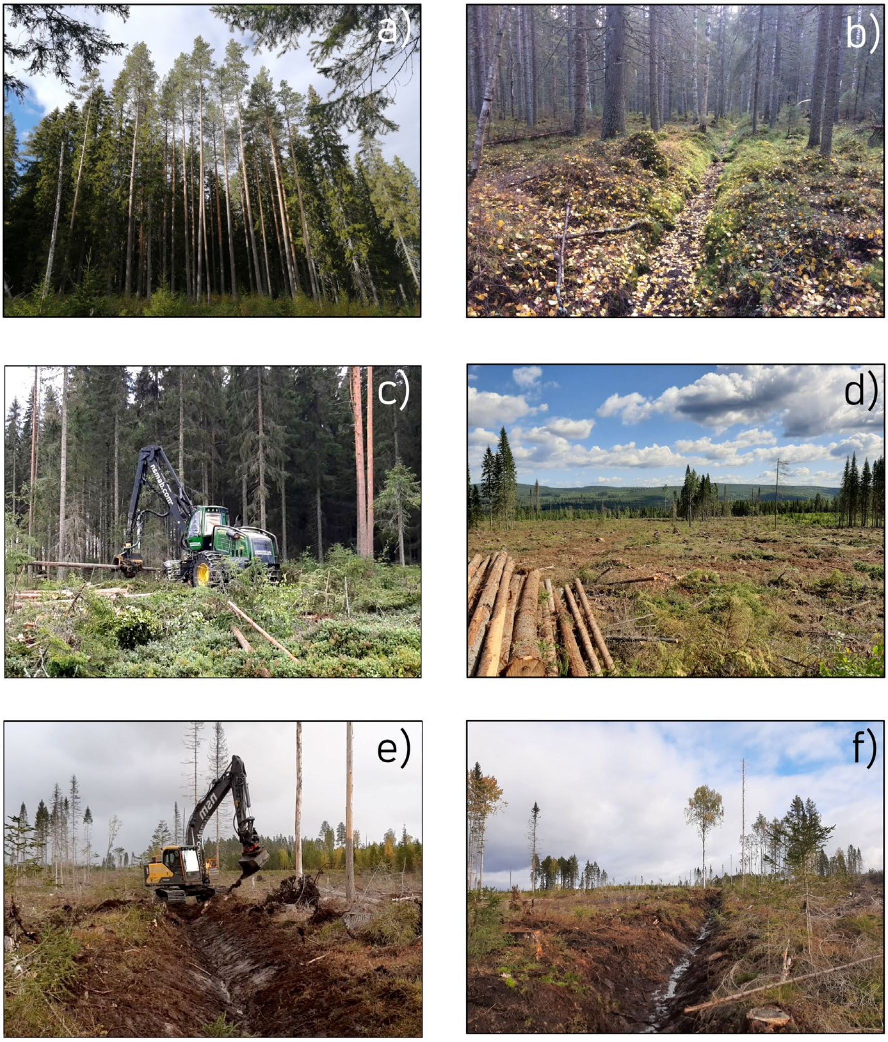

Figure 2. Forest management operations in TEA. Boreal forest before disturbance (a) with naturally infilled ditch (b), forest harvest by clear cutting during summer 2020 (c and d), and ditch network maintenance by ditch cleaning during autumn 2021 (e and f). Photos: a) Alejandro Gándara, b) Eliza Hasselquist.

3.1.3 Field measurements

Water samples (Paper I-III)

At the KCS I compiled data for dissolved organic carbon (DOC), total dissolved nitrogen (TDN), nitrate (NO_3), ammonium (NH_4), and phosphate or soluble reactive phosphorus (PO_4), from the KCS regular monitoring program for streams during the period between 2008 and 2020. The sampling regime is flow weighted, meaning that during spring flood, when discharge is the highest, samples are collected as frequently as twice per week, during the terrestrial growing season sampling occurs every 2 weeks, and during winter base-flow sampling occurs once per month. For paper I and II, I analyzed data from 13 streams in the KCS, where 11 of these had data for the entire period, ranging from 262 to 311 observations per stream, while for the other two streams (C14 and C15) the monitoring program started in 2012, and thus included data from fewer years, or 144 and 133 observations, respectively. For DOC, the monitoring program started in 2003 for the 13 sites, thus I took advantage of this longer period, having 478–408 observations per stream. For paper III, I compiled the data for C1 and C2 from 2019 until 2023 as this corresponded to TEA experiment.

At the TEA, starting in 2019, pre-disturbance water samples for analysis of DOC, TDN, NO_3, NH_4, and PO_4 were taken at the weirs in the outlets of the four treated catchments. In late August 2020, the post clear-cut period began and lasted approximately one year. In mid-September 2021, ditch cleaning started and the post-drainage period began in late September of 2021 and lasted until June 2023, when I completed the last sampling. For the pre-disturbance, post-clear cut and post-drainage period I sampled 33, 36 and 45 sampling occasions per period, respectively. The same protocols and sampling intensities were followed in the four experimental catchments as within the regular KCS monitoring program, during the pre-treatment and post-treatment periods. Finally, for paper IV, water sampling points were established at the weir in the outlets of the four treated catchments, above the biochar (inlet) and ~1 m below the biochar (outlet). Water samples were taken daily for the first 2 weeks after ditch cleaning operations (September 27–October 10) and twice a week until ditch water froze (November 3), following the same protocols as in the regular KCS and TEA sampling.

Discharge data (Paper I and III)

At the KCS and TEA, for the same period, water levels were continuously measured using automatic stage loggers at all sites and discharge was estimated using site-specific rating curves. Rating curves were created from salt dilution velocity-area, and time-volume flow measurements covering most of the observed flow range (Karlsen, Grabs, et al., 2016). For the KCS, year round flow measurements were possible for six gauging stations in heated houses, one of which is a reference catchment for paper III (i.e., C2) and discharge during winter periods for locations without frost-free gauging station in the KCAS and TEA was modeled according to established flow relationships (see Karlsen, Seibert, et al., 2016 for further details on hydrological measurements).

Groundwater table depth data (Paper III)

At the TEA, water table depth (WTD) was measured using 36 continuously monitored wells (Solinst Levelogger 5; see Figure 1 for locations). For the post-clear cut and post-drainage period, daily continuous data were analyzed, with 237 and 204 observations per sampling period, respectively. At all sites, WTD was measured relative to the ground surface.

3.1.4 Biochar field experiment setup (Paper IV)

After evaluating two different biochar feedstocks in laboratory conditions for nutrient adsorption, a wood-based biochar adsorbed the most nutrients and therefore was used to upscale the experiment to field conditions in the TEA. The wood-based biochar was placed in jute sacks (Granngården AB, Malmö, Sweden) and placed in the ditches that drain the four experimental catchments (i.e., DC1, DC2, DC3, and DC4, n = 4). I expected different solute concentration in the runoff from the catchments with ditch cleaning and the catchments without ditch cleaning (Nieminen et al., 2018), thus, testing the effectiveness of biochar adsorption with different nutrient concentrations in field conditions. Sacks were filled with approximately 100 L of biochar and 4–5 sacks, depending on flow and geomorphology of the channel, were placed in each catchment outlet below the weir aimed to direct the ditch water flow through the biochar and to avoid bypass flow around and under the sacks. I took water samples before the biochar filter (inlet) and afterwards (outlet) daily for the first 2 weeks after ditch cleaning operations

(September 27–October 10) and twice a week until ditch water froze (November 3).

3.1.5 Analytical methods (Paper I-IV)

All samples were collected in acid-washed high-density polyethylene bottles, stored in cold conditions and filtered (0.45 µm) in the lab within 24–72 hr. Filtered subsamples were frozen (−20°C) immediately after subsampling and stored for later analysis of NO_3-N, NH_4-N, and PO_4-P, samples for DOC and TDN were refrigerated (+4°C) and analyzed within 10 days after field collection. DOC and TDN were analyzed via the combustion catalytic oxidation method on a Shimadzu TOC VCPH analyzer (Shimadzu, Duisburg, Germany). PO_4, NH_4 and NO_3 were quantified colorimetrically using a SEAL Analytical Autoanalyzer 3 (SEAL Analytical, Wisconsin, USA). Dissolved inorganic phosphorus was analyzed as PO_4 using the ascorbic acid method following G-297-03. NH_4 was analyzed using the Berthelot reaction following the method G-171-96 Rev. 12 and NO_3 analysis was performed by reduction to NO_2 following the method G-384-08 Rev. 2 (Blackburn, Ledesma, Näsholm, Laudon, & Sponseller, 2017). Dissolved inorganic nitrogen (DIN) was calculated as the sum of NO_3 (including nitrite) and NH_4, while dissolved organic nitrogen (DON) was calculated as the difference between TDN and DIN. Annual exports was estimated using daily discharge and interpolated (daily) stream concentration data. Daily concentration of stream nutrients was estimated via linear interpolation to gap fill between sampling occasions. Daily export was then calculated as the product of the interpolated daily concentration and the specific daily discharge. Daily values were summed to estimate cumulative daily exports (mg ha^{-1} day^{-1}).

3.1.6 Season delimitation

The seasons were determined using the World Meteorological Organization (WMO) standard definition based on air temperature measured at Svartberget Field Station located in the center of the KCS (Laudon et al., 2013). Accordingly, spring begins when mean air temperature reaches above 0°C for five consecutive days and the maximum temperature is still below 20°C. Summer begins when the 5-day mean temperature rises above 10°C for 10 consecutive days. Autumn starts when the mean daily temperature falls below 10°C and the minimum temperature is below 0°C, and winter starts when the daily mean temperature is below 0°C for five consecutive days.

3.2 Statistical analysis

All statistical analyses were conducted in R (R Core Team, 2022) and significance levels were set at $p < 0.05$ for all tests. Furthermore, all the graphics of this study were produced using the R package "ggplot2" (Wickham, 2016).

3.2.1 Concentration-discharge curves (Paper I)

I evaluated relationships between PO_4, NO_3, NH_4, DON and DOC concentration and discharge (c–Q) on a yearly basis by calculating the slope (β) of the log c - log specific Q using ordinary least square fit (Zimmer, Pellerin, Burns, & Petrochenkov, 2019) and the ratio of the coefficients of variation between concentration and discharge (CVc/CVq) (Andreas Musolff, Schmidt, Selle, & Fleckenstein, 2015). Hereafter, I refer to log c - log specific Q ordinary least square (OLS) as the "c-Q relationship" and CVc/CVq as the "c-Q ratio". The (log)c-(log)Q relationships was calculated as follows:

$$C = aQ^{\beta}$$

where C is concentration, a is a coefficient with units of concentration, Q is discharge, and β is a unit-less exponent representing the slope of the log-transformed c-Q relationship. Furthermore, the coefficient of variation (CV) is the standard deviation σ of a variable normalized by its mean μ (Thompson, Basu, Lascurain, Aubeneau, & Rao, 2011). The metric is the ratio as follows:

$$\frac{CV_c}{CV_Q} = \frac{\mu_Q}{\mu_c}\frac{\sigma_c}{\sigma_Q}$$

I classified c-Q relationships based on three responses from the slope (β) of the c-Q relationship: i) 'up', classified as transport-limited (β is positive), ii) 'down', classified as source-limited (β is negative), and iii) 'flat', classified as constant ($\beta \approx 0$; Ducharme et al. 2021; Moatar et al. 2017; Musolff et al. 2017). Positive slopes ($\beta > 0$) occur when solute concentrations increase with discharge and this is described as transport-limited because delivery to the stream is dependent on the capacity of the catchment to move a solute and not by the availability or production of the solute. Negative slopes ($\beta < 0$) indicate a dilution of stream solute concentrations with increasing flow, and are described as source-limited because delivery to the stream is determined by the solute abundance rather than the ability of the catchment to transport them (Ducharme et al., 2021; Moatar et al., 2017; Zimmer et al., 2019). Finally, constant behavior indicates that changes in hydrological connectivity and flowpath do not affect the solute concentration in the stream and this is often attributed to homogenous and uniform distribution of elements in the catchment.

I considered the parameter β to be approximately 0, when β and r^2 values were low and the slope of the c–Q line was not significant ($p>0.05$) (Ducharme et al., 2021). As an alternative to a classification based on fixed ranges (i.e., $\beta > 0.2$ or $\beta < -0.2$; Zimmer et al. 2019), I resolved c-Q behaviors based on significant differences in the slope β from zero (t-test, 95% confidence level) (Ebeling et al., 2021). Similarly, I defined a dilution response as β less than 0 and enrichment response as β above 0, but only when the relationship was significant ($p<0.05$) and the r^2 was high (Zimmer et al., 2019). I further defined weak responses when c-Q relationship was significant ($p<0.05$) but the r^2 was low (M. Z. Bieroza, Heathwaite, Bechmann, Kyllmar, & Jordan, 2018; Ducharme et al., 2021). Finally, I used the ratio of the coefficients of variation between concentration and discharge (CV_C/CV_Q) to characterize whether export regimes are chemostatic or chemodynamic. Following Musolff et al. (2017), chemodynamic refers to solutes that vary strongly and independently from discharge ($CV_c/CV_Q > 0.5$), whereas chemostasis refers to situations where solute concentrations are less variable than discharge ($CV_c/CV_Q < 0.5$).

3.2.2 Trends (Paper II)

I analyzed organic C and N and inorganic N and P concentration and molar ratios for overall significant monotonic time series trends by performing a non-parametric Seasonal Mann–Kendall test with seasons as the blocking variable using the “rkt” package (Marchetto, 2017). The Seasonal Mann–Kendall is well suited to dis- tinguish between random fluctuations and monotonic trends and is applicable to data sets with seasonality. It is not biased by missing values or values reported as “below detection limit” and requires no assumption of normality (Hirsch and Slack 1984). Specifically, I determined the Seasonal Kendall slope (unit yr^{-1}), an extension of the Theil Sen slope, to estimate the magnitude of statistically significant trends. If the Seasonal Kendall slope is positive it means that the variable consistently increases and if it is negative the variable decreases, yet, does not imply a linear regression (Hirsch et al. 1982). To further understand the seasonal differences in the trends I used the Seasonal Mann–Kendall to test for trends of the different seasons and individual months using the median of samples collected within each month or season (Hirsch, Slack, & Smith, 1982). Finally, to capture and illustrate the general pattern of nutrient concentration and molar ratio over time, a locally weighted scatterplot smoothing (loess) fitting curve was applied using the "ggplot" package in R (Wickham 2009).

3.2.3 BACI experimental design (Paper III)

The statistical design used in this study focuses on the BACI experimental design as used previously in hydrological studies (Laudon et al., 2023). To compare treatments and reference WTD and nutrient concentration, at each sampling occasion, I calculated the difference in mean value of the two clear cut-only sites (DC2 and DC4), the two clear cut and ditch cleaned sites (DC1 and DC3), and the mean value of their reference sites (C1 and C2). Linear mixed effect model (LMM) was the used to evaluate whether clear-cut and drainage resulted in significant response in WTD, PO_4, DIN, DON and DOC. The analysis was performed using lme model from the *nlme package* (Pinheiro, Bates, DebRoy, Sarkar, & Heisterkamp, 2022). The fixed effects considered in this study were the forest management interventions (i.e., clear cut and ditch cleaning) and the random effects included were catchment ID and sampling time to account for repeated measures. Finally, to capture and illustrate the general pattern of nutrient concentration over time, a General Additive Model (GAM) fitting curve was applied using the "ggplot" package in R (Wickham 2009).

3.2.4 Biochar field experiment (Paper IV)

Response variables consisted of dissolved nutrient concentration in water (mg L^{-1} TDN and DOC and µg L^{-1} PO_4) and available nutrient concentration in biochar (% of Tot- C and Tot- N, and mg kg^{-1} of Tot- P). I used a linear mixed- effect model (LMM) to analyze differences in the concentration of

PO_4, DOC, and TDN between the inlet and the outlet, before and after the biochar. The analysis was performed using lme model from the *nlme package* (Pinheiro et al., 2022). The LMM provided a nonparametric approach to explain variability in the response variables by fixed effects (factors that were included in the study design) and random effects, which accounted for factors that were not part of the study design, but possibly affected variability in the concentration of PO_4, DOC, and TDN between the inlet and the outlet. The fixed effects considered in this study were the biochar treatment (inlet–outlet) and sampling time (i.e., day number); the random effects included were catchment ID and sampling time to account for repeated measures.

4. Results and discussion

To predict future water quality changes and developing sustainable management practices, it is crucial to understand current and long-term catchment functions that supply essential elements to aquatic ecosystems. Moreover, it is necessary to understand how these functions interact with anthropogenic activities co-occurring in the landscape and if there are feasible ways to mitigate an impact. In this research, I focused in the essential limiting nutrients of aquatic ecosystems, C, N and P, as their variation in supply and stoichiometry can influence a wide range of ecological and biogeochemical processes in streams, rivers, and lakes (Sardans et al., 2012). I first tried to provide fundamental understandings of the regulating interaction between hydrological flow paths and the terrestrial storage in the simultaneous supply to streams of essential nutrients from boreal landscape with different catchment characteristics but with limited anthropogenic activities. Further, I presented the long term trend of these essential nutrients in the boreal streams of these different catchments providing a glimpse of where stream chemistry might be heading. From there, I evaluated the effect that forestry, the main anthropogenic activity in boreal landscapes, could have in the supply of these essential nutrients; and finally, I tested a new method to potentially alleviate the impact of this anthropogenic activity on the stream concentration of these essential nutrients.

4.1 **Distinct chemical signature in boreal streams.** Catchment controls on the supply of carbon and nutrients to boreal streams (Paper I)

The variability in supply of C, N and P across land-water boundaries is regulated by the capacity of hydrological transport mechanisms to mobilize dissolved forms in the face of biotic and abiotic processes that mediate their uptake or removal in soils or groundwater (Gerber & Brookshire, 2014). In this regard, for paper I, I analyzed the c-Q relationships from 12 years of data to test how seasonal flow regulates the concentrations of DIN and PO_4, DON, DOC and their respective ratios across 12 streams in the boreal KCS. At inter-annual times scales, I observed export regimes predominantly chemostatic for all solutes, yet opposing c-Q relationships between organic and inorganic solutes (Figure 3a). DOC and DON tended toward transport limitation, with significant and moderately positive c-Q slopes ($p < 0.0001$; $\beta = +0.09$ and $+0.08$, respectively) and with little year-to-year change, whereas NH_4 and PO_4 were source limited, with significant negative c-Q slopes ($p < 0.0001$ and $\beta = -0.19$ and -0.13, respectively) and with a tendency of becoming more source limited over time. However, NO_3 had generally constant behavior ($p > 0.05$ and $\beta = 0.01$), regardless of time and catchment characteristic. Our results showed that organic and inorganic nutrients were differently mobilized by increases in discharge, consistent with the idea that organic and inorganic solutes have distinct vertical patterns of storage in the soils and groundwater (Stewart et al., 2022). Specifically, DON and DOC in streams were often enriched at high flows, ostensibly because their concentrations and the degree of soil hydrological conductivity are highest near the soil surface where soil organic matter storage is greatest (Bishop et al., 2004). Thus, the activation of these strata with increasing discharge mobilizes large amounts of dissolved organic material (Ledesma et al., 2018). By contrast, NH_4 and PO_4 are unlikely to accumulate in surficial, organic soils, where both microbial and plant demand are highest. Instead, these solutes are more likely to increase in concentration with depth: for PO_4 as a consequence of proximity to mineral P sources (Ebeling et al., 2021) and for NH_4 as a consequence of low redox conditions in riparian soils and groundwater that constrain nitrification and promote accumulation of reduced N (Blackburn et al., 2017). Regardless of the mechanism, and as may be expected for a nutrient-poor landscape (Thompson et al., 2011), mobilization of inorganic N and P from biologically active surface soils typically cannot keep pace with hydrologic flushing as water tables rise, leading to dilution of these solutes in streams. Finally, change in c-Q relationships for inorganic nutrients over time suggest that source limitation is intensifying as a result of oligotrophication during this period of record (Mosquera et al., 2022).

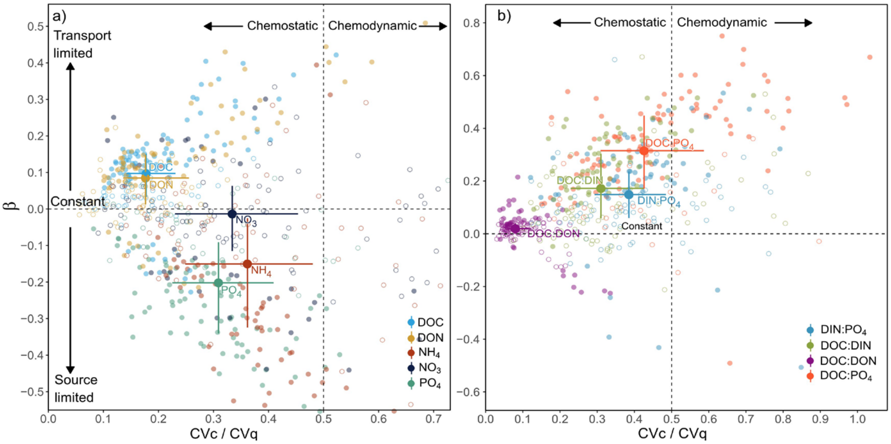

Figure 3. Slope of the linear regression relationship (β) of concentration and ratio versus the coefficient of variation (CV) of concentration divided by the CV of discharge. (a) Slope of the linear log(concentration)-log(discharge) relationships (β) of PO_4, NH_4, NO_3, dissolved organic nitrogen (DON), and dissolved organic carbon (DOC) and (b) slope of the linear log(ratio)-log(discharge) relationships (β) of DON:DON, DOC:DIN, DOC:PO_4, and DIN:PO_4. Points are coloured by (a) solute or (b) ratio and show c-Q relationships for each site and year. Hollow points represent non-significant c-Q or ratio-Q relationships ($p > 0.05$). The larger points represent the median for each group. Error bars represent the interquartile range.

Our results also highlight strong influences of catchment structure on c-Q patterns, regardless of solute, season, longer-term directional changes and despite the general difference between organic and inorganic c-Q patterns. DON, DOC, PO_4, and NH_4 were all positively correlated ($p < 0.05$) with large-scale, catchment properties such as mire versus forest cover (PCA2). Specifically, the organic solute c-Q responses became less constant, while inorganic solute responses became more constant along this axis of catchment properties. For DOC and DON, c-Q slopes from sub catchments with less mire cover, more sorted sediment, larger area and longer channel lengths, indicated transport limitation (i.e., positive β in Figure 4a and b, respectively), while for PO_4 and NH_4, these same sub catchments had a constant response. In contrast, for PO_4 and NH_4, sub catchments with more mire cover, smaller area and shorter river lengths, showed a source limited behavior (i.e., negative β in Figure 4d and e, respectively), while for DOC and DON these same sub catchments had a constant response. Our results are in hand with others that have found that catchment characteristics such as land-use, soil type, or drainage size can influence the complex interactions between hydrological and biogeochemical processes that underpin c-Q relationships (Andreas Musolff et al., 2015; Thompson et al., 2011). Sites with particularly strong influence from upstream mires stood out in our analyses of c-Q relationships for most solutes. In particular, stream draining the mire (C4) showed persistent source limitation for DOC and DON (−0.14 and −0.15, respectively) and the strongest source limitation for PO_4 and NH_4 (-0.45 and -0.47, respectively). For DOC and DON, these observations are consistent with mechanisms suggested by Laudon et al. (Laudon, Berggren, et al., 2011), where dilution during spring flood results from the substantial contribution of direct snow-melt flow running atop surficial ice in the mire with little peat contact. Further, source limitation for NH_4, or even PO_4, could be explained by the dominance of preferential flow paths through the mire (Peralta-Tapia et al., 2015), such that solute exports are supported by an exhaustible pool that accumulates at depth during low flow (winter) months (Sponseller et al., 2018). Overall, across the KCS network, our inter-annual assessment revealed a range of c-Q relationships among organic and inorganic solutes, which in most cases appear to reflect the specific biogeochemical and hydrological conditions of either the riparian-stream or mire-stream interface.

These different c-Q relationships translated into strongly dynamic ratio-Q responses, particularly when considering resource pairs that have the most distinct subsurface storage and turnover patterns. Most notably, I found that the opposing mobilization patterns for organic versus inorganic solutes combine to create sharp increases in DOC:DIN ($p < 0.05$ and $\beta = +0.11$) and DOC:PO_4 ($p < 0.05$ and $\beta = +0.25$) ratios in streams during high flow events. By comparison, DOC:DON, was relatively invariant with discharge across most catchments, ($p < 0.05$ and $\beta = 0.0$). Overall, differences in timing of catchment exports for C, N, and P, create dynamic variation in solute concentrations in streams, likely supplying aquatic ecosystems with far more organic energy than inorganic building blocks needed to support microbial metabolism. Thus, high flows potentially exacerbate the seasonal imbalance of energy versus nutrient supply to aquatic systems with subsequent impacts on resource stoichiometry that is central to aquatic ecological processes even though N and P deficits could be met to some degree by organic forms (Rulli et al., 2022). Such observations gain even more importance when considered in the context of general “browning trends” observed across northern aquatic systems (Kritzberg et al., 2020), oligotrophication of boreal streams (Mosquera, Hasselquist, Sponseller, & Laudon, 2022), “wetter autumns/winters” arising from altered precipitation patterns (Teutschbein, Grabs, Laudon, Karlsen, & Bishop, 2018), and the likelihood of more frequent flood events in the future (Vormoor, Lawrence, Heistermann, & Bronstert, 2015), all of which may contribute to amplifying the supply of DOC and DON relative to inorganic nutrients across land-water boundaries.

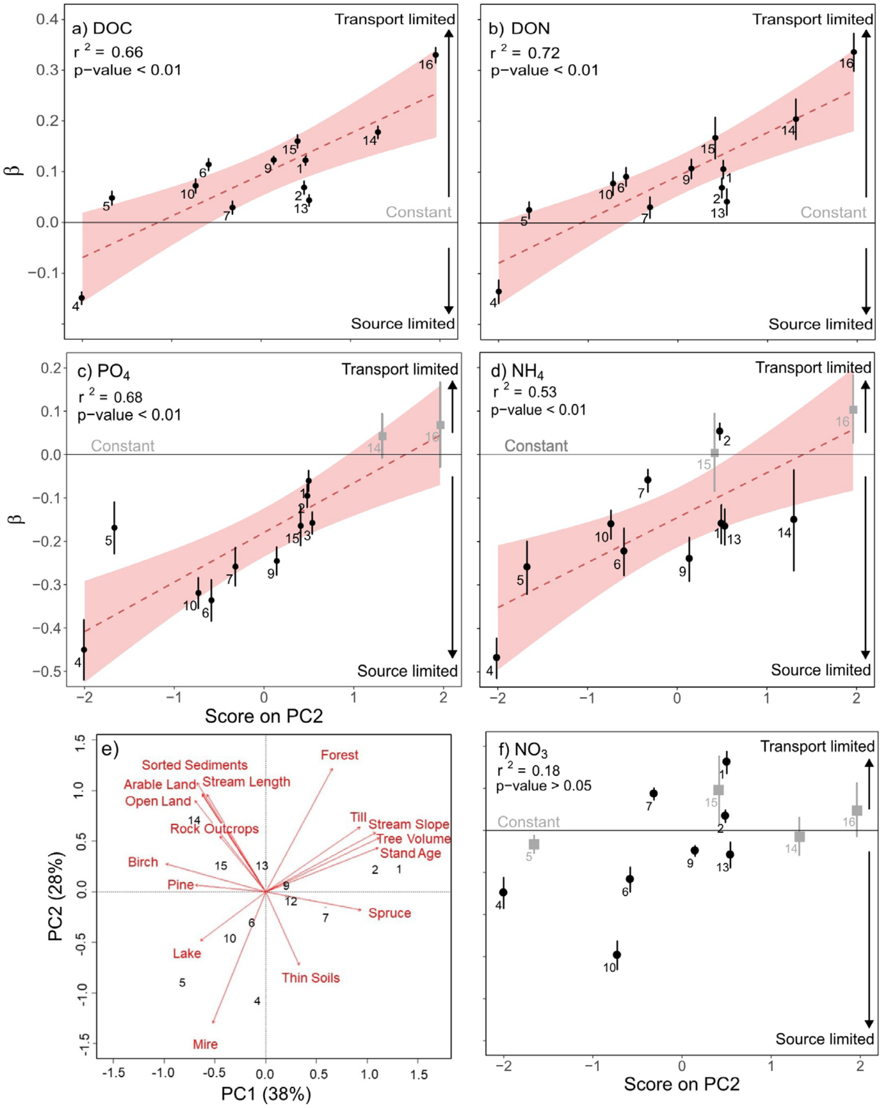

Figure 4. Relationship between principal component analysis (PCA) scores of catchment characteristics and c-Q relationships (β); streams with significant β ($p < 0.05$) are shown in black circles, non-significant ($p > 0.05$) in light gray, (overall inter-annual ±1 SE β for a given stream). Linear regression of PCA2 versus (a) dissolved organic carbon β, (b) dissolved organic nitrogen β, (c) PO_4 β,(d) NH_4 β, and (f) NO_3 β and (e) PCA of catchment characteristics for Krycklan Catchment Study. In panel (b–e), red dotted line is the significant linear regression with ±1 SE (in light red). The numbers shown are the ID for each stream (Figure 1).

4.2 **Understanding past behavior to foresee future consequences.** Oligotrophication in a browning boreal stream network (Paper II)

Understanding the long-term trends of relative supply of C, N and P to freshwater ecosystems is of significant concern in environmental research mainly due to their fundamental importance to aquatic productivity and the future of nutrient cycling and food web dynamics of streams and lakes. Thus, in paper II I analyzed the long-term simultaneous trends of C, N and P in the KCS, a boreal landscape with different catchment characteristics and limited direct anthropogenic influence. Our results revealed widespread declines for PO_4 and DIN co-occurring with a well-established DOC increased in streams over the 13-year period (2008-2020). All KCS streams ($n = 13$) showed statistically significant ($p < 0.05$) declines in PO_4 concentration (Figure 5a) and almost all (11 out of 13 streams) showed a statistically significant decline in DIN concentrations (Figure 5b). The other two streams also showed a negative trend but with no statistical significance ($p > 0.05$). The overall magnitude of concentration trends varied between DIN and PO_4 and among sub catchments, but was broadly similar as an annual percentage. Specifically, the annual magnitude of DIP and DIN decrease (Seasonal Kendall slope estimator) averaged a decrease of -5.4% (±1.6) and -7.1% (±1.6), respectively. Contrary to N and P trends, DOC concentrations increased in most of the KCS streams, however with a halt in increase after 2011 (Eklöf et al., 2021). Specifically, for the period of 2003–2020, 9 out of 13 streams had statistically significant ($p < 0.05$) increase of DOC, with an averaging increase of 1.2% (±0.6) annually (Figure 5d). Furthermore, while both DIN and PO_4 concentrations show declines for most of the KCS sub catchments at annual scales, a more detailed assessment using the Seasonal Kendall test revealed distinct seasons during which most of this long-term change. Specifically, the pooled significant ($p < 0.05$) decline for DIN trends was dominated by changes during the open water season (April–October), but declines were also observed during winter months (Figure 6a). By comparison, significant declines ($p < 0.05$) for PO_4 occurred during spring (April–June), as well as from autumn to early winter (October–January;Figure 6), both periods that begin with relatively elevated stream discharge. Overall, even though the mechanisms that regulate C, N and P mineralization and immobilization in soils can differ in fundamental ways

(Neff, Hobbie, & Vitousek, 2000), I found trends, declining for PO_4 and DIN and increasing for DOC concentration, in nearly all study streams, which occur regardless of catchment characteristic and independent of hydrological change. Therefore, given the spatial extent of observed changes, I suggest that these decadal-scale trends are most likely shaped by drivers operating at broader spatial scales, including ongoing climate changes and the legacy of atmospheric deposition (Laudon, Sponseller, & Bishop, 2021). However, our results point toward independent sets of drivers acting in different seasons on all three solutes. DOC change is likely regulated by SO_4 decline (Fork, Karlsson, & Sponseller, 2020), whereas DIN appears linked to biological processes in the catchment, as the decline was strongest during the growing season and together with increases in DOC:DON at several sites, suggests increasing N retention by plants and soil microbes across this landscape. Finally, changes in P are likely connected to geochemical changes in near-stream soils occurring primarily during late autumn and winter.

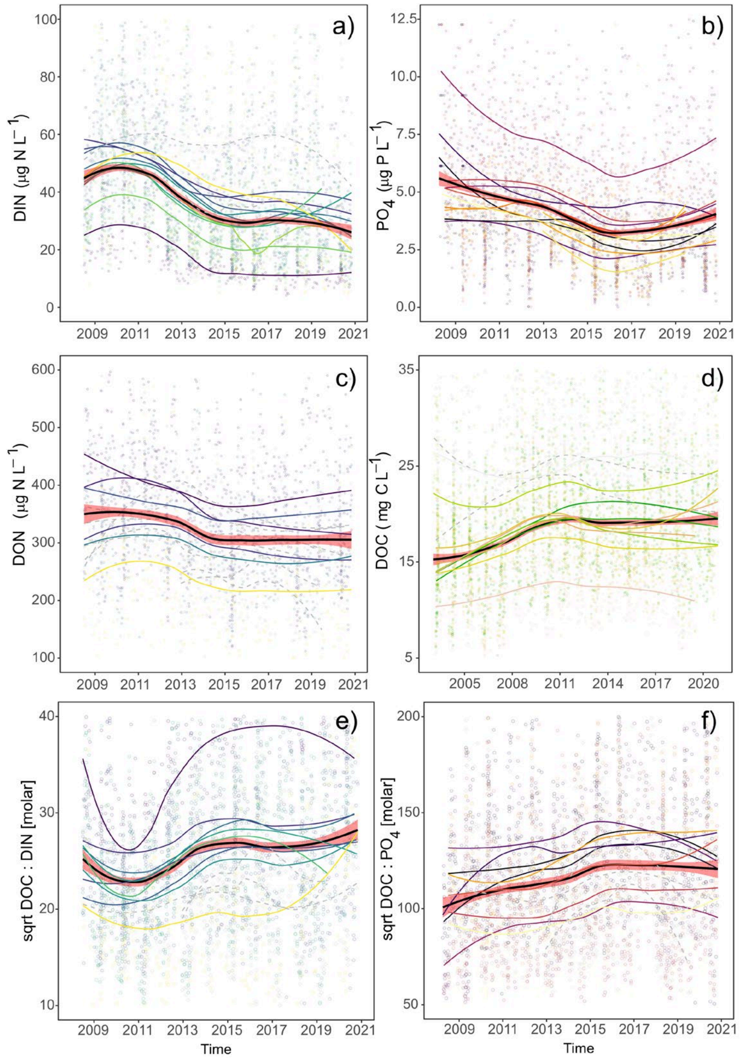

Figure 5. Time series of organic and inorganic nutrient concentration and ratios for the period 2008–2020 shown with locally weighted scatterplot smoothing (loess). (a) Dissolved inorganic nitrogen (DIN), (b) dissolved inorganic phosphorus (PO$_4$), (c) dissolved organic nitrogen (DON)), (d) dissolved organic carbon (DOC) (all streams have data from 2003 to 2020), molar ratio of DOC and DIN (DOC:DIN), and molar ratio of DOC and PO$_4$ (DOC:PO$_4$) for 13 streams of the KCS (C14 and C15 have data from 2012 to 2020). Statistically significant trends (seasonal Mann–Kendall test) per stream are shown in solid lines, streams with no significant trend are shown with gray dashed lines, and the mean trend for all rivers combined is shown in black line with ± 1 SE in shaded red.

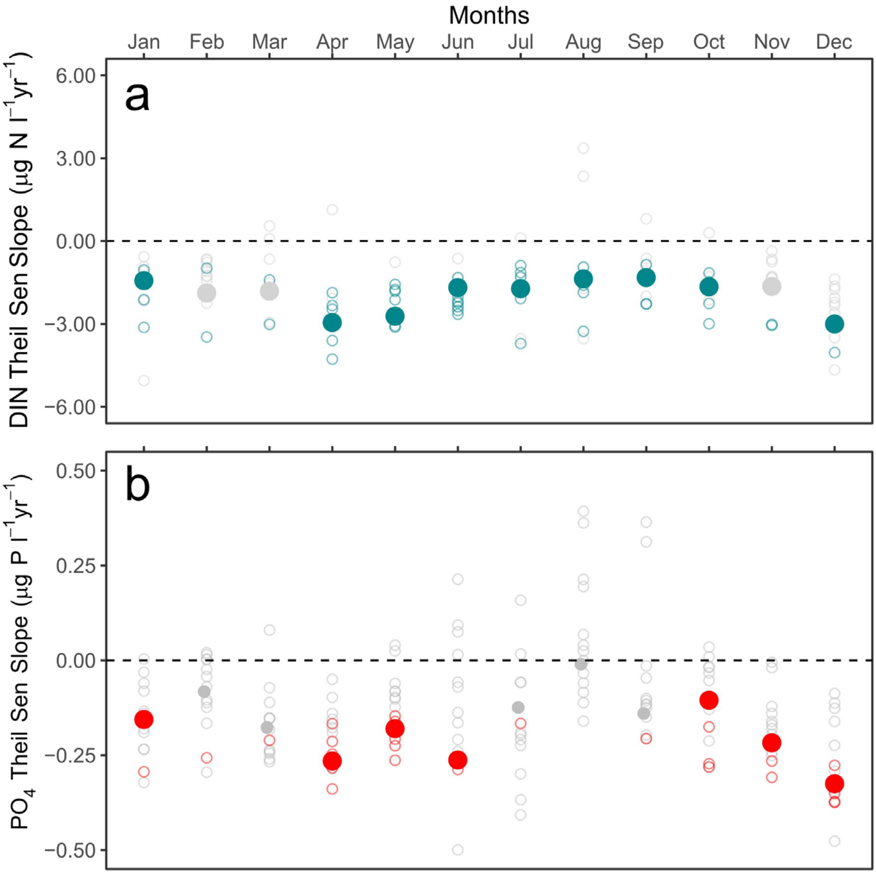

Figure 6. Seasonal Kendall test for inorganic nutrients in stream waters. (a) DIN Seasonal Kendall test and (b) PO_4 Seasonal Kendal test. Pooled Theil Sen slope is shown with filled circles and site-specific Theil Sen slope is shown with hollow circles. Streams with non-significant monthly declines ($p > 0.05$) are shown in light gray. Note that the scales in y-axis show different magnitudes of decline.

Given declining trends in PO_4 and DIN, together with increasing trends for DOC, I found that the ratios between C:N and C:P increased over time in almost all the streams in the KCS (Figure 5e and f). Specifically, 11 of 13 streams showed a significant increase ($p < 0.05$) in the DOC:DIN ratio (Figure 5e) and 12 of 13 streams showed a significant increase ($p < 0.05$) in the DOC:PO_4 ratio (Figure 5f). Moreover, the decline of PO_4 and DIN seems to be stronger in seasons when concentration in streams are already low and

DOC concentration is high. Specifically, in paper I, I found that PO_4 and NH_4 concentration reached minimum values for all streams during spring (Figure 7e and c) and NO_3 concentrations were lowest from late spring into summer (Figure 7d), while DOC and DON concentrations tended to first peak during spring flood, and then again, reaching maximum values between end of summer and start of autumn (Figure 7a and b). The observed imbalance in energy vs. nutrient supply potentially has a long-term effect on the oligotrophication process (i.e., decline of nutrients and ecosystem productivity) in KCS streams, since most are becoming richer in organic carbon but poorer in inorganic nutrients. Several studies have demonstrated the importance of interactions among N, P, and DOC stream water concentrations in freshwater systems (Bechtold, Marcarelli, Baxter, & Inouye, 2012; J. Elser et al., 2007; Francoeur, 2001; Peñuelas, Sardans, Rivas-Ubach, & Janssens, 2012) where there are strong ecological and bio-geochemical connections among these elements (Dodds et al., 2004). For example, declines in inorganic N and P could influence C cycling in streams either by limiting or co-limiting nutrients for primary production (Burrows, Jonsson, Fältström, Andersson, & Sponseller, 2021) and heterotrophic respiration (Burrows et al., 2015) and/or by altering how these nutrients facilitate litter decomposition (Maranger, Jones, & Cotner, 2018). Overall, our observations from this stream network point to ongoing oligotrophication, with possible consequences for aquatic ecosystems in boreal landscapes.

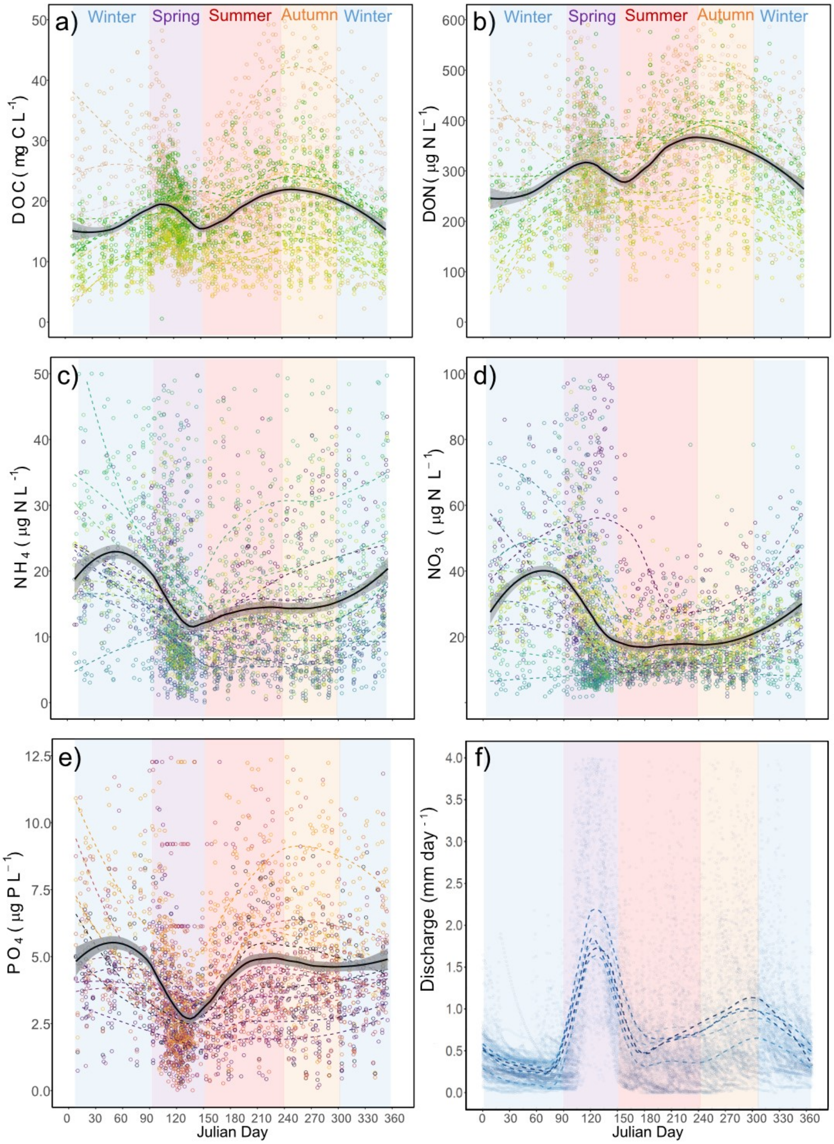

Figure 7. Intra-annual variability of organic and inorganic nutrients for the period 2008–2020 shown with locally weighted scatterplot smoothing (loess). (a) Phosphorus (PO_4), (b) ammonium (NH_4), (c) nitrate (NO_3), (d) dissolved organic nitrogen, (e) dissolved organic carbon, and (f) specific discharge for 12 headwater streams in the Krycklan Catchment Study. Colored circles represent each observation for each stream, dashed lines represent loess trend per stream, black line represent the overall temporal variability with ±SE shaded in gray. Background colors delimitates average seasons.

4.3 **Putting humans in the picture.** Cumulative and discrete effects of forest management on carbon and nutrient exports (Paper III)

In boreal landscapes, forest management has the potential to become a major driver of surface water quality due to the large area of actively managed forest combined with the intensity of forestry operations. Therefore, in paper III, I analyzed the single and combined effect of two forest management operations (i.e., final harvest by clear cutting and subsequent ditch cleaning to increase drainage capacity) on the catchment outflow concentrations and exports of DOC, DON, DIN and PO_4 in boreal Sweden. I found that concentration of all nutrients (i.e., PO_4, DIN, DON and DOC) in ditch water increased significantly ($p < 0.05$) post-clear cut in all treated catchments compared to the pre-disturbance period, however the DIN concentration increase was not significant ($p > 0.05$, Figure 8). Specifically, on average in the clear-cut catchments, PO_4 increased from 1.3 ± 0.2 to 8.1 ± 1 μg P L^{-1}, DIN from 47 ± 6 to 137 ± 13 μg N L^{-1}, DON from 461 ± 17 to 864 ± 70 μg N $L^{-}1$ and DOC from 25 ± 1 to 46± 3 mg C L^{-1}, from pre-disturbance to after-clear cut period, respectively. Furthermore, after clear cut, due to the removal of tree transpiration, WTD rose on average 10 cm reaching approximately 32cm below ground surface. The rise in WTD is one of the clearest effects of clear cutting on drained soils and this has consequences for nutrient mobility; where elevated water tables reach soil layers with greater nutrient concentrations and induce anoxic conditions in more surficial strata, driving changes in biogeochemical processes and increasing nutrient leaching (Nieminen, Sarkkola, & Laurén, 2017; Stewart et al., 2022). However, for DIN mobilization, clear cutting seemed to have a delayed effect as there was an increase in DIN concentrations only after the next growing season after clear cutting. Such a response seems to be attributed to a combination of the loss of plant nutrient demand during growing season (Hughes & Quinn, 2019), and eventually higher rates soil N mineralization, also shown by our results with a delayed increase of NH_4, and a higher hydrologic flux due to the increase in WTD (Schelker et al., 2016).

Conversely, during the post-drainage period, the organic nutrient concentration (i.e., DON and DOC) in the catchments with ditch cleaning decreased to almost pre-disturbance levels, while in the catchments with no ditch cleaning the concentration remained high (Figure 8c and d). The catchments that were ditch cleaned decreased from an average of 579 ± 35 to 385 ± 16 for DON and 31 ± 2 to 20 ± 1 for DOC, from the post-clear cut to post-drainage period, respectively; while the catchments without ditch cleaning on average had a DON concentration of 1157 ± 128 μg N L^{-}1 in the post-clear cut period and of 970 ± 61 μg N L^{-}1 in the post drainage period, and DOC maintained an average of 56 ± 4 mg C L^{-1} during both periods. Once more, the difference in nutrient concentration seems to be an effect of the decrease in WTD after ditch cleaning, decreasing 14cm and reaching 50cm below ground surface on average. DOC and DON declined to almost pre-disturbance levels after drainage, which likely reflects the combined effect of (1) water table not reaching the upper organic soil layer with its easily releasable, high organic nutrient concentrations (Nieminen, Piirainen, et al., 2018) and (2) greater fraction of lateral water flowing through deeper soil layers with positively charged mineral soil oxohydroxides that yield less organic material and could in fact act as sorption sites for the negatively charged organic moieties (Åström, Aaltonen, & Koivusaari, 2001). The inorganic nutrient concentration (i.e., PO$_4$ and DIN) simultaneously increased further during the post-drainage period in the catchments without ditch cleaning, from 10.3 ± 2 to 20.5 ± 3 for PO$_4$ μg P L^{-}1 and from 144 ± 21 to 1003 ± 84 μg N L^{-}1 for DIN, from the post-clear cut to the post drainage period, respectively (Figure 8a and b); while for catchments with ditch cleaning, DIN concentration increased from 131 ± 17 to 551 ± 49 μg N L^{-}1, from post-clear cut to post-drainage period, respectively, and PO$_4$ stayed in the same concentration level of 6.8 ± 0.6 μg P L^{-1} after ditch cleaning (Figure 8a and b). Here, the lower WTD likely increases the oxygen in peat and mineral soil layers, which theoretically will increase adsorption of PO$_4$ by Fe and Al and consequently decreasing nutrient concentration (Kaila et al., 2014; Laudon et al., 2023). Similarly, the differentiated increase of DIN could also be explained by the difference in lateral flow due to changes in WTD, as clear cutting likely mobilized N near the soil surface and this pool could become inaccessible when WTD drops after ditch cleaning (Nieminen, Palviainen, et al., 2018). Moreover, this can further be explained by understanding the differentiated effect of WTD change on NO$_3$ and NH$_4$ (Åström, Aaltonen, & Koivusaari, 2005). Specifically, the increase of nitrate in response to ditch cleaning, from an average of 66 ± 9 to 373 ± 36 μg N L^{-1}, could be related to higher nitrification rates due to oxygenated soil layers and higher nitrate mobilization; while ammonium mitigated increase, from an average of 65 ± 9 to 178 ± 21 μg N L^{-1}, could be related to a greater accumulation of mineralized NH_4 in the post-clear cut period in more surficial soils that become disconnected as the water table drops (Kaila et al., 2016).

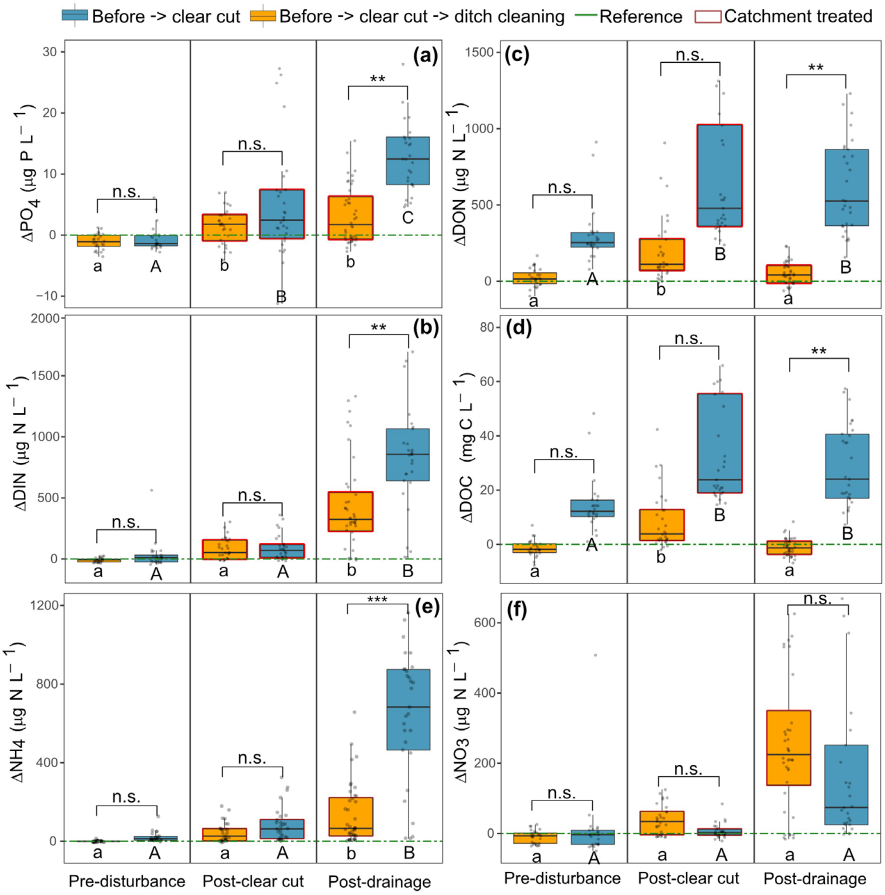

Figure 8. Difference in nutrient concentration between treatment and reference catchments before and after interventions for PO_4 (a), DIN (b), DON (c), DOC (d), NH_4 (e) and NO_3 (f). Black circles represent individual data points. *denotes significant difference ($p < 0.05$) between treatments during each intervention period; different uppercase letters indicate significant difference ($p < 0.05$) for catchments with clear cut and ditch cleaning after each intervention; and different lower case letters indicate significant difference ($p < 0.05$) for catchments with clear cut but without ditch cleaning after each intervention . Green dotted line denotes the control zero reference. Solid line in box plots is the median value, box extents are the interquartile range (IQR) and whiskers show the 1.5IQR value.

Forest management operations increased exports of all nutrients, where the catchments with only clear cut had the highest total exports of all nutrients (i.e., PO_4, DIN, DON and DOC), followed by the catchments with clear cut and ditch cleaning (Figure 9). However, our results also showed that ditch cleaning could help mitigate, or even reverse, the effect of clear cut on organic and inorganic exports, as the highest exports of all organic and inorganic nutrients were reached by the catchments without ditch cleaning. In total, for the entire study period, the reference catchment exported 0.03 kg P ha^{-1}, the catchment with clear cut and ditch cleaning exported 0.1 kg P ha^{-1} and the catchment with only clear cut exported 0.6 kg P ha^{-1} of PO_4. For inorganic and organic nitrogen, the reference catchment exported 0.12 and 3.5 kg N ha^{-1}, the catchment with clear cut and ditch cleaning exported 7.0 and 13.8 kg N ha^{-1} and the catchment with only clear cutting exported 9.1 and 27.6 kg N ha^{-1}, respectively. For DOC, the reference catchment exported, 226 kg C ha^{-1}, the catchment with clear cut and ditch cleaning exported 700 kg C ha^{-1} and the catchment with only clear cut exported over twice this amount, 1463 kg C ha^{-1}. Overall, this reversible effect on the total organic and inorganic C, N and P export seems to be a joint effect of lower nutrient concentration and a decrease in base flow as both concentration and water fluxes act simultaneously on exports (Schelker et al., 2012). Nevertheless, although ditch cleaning did show a short-term mitigating effect on nutrient exports following clear-cutting, catchments with ditch cleaning still showed an increase in organic and inorganic nutrient exports when compared to both the reference catchments and the pre-disturbance period. These increases in organic and inorganic nutrients after forest management operations could have important effects on water quality and the aquatic ecosystem, contributing to brownification due to an increase of DOC or downstream eutrophication due to an increase of N and P in receiving water bodies (Nieminen, Sarkkola, Sallantaus, Hasselquist, & Laudon, 2021; Smith & Schindler, 2009).

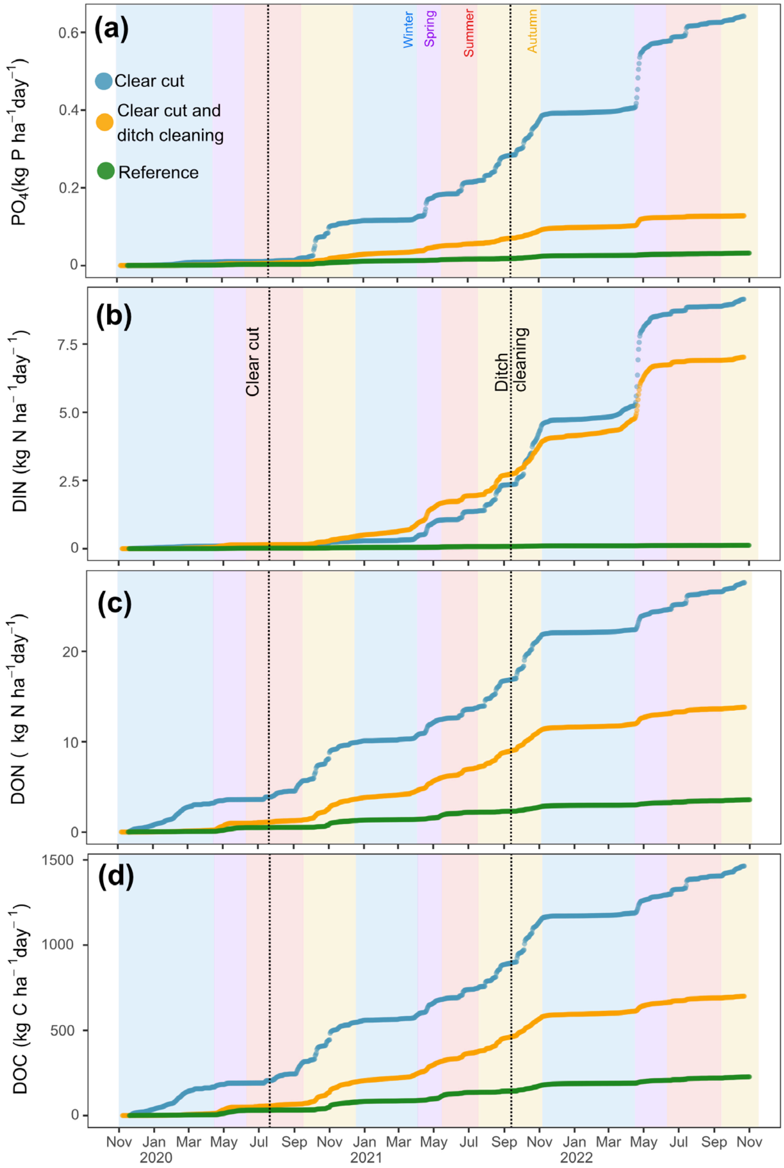

Figure 9. Time series of organic and inorganic nutrients cumulative exports for the pre-disturbance, post-clear cut and post-drainage period. (a) PO_4, (b) DIN, (c) DON and (d) DOC for catchments with clear cut and ditch cleaning shown with yellow line (i.e., DC3), catchments with only clear cut shown with blue line (i.e., DC2) and reference catchments shown with green line (i.e., C2). Background colors delimitates average seasons.

4.4 **Can we do something about it?** Biochar as a potential tool to mitigate nutrient exports from managed boreal forests. (Paper IV)

As shown in paper III, forest management in drained forested peatlands can negatively affect water quality due to the increase in exports of organic matter and nutrients. Therefore, in paper IV, I tested a wood-based biochar filter as a potential method to alleviate the impact of catchment exports by adsorbing the PO_4, TDN and DOC concentration in outlets of two catchments that underwent clear cut and two that underwent clear cut (i.e., DC2 and DC4) and ditch cleaning (DC1 and DC3) in the TEA (Figure 1). Our results showed a removal by wood-based biochar of TDN and DOC ($p < 0.05$) in discharge water of one experimental catchment and no removal of PO_4 ($p > 0.05$) in discharge water (Figure 10), revealing that the efficiency of biochar to remove DOC and TDN in the field was dependent on the initial concentration of the incoming water ($p < 0.05$), with higher initial nutrient concentrations having a higher efficiency of removal. The reduction in DOC and TDN concentration in solution could be explained by a wood biochar with large specific surface area, high porosity, and active sites on the adsorbent surface interacting with the arriving organic molecules from DOC and the organic part of TDN (i.e., DON) (Lee, Cheng, Wong, & Wang, 2018). Specifically, the experimental catchment with only clear cut (i.e., DC4) and the highest initial (upstream) concentration of TDN (2.6 mg N L^{-1}) and DOC (95.6 mg C L^{-1}), was the only site where the biochar filter significantly lowered the mean concentration ($p < 0.05$; Figure 10b and c). This is likely due to an increase in adsorption in response to the increased organic N and C availability in the water which improves the adsorption of organic compounds onto biochar surfaces (Saarela et al., 2020). These results are consistent with laboratory experiment results (Kakaei Lafdani et al., 2021; Mosquera et al., 2024), where in controlled environments, the higher adsorption rate was found when the initial solute concentration in the water was higher. However, even in the catchment with the highest initial solute concentration in our field study (i.e., DC4), the mean percent of removal over the length of the experiment was only 7% for TDN and 6% for DOC, with a maximum removal of 20% and 15%, respectively. These removal percentages seem low when compared to other studies where the biochar was shown to reduce 58% of the TN concentration (Kakaei Lafdani et al., 2020) or even with the increase in DOC and TN after clear- cut (i.e., an average increase of 42% ± 8 and 56% ± 12, respectively) in our study sites (Laudon et al., 2023). Yet, the observed low adsorption capacity might be an artifact of our filter setup, particularly when compared with other configurations such as horizontally oriented columns with longer residence time (Kakaei Lafdani et al., 2020). Overall, our results suggest that a wood- based biochar filter has the potential to be a water protection tool for reducing the export of nutrients from catchments with high nutrient concentration.

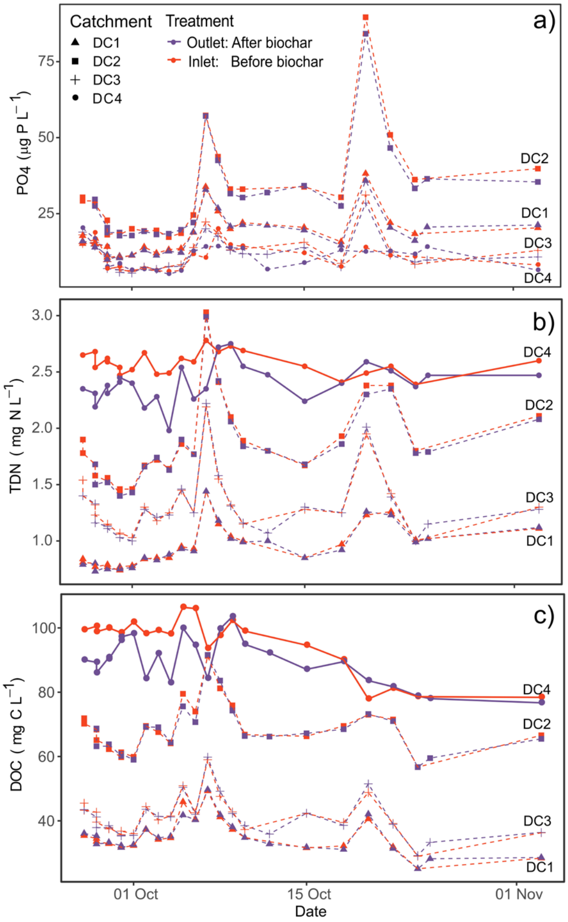

Figure 10. Nutrient concentrations of water from the inlet and outlet of the biochar filter for each experimental catchment. Solid lines represent a significant difference between inlet (red) and outlet (purple) over time according to the LMM ($p < 0.5$). The dotted lines represent non-significant relationships. Shape of the points identifies catchments, where circle is DC4, triangle DC1, square DC2, and cross DC3.

Photo: Alejandro Gándara

5. Concluding remarks

The work described in this thesis aimed to examine the long term, seasonal and anthropogenic supply of C, N and P from catchments to streams in a boreal landscape and to develop new ways to mitigate the anthropogenic influence on the export of these elements. Although the importance of the concentration and stoichiometry of C, N and P on freshwater ecosystems is well established, few earlier studies have attempted to understand these dynamics, and even fewer in a boreal context. Specifically, as C, N and P are individually and collectively essential to aquatic productivity, nutrient cycling, and food web dynamics of streams and lakes, all studies in this thesis were focused on the simultaneous response of these three nutrients and therefore the response in ratios exported to freshwater ecosystems. Using over ten years of data from the KCS, I was able to demonstrate that catchment characteristics directly influenced the opposing mobilization response of inorganic N and P and organic C and N to increases in flow (paper I), while opposing long-term trends, increasing organic C and decreasing trends of inorganic N and P, were widespread and unrelated to catchment characteristics (paper II). Furthermore, these dynamic variations in solute concentrations in streams had subsequent impacts on resource stoichiometry (paper I and II), regardless of catchment characteristics, with strong increasing trends in the balance between the supply of energy vs. nutrient ratios (i.e., DOC:DIN and DOC: PO_4) and sharp increases in DOC:DIN and DOC:PO_4 ratios in streams during high flow events. Alongside, we demonstrated that anthropogenic activities, such as forestry operations, can also have differentiated effects, in magnitude and timing, in the supply of C, N and P (paper III) and that protection tools, such as biochar filters, will not mitigate the effect in exports equally or universally (paper IV). Therefore, given the critical interplay between the supply of resources from catchments and their demand in aquatic ecosystems, understanding the spatial-temporal variability of C, N, and P concentrations and their ratios is key to predicting how northern rivers and downstream lakes may respond to ongoing and future environmental changes. For that reason, the information developed in my thesis is crucial for those managing these landscapes to understand the variability and controls over C, N, and P exports from diverse catchments, and it is central to predicting the consequences for water-quality.

6. Future perspective

It has been very interesting to try and understand the C, N and P export dynamics, natural and anthropogenic, in a boreal landscape and ways to mitigate possible effects. Nonetheless, there are still many questions to be answered before we can fully understand C, N and P dynamics in boreal freshwater ecosystems. One recurring question at the completion of this thesis is whether and to what extent the results obtained in paper I, II and III can impact life and functions of aquatic ecosystems. For example, throughout all studies, I questioned and discussed how the stoichiometry of C, N, and P supplied to aquatic ecosystems can influence a wide range of processes, including rates of autotrophic and heterotrophic activity and the strength of resource limitation, and how differences in seasonality, nutrient exports and trends could trigger ecological unforeseen responses. Consequently, although there are many ways forward in this direction, I propose starting by understanding more about the resource limitation of autotrophic and heterotrophic organisms in these ecosystems. Furthermore, I found contrasting results for N versus P concentration dynamics in streams in the face of different environmental drivers. Specifically, in paper II, I found decreasing trends of inorganic N and P in streams draining natural catchments, while in paper III, I found that forest management increases the concentration of N and P. Therefore, given the extent of forest management in these boreal systems, understanding the effect in receiving rivers and lakes of contrasting exports of C, N and P draining from natural catchments and catchments more directly influenced by anthropogenic activities is an interesting way forward. Specifically, trying to understand the capacity of boreal stream networks to buffer or propagate nutrient mobilization in light of brownification and oligotrophication trends in streams. Additionally, while in paper I and II I was able to use decadal-scale data from the KCS on

C, N and P at the catchment scale, I strongly recommend continuous and longer-term analysis of catchment functions and stream concentration trends on a larger scale (e.g., Baltic Sea catchment scale), since climate change and land use changes could have unforeseen, but important future impacts. In this context, while I focused this thesis on C, N and P due to its clear importance to water quality and freshwater ecology, further analysis of trends, triggers, and ways to mitigate exports of other solutes such as sulphate (SO_4), iron (Fe), or calcium (Ca) would add to the understanding of boreal freshwater ecosystem and ways to correctly manage them in a changing environment. Finally, although our research showed promising results for using biochar as a tool to mitigate nutrient exports from managed catchments, there are still many ways forward, such as improving the biochar filter, determining the lower limits of nutrient exports where biochar is still effective or evaluating if re-introducing the enriched biochar to the catchment´s soils could improve forest growth.

Photo: Alejandro Gándara

Photo: Alejandro Gandara

7. References

Ågren, A., Lidberg, W., & Ring, E. (2015). Mapping temporal dynamics in a forest stream network-implications for riparian forest management. *Forests*, *6*(9), 2982–3001. https://doi.org/10.3390/f6092982

Ågren, A. M., Buffam, I., Cooper, D. M., Tiwari, T., Evans, C. D., & Laudon, H. (2014). Can the heterogeneity in stream dissolved organic carbon be explained by contributing landscape elements? *Biogeosciences*, *11*(4), 1199–1213. https://doi.org/10.5194/bg-11-1199-2014

Ahmad, M., Rajapaksha, A. U., Lim, J. E., Zhang, M., Bolan, N., Mohan, D., … Ok, Y. S. (2014). Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere*, *99*, 19–33. https://doi.org/10.1016/j.chemosphere.2013.10.071

Andersen, J. H., Carstensen, J., Conley, D. J., Dromph, K., Fleming-Lehtinen, V., Gustafsson, B. G., … Murray, C. (2017). Long-term temporal and spatial trends in eutrophication status of the Baltic Sea. *Biological Reviews*, *92*(1), 135–149. https://doi.org/10.1111/brv.12221

Asmala, E., Carstensen, J., & Raike, A. (2019). Multiple anthropogenic drivers behind upward trends in organic carbon concentrations in boreal rivers. *Environmental Research Letters*, *14*(12). https://doi.org/10.1088/1748-9326/ab4fa9

Åström, M., Aaltonen, E. K., & Koivusaari, J. (2001). Effect of ditching operations on stream-water chemistry in a boreal forested catchment. *Science of the Total Environment*, *279*(1–3), 117–129. https://doi.org/10.1016/S0048-9697(01)00757-4

Åström, M., Aaltonen, E. K., & Koivusaari, J. (2005). Changes in leaching patterns of nitrogen and phosphorus after artificial drainage of a boreal forest - A paired catchment study in Lappajärvi, western Finland. *Boreal Environment Research*, *10*(1), 67–78.

Bechtold, H. A., Marcarelli, A. M., Baxter, C. V, & Inouye, R. S. (2012). Effects of N , P , and organic carbon on stream biofilm nutrient limitation and uptake in a semi-arid watershed. *Limnology and Oceanography*, *57*(5), 1544–1554. https://doi.org/10.4319/lo.2012.57.5.1544

Bieroza, M., Baker, A., & Bridgeman, J. (2009). Relating freshwater organic matter fluorescence to organic carbon removal efficiency in drinking water treatment. *Science of the Total Environment*, *407*(5), 1765–1774. https://doi.org/10.1016/j.scitotenv.2008.11.013

Bieroza, M. Z., Heathwaite, A. L., Bechmann, M., Kyllmar, K., & Jordan, P. (2018). The concentration-discharge slope as a tool for water quality management. *Science of the Total Environment*, *630*, 738–749. https://doi.org/10.1016/j.scitotenv.2018.02.256

Birdsey, R., & Pan, Y. (2015). Trends in management of the world's forests and impacts on carbon stocks. *Forest Ecology and Management*, *355*, 83–90. https://doi.org/10.1016/j.foreco.2015.04.031

Bishop, K., Seibert, J., Köhler, S., & Laudon, H. (2004). Resolving the Double Paradox of rapidly mobilized old water with highly variable responses in runoff chemistry. *Hydrological Processes*, *18*(1), 185–189. https://doi.org/10.1002/hyp.5209

Bishop, K., Shanley, J. B., Riscassi, A., de Wit, H. A., Eklöf, K., Meng, B., … Zhu, W. (2020). Recent advances in understanding and measurement of mercury in the environment: Terrestrial Hg cycling. *Science of the Total Environment*, *721*. https://doi.org/10.1016/j.scitotenv.2020.137647

Blackburn, M., Ledesma, J. L. J., Näsholm, T., Laudon, H., & Sponseller, R. A. (2017). Evaluating hillslope and riparian contributions to dissolved nitrogen (N) export from a boreal forest catchment. *Journal of Geophysical Research: Biogeosciences*, *122*(2), 324–339. https://doi.org/10.1002/2016JG003535

Bradshaw, C. J. A., & Warkentin, I. G. (2015). Global estimates of boreal forest carbon stocks and flux. *Global and Planetary Change*, *128*, 24–30. https://doi.org/10.1016/j.gloplacha.2015.02.004

Buffam, I., Laudon, H., Temnerud, J., Mörth, C. M., & Bishop, K. (2007). Landscape-scale variability of acidity and dissolved organic carbon during spring flood in a boreal stream network. *Journal of Geophysical Research: Biogeosciences*, *112*(1), 1–11. https://doi.org/10.1029/2006JG000218

Burrows, R. M., Hotchkiss, E. R., Jonsson, M., Laudon, H., Mckie, B. G., & Sponseller, R. A. (2015). Nitrogen limitation of heterotrophic biofilms in boreal streams. *Freshwater Biology*, *60*(7), 1237–1251. https://doi.org/10.1111/fwb.12549

Burrows, R. M., Jonsson, M., Fältström, E., Andersson, J., & Sponseller, R. A. (2021). Interactive effects of light and nutrients on stream algal growth modified by forest management in boreal landscapes. *Forest Ecology and Management*, *492*(March). https://doi.org/10.1016/j.foreco.2021.119212

Clark, J. M., Bottrell, S. H., Evans, C. D., Monteith, D. T., Bartlett, R., Rose, R., … Chapman, P. J. (2010). The importance of the relationship between scale and process in understanding long-term DOC dynamics. *Science of the Total Environment*, *408*(13), 2768–2775. https://doi.org/10.1016/j.scitotenv.2010.02.046

Cloern, J. (2001). Our evolving conceptual model of the coastal eutrophication problem. *Marine Ecology Progress Series*, *210*, 223–253.

Conley, D. J., Paerl, H. W., Howarth, R. W., Boesch, D. F., Seitzinger, S. P., Havens, K. E., … Likens, G. E. (2009). Ecology - Controlling eutrophication: Nitrogen and phosphorus. *Science*, *323*(5917), 1014–1015. https://doi.org/10.1126/science.1167755

Creed, I. F., & Beall, F. D. (2009). Distributed topographic indicators for predicting nitrogen export from headwater catchments. *Water Resources Research*, *45*(10), 1–12. https://doi.org/10.1029/2008WR007285

Creed, I. F., Beall, F. D., Clair, T. A., Dillon, P. J., & Hesslein, R. H. (2008). Predicting export of dissolved organic carbon from forested catchments in glaciated landscapes with shallow soils. *Global Biogeochemical Cycles*, *22*(4). https://doi.org/10.1029/2008GB003294

Creed, Irena F., Bergström, A., Trick, C. G., Grimm, N. B., Hessen, D. O., Karlsson, J., … Weyhenmeyer, G. A. (2018). Global change-driven effects on dissolved organic matter composition: Implications for food webs of northern lakes. *Global Change Biology*, *24*(8), 3692–3714. https://doi.org/10.1111/gcb.14129

De Paolis, F., & Kukkonen, J. (1997). Binding of organic pollutants to humic and fulvic acids: Influence of pH and the structure of humic material. *Chemosphere*, *34*(8), 1693–1704. https://doi.org/10.1016/S0045-6535(97)00026-X

de Wit, H. A., Austnes, K., Hylen, G., & Dalsgaard, L. (2015). A carbon balance of Norway: terrestrial and aquatic carbon fluxes. *Biogeochemistry*, *123*(1–2), 147–173. https://doi.org/10.1007/s10533-014-0060-5

De Wit, H. A., Lepistö, A., Marttila, H., Wenng, H., Bechmann, M., Blicher-Mathiesen, G., … Rakovic, J. (2020). Land-use dominates climate controls on nitrogen and phosphorus export from managed and natural Nordic headwater catchments. *Hydrological Processes*, *34*(25), 4831–4850. https://doi.org/10.1002/hyp.13939

De Wit, H. A., Stoddard, J. L., Monteith, D. T., Sample, J. E., Austnes, K., Couture, S., … Evans, C. D. (2021). Cleaner air reveals growing influence of climate on dissolved organic carbon trends in northern headwaters. *Environmental Research Letters*, *16*(10). https://doi.org/10.1088/1748-9326/ac2526

De Wit, H. A., Valinia, S., Weyhenmeyer, G. A., Futter, M. N., Kortelainen, P., Austnes, K., … Vuorenmaa, J. (2016). Current Browning of Surface Waters

Will Be Further Promoted by Wetter Climate. *Environmental Science and Technology Letters*, *3*(12), 430–435. https://doi.org/10.1021/acs.estlett.6b00396

Deininger, A., Kaste, Ø., Frigstad, H., & Austnes, K. (2020). Organic nitrogen steadily increasing in Norwegian rivers draining to the Skagerrak coast. *Scientific Reports*, *10*(1), 18451. https://doi.org/10.1038/s41598-020-7553232-5

Deval, C., Brooks, E. S., Gravelle, J. A., Link, T. E., Dobre, M., & Elliot, W. J. (2021). Long-term response in nutrient load from commercial forest management operations in a mountainous watershed. *Forest Ecology and Management*, *494*(April), 119312. https://doi.org/10.1016/j.foreco.2021.119312

Dodds, W. K., Martí, E., Tank, J. L., Pontius, J., Hamilton, S. K., Grimm, N. B., … Gregory, S. (2004). Carbon and nitrogen stoichiometry and nitrogen cycling rates in streams. *Oecologia*, *140*(3), 458–467. https://doi.org/10.1007/s00442-004-1599-y

Ducharme, A. A., Casson, N. J., Higgins, S. N., & Friesen-Hughes, K. (2021). Hydrological and catchment controls on event-scale dissolved organic carbon dynamics in boreal headwater streams. *Hydrological Processes*, *35*(7), 1–12. https://doi.org/10.1002/hyp.14279

Duffy, C., O'Donoghue, C., Ryan, M., Kilcline, K., Upton, V., & Spillane, C. (2020). The impact of forestry as a land use on water quality outcomes: An integrated analysis. *Forest Policy and Economics*, *116*(May), 102185. https://doi.org/10.1016/j.forpol.2020.102185

Ebeling, P., Kumar, R., Weber, M., Knoll, L., Fleckenstein, J. H., & Musolff, A. (2021). Archetypes and Controls of Riverine Nutrient Export Across German Catchments. *Water Resources Research*, *57*(4), 1–29. https://doi.org/10.1029/2020WR028134

Eimers, M. C., Watmough, S. A., Paterson, A. M., Dillon, P. J., & Yao, H. (2009). Long-term declines in phosphorus export from forested catchments in south-central Ontario. *Canadian Journal of Fisheries and Aquatic Sciences*, *66*, 1682–1692. https://doi.org/10.1139/F09-101

Eklöf, K., von Brömssen, C., Amvrosiadi, N., Fölster, J., Wallin, M. B., & Bishop, K. (2021). Brownification on hold: What traditional analyses miss in extended surface water records. *Water Research*, *203*(August). https://doi.org/10.1016/j.watres.2021.117544

Elser, J., Bracken, M., Cleland, E., Gruner, D., Harpole, S., Hillebrand, H., … Smith, J. (2007). Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater , marine and terrestrial ecosystems. *Ecology Letters*, *10*, 1135–1142. https://doi.org/10.1111/j.1461-0248.2007.01113.x

Elser, J. J., Fagan, W. F., Denno, R. F., Dobberfuhl, D. R., Folarin, A., Huberty, A., … Sterner, R. W. (2000). Nutritional constraints in terrestrial and freshwater food webs. *Nature*, *408*(6812), 578–580. https://doi.org/10.1038/35046058

Esseen, P., Ehnström, B., Ericson, L., & Sjöberg, K. (1997). Boreal forests. *Ecological Bulletins*, (46), 16–47.

Evans, C. D., Monteith, D. T., & Cooper, D. M. (2005). Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environmental Pollution*, *137*(1), 55–71. https://doi.org/10.1016/j.envpol.2004.12.031

Evans, Chris D., Jones, T. G., Burden, A., Ostle, N., Zieliński, P., Cooper, M. D. A., … Freeman, C. (2012). Acidity controls on dissolved organic carbon mobility in organic soils. *Global Change Biology*, *18*(11), 3317–3331. https://doi.org/10.1111/j.1365-2486.2012.02794.x

Fork, M. L., Karlsson, J., & Sponseller, R. A. (2020). Dissolved organic matter regulates nutrient limitation and growth of benthic algae in northern lakes through interacting effects on nutrient and light availability. *Limnology and Oceanography Letters*, *5*(6), 417–424. https://doi.org/10.1002/lol2.10166

Fork, M. L., Sponseller, R. A., & Laudon, H. (2020). Changing Source-Transport Dynamics Drive Differential Browning Trends in a Boreal Stream Network. *Water Resources Research*, *56*(2). https://doi.org/10.1029/2019wr026336

Francoeur, S. N. (2001). Meta-analysis of lotic nutrient amendment experiments: detecting and quantifying subtle responses. *Journal of the North American Benthological Society*, *20*(3), 358–368. https://doi.org/10.2307/1468034

Gerber, S., & Brookshire, E. N. J. (2014). Scaling of Physical Constraints at the Root-Soil Interface to Macroscopic Patterns of Nutrient Retention in Ecosystems. *The American Naturalist*, *183*(3), 418–430. https://doi.org/10.1086/674907

Gleick, P. H., Singh, A., & Shi, H. (2001). Emerging Threats to the World's Freshwater Resources. A Report of the Pacific Institute for Studies in Development, Environment, and Security. In *Security* (Vol. 261). Oakland, California USA: Pacific Institute for Studies in Development, Environment, and Security.

Gwenzi, W., Chaukura, N., Noubactep, C., & Mukome, F. N. D. (2017). Biochar-based water treatment systems as a potential low-cost and sustainable technology for clean water provision. *Journal of Environmental Management*, *197*, 732–749. https://doi.org/10.1016/j.jenvman.2017.03.087

Hartikainen, H. (1979). Phosphorus and its reactions in terrestrial soils and lake sediments. *Journal of the Scientific Agricultural Society of Finland*, *51*(8), 537–624.

Hasselquist, E., Kuglerová, L., Sjögren, J., Hjältén, J., Ring, E., Sponseller, R. A., … Laudon, H. (2021). Moving towards multi-layered, mixed-species forests in riparian buffers will enhance their long-term function in boreal landscapes. *Forest Ecology and Management*, *493*(December 2020). https://doi.org/10.1016/j.foreco.2021.119254

Hasselquist, E. M., Mancheva, I., Eckerberg, K., & Laudon, H. (2020). Policy change implications for forest water protection in Sweden over the last 50 years. *Ambio*, *49*(7), 1341–1351. https://doi.org/10.1007/s13280-019-01274-y

Hirsch, R. M., Slack, J. R., & Smith, R. A. (1982). Techniques of trend analysis for monthly water quality data. *Water Resources Research*, *18*(1), 107–121. https://doi.org/10.1029/WR018i001p00107

Högberg, P., Näsholm, T., Franklin, O., & Högberg, M. N. (2017). Tamm Review: On the nature of the nitrogen limitation to plant growth in Fennoscandian boreal forests. *Forest Ecology and Management*, *403*, 161–185. https://doi.org/10.1016/j.foreco.2017.04.045

Hughes, A. O., & Quinn, J. M. (2019). The effect of forestry management activities on stream water quality within a headwater plantation Pinus radiata forest. *Forest Ecology and Management*, *439*(August 2018), 41–54. https://doi.org/10.1016/j.foreco.2019.02.035

Huser, B. J., Futter, M. N., Wang, R., & Fölster, J. (2018). Persistent and widespread long-term phosphorus declines in Boreal lakes in Sweden. *Science of The Total Environment*, *613–614*, 240–249. https://doi.org/10.1016/j.scitotenv.2017.09.067

Huser, B. J., & Rydin, E. (2005). Phosphorus inactivation by aluminum in Lakes Gårdsjön and Härsvatten sediment during the industrial acidification period in Sweden. *Canadian Journal of Fisheries and Aquatic Sciences*, *62*(8), 1702–1709. https://doi.org/10.1139/f05-083

Hynninen, A., Sarkkola, S., Laurén, A., Koivusalo, H., & Nieminen, M. (2011). Capacity of riparian buffer areas to reduce ammonium export originating from ditch network maintenance areas in peatlands drained for forestry. *Boreal Environment Research*, *16*(5), 430–440.

Ivanov, K. E. (1981). *Water movement in mirelands.* London, UK: Academic Press Inc. (London) Ltd.

Jutebring Sterte, E., Lidman, F., Lindborg, E., Sjöberg, Y., & Laudon, H. (2021). How catchment characteristics influence hydrological pathways and travel times in a boreal landscape. *Hydrology and Earth System Sciences*, *25*(4), 2133–2158. https://doi.org/10.5194/hess-25-2133-2021

Kaila, A., Asam, Z., Koskinen, M., Uusitalo, R., Smolander, A., Kiikkilä, O., … Nieminen, M. (2016). Impact of Re-wetting of Forestry-Drained Peatlands on Water Quality—a Laboratory Approach Assessing the Release of P, N, Fe, and Dissolved Organic Carbon. *Water, Air, and Soil Pollution*, *227*(8). https://doi.org/10.1007/s11270-016-2994-9

Kaila, A., Sarkkola, S., Laurén, A., Ukonmaanaho, L., Koivusalo, H., Xiao, L., … Nieminen, M. (2014). Phosphorus export from drained Scots pine mires after clear-felling and bioenergy harvesting. *Forest Ecology and Management*, *325*, 99–107. https://doi.org/10.1016/j.foreco.2014.03.025

Kakaei Lafdani, E., Laurén, A., Cvetkovic, J., Pumpanen, J., Saarela, T., & Palviainen, M. (2021). Nitrogen Recovery from Clear-Cut Forest Runoff Using Biochar: Adsorption–Desorption Dynamics Affected by Water Nitrogen Concentration. *Water, Air, and Soil Pollution*, *232*(10). https://doi.org/10.1007/s11270-021-05366-y

Kakaei Lafdani, E., Saarela, T., Laurén, A., Pumpanen, J., & Palviainen, M. (2020). Purification of forest clear-cut runoff water using biochar: A meso-scale laboratory column experiment. *Water (Switzerland)*, *12*(2). https://doi.org/10.3390/w12020478

Karlsen, R. H., Grabs, T., Bishop, K., Buffam, I., Laudon, H., & Seibert, J. (2016). Landscape controls on spatiotemporal discharge variability in a boreal catchment. *Water Resources Research*, *52*(8), 6541–6556. https://doi.org/10.1002/2016WR019186

Karlsen, R. H., Seibert, J., Grabs, T., Laudon, H., Blomkvist, P., & Bishop, K. (2016). The assumption of uniform specific discharge: unsafe at any time? *Hydrological Processes*, *30*(21), 3978–3988. https://doi.org/10.1002/hyp.10877

Kļaviņa, Z., Bārdule, A., Eklöf, K., Bitenieks, K., Kļaviņš, I., & Lībiete, Z. (2021). Carbon, nutrients and methylmercury in water from small catchments affected by various forest management operations. *Forests*, *12*(9), 1–18. https://doi.org/10.3390/f12091278

Koivusalo, H., Ahti, E., Laurén, A., Kokkonen, T., Karvonen, T., Nevalainen, R., & Finér, L. (2008). Impacts of ditch cleaning on hydrological processes in a drained peatland forest. *Hydrology and Earth System Sciences*, *12*(5), 1211–1227. https://doi.org/10.5194/hess-12-1211-2008

Koivusalo, H., Kokkonen, T., Laurén, A., Ahtiainen, M., Karvonen, T., Mannerkoski, H., … Finér, L. (2006). Parameterisation and application of a hillslope hydrological model to assess impacts of a forest clear-cutting on runoff generation. *Environmental Modelling and Software*, *21*(9), 1324–1339. https://doi.org/10.1016/j.envsoft.2005.04.020

Kozii, N., Haahti, K., Tor-Ngern, P., Chi, J., Maher Hasselquist, E., Laudon, H., … Hasselquist, N. J. (2020). Partitioning growing season water balance within a forested boreal catchment using sap flux, eddy covariance, and a process-based model. *Hydrology and Earth System Sciences*, *24*(6), 2999–3014. https://doi.org/10.5194/hess-24-2999-2020

Kreutzweiser, D. P., Hazlett, P. W., & Gunn, J. M. (2008). Logging impacts on the biogeochemistry of boreal forest soils and nutrient export to aquatic systems: A review. *Environmental Reviews*, *16*(NA), 157–179. https://doi.org/10.1139/A08-006

Kritzberg, E. S., Hasselquist, E. M., Škerlep, M., Löfgren, S., Olsson, O., Stadmark, J., … Laudon, H. (2020). Browning of freshwaters: Consequences to ecosystem services, underlying drivers, and potential mitigation measures. *Ambio*, *49*(2), 375–390. https://doi.org/10.1007/s13280-019-01227-5

Kuglerová, L., Hasselquist, E. M., Sponseller, R. A., Muotka, T., Hallsby, G., & Laudon, H. (2021). Multiple stressors in small streams in the forestry context of Fennoscandia: The effects in time and space. *Science of the Total Environment*, *756*. https://doi.org/10.1016/j.scitotenv.2020.143521

Kuglerová, L., Muotka, T., Chellaiah, D., Jyväsjärvi, J., & Richardson, J. S. (2024). Protecting our streams by defining measurable targets for riparian management in a forestry context. *Journal of Applied Ecology*, *61*(2), 206–214. https://doi.org/10.1111/1365-2664.14549

Laird, D., Fleming, P., Wang, B., Horton, R., & Karlen, D. (2010). Biochar impact on nutrient leaching from a Midwestern agricultural soil. *Geoderma*, *158*(3–4), 436–442. https://doi.org/10.1016/j.geoderma.2010.05.012

Laudon, H., Berggren, M., Ågren, A., Buffam, I., Bishop, K., Grabs, T., … Köhler, S. (2011). Patterns and Dynamics of Dissolved Organic Carbon (DOC) in Boreal Streams: The Role of Processes, Connectivity, and Scaling. *Ecosystems*, *14*(6), 880–893. https://doi.org/10.1007/s10021-011-9452-8

Laudon, H., & Hasselquist, E. (2023). Applying continuous-cover forestry on drained boreal peatlands; water regulation, biodiversity, climate benefits and remaining uncertainties. *Trees, Forests and People*, *11*(August 2022), 100363. https://doi.org/10.1016/j.tfp.2022.100363

Laudon, H., Hasselquist, E. M., Peichl, M., Lindgren, K., Sponseller, R., Lidman, F., … Ågren, A. M. (2021). Northern landscapes in transition: Evidence, approach and ways forward using the Krycklan Catchment Study. *Hydrological Processes*, *35*(4), 1–15. https://doi.org/10.1002/hyp.14170

Laudon, H., Lidberg, W., Sponseller, R. A., Maher Hasselquist, E., Westphal, F., Östlund, L., … Ågren, A. M. (2022). Emerging technology can guide ecosystem restoration for future water security. *Hydrological Processes*, *36*(10), 1–5. https://doi.org/10.1002/hyp.14729

Laudon, H., & Löfvenius, M. O. (2016). Adding snow to the picture – providing complementary winter precipitation data to the Krycklan Catchment Study database. *Hydrological Processes*, *30*(13), 2413–2416. https://doi.org/10.1002/hyp.10753

Laudon, H., Mosquera, V., Eklöf, K., Järveoja, J., Karimi, S., Krasnova, A., … Hasselquist, E. M. (2023). Consequences of rewetting and ditch cleaning on hydrology, water quality and greenhouse gas balance in a drained northern landscape. *Scientific Reports*, *13*(1), 20218. https://doi.org/10.1038/s41598-023-47528-4

Laudon, H., & Sponseller, R. A. (2018). How landscape organization and scale shape catchment hydrology and biogeochemistry: insights from a long-term catchment study. *Wiley Interdisciplinary Reviews: Water*, *5*(2). https://doi.org/10.1002/WAT2.1265

Laudon, H., Sponseller, R. A., & Bishop, K. (2021). From legacy effects of acid deposition in boreal streams to future environmental threats. *Environmental Research Letters*, *16*(1), 015007. https://doi.org/10.1088/1748-9326/abd064

Laudon, H., Sponseller, R. A., Lucas, R. W., Futter, M. N., Egnell, G., Bishop, K., … Högberg, P. (2011). Consequences of more intensive forestry for the sustainable management of forest soils and waters. *Forests*, *2*(1), 243–260. https://doi.org/10.3390/f2010243

Laudon, H., Taberman, I., Ågren, A., Futter, M., Ottosson-Löfvenius, M., & Bishop, K. (2013). The Krycklan Catchment Study - A flagship infrastructure for hydrology, biogeochemistry, and climate research in the boreal landscape. *Water Resources Research*, *49*(10), 7154–7158. https://doi.org/10.1002/wrcr.20520

Lavonen, E. E., Gonsior, M., Tranvik, L. J., Schmitt-Kopplin, P., & Köhler, S. J. (2013). Selective chlorination of natural organic matter: Identification of previously unknown disinfection byproducts. *Environmental Science and Technology*, *47*(5), 2264–2271. https://doi.org/10.1021/es304669p

Lawrence, G. B., & Roy, K. M. (2021). Ongoing increases in dissolved organic carbon are sustained by decreases in ionic strength rather than decreased acidity in waters recovering from acidic deposition. *Science of the Total Environment*, *766*, 142529. https://doi.org/10.1016/j.scitotenv.2020.142529

Ledesma, J. L. J., Futter, M. N., Blackburn, M., Lidman, F., Grabs, T., Sponseller, R. A., … Köhler, S. J. (2018). Towards an Improved Conceptualization of Riparian Zones in Boreal Forest Headwaters. *Ecosystems*, *21*(2), 297–315. https://doi.org/10.1007/s10021-017-0149-5

Ledesma, J. L. J., Futter, M. N., Laudon, H., Evans, C. D., & Köhler, S. J. (2016). Boreal forest riparian zones regulate stream sulfate and dissolved organic carbon. *Science of the Total Environment*, *560–561*, 110–122. https://doi.org/10.1016/j.scitotenv.2016.03.230

Lee, D. J., Cheng, Y. L., Wong, R. J., & Wang, X. D. (2018). Adsorption removal of natural organic matters in waters using biochar. *Bioresource Technology*, *260*(April), 413–416. https://doi.org/10.1016/j.biortech.2018.04.016

Lehmann, J., & Joseph, S. (2012). *Biochar for environmental management - science and technology*. MBG Book, UK.

Liljaniemi, P., Vuori, K. M., Tossavainen, T., Kotanen, J., Haapanen, M., Lepistö, A., & Kenttämies, K. (2003). Effectiveness of Constructed Overland Flow Areas in Decreasing Diffuse Pollution from Forest Drainages. *Environmental Management*, Vol. 32, pp. 602–613. https://doi.org/10.1007/s00267-003-2927-4

Loehle, C., Wigley, T. B., Lucier, A., Schilling, E., Danehy, R. J., & Ice, G. (2014). Toward improved water quality in forestry: Opportunities and challenges in a changing regulatory environment. *Journal of Forestry*, *112*(1), 41–47. https://doi.org/10.5849/jof.12-111

Lucas, R. W., Sponseller, R. A., Gundale, M. J., Stendahl, J., Fridman, J., Högberg, P., & Laudon, H. (2016). Long-term declines in stream and river inorganic nitrogen (N) export correspond to forest change. *Ecological Applications*, *26*(2), 545–556. https://doi.org/10.1890/14-2413

Maranger, R., Jones, S. E., & Cotner, J. B. (2018). Stoichiometry of carbon, nitrogen, and phosphorus through the freshwater pipe. *Limnology and Oceanography Letters*, *3*(3), 89–101. https://doi.org/10.1002/lol2.10080

Marchetto, A. (2017). *Mann-Kendall Test, Seasonal and Regional Kendall Tests* (p. 10). p. 10.

Mason, R. E., Craine, J. M., Lany, N. K., Jonard, M., Ollinger, S. V., Groffman, P. M., … Elmore, A. J. (2022). Evidence, causes, and consequences of declining nitrogen availability in terrestrial ecosystems. *Science*, *376*(6590). https://doi.org/10.1126/science.abh3767

Moatar, F., Abbott, B. W., Minaudo, C., Curie, F., & Pinay, G. (2017). Elemental properties, hydrology, and biology interact to shape concentration-discharge curves for carbon, nutrients, sediment, and major ions. *Water Resources Research*, *53*(2), 1270–1287. https://doi.org/10.1002/2016WR019635

Monteith, D. T., Stoddard, J. L., Evans, C. D., De Wit, H. A., Forsius, M., Høgåsen, T., … Vesely, J. (2007). Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature*, *450*(7169), 537–540. https://doi.org/10.1038/nature06316

Mosquera, V., Gundale, M. J., Palviainen, M., Laurén, A., Laudon, H., & Hasselquist, E. M. (2024). Biochar as a potential tool to mitigate nutrient exports from managed boreal forest: A laboratory and field experiment. *GCB Bioenergy*, *16*(3), 1–14. https://doi.org/10.1111/gcbb.13131

Mosquera, V., Hasselquist, E. M., Sponseller, R. A., & Laudon, H. (2022). Co-occurrence of browning and oligotrophication in a boreal stream network. *Limnology and Oceanography*, *67*(10), 2325–2339. https://doi.org/10.1002/lno.12205

Mulqueen, J. (1986). Hydrology and drainage of peatland. *Environmental Geology and Water Sciences*, *9*(1), 15–22. https://doi.org/10.1007/BF02439882

Musolff, A., Fleckenstein, J. H., Rao, P. S. C., & Jawitz, J. W. (2017). Emergent archetype patterns of coupled hydrologic and biogeochemical responses in catchments. *Geophysical Research Letters*, *44*(9), 4143–4151. https://doi.org/10.1002/2017GL072630

Musolff, Andreas, Schmidt, C., Selle, B., & Fleckenstein, J. H. (2015). Catchment controls on solute export. *Advances in Water Resources*, *86*, 133–146. https://doi.org/10.1016/j.advwatres.2015.09.026

Neff, J. C., Hobbie, S. E., & Vitousek, P. M. (2000). Nutrient and mineralogical control on dissolved organic C, N and P fluxes and stoichiometry in Hawaiian soils. *Biogeochemistry*, *51*(3), 283–302. https://doi.org/10.1023/A:1006414517212

Nieminen, M., Ahti, E., Nousiainen, H., Joensuu, S., & Vuollekoski, M. (2005). Capacity of riparian buffer zones to reduce sediment concentrations in discharge from peatlands drained for forestry. *Silva Fennica*, *39*(3), 331–339. https://doi.org/10.14214/sf.371

Nieminen, M., Palviainen, M., Sarkkola, S., Laurén, A., Marttila, H., & Finér, L. (2018). A synthesis of the impacts of ditch network maintenance on the quantity and quality of runoff from drained boreal peatland forests. *Ambio*, *47*(5), 523–534. https://doi.org/10.1007/s13280-017-0966-y

Nieminen, M., Piirainen, S., Sikström, U., Löfgren, S., Marttila, H., Sarkkola, S., … Finér, L. (2018). Ditch network maintenance in peat-dominated boreal forests: Review and analysis of water quality management options. *Ambio*, *47*(5), 535–545. https://doi.org/10.1007/s13280-018-1047-6

Nieminen, M., Sarkkola, S., & Laurén, A. (2017). Impacts of forest harvesting on nutrient, sediment and dissolved organic carbon exports from drained peatlands: A literature review, synthesis and suggestions for the future. *Forest Ecology and Management*, *392*, 13–20. https://doi.org/10.1016/j.foreco.2017.02.046

Nieminen, M., Sarkkola, S., Sallantaus, T., Hasselquist, E. M., & Laudon, H. (2021). Peatland drainage - a missing link behind increasing TOC concentrations in waters from high latitude forest catchments? *Science of the Total Environment*, *774*, 145150. https://doi.org/10.1016/j.scitotenv.2021.145150

Norstedt, G., Hasselquist, E. M., & Laudon, H. (2021). From haymaking to wood production: Past use of mires in northern sweden affect current ecosystem services and function. *Rural Landscapes*, *8*(1), 1–15. https://doi.org/10.16993/rl.70

Paavilainen, E., & Päivänen, J. (2013). *Peatland forestry: ecology and principles*. Springer Science & Business Media.

Päivänen, J., & Hånell, B. (2012). *Peatland ecology and forestry: a sound approach*. Department of Forest Ecology, University of Helsinki.

Palviainen, M., Aaltonen, H., Laurén, A., Köster, K., Berninger, F., Ojala, A., & Pumpanen, J. (2020). Biochar amendment increases tree growth in nutrient-poor, young Scots pine stands in Finland. *Forest Ecology and Management*, *474*(May), 118362. https://doi.org/10.1016/j.foreco.2020.118362

Peñuelas, J., Sardans, J., Rivas-Ubach, A., & Janssens, I. (2012). The human-induced imbalance between C , N and P in Earth ’ s life system. *Global Change Biology*, *18*, 3–6. https://doi.org/10.1111/j.1365-2486.2011.02568.x

Peralta-Tapia, A., Sponseller, R. A., Ågren, A., Tetzlaff, D., Soulsby, C., & Laudon, H. (2015). Scale-dependent groundwater contributions influence patterns of winter baseflow stream chemistry in boreal catchments. *Journal of Geophysical Research: Biogeosciences*, *120*(5), 847–858. https://doi.org/10.1002/2014JG002878

Pinheiro, J., Bates, D., DebRoy, S., Sarkar, D., & Heisterkamp, S. (2022). *nlme: Linear and Nonlinear Mixed Effects Models* (p. 338). p. 338. Retrieved from https://cran.r-project.org/package=nlme.

R Core Team. (2022). *R: A language and environment for statistical computing.* Retrieved from https://www.r-project.org/.

Richardson, J. S., Naiman, R. J., & Bisson, P. A. (2012). How did fixed-width buffers become standard practice for protecting freshwaters and their riparian areas from forest harvest practices? *Freshwater Science*, *31*(1), 232–238. https://doi.org/10.1899/11-031.1

Rodgers, M., O’Connor, M., Healy, M. G., O’Driscoll, C., Asam, Z. U. Z., Nieminen, M., … Xiao, L. (2010). Phosphorus release from forest harvesting on an upland blanket peat catchment. *Forest Ecology and Management*, *260*(12), 2241–2248. https://doi.org/10.1016/j.foreco.2010.09.037

Saarela, T., Kakaei Lafdani, E., Laurén, A., Pumpanen, J., & Palviainen, M. (2020). Biochar as adsorbent in purification of clear-cut forest runoff water: adsorption rate and adsorption capacity. *Biochar*, *2*(2), 227–237. https://doi.org/10.1007/s42773-020-00049-z

Sardans, J., Rivas-Ubach, A., & Peñuelas, J. (2012). The elemental stoichiometry of aquatic and terrestrial ecosystems and its relationships with organismic lifestyle and ecosystem structure and function: A review and perspectives. *Biogeochemistry*, *111*(1–3), 1–39. https://doi.org/10.1007/s10533-011-9640-9

Schelker, J., Eklöf, K., Bishop, K., & Laudon, H. (2012). Effects of forestry operations on dissolved organic carbon concentrations and export in boreal first-order streams. *Journal of Geophysical Research: Biogeosciences*, *117*(1), 1–12. https://doi.org/10.1029/2011JG001827

Schelker, J., Sponseller, R., Ring, E., Högbom, L., Löfgren, S., & Laudon, H. (2016). Nitrogen export from a boreal stream network following forest harvesting: seasonal nitrate removal and conservative export of organic forms. *Biogeosciences*, *13*(1), 1–12. https://doi.org/10.5194/bg-13-1-2016

Schindler, D. W. (1974). Eutrophication and recovery in experimental lakes: Implications for lake management. *Science*, *184*(4139), 897–899. https://doi.org/10.1126/science.184.4139.897

Shah, N. W., Baillie, B. R., Bishop, K., Ferraz, S., Högbom, L., & Nettles, J. (2022). The effects of forest management on water quality. *Forest Ecology and Management*, *522*(August). https://doi.org/10.1016/j.foreco.2022.120397

Shousha, S., Maranger, R., & Lapierre, J. F. (2021). Different forms of carbon, nitrogen, and phosphorus influence ecosystem stoichiometry in a north temperate river across seasons and land uses. *Limnology and Oceanography*, *66*(12), 4285–4298. https://doi.org/10.1002/lno.11960

Sikström, U., Jansson, G., & Pettersson, F. (2020). Growth responses of Pinus sylvestris and Picea abies after ditch cleaning–a survey in Sweden. *Scandinavian Journal of Forest Research*, *35*(1–2), 69–84. https://doi.org/10.1080/02827581.2019.1705891

Smith, V. H., Joye, S. B., & Howarth, R. W. (2006). Eutrophication of freshwater and marine ecosystems. *Limnology and Oceanography*, *51*(1 II), 351–355. https://doi.org/10.4319/lo.2006.51.1_part_2.0351

Smith, V. H., & Schindler, D. W. (2009). Eutrophication science: where do we go from here? *Trends in Ecology and Evolution*, *24*(4), 201–207. https://doi.org/10.1016/j.tree.2008.11.009

Sponseller, R. A., Blackburn, M., Nilsson, M. B., & Laudon, H. (2018). Headwater Mires Constitute a Major Source of Nitrogen (N) to Surface Waters in the Boreal Landscape. *Ecosystems*, *21*, 31–44. https://doi.org/10.1007/s10021-017-0133-0

Stetler, J. T., Knoll, L. B., Driscoll, C. T., & Rose, K. C. (2021). Lake browning generates a spatiotemporal mismatch between dissolved organic carbon and limiting nutrients. *Limnology and Oceanography Letters*, *6*(4), 182–191. https://doi.org/10.1002/lol2.10194

Stewart, B., Shanley, J. B., Kirchner, J. W., Norris, D., Adler, T., Bristol, C., … Li, L. (2022). Streams as Mirrors: Reading Subsurface Water Chemistry From Stream Chemistry. *Water Resources Research*, *58*(1), 1–20. https://doi.org/10.1029/2021WR029931

Teutschbein, C., Grabs, T., Laudon, H., Karlsen, R. H., & Bishop, K. (2018). Simulating streamflow in ungauged basins under a changing climate: The importance of landscape characteristics. *Journal of Hydrology*, *561*(December 2016), 160–178. https://doi.org/10.1016/j.jhydrol.2018.03.060

Teutschbein, C., Sponseller, R. A., Grabs, T., Blackburn, M., Boyer, E. W., Hytteborn, J. K., & Bishop, K. (2017). Future Riverine Inorganic Nitrogen Load to the Baltic Sea From Sweden: An Ensemble Approach to Assessing Climate Change Effects. *Global Biogeochemical Cycles*, 1–28. https://doi.org/10.1002/2016GB005598

Thompson, S. E., Basu, N. B., Lascurain, J., Aubeneau, A., & Rao, P. S. C. (2011). Relative dominance of hydrologic versus biogeochemical factors on solute export across impact gradients. *Water Resources Research*, *47*(7), 1–20. https://doi.org/10.1029/2010WR009605

Troch, P. A., Carrillo, G. A., Heidbüchel, I., Rajagopal, S., Switanek, M., Volkmann, T. H. M., & Yaeger, M. (2009). Dealing with landscape heterogeneity in watershed hydrology: A review of recent progress toward new hydrological theory. *Geography Compass*, *3*(1), 375–392. https://doi.org/10.1111/j.1749-8198.2008.00186.x

Väänänen, R., Nieminen, M., Vuollekoski, M., Nousiainen, H., Sallantaus, T., Tuittila, E. S., & Ilvesniemi, H. (2008). Retention of phosphorus in peatland buffer zones at six forested catchments in southern Finland. *Silva Fennica*, *42*(2), 211–231. https://doi.org/10.14214/sf.253

van Dorst, R. M., Gårdmark, A., Svanbäck, R., Beier, U., Weyhenmeyer, G. A., & Huss, M. (2019). Warmer and browner waters decrease fish biomass production. *Global Change Biology*, *25*(4), 1395–1408. https://doi.org/10.1111/gcb.14551

Vormoor, K., Lawrence, D., Heistermann, M., & Bronstert, A. (2015). Climate change impacts on the seasonality and generation processes of floods – Projections and uncertainties for catchments with mixed snowmelt/rainfall regimes. *Hydrology and Earth System Sciences*, *19*(2), 913–931. https://doi.org/10.5194/hess-19-913-2015

Wachholz, A., Dehaspe, J., Ebeling, P., Kumar, R., Musolff, A., Saavedra, F., … Graeber, D. (2023). Stoichiometry on the edge—humans induce strong imbalances of reactive C:N:P ratios in streams. *Environmental Research Letters*, *18*(4), 044016. https://doi.org/10.1088/1748-9326/acc3b1

Wickham, H. (2016). *ggplot: Elegant Graphics for Data Analysis (Version 3.4.2) [R package]*. Retrieved from https://cran.r-project.org/web/packages/ggplot2/index.html

Zannella, A., Eklöf, K., Lannergård, E., Laudon, H., Hasselquist, E., & Wallin, M. B. (2023). Metabolic processes control carbon dioxide dynamics in a boreal forest ditch affected by clear-cut forestry. *Frontiers in Water*, *5*. https://doi.org/10.3389/frwa.2023.1250068

Zimmer, M. A., Pellerin, B., Burns, D. A., & Petrochenkov, G. (2019). Temporal Variability in Nitrate-Discharge Relationships in Large Rivers as Revealed by High-Frequency Data. *Water Resources Research*, *55*(2), 973–989. https://doi.org/10.1029/2018WR023478

Photo: Joel Norén

8. Popular science summary

Carbon, nitrogen, and phosphorus are important nutrients in freshwater ecosystems. If there is too little, too much, or an imbalance of these nutrients, it can affect many ecological processes and the aquatic life in streams and lakes. These nutrients usually move from the land to streams, and this movement is controlled by how water can mobilize them from the soil as it flows through the catchment. In northern regions, climate change and past pollution are likely changing how these nutrients are use on land and flow into streams. While we already know that organic carbon dissolved in water (DOC) moves from the soil to streams during rain and snow melt, and that this levels of carbon are rising in many northern streams, mainly because of large-scale human activities, we do not know as much about N and P levels, the balance between C, N and P in streams, how these three elements move with changes in water flow, and how human activities affect all of these. In an attempt to better understand these interactions, I first looked at over ten years of data from 13 streams in a boreal catchment with different land uses, like mires or forests, but minimal human activity. I started by analyzing the relationship between concentrations of carbon, nitrogen, phosphorus and stream flow and found that organic and inorganic nutrients are mobilized differently when water flow increases. As shown in Figure 11, more organic carbon and nitrogen are carried into streams as the water flow increases, while inorganic nitrogen and phosphorus are diluted. I also found that the type of land cover affects this process, where areas with more mire cover dilutes inorganic nitrogen and phosphorus, while areas with more forest cover increases organic carbon and nitrogen in streams as the flow increases. These differences in how nutrients move with water flow can cause big changes in the balance of carbon, nitrogen and phosphorus in streams throughout the year. Because of this, in some seasons, streams can have too much carbon and not enough nitrogen and phosphorus, which could disturb the aquatic ecosystem.

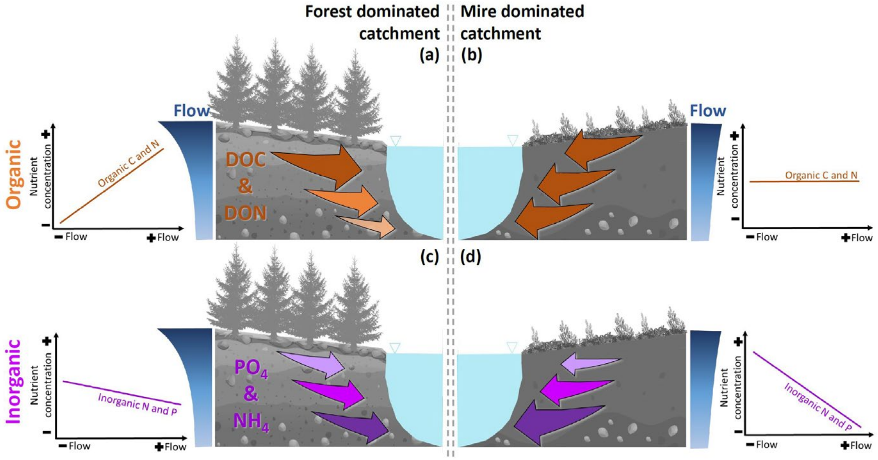

Figure 11. Illustration showing the main ways of how organic (a, b) and inorganic (c, d) nutrients move in catchments with lots of forest (a, c) and catchments influenced by mires (b, d).

In over ten years of data, I noticed that the connection between inorganic nutrients and water flow changed, suggesting that the levels of these nutrients might be changing over time. That is why in paper II, I investigated these changes, looking at not just inorganic nitrogen and phosphorus but also organic carbon and nitrogen, and how these levels vary by season. I found that the levels of inorganic phosphorus and nitrogen are dropping in streams, no matter the surrounding characteristics, as shown in the top illustration in Figure 12. The drop in inorganic nitrogen is most noticeable during the growing season, suggesting that plants and soil microbes are holding onto more nitrogen. On the other hand, the drop in inorganic P mainly happens in late autumn and winter, showing that significant biogeochemical changes occur outside the growing season too. So, as organic carbon levels in the water increase over time, streams are getting richer in carbon but poorer in nutrients, especially during critical seasons for aquatic organisms. If these trends continue in time the balance of aquatic life in streams and lakes could be disrupted.

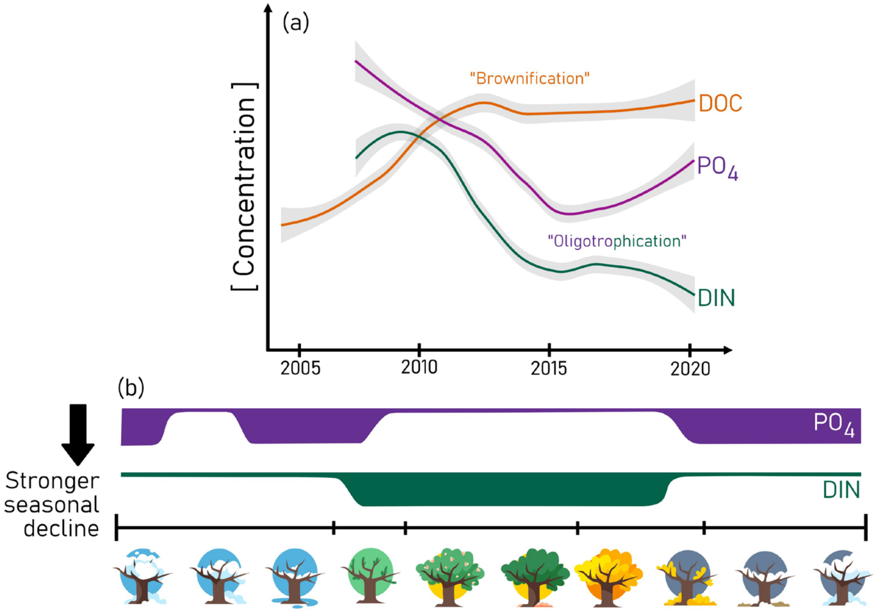

Figure 12. Trends of organic and inorganic nutrients. The upper illustration (a) shows the increase in time of levels of organic C dissolved in water and the decrease of inorganic N and P dissolved in water and in the lower illustration (b) shows the seasons when the decline is stronger.

To fully understand how carbon, nitrogen and phosphorus behave in northern streams, I needed to understand how human activities affect these nutrients. In boreal ecosystems, forest management is a major human activity that could alter carbon, nitrogen and phopshorus levels in streams because it is widespread and intensive. Therefore, I studied the forest operations that likely have the biggest impact on water quality in Sweden, including harvesting all trees and afterwards cleaning out old forest-ditches to be able to increase the success of replanting trees. I found that after harvesting the trees, the ground water levels increased and levels of carbon, nitrogen and phosphorus dissolved in the water went up. However, after ditches were cleaned out, ground water lowered and the levels of the organic carbon and nitrogen dissolved in the water went back to normal and inorganic nitrogen and phosphorus levels did not continue to increase. Even though cleaning the ditches helped reduce the impact of forest harvesting on nutrient levels, both the catchments with only harvest and the areas with harvest and cleaned ditches still had higher exports of both organic and inorganic nutrients than before, as explained in the illustration of Figure 13. This is why, I set up a small experiment in these areas to see if using biochar filters could help reduce this impact on water quality. I found that biochar filters do reduce nitrogen and carbon levels, but not phosphorus, in water coming from areas with forest operations. However, the reduction happens only when nitrogen and carbon levels are sufficiently high. Finally, I also found that it might be possible to return the nutrient enriched biochar to the catchments and help trees grow again.

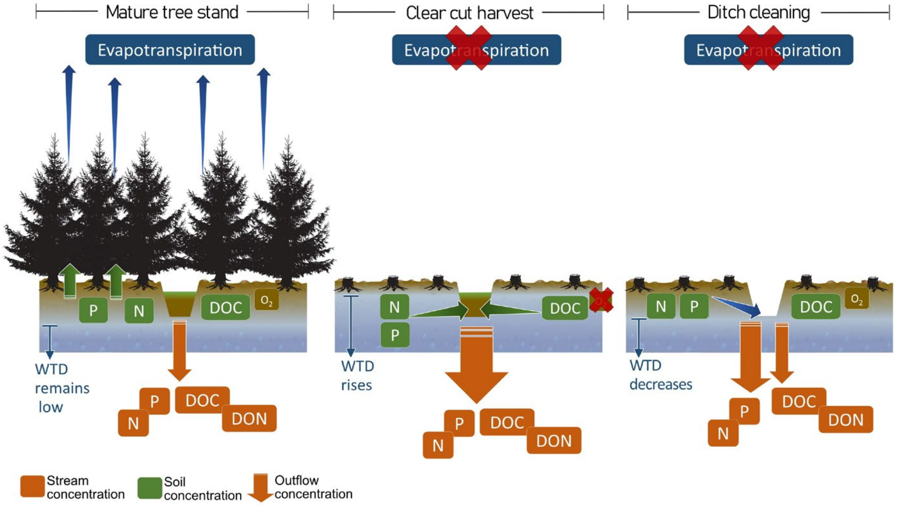

Figure 13. Summary of how C, N and P nutrient concentration exports change after sequential forest management operations typical of wet forests in Sweden.

9. Populärvetenskaplig sammanfattning

Kol (C), kväve (N) och fosfor (P) är viktiga näringsämnen i sötvattensekosystem. Om det finns för lite, för mycket eller en obalans av dessa näringsämnen kan det påverka många ekologiska processer och det akvatiska livet i sjöar och vattendrag. Dessa viktiga näringsämnen rör sig vanligtvis från land till bäck, ett flöde som styrs av hur vatten tar upp dem i marken och transporterar ut dem till närliggande vattendrag. I nordliga regioner kommer klimatförändringar och tidigare föroreningar sannolikt att förändra dynamiken i hur dessa näringsämnen tas upp och används på land och vad som blir över till vattendragen. Även om vi redan vet mycket om hur organiskt kol löst i vatten (DOC) rör sig från mark till vattendrag under regn och snösmältning, så är kunskapen inte lika stor om hur N- och P, eller balansen mellan C, N och P i vattendrag påverkas av mänskliga och naturliga processer. I ett försök att bättre förstå dessa interaktioner använde jag först över tio års data från 13 vattendrag i ett Västerbottniskt avrinningsområde med olika marktyper, som myr och/eller skog, men med liten pågående mänsklig aktivitet. Jag började med att analysera sambandet mellan koncentrationer av C, N och P och hydrologi och fann att organiska och oorganiska näringsämnen mobiliseras på olika sätt när vattenflödet ökar. Jag fann att mer organiskt C och N förs ut i bäckar när vattenflödet går upp, medan oorganiskt N och P späds ut. Jag fann också att marktypen påverkar dessa processer, där områden dominerade av myr späder ut oorganiskt N och P, medan skogbeklädda områden ledde till högre halter organiskt C och N i vattendrag när flödet ökade. Dessa skillnader i hur näringsämnen rör sig med vattenflödet kan orsaka stora förändringar i balansen mellan C, N och P i vattendrag under hela året och resulterar i att vissa årstider har mycket höga halter kol och inte tillräckligt med kväve och fosfor, vilket kan störa det akvatiska ekosystemet. Med mer än tio års data kunde jag också visa att sambandet mellan oorganiska näringsämnen och vattenflöde förändrades, vilket tyder på att nivåerna av näringsämnena kan förändras över tid. Jag undersökte dessa förändringar närmare, och fann att både oorganiskt kväve N och P, samt organiskt kol C och N, varierade under olika säsonger och att nivåerna av oorganiskt P och N minskade, oavsett omgivningens egenskaper. Minskningen av oorganiskt kväve är mest märkbar under växtsäsongen, vilket tyder på att växter och markmikrober tar hand om tillgängligt kväve. Och andra sidan minskade halterna oorganiskt P främst på senhösten och vintern, vilket tyder på betydande biogeokemiska förändringar även sker utanför växtsäsongen. Så när halterna av organiskt kol i vattnet ökar med tiden, blir vattendragen rikare på kol men fattigare på näringsämnen, särskilt under kritiska säsonger för vattenlevande organismer. Om dessa trender fortsätter kan balansen mellan vattenlevande liv i vattendrag och sjöar påverkas negativt.

Slutligen, för att helt förstå hur C, N och P beter sig i nordliga vattendrag, behövde jag förstå hur mänskliga aktiviteter påverkar dessa näringsämnen. I boreala ekosystem är skogsbruk en viktig aktivitet som kan förändra C-, N- och P-nivåerna i vattendrag eftersom de är så utbredda. Därför studerade jag de skogsskötselmetoder som sannolikt har störst påverkan på vattenkvaliteten i Sverige. Detta inkluderade slutavverkning av helt skogsbestånd, följt av dikesrensning av gamla skogsdiken med syfte att förbättra potentialen att lyckas med återplanteringen av nya skogsplantor. I mitt arbete fann jag att avverkningen ledde till stigande grundvattennivåer och ökande halter av C, N och P i vattendragen. Efter att diken rensats sjönk grundvattnet tillbaka och halterna av organiskt C och N i vattendragen återgick till de flesta fall till liknande nivåer som innan, eller slutade att stiga i andra fall. Även om rensningen av diken bidrog till att minska skogsavverkningens påverkan på näringshalterna, hade avrinningsområdena med enbart avverkning, och de med avverkning samt rensade diken fortfarande högre export av både organisk och oorganisk näring än tidigare. Av den anledningen satte jag upp ett experiment för att se om användningen av biokolfilter kunde bidra till att minska påverkan på vattenkvaliteten. Jag fann att kolfilterna minskade N- och C-nivåerna, men inte P-halterna, i vatten som kommer från områden med avverkning. Reduktionen skedde dock endast när N- och C-nivåerna var tillräckligt höga. Slutligen fann jag att det kan var möjligt att återföra den näringsberikade biokolen till avrinningsområdena och på så sätt återföra näringen till marken och få framtida träd att växa bättre.

Photo: Alejandro Gándara

Photo: Alejandro Gándara

10. Acknowledgment

A PhD represents a significant commitment with advancing knowledge in a particular field through rigorous and original research. It typically involves several years of hard work with multiple setbacks, it is a bumped road that needs perseverance and hard work. But above all, it is road that needs companionship, encouragement and support, it needs a tribe to get one of us to walk and fulfill the commitment. I was immensely lucky to have found the perfect tribe for my journey, Umeå, SLU and the FEM department has provided all that I needed, and for that, I am grateful.

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In the academic world, mobility is encouraged to broad our understanding and be able to see different perspective, however with this constant academic mobility comes the dreadful and wonderful reality of friends coming and going, and our support tribe to survive the PhD evolves constantly. Through my PhD I have had waves of friends with their own love and support that has been key actors in my PhD journey and have left a forever footprint in my heart. **Thanks to all!** However, special thanks and in chronological order to: In the welcoming wave, **Heli and Eduardo**, you two helped us survive the winter, without you two I am not sure we could have learn to enjoy the way we have our lives in Winterwonderland. **Anne and José**, our first neighbors, thanks for making us feel like home, with the morning coffees and the fresh baked cakes. **Lara and Joss**, your house(s) have been a refuge to several of us, thanks for always opening them to us. Later, in the second wave, came **Kishore**, our upstairs neighbor, whom became part of our family and allowed us to be part of his, your enthusiasm is contagious, it was a blast. **Stefan and Paul**, whose presence always makes it better, thanks for being there. **Karim**, your kind soul was comforting, even in the coldest days you always gave us warmth. And, **Ruth**, whom by chance has been my best support as an academia mom, our lives changed together and for that I am grateful forever. The third wave, the wave we are now riding, comes with unconditional friendship such as that given by **Barry**; sincere support given by **Francesco and Lin;** an everlasting positive perspective of life given by **Vincent** and some positive pressure from **Martha** to attend our swimming sessions that became the best way to blow off some pressure in the last stretch of the PhD. Finally, riding with me the constant going and coming of friends are my generation of PhDs and the core Krycklan crew. Specially, **Shirin**, I learned so much from you, I could not have asked for a better office mate. Honorable mention to **Ash** and **Mariana.** And, **Gosia**, you being stuck here with us has made our time better, happier, even easier. Let´s see who leaves first or at all. **Clydecia and Betty**, becoming a mom during the PhD journey is not an easy task, thank you for supporting me in both these journeys. **Viktor Böstrom, Johannes Tiwari, Joel and Meredith**, without you all, not only would I have not finished my PhD but I think I would not have survived field and lab work. And finally, thanks to all the FEM admin, but specially to **Ulf** for always answering all out hard and easy questions in such a good spirit and **Inger** for all the sincere conversations in the morning.

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Photo: Alejandro Gándara

JGR Biogeosciences

RESEARCH ARTICLE
10.1029/2022JG007179

Key Points:

- *c-Q* relationships differed between organic C and N (transport limited) and inorganic N and P (source limited) across boreal streams
- Catchment properties regulated variation in *c-Q* relationships among streams, regardless of solute, seasonal timing, and longer-term change
- Different *c-Q* relationships for organic and inorganic solutes drove shifts in the energy:nutrient stoichiometry of resource supply to streams

Supporting Information:

Supporting Information may be found in the online version of this article.

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Concentration-Discharge Patterns Reveal Catchment Controls Over the Stoichiometry of Carbon and Nutrient Supply to Boreal Streams

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Abstract Carbon (C), nitrogen (N), and phosphorus (P) export from catchments is strongly regulated by interactions between hydrological flowpaths and their terrestrial use/storage. While concentration-discharge (*c-Q*) relationships have been widely used to understand this interplay for C, N, and P individually, how flow regulates the relative supply of these resources across spatial and temporal scales is not well documented. Here, we analyze *c-Q* relationships from 12 years of data to test how seasonal flow regulates the concentrations of inorganic N (Dissolved inorganic nitrogen [DIN]) and P (Dissolved inorganic phosphorus [DIP]), dissolved organic N (DON) and C (dissolved organic carbon [DOC]) and their respective ratios across 12 streams in a boreal landscape. We observed opposing *c-Q* relationships between organic and inorganic solutes. DOC and DON tended toward transport limitation with little year-to-year change, whereas ammonium (NH_4) and DIP were increasingly source limited over time. These different *c-Q* relationships translated into large (up to three-fold) shifts in resource ratios (e.g., DOC:DIN) in response to changes in flow. Our results also highlight strong influences of catchment structure on *c-Q* patterns, regardless of solute, season, and longer-term directional changes. Here, the organic solute *c-Q* responses became less transport limited over time; while inorganic solute responses became less source limited with increasing mire/decreasing forest cover. Overall, differences in timing of catchment exports for C, N, and P, create dynamic variation in solute concentrations in streams with subsequent impacts on resource stoichiometry that is central to aquatic ecological processes.

Plain Language Summary Carbon (C), Nitrogen (N), and Phosphorus (P) are essential elements in freshwater ecosystems. Too little, too much, or an imbalance of these elements in waters can influence a wide range of ecological processes in streams and lakes. The movement of these resources from a given source area to the stream is controlled by the ability of water to mobilize them from soils as it flows through catchments. By analyzing the relationship between concentrations of C, N, and P and stream flow in a boreal catchment, we found that more *organic* C and N is exported as stream flow increases, while *inorganic* N and P are diluted. These relationships are modified by catchment characteristics, where greater proportion of mire cover dilutes *inorganic* N and P, whereas greater forest cover increases *organic* C and N in streams as flow increases. These individual relationships with flow lead to dramatic changes in the ratios between organic C and inorganic N and P supplied to streams throughout the year. Given the projections for climate-driven changes in precipitation, understanding controls over C, N, and P delivery to freshwater ecosystems is key to predict ecological effects and develop potential management responses.

1. Introduction

Carbon (C), nitrogen (N), and phosphorus (P) are essential limiting resources for growth and reproduction of all organisms in freshwater ecosystems. Seasonal variation in the supply and stoichiometry of these elements thus influences a wide range of ecological and biogeochemical processes in streams, rivers, and lakes (Sardans et al., 2012). The intra- and inter-annual variability in C, N, and P supply across land-water boundaries is in turn regulated by the capacity of hydrological transport mechanisms to mobilize dissolved forms in the face of biotic and abiotic processes that mediate their uptake or removal in soils or groundwater (e.g., Gerber & Brookshire, 2014). Consequently, understanding the variability and controls over C, N, and P exports from diverse catchments is central to predicting the water-quality consequences of changing environmental conditions,

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including increases in anthropogenic nutrient loading (e.g., Wachholz et al., 2023), various land management activities (Shousha et al., 2021), and ongoing climate change (e.g., Teutschbein et al., 2017).

In northern boreal landscapes, there is increasing evidence that catchment exports of C, N, and P to lakes and streams are changing in response to multiple environmental drivers (Deininger et al., 2020; De Wit et al., 2020; Fork et al., 2020). For example, dissolved organic carbon (DOC) concentrations in surface waters have increased throughout northern Europe and North America, as a result of recovery from acid deposition (Clark et al., 2010; Evans et al., 2012; Monteith et al., 2007), but also from changes in climate and land use (Kritzberg et al., 2020). At the same time, inorganic N and P appear to be declining, reflecting a reduction in atmospheric deposition but also tightening of biogeochemical cycles on land in response to climate warming and elevated CO_2 (Lucas et al., 2016; Mason et al., 2022) as well as emergent geochemical sinks (Huser & Rydin, 2005). Yet, despite progress toward understanding the mechanisms behind these longer-term trends, considerable uncertainty remains regarding short-term, hydrologically driven variation in the supply of these resources from soils and groundwater, which ultimately determines whether seasonal inputs of energy and nutrients align with biological demand in streams, rivers, and lakes.

Assessment of concentration-discharge (*c*-*Q*) relationships has emerged as a widely used approach to understand the interplay between catchment hydrology and biogeochemistry (Godsey et al., 2009). *c*-*Q* analysis yields classes of behaviors that describe whether solute concentrations in streams remain the same (i.e., are constant) or change as discharge increases (Moatar et al., 2017; Musolff et al., 2015). These behaviors reflect, in part, how different solutes are stored vertically in the subsurface, and thus whether rising water tables intersect soil strata with a greater, lesser, or equal capacity to mobilize a given solute, leading to increases, decreases, or no change in stream concentrations (Gómez-Gener et al., 2021; Stewart et al., 2022). While many studies have applied this framework to understand the dynamics of individual solutes, it may also be an effective tool for thinking about the stoichiometry of energy and nutrient supply (i.e., C:N:P) from catchments to streams (Gao et al., 2021). For example, pairs of resources that likely share similar storage patterns on land (e.g., organic C and N) should have a relatively constant supply ratio in response to changes in flow. By contrast, if resource pairs have opposing patterns of subsurface storage and/or production in the catchment, then the emergent ratio of supply is likely to be highly dynamic as discharge increases. In this way, the relative supply of elements that form the resource base of aquatic ecosystems at any one time could reflect the outcome of solute-specific patterns in hydrological mobilization that give rise to unique *c*-*Q* and thus ratio-*Q* relationships.

Given that *c*-*Q* relationships reflect how solutes are stored and mobilized on land, it is not surprising that the resulting metrics are also sensitive to the details of catchment structure, as well as to the temporal scales of assessment. For example, across northern boreal landscapes, we know that differences in forest, wetland, and lake cover can determine whether stream DOC is constant or dynamic with changes in flow, based on how these different patches store carbon and/or convey water (Ducharme et al., 2021; Fork et al., 2020; Laudon et al., 2011). By comparison, we know less about how the same factors influence *c*-*Q* relationships for different forms of N and P in these remote landscapes. For example, for inorganic N, strong demand by N-limited boreal forests should drive source limitation for ammonium (NH_4) and nitrate (NO_3) (e.g., Basu et al., 2010), but the potential for inorganic N production in organic-rich riparian soils might disconnect stream signals from the surrounding landscape (Blackburn et al., 2017). We know even less about *ratio-Q* relationships in northern boreal settings, but assuming that organic solutes are at least constant, if not transport limited (Thomas et al., 2016), and that inorganic solutes are potentially source limited (Bieroza et al., 2018), increases in discharge should be linked to periods of greater energy versus nutrient supply to aquatic systems. Finally, while most studies explore *c*-*Q* relationships at annual time scales, these relationships may also vary across seasons (Duncan et al., 2017; Gómez-Gener et al., 2021), or even across years in the response to changes in solute storage in the subsurface (Fork et al., 2020). In northern landscapes, seasonality may be pronounced given the powerful influence of the spring snowmelt followed by a rapid upregulation of biotic activity during the short, intense growing season. At even longer-time scales, it is unclear whether documented declines in inorganic nutrient concentrations (e.g., Mosquera et al., 2022) also correspond to changes in *c*-*Q* or ratio-*Q* relationships.

In this study, we ask (a) how the dynamics of C, N, and P supply to a boreal stream network are regulated by hydrology, (b) how catchment characteristics influence this supply, and (c) how *c*-*Q* and ratio-Q relationships vary at seasonal, annual, and decadal time scales. To answer these questions, we analyzed long-term water quality and discharge records (2008–2019) for 12 streams within the Krycklan Catchment Study (KCS) located in boreal

Sweden (Laudon et al., 2021). Specifically, we used different thresholds and metrics based on the *c-Q* and ratio-Q relationships to test whether DOC and organic and inorganic nutrients (NO_3, NH_4, DON, and PO_4), as well as key ratios (DOC:DON, DOC:DIN, DOC:PO_4, and DIN:PO_4) show contrasting responses due to differences in subsurface sources and dominating flow paths across sub-catchments and over the time-period. We then used regression approaches to explore how landscape characteristics such as topography, surficial geology, land use, and catchment size act as controls over these relationships.

2. Methods

2.1. Study Site

We conducted this study in the KCS, which has continuous hydrological measurements dating back to the early 1980s. The 68 km^2 KCS, is located in the boreal zone of northern Sweden (64°14′N, 19°46′E), approximately 60 km from the Baltic Sea coast and is composed of 14 monitored sub-catchments (Figure S1 in Supporting Information S1) ranging in size from 0.12 to over 19 km^2 (see Laudon et al. (2021, 2021)). Briefly, forest covers 87% of the KCS and is dominated by Scots Pine (*Pinus sylvestris*, 63% cover) found mostly on the dry uplands, Norway Spruce (*Picea abies*, 26%) in wetter low-lying areas, and relatively low cover of deciduous trees (∼10%), primarily birch (*Betula* spp.). Sub-catchments range from 100% forest cover to up to 44% of open peatlands, with two monitoring stations located in outlets of a S*phagnum*-dominated mire (acid, oligotrophic, and minerogenic mire; C4), and a small humic lake (C5) (Table S1 in Supporting Information S1). This landscape is underlain by quaternary deposits dominated by till soils (51%), that vary in thickness from a few centimeters to tens of meters, and sorted sediments (30%) (Laudon et al., 2021).

Mean annual air temperature at the KCS is 2.1°C (30 years mean, 1986–2015) with the highest mean monthly temperature in July and the lowest in January (+14.6 and −8.6°C, respectively; Kozii et al., 2020). The study site receives around 614 mm yr^{-1} of precipitation, which generates approximately 311 mm yr^{-1} of runoff. 35%–50% of this precipitation arrives as snow (Laudon et al., 2013), which maintains snow cover on average for 167 days, typically from late October to early May, but this duration has been declining at a rate of ∼0.5 days yr^{-1} since 1980 (Laudon & Löfvenius, 2016). The hydrologic regime is characterized by high flow during the spring snowmelt (April–May), which accounts for 40%–60% of annual discharge and represents the largest single hydrological event of the year. In addition, hydrologic inputs to KSC streams are dominated by shallow groundwater flowpaths (Bishop et al., 2004), although this can vary across the channel network. More specifically, in smaller sub-catchments, lateral subsurface flowpaths contribute ∼80% of stream baseflow due to a compact layer of basal till with substantially lower hydraulic conductivity (Jutebring Sterte et al., 2021). By comparison, for sub-catchments larger than 10 km^2 (i.e., C15 and the KCS outlet C16), deeper groundwater sources can contribute 70%–80% of surface water during baseflow periods (Peralta-Tapia et al., 2015).

This region is also subject multiple environmental changes (Laudon et al., 2021). Most importantly, mean annual temperature has increased by 2.5°C over the last 40 years, with the largest changes in the autumn and winter months. For the period of our study (2008–2020), mean annual temperature has a positive Sen slope of 0.02°C yr^{-1} ($p < 0.05$). Total annual average precipitation does not show significant trend over the last 40 years, and for our study period there is no evidence of directional changes in annual discharge (Mosquera et al., 2022). However, an extreme drought in the summer of 2018, which was considered the most severe in the last 250 years (Schuldt et al., 2020), had major transient consequences on stream chemistry (Tiwari et al., 2022). Finally, while inorganic N deposition at the KCS has been low historically, these rates have dropped from ca. 2.5 to 1.0 kg N ha y^{-1} between 1990 and 2020 (Laudon et al., 2021).

2.2. Data Collection and Analytical Methods

We compiled a combination of hydrological and biogeochemical data from 12 streams of the KCS regular monitoring program for the period of 2008–2019. Stream water levels were continuously measured using automatic stage loggers at all sites and discharge was estimated using site-specific rating curves. Rating curves were created from salt dilution velocity-area, and time-volume flow measurements covering most of the observed flow range (Karlsen et al., 2016a). Year round flow measurements were possible for six gauging stations in heated houses and discharge during winter periods for locations without frost-free gauging station was modeled according to established flow relationships (see Karlsen et al. (2016b) for further details on hydrological measurements in the KCS). For the same period and streams, data for DOC, total dissolved nitrogen (TDN), nitrate ($NO_3{}^-$), ammonium (NH_4), and phosphate or soluble reactive phosphorus (PO_4) was compiled, ranging from 262 to 311 observations per stream. For two of these 12 streams (C14 and C15), the monitoring program stopped in 2012, and thus included data from fewer years, or 144 and 133 observations, respectively (see Figure S2 in Supporting Information S1 for ranges of solute concentrations and discharge). The sampling regime is flow weighted, with more frequent sampling during spring flood (as frequently as twice per week), every 2 week sampling during the terrestrial growing season, and once per month sampling during winter base-flow.

All samples were collected in acid-washed high-density polyethylene bottles, stored in cold conditions and filtered (0.45 μm) in the lab within 24–72 hr. Filtered subsamples were frozen (−20°C) immediately after subsampling and stored for later analysis of NO_3-N, NH_4-N, and PO_4-P, samples for DOC and TDN were refrigerated (+4°C) and analyzed within 10 days after field collection. The analytical methods for DOC, TDN, NO_3^-, and $NH_4{}^+$ have been described in detail by Blackburn et al. (2017). Dissolved inorganic nitrogen (DIN) was calculated as the sum of NO_3 (including nitrite) and NH_4, while dissolved organic nitrogen (DON) was calculated as the difference between TDN and DIN. Dissolved inorganic phosphorus was analyzed as PO_4 on a Seal Analytical Autoanalyzer 3 HR using method G-297-03.

2.3. Data Analysis and Statistical Methods

We evaluated relationships between PO_4, NO_3, NH_4, DON, and DOC concentration and discharge (*c*-*Q*) on a yearly and seasonal basis by calculating the slope (β) of the log *c*-log specific *Q* using ordinary least squares (OLS) fit (Zimmer et al., 2019) and the ratio of the coefficients of variation between concentration and discharge (CV_c/CV_q) (Musolff et al., 2015). Hereafter, we refer to log *c*-log specific *Q* OLS as the "*c*-*Q* relationship" and CV_c/CV_q as the "*c*-*Q* ratio." The (log)*c*-(log)*Q* relationships was calculated as follows:

$$C = aQ^{\beta}$$

where C is concentration, a is a coefficient with units of concentration, Q is discharge, and β is a unit-less exponent representing the slope of the log-transformed *c*-*Q* relationship. Furthermore, the coefficient of variation is the standard deviation σ of a variable normalized by its mean μ (Thompson et al., 2011). The metric is the ratio as follows:

$$\frac{\mathrm{CV}_c}{\mathrm{CV}_Q} = \frac{\mu_Q}{\mu_c}\frac{\sigma_c}{\sigma_Q}$$

We classified *c*-*Q* relationships based on three responses from the slope (β) of the log *c*-log specific *Q* regression: (a) "up," classified as transport-limited (β is positive), (b) "down," classified as source-limited (β is negative), and (c) "flat," classified as constant ($\beta \approx 0$, Ducharme et al., 2021; Moatar et al., 2017; Musolff et al., 2017). Positive slopes ($\beta > 0$) occur when solute concentrations increase with discharge and this is described as transport-limited because delivery to the stream is dependent on the capacity of the catchment to move a solute and not by the availability or production of the solute. Negative slopes ($\beta < 0$) indicate a dilution of stream solute concentrations with increasing flow, and are described as source-limited because delivery to the stream is determined by the solute abundance rather than the ability of the catchment to transport them (Ducharme et al., 2021; Moatar et al., 2017; Zimmer et al., 2019). Finally, constant behavior indicates that changes in hydrological connectivity and flowpath do not affect the solute concentration in the stream and this is often attributed to homogenous and uniform distribution of elements in the catchment. Note that others have described this last pattern as "chemostatic" (e.g., Godsey et al., 2009), even in recent KCS studies (e.g., Fork et al., 2020; Gómez-Gener et al., 2021), but here we adopt newer terminology from Musolff et al. (2017) and use chemostatic to represent the export regimes rather than *c*-*Q* patterns (see below).

We considered the parameter β to be approximately 0, when β and r^2 values were low and the slope of the *c*-*Q* line was not significant ($p > 0.05$) (Ducharme et al., 2021). As an alternative to a classification based on fixed ranges (i.e., $\beta > 0.2$ or $\beta < -0.2$, Zimmer et al., 2019), we resolved *c*-*Q* behaviors based on significant differences in the slope β from zero (*t*-test, 95% confidence level) (Ebeling et al., 2021). Similarly, we defined a dilution response as β less than 0 and enrichment response as β above 0, but only when the relationship was significant ($p < 0.05$) and the r^2 was high (Zimmer et al., 2019). We further defined weak responses when *c*-*Q* relationship was significant ($p < 0.05$) but the r^2 was low (Bieroza et al., 2018; Ducharme et al., 2021). Finally, we used the ratio of the coefficients of variation between concentration and discharge (CV_C/CV_Q) to characterize whether export regimes are chemostatic or chemodynamic. Following Musolff et al. (2017), chemodynamic refers to solutes that vary strongly and independently from discharge ($CV_C/CV_Q > 0.5$), whereas chemostasis refers to situations where solute concentrations are less variable than discharge ($CV_C/CV_Q < 0.5$).

To explore how the relationship between DOC:DON, DOC:DIN, DOC:PO_4, and DIN:PO_4 stoichiometric ratios change with discharge (ratio-*Q*) we applied the same approach as the *c*-*Q* relationships (log ratio—log specific *Q*) (Gao et al., 2021), with calculated molar ratios. In this case, a positive/negative slope would indicate an increase/decrease of a ratio with an increase in discharge and this should occur whenever the two solutes in question have distinct flow responses. In contrast, constant response would indicate that a ratio does not change in response to flow because both solute change similarly with flow. We excluded left censored values (below detection limit) due to the low proportion of non-detects (USEPA, 2000), being <5% for PO_4, <2% for NH_4, and less <1% for NO_3. This small proportion of non-detects in our database is influenced by the low detection limits of the analytical method (0.4, 0.3, and 0.4 μg/L, respectively).

To test the controls over the organic and inorganic *c*-*Q* relationships, we first conducted a principal component analysis (PCA) of sub-catchment characteristics using the "vegan" package in R (Oksanen et al., 2019) with standardized parameters. The sub-catchment characteristics used in the PCA (Table S1 in Supporting Information S1) include those reported in Laudon et al. (2013), but also ditch density (km km^2) for each sub-catchment (Hasselquist et al., 2018). To assess the correlation between integrated catchment characteristics, specifically focusing in large-scale, landscape factors like mire versus forest cover (i.e., PC2 scores) and β for each stream, we used ordinary least-squared analysis (lm) with step procedure in R. Further, to assess monotonic trends in the annual β we performed a non-parametric Mann-Kendall test using the "rkt" package in R (Marchetto, 2017). Finally, to capture and illustrate the general nutrient concentration seasonal variability, a locally weighted scatterplot smoothing (loess) fitting curve was applied using the "ggplot" package in R (Wickham, 2016). Note that seasons were defined on the basis of local air temperature measured at the center of the KCS using World Meteorological Organization standards (Laudon et al., 2013). Accordingly, spring begins when average air temperature reaches above 0°C for five consecutive days and the maximum temperature is still below 20°C. Summer begins when the 5-day mean temperature rises above 10°C for 10 consecutive days. Autumn begins when the mean daily temperature fell below 10°C and the minimum temperature is below 0°C, and winter starts when daily mean temperature is below 0°C for five consecutive days. Finally, all the graphics of this study were produced using the R package "ggplot2" (Wickham, 2016). All statistical analyses, as well as graphics were conducted using the freely available software R (R Core Team, 2022).

3. Results

3.1. Intra-Annual Variation of Carbon and Nutrients Concentration and Ratios in Streams

Seasonal variability in stream concentrations were distinct between organic and inorganic solutes, but were nonetheless in phase across most streams (cf. "seasonal maximum and minimum" in Figures 1 and 2). DOC and DON concentrations tended to first peak during spring flood, between Julian days 100–130, and then again, reaching maximum values between days 220 (i.e., end of summer) and 270 (i.e., start of autumn). DOC and DON generally reached minimum values during winter, between days 20–90. For DON, annual minima were also observed in early spring (i.e., days 100–120) for some years and streams. Here, the stream draining the mire (C4) was an exception, with minimum DOC and DON concentrations observed during spring flood, between Julian days 110–135. By comparison, inorganic nutrients (PO_4, NH_4, and NO_3) typically reached annual maximum concentrations during winter, between days 20–100. For PO_4, the stream draining the mire (C4) was again an exception, with maximum values observed during summer, between days 170–240. Similarly, for NH_4, streams draining the mire (C4) and the lake (C5) reached maximum values either in late spring or in summer, respectively. Finally, PO_4 and NH_4 reached minimum values for all streams during spring, between days 110 and 160, whereas NO_3 concentrations were lowest from late spring (day 160) into summer (day 190); for some streams and years, low NO_3 concentrations were observed until mid-autumn (day 270).

These distinct seasonal patterns in concentrations underpinned strong seasonality in key resource ratios (Figure 2). For example, DOC:DIN ratios on average almost doubled from the lowest in winter to autumn, increasing from spring flood, throughout the summer, and peaking during autumn (Figure 2a). By comparison, DOC:PO_4 was

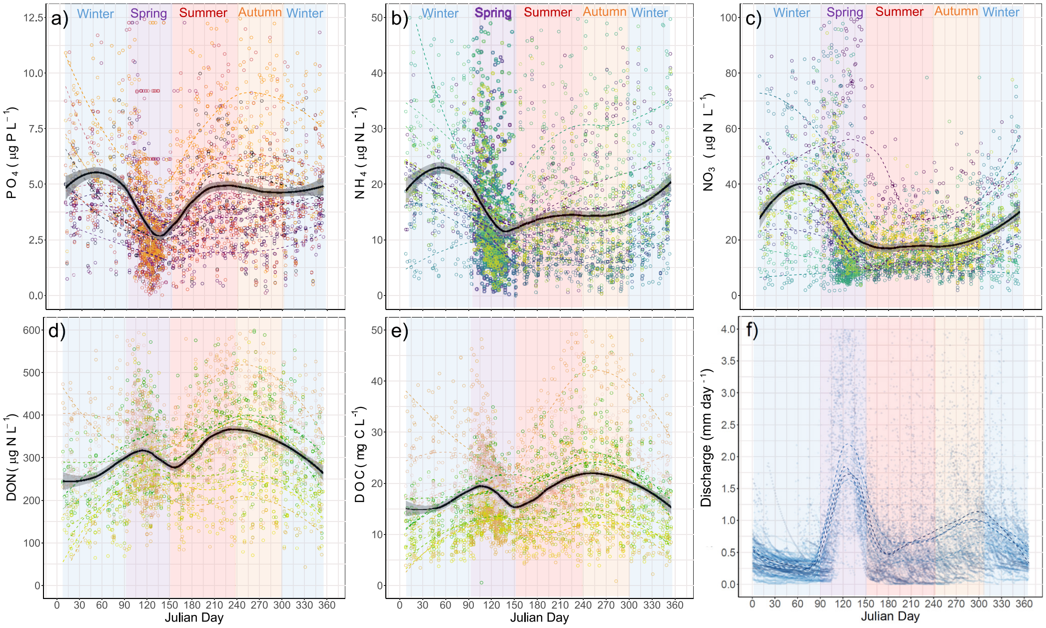

Figure 1. Intra-annual variability of organic and inorganic nutrients for the period 2008–2020 shown with locally weighted scatterplot smoothing (loess). (a) Phosphorus (P-PO_4), (b) ammonium (N-NH_4), (c) nitrate (N-NO_3), (d) dissolved organic nitrogen, (e) dissolved organic carbon, and (f) specific discharge for 12 headwater streams in the Krycklan Catchment Study. Colored circles represent each observation for each stream, dashed lines represent loess trend per stream, black line represent the overall temporal variability with ±SE shaded in gray. Background colors delimitates average seasons.

greatest following the spring flood, moderate throughout summer and autumn, and then dropped considerably during winter (Figure 2b). Again, the stream draining the mire (C4) was the exception for DOC:DIN and DOC:PO_4 seasonality, in that both ratios decreased during summer and peaked during autumn and early winter, respectively. The DIN:PO_4 ratio showed weaker seasonal patterns across catchments, but generally fell to the lowest levels during summer and autumn (on average ratios of 2.5 and 2.3, respectively, Figure 2c). Here, the KCS outlet (C16) was an exception, as the DIN:PO_4 ratio increased during early autumn reaching the highest ratio during winter. Finally, the ratio between organic C and N (DOC:DON) was remarkably constant throughout the year with only a small decrease in early summer (Figure 2d).

3.2. Inter-Annual Concentration/Ratios Versus Discharge Relationships and the Influence of Catchment Characteristics

Inter-annual *c*-*Q* relationships for organic C and N and inorganic P and N across catchments also showed opposing regimes (Figure 3a). The overall *c*-*Q* slopes for DOC and DON were significant and moderately positive ($p < 0.0001$; $\beta = +0.09$ and $+0.08$, respectively). For DOC, 58% of annual *c*-*Q* relationships across all streams and for each year indicated weak transport limitation, whereas 35% suggested a constant response; for DON, observations of constant response (47%) and weak transport limitation (46%) were essentially equal in frequency. By comparison, inter-annual slopes for PO_4 and NH_4 were characteristic of weak source limitation ($p < 0.0001$ and $\beta = -0.19$ and -0.13, respectively) while NO_3 had generally constant behavior ($p > 0.05$ and $\beta = 0.01$). More specifically, for PO_4, source limitation was observed for 67% of sites and years, whereas constant responses occurred 25% of the time. For NH_4, 39% of occurrences were classified as source limited and 28% as constant. Finally, for NO_3, constant responses occurred most of the time (68%). Furthermore, all solutes showed lower variability in C than in *Q*, such that the predominant solute export regime across this network was chemostatic ($CV_c/CV_q < 0.5$). Specifically, for DOC and DON, 99% and 96% of observations were chemostatic, respectively, while these values were slightly lower for PO_4 (88%), NH_4 (81%), and NO_3 (78%).

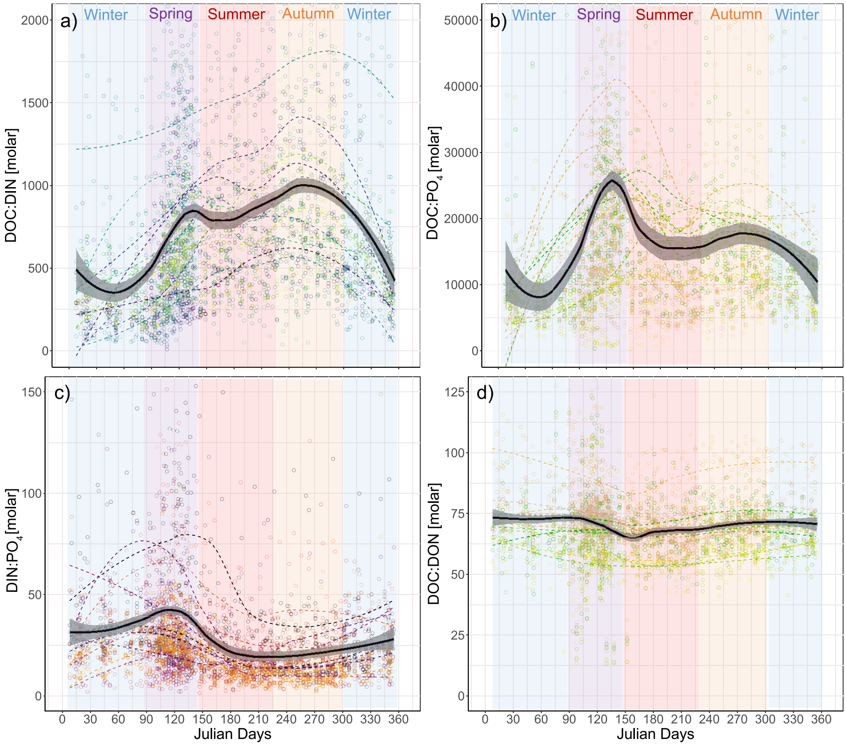

Figure 2. Intra-annual variability of nutrient ratios for the period 2008–2020 shown with locally weighted scatterplot smoothing (loess). (a) dissolved organic carbon (DOC):dissolved organic nitrogen, (b) DOC:Dissolved inorganic nitrogen (DIN), (c) DOC:PO$_4$, and (d) DIN:PO$_4$ for 12 headwater streams in the Krycklan Catchment Study. Colored circles represent individual observations for each stream, dashed lines represent loess trend per stream, and the black line represents the overall temporal variability with ±SE shaded in gray. Background colors delimitates average seasons.

The average slopes incorporated considerable variability in *c*-*Q* behavior across the 12 sub-catchments (Figure 3a, Tables S2 and S3 in Supporting Information S1). For example, DON and DOC showed generally similar regimes across sites and years, with average slopes ranging from -0.15 ($p < 0.05$, non-zero β) to $+0.34$ ($p < 0.05$) for DON and from -0.14 ($p < 0.05$) to $+0.33$ ($p < 0.05$) for DOC. For both solutes, the lake outlet (C5) showed the weakest and the catchment outlet (C16) the strongest degree of transport limitation (Table S3 in Supporting Information S1). Only the stream draining the mire (C4) showed persistent source limitation (-0.14 and -0.15 for DOC and DON, respectively). By comparison, this variation across streams was greater for PO$_4$, with *c*-*Q* slopes ranging from -0.45 ($p < 0.05$) to $+0.07$ ($p < 0.05$), similar to NH$_4$, which ranged from -0.47 ($p < 0.05$) to $+0.10$ ($p < 0.05$). For both solutes, the mire outlet (C4) showed the strongest source limitation, whereas the KCS catchment outlet (C16) the most constant behavior (Table S2 in Supporting Information S1). Finally, although the general *c*-*Q* relationship for NO$_3$ was constant, site C10 and C1 showed weak source and transport limitation, ranging on average from -0.3 ($p > 0.05$) to $+0.16$, respectively.

Inter-annual ratio-*Q* relationships also varied among resource combinations and for some sites (Figure 3b, Table S4 in Supporting Information S1). For example, DOC:DON, was relatively invariant with discharge across most catchments, ($p < 0.05$ and $\beta = 0.0$). By comparison, DOC:PO$_4$ ratios increased with discharge ($p < 0.05$ and $\beta = +0.25$) in all sub-catchments, whereas DOC:DIN and DIN:PO$_4$ showed a weak increase with discharge ($p < 0.05$ and $\beta = +0.11$ and $+0.16$, respectively). However, DOC:DIN ratios for the forested catchments (C1 and C2) and DIN:PO$_4$ ratios for the lake outlet (C5) and the KCS catchment outlet (C16) were primarily constant.

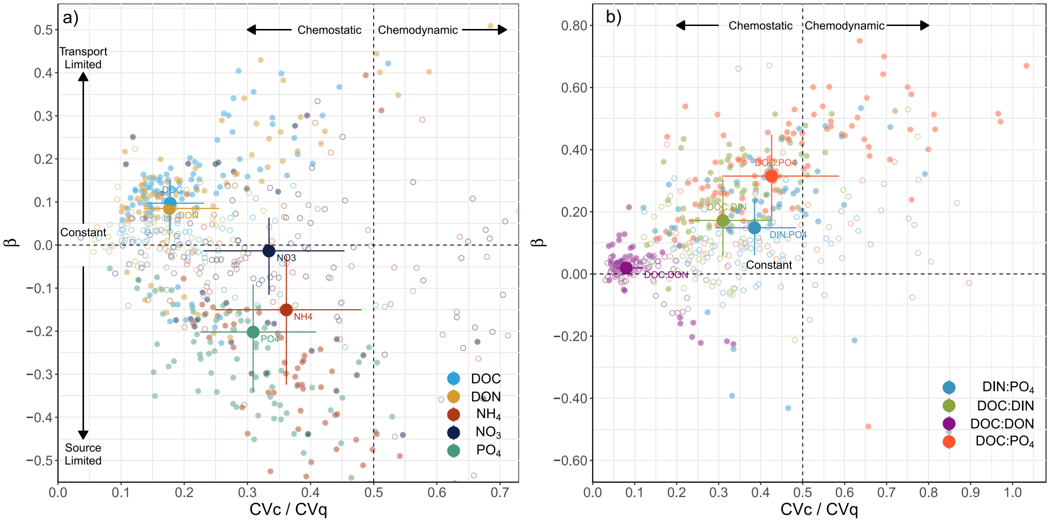

Figure 3. Slope of the linear regression relationship (*β*) of concentration and ratio versus the coefficient of variation (CV) of concentration divided by the CV of discharge. (a) Slope of the linear log(concentration)-log(discharge) relationships (*β*) of PO_4, NH_4, NO_3, dissolved organic nitrogen (DON), and dissolved organic carbon (DOC) and (b) slope of the linear log(ratio)-log(discharge) relationships (*β*) of DON:DON, DOC:Dissolved inorganic nitrogen (DIN), DOC:PO_4, and DIN:PO_4. Points are colored by (a) solute or (b) ratio and show *c*-*Q* relationships for each site and year. Hollow points represent non-significant *c*-*Q* or ratio-*Q* relationships ($p > 0.05$). The larger points represent the median for each group. Error bars represent the interquartile range.

To evaluate the effect of catchment characteristics (Table S1 in Supporting Information S1) on the average annual *c*-*Q* slopes, we used regression to relate the slopes for each site to catchment structure represented by a PCA (Figure 4). PCA metrics explained 38% of the variation on axis 1% and 28% of the variation on axis 2 (Figure 4c). PCA1 largely represents variation tree volume (m^3 ha^{-1}); stand age (year), ditch density (km km^2) and quaternary deposits made up of till (%), whereas PCA2 was associated with large-scale, landscape factors like mire versus forest cover. We did not observe a correlation between any solute *c*-*Q* slope and PCA1 ($p > 0.05$, Figure S3 in Supporting Information S1), nor was NO_3 correlated with any integrated catchment characteristic (Figure 4f). However, DON, DOC, PO_4, and NH_4 were all positively correlated ($p < 0.05$) with PCA2 (Figures 4a, 4b, 4d, and 4e, respectively). In this case, the organic solute *c*-*Q* responses became less constant, while inorganic solute responses became more constant along this axis of catchment properties. Specifically, for DOC and DON, *c*-*Q* slopes from sub-catchments with less mire cover, more sorted sediment, larger area and longer channel lengths, indicated transport limitation (i.e., positive *β* in Figures 4a and 4b, respectively). For PO_4 and NH_4, these same sub-catchments had a constant response. In contrast, for PO_4 and NH_4, sub-catchments with more mire cover, smaller area and shorter river lengths, showed a source limited behavior (i.e., negative *β* in Figures 4d and 4e, respectively), while for DOC and DON these same sub-catchments had a constant response. Finally, unlike the analyses with individual solutes, we did not observe any relationship between catchment characteristics and ratio-*Q* relationships ($p > 0.05$) for any of the ratios analyzed (i.e., DOC:DON, DOC:DIN, DOC:PO_4, and DIN:PO_4). Yet, for DOC:DIN ratio-*Q* slopes, we did find that the forested catchments (C1 and C2) had a constant response while these ratios for the mire (C4) and lake (C5) outlet increased with discharge.

3.3. Seasonal Variability in *c*-*Q* Relationships

Within seasons, we observed a broader set of hydrological responses for the dynamic solutes, especially for the inorganic nutrients (Figure 5), when compared to annual assessments. Specifically, DOC and DON showed only subtle variation in the average *c*-*Q* behavior between seasons, including a shift between weak transport limitation to a constant pattern during spring ($p > 0.05$, $\beta = 0.06$). Across sub-catchments (Tables S2 and S3 in Supporting Information S1), we observed constant behavior during spring in 50% of the sites for DON but only on 25%

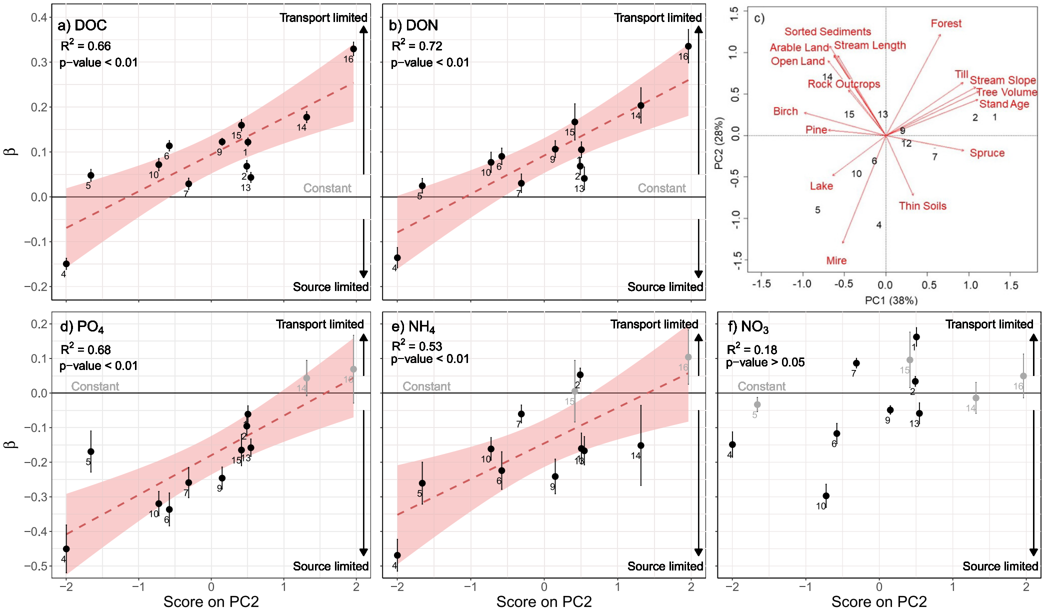

Figure 4. Relationship between principal component analysis (PCA) scores of catchment characteristics and *c*-*Q* relationships (β); streams with significant β ($p < 0.05$) are shown in black circles, non-significant ($p > 0.05$) in light gray, (overall inter-annual ±1 SE β for a given stream). Linear regression of PCA2 versus (a) dissolved organic carbon β, (b) dissolved organic nitrogen β, (d) PO_4 β,(e) NH_4 β, and (f) NO_3 β and (c) PCA of catchment characteristics for Krycklan Catchment Study. In panel (b–e), red dotted line is the significant linear regression with ±1 SE (in light red). The numbers shown are the ID for each stream; the full description of catchment characteristics is given in Table S1 in Supporting Information S1.

of sites for DOC. For both solutes, the majority of sub-catchments showed weak-to-strong transport limitation during winter, summer, and autumn (83%, 100%, and 92%, respectively for DON, and 92%, 100%, and 92% respectively for DOC). For PO_4, the majority (73%) of sub-catchments showed source limitation during summer; however, for autumn and spring the percentage was lower (45% and 50%, respectively) and concentrations were often constant in winter. For NH_4, the majority (82%) of sub-catchments showed source limitation during winter, while for spring and summer this was only 45%, with the remainder showing constant behavior. For NO_3, during summer and autumn, the majority of sub-catchments showed a constant behavior (75% and 58%, respectively), but both transport and source limitation were observed during winter. Analysis of these seasonal *c*-*Q* relationships with land cover suggest that such relationships change throughout the year, particularly for inorganic solutes (Figure S4 in Supporting Information S1). Specifically, for PO_4, summer and autumn *c*-*Q* slopes are not statistically correlated ($p > 0.05$) with any integrated catchment characteristics, neither were the *c*-*Q* slopes for NH_4 during winter. Conversely, all seasonal *c*-*Q* slopes of DON and DOC were correlated with PCA2, being stronger during spring and weaker during summer (Figure S4 in Supporting Information S1). Finally, and in contrast to our inter-annual assessment above, export regimes for inorganic nutrient were more commonly chemodynamic ($CV_c/CV_q > 0.5$) when assessed as at the seasonal scale, particularly so for NH_4, but also for PO_4 and NO_3 during spring.

3.4. Trends in *c*-*Q* Relationships Over Time

c-*Q* slopes in the KCS have tended to become more source limited over time for inorganic solutes (i.e., PO_4 and NH_4). Mann Kendall trend analysis showed a negative Sen slope for *c*-*Q* slopes in 11 out of 12 streams for NH_4 and 10 out of 12 streams for PO_4; however this trend was not statistically significant ($p > 0.05$) for most streams (Table S5 in Supporting Information S1), largely due to a change in solute dynamics after 2017. As an example, for the forest-dominated headwaters (C2 and C1), the PO_4 and NH_4 (Figures S5a and S5c in Supporting

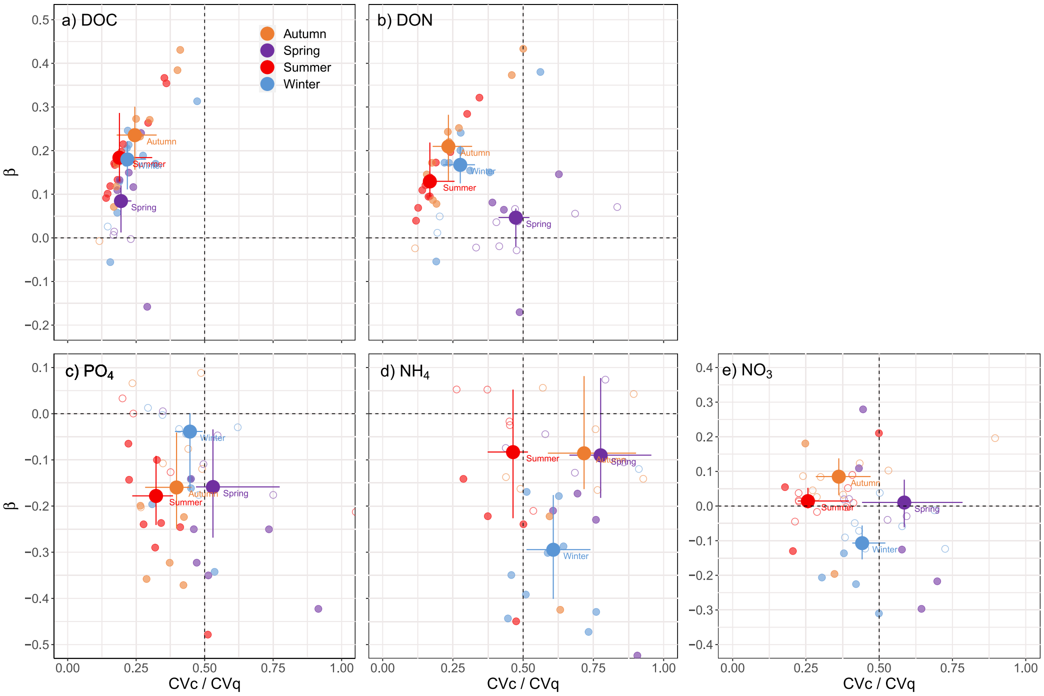

Figure 5. Slope of the linear log(concentration)-log(discharge) relationships (β) versus the coefficient of variation for (a) dissolved organic carbon, (b) dissolved organic nitrogen, (c)PO_4, (d) NH_4, and (e) NO_3 for winter, spring, summer, and autumn. Points are colored by season and show *c*-*Q* relationships for each stream. Hollow points represent non-significant *c*-*Q* relationships ($p > 0.05$). The larger points represent the median for each group and their error bars represent the interquartile range. The horizontal black hashed line shows the limit between positive and negative β, while the vertical line shows the limit to independence of solute export to flow. Note that the scales for the *y*-axes show different magnitudes of slopes.

Information S1) annual *c*-*Q* relationship slope changed from constant (−0.01 and +0.06, $p > 0.05$, respectively) to source limited (−0.22 and −0.38, $p < 0.05$, respectively) over time, but returned to a more constant state during and after the 2018 drought (−0.05 and −0.16, $p < 0.05$, respectively). The mire-dominated headwater (C4) showed the same trend for PO_4 and NH_4, with increasing source limitation over time (−0.17 to −0.76, $p < 0.05$ and −0.32 to −0.6, $p < 0.05$, respectively), until these slopes changed in 2018 (−0.34 to −0.54, $p < 0.05$, respectively) (Figures S5b and S5d in Supporting Information S1). Together, the percentage of sub-catchments in the KCS showing different *c*-*Q* behaviors also changed over time (Figure 6). For example, for PO_4, only 20% of the sub-catchments showed source limitation at the start of the record, but this reached 92% by 2016 and was 66% by the end of the period. Likewise, for NH_4, only 10% of the sub-catchments showed source limitation at the start of the period; by 2016 this reached 75%, and by the end of the period, 58% of sites had negative *c*-*Q* slopes. Despite these changes over time, both for PO_4 and NH_4, the relationship between *c*-*Q* slopes and catchment characteristics remained qualitatively unchanged and significant ($p < 0.05$) across all years, except for 2009 and 2016–2017 for PO_4 and NH_4, respectively (Figure S6 in Supporting Information S1). Only the intercepts of these regression lines showed variance over time, decreasing as a result of overall, longer-term declines nutrient concentrations across this landscape.

In contrast to NH_4 and PO_4, changes in the *c*-*Q* slope over time for NO_3 were not as widespread, with significant trends ($p < 0.05$) in only three of 12 streams (Table S5 in Supporting Information S1). Specifically, two mire-dominated catchments (C4 and C10) and the outlet of the lake (C5), shifted between transport limitation in 2008 to source limitation by the end of the period ($p < 0.05$). Similarly, DOC and DON showed no trends in the slopes of *c*-*Q* relationships during this time-period at most streams, the only exception being the lake outlet (C5)

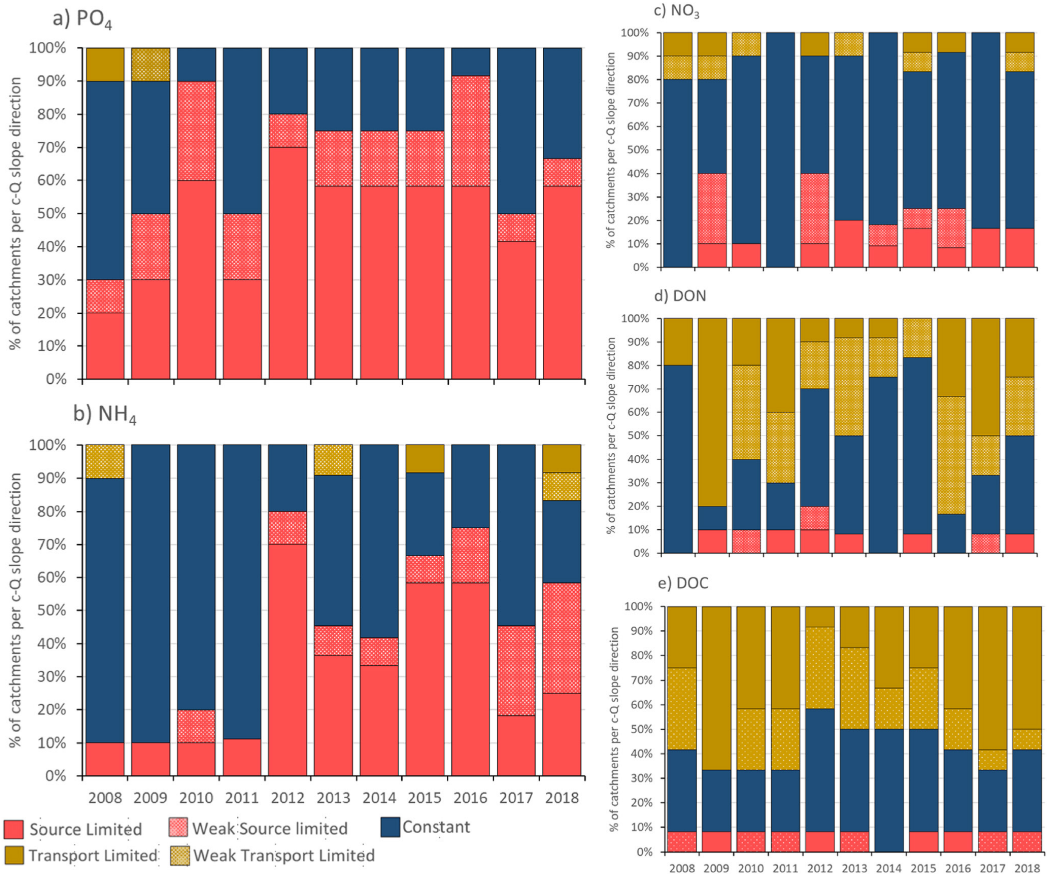

Figure 6. Percentage of sub-catchments *c-Q* archetypes for the following solutes: (a) PO$_4$ and (b) NH$_4$ responses across the study period (2008–2018). Constant pattern is presented in blue, transport limited (positive slope) in yellow, weak transport limited (positive slope with low r^2) in dotted yellow, source limited (negative slope) in pink and weak source limited (negative slope with low r^2) in dotted pink.

that showed a positive trend (Table S5 in Supporting Information S1). Similarly, the percentage of sub-catchments categorized by different *c-Q* relationship regimes did not shift over time for DOC and DON (Figure 6). Finally, DOC:DON and DIN:PO$_4$ ratios did not show any decadal-scale trends in the slopes of ratio-*Q* relationships for any streams during this time period. Intra-annual patterns in the relationship between discharge and DOC:DIN and DOC:PO$_4$ were generally subtle and similar across sub-catchments, except for C4 (mire outlet) and C5 (lake outlet), which changed from a constant response to positive relationships by the end of the period. This same change for DOC:PO$_4$ was also observed for the catchment outlet (C16).

4. Discussion

Understanding the nature of hydrological controls over C, N, and P export in northern boreal landscapes is critical for projecting nutrient losses from catchments to receiving waters in the face of environmental change. Here, we classified *c-Q* relationships from low-frequency concentration data to provide insight into organic and inorganic resource supply to streams with different catchment characteristics but limited direct anthropogenic influences. At inter-annual time scales, export regimes across the KCS were predominately chemostatic for all solutes, yet *c*-*Q* relationships were often opposing: organic C and N tended toward transport limitation, whereas inorganic P and N were more often source limited. Further, for nearly all solutes considered, variability in *c*-*Q* relationships across streams could be predicted from relatively simple catchment properties (Figure 4). Yet, at seasonal time scales, we observed an even broader set of hydrological responses for the non-constant solutes, and *c*-*Q* relationships for inorganic nutrients over time suggest that source limitation is intensifying as a result of oligotrophication during this period of record (Mosquera et al., 2022). Collectively, shifts in the timing of catchment exports, together with distinct *c*-*Q* relationships for C, N, and P, create dynamic temporal variation in the stoichiometry of these resources in streams, which may in turn influence a range of ecological and biogeochemical processes (Elser et al., 2007; Francoeur, 2001; Peñuelas et al., 2012).

4.1. Inter-Annual *c*-*Q* Dynamics for Individual Solutes

Consistent with the idea that organic and inorganic solutes have distinct vertical patterns of storage in the soils and groundwater (Stewart et al., 2022), organic and inorganic nutrients were differently mobilized by increases in discharge, showing opposing annual *c*-*Q* relationships at most streams. Specifically, DON and DOC in streams were often enriched at high flows, ostensibly because their concentrations and the degree of soil hydrological conductivity are highest near the soil surface where soil organic matter storage is greatest (Bishop et al., 2004). Thus, the activation of these strata with increasing discharge mobilizes large amounts of dissolved organic material (Ledesma et al., 2018). By contrast, NH_4 and PO_4 are unlikely to accumulate in surficial, organic soils, where both microbial and plant demand are highest. Instead, these solutes are more likely to increase in concentration with depth: for PO_4 as a consequence of proximity to mineral P sources (Ebeling et al., 2021) and for NH_4 as a consequence of low redox conditions in riparian soils and groundwater that constrain nitrification and promote accumulation of reduced N (Blackburn et al., 2017). Regardless of the mechanism, and as may be expected for a nutrient-poor landscape (Thompson et al., 2011), mobilization of inorganic N and P from biologically active surface soils typically cannot keep pace with hydrologic flushing as water tables rise, leading to dilution of these solutes in streams. Of course, dilution of inorganic N and P is not universal, and many studies show transport limitation of these elements, particularly in agricultural landscapes (e.g., Moatar et al., 2017), but also in less-pristine forested landscapes where anthropogenic inputs create larger and mobilizable pools in surface soils (Rose et al., 2018). Yet, for much of the global north, rates of external nutrient inputs to forests are low (e.g., Gundale et al., 2011), and thus the opposing controls over organic versus inorganic solute supply reported here are likely widespread.

Compared to other solutes, stream NO_3 dynamics for most sites and years were unique in showing little to no relationship with hydrology ($\beta = 0$). This lack of clear pattern could be attributed to low NO_3 concentrations throughout the subsurface vertical profile (Blackburn et al., 2017), to discrete groundwater inputs that support low but constant NO_3 supplies to the stream, and/or to rapid nitrification of NH_4 either when dry surface soils become rewetted (Thomas et al., 2016) or when anoxic groundwater reach oxic surface waters (Lupon et al., 2020). In this sense, we know that organic-rich soils and sediments at the riparian-hyporheic-stream interface can act as NH_4 sources to boreal headwaters (Blackburn et al., 2017). During elevated flows, nitrification of this pool could maintain NO_3 supply while at the same time diluting NH_4, thus shaping the different *c*-*Q* relationships between these two N forms (Lupon et al., 2020; Thomas et al., 2016). Whatever the mechanisms, the observed constant pattern for NO_3 suggests that near-stream processes regulate the supply of a key inorganic N form in ways that deviate from what would be expected for a landscape dominated by N limited vegetation, which should promote source limitation in streams (Thompson et al., 2011).

Sites with particularly strong influence from upstream mires stood out in our analyses of *c*-*Q* relationships for most solutes. In particular, inter-annual *c*-*Q* patterns for inorganic (i.e., PO_4 and NH_4) and organic (i.e., DOC and DON) solutes at the mire outlet (C4) were remarkably persistent across years and are uniquely source limited relative to other KCS sites. For DOC and DON, these observations are consistent with mechanisms suggested by Laudon et al. (2011), where dilution during spring flood results from the substantial contribution of direct snowmelt flow running atop surficial ice in the mire with little peat contact. Further, source limitation for NH_4, or even PO_4, could be explained by the dominance of preferential flowpaths through the mire (Peralta-Tapia et al., 2015), such that solute exports are supported by an exhaustible pool that accumulates at depth during low flow (winter) months (Sponseller et al., 2018). Overall, across the KCS network, our inter-annual assessment revealed a range of *c*-*Q* relationships among organic and inorganic solutes, which in most cases appear to reflect the specific biogeochemical and hydrological conditions of either the riparian-stream or mire-stream interface.

Finally, an important limitation of the solute dynamics reported here lies in the relatively low frequency of our sampling program, such that even a 12-year record of flow weighted samples may be too short and/or coarse to fully capture *c*-*Q* dynamics, particularly during hydrological events (Duncan et al., 2017; Fazekas et al., 2020). In our case, the snowmelt period is reasonable well captured, but flood events during summer and autumn are not targeted and are thus sometimes missed by the stream monitoring program. Thus, at annual time scales, *c*-*Q* relationships reported here are potentially too strongly shaped by the snowmelt season. Yet, despite limitations linked to sample timing and frequency, the resulting errors in *c*-*Q* slopes are unlikely to qualitatively change the overall solute behavior (e.g., shifting between enrichment to dilution) (Cassidy & Jordan, 2011; Dupas et al., 2016) but could instead reduce the strength of these relationships (e.g., from strong to weak limitation) (Bieroza et al., 2018). Furthermore, and consistent with our results, asynchronous and land-cover dependent source limitation of inorganic N and P (Bowes et al., 2015), as well as constant NO_3 patterns (Vaughan et al., 2017; Wymore et al., 2021), have been documented elsewhere using high frequency data. Thus, the *c*-*Q* slopes reported here should adequately capture the overall direction and variation of dominant behaviors in terms of solute storage and transport across sub-catchments at annual time scales.

4.2. Seasonal Variation in *c*-*Q* Relationships

Seasonal changes in hydroclimatic conditions and/or biogeochemical processes can modulate the contribution of solutes from a range of permanently and seasonally saturated zones that collectively alter *c*-*Q* relationships (Dupas et al., 2017; Thomas et al., 2016). Indeed, our within-season assessment revealed a much larger range of *c*-*Q* relationships than observed across years with distinct changes for inorganic versus organic solutes. Specifically, seasonal transport limitation ($\beta > 0$) for organic solutes suggests that the reconnection of more surficial catchment soils, where DOC and DON are more abundant, may be particularly influential during summer and autumn events, with flushing of organic resources produced and accumulated during the growing season (Tiwari et al., 2022). The clearest example of this is observed in the mire-dominated sub-catchment (C4), where the *c*-*Q* relationship for DON and DOC changed from a strong source limitation during snowmelt to transport limitation during summer. This shift indicates that rates of C and N production and accumulation in hydrologically active peat layers during summer and autumn are sufficient to keep pace with elevated flow during those seasons (Gómez-Gener et al., 2021).

Our assessment also showed seasonally changing hydrological responses for NH_4 and PO_4. For NH_4, which was source limited and chemostatic inter-annually, we observed a shift toward constant *c*-*Q* relationships and even some cases of chemodynamic export regimes (i.e., $CV_c/CV_q > 0.5$) when assessed seasonally. As suggested above for NO_3, constant behavior for NH_4 indicates sustained but minor losses to streams during the growing season, even though this is when N demand in surrounding landscape is greatest. In the KCS, this likely reflects some leaking of NH_4 from deep, peat-rich riparian and mire soils, which are functionally disconnected from surface vegetation and shallow rooting zones (Sponseller et al., 2018). Why NH_4 shifts toward a chemodynamic export regime during autumn and spring is less clear, but this is consistent with the relatively high biological reactivity of this solute in stream and near-stream environments (e.g., Lupon et al., 2020), which may uncouple variability in concentrations from that of discharge (Musolff et al., 2015). Finally, for PO_4, as observed at inter-annual scales, source limitation persisted throughout summer and autumn for most sub-catchments and only shifted toward constant behavior in winter. Persistent source limitation across seasons reflects the deeper mineral source of PO_4 across this landscape, but is also consistent with studies showing that, while biogeochemical processes (e.g., reductive dissolution of iron oxy-hydroxide) can release PO_4 during summer low flows, this source is readily diluted as discharge increases (Dupas et al., 2017; Ebeling et al., 2021). Such patterns are also consistent with the same P sources being repeatedly mobilized and depleted by successive wetting cycles during autumn (Ali et al., 2017).

4.3. Non-Stationary *c*-*Q* Patterns Over Time

We assessed whether previously documented directional changes in solute concentrations coincide with shifts in *c*-*Q* relationships that reflect differences in the patterns of solute storage in catchment soils (Fork et al., 2020). For example, both NH_4 and PO_4 concentrations have declined in KCS streams over the last decade (Mosquera et al., 2022), and our results here show that these solutes have also become more source limited in almost all study catchments. Together, these patterns indicate that all sub-catchments are becoming better at retaining these nutrients on land and that supply is particularly declining in surficial layers activated during higher flows. By comparison, NO_3 concentrations are also declining at most KCS streams (Mosquera et al., 2022), yet *c*-*Q* patterns are largely stationary over this time period, indicating a more diffuse weakening in catchment source strength, which may be consistent with a more complex set of mechanisms underpinning NO_3 supply (e.g., coupling with nitrification). Regardless, our results are generally consistent with other studies in the region showing widespread declines in DIN (Lucas et al., 2016) and P (Huser et al., 2018) concentrations in aquatic ecosystems. Such declines have been observed elsewhere (Mason et al., 2022) and have been linked to several regional processes, including reduced atmospheric N deposition (Deininger et al., 2020), increased nutrient retention in vegetation triggered by climate warming (Lucas et al., 2016) and strengthening geochemical sinks (Huser & Rydin, 2005). However, the intensification of source limitation observed for NH_4 and PO_4 in the KCS could also be part of a cyclical fluctuation between wet and dry years that affect catchment processes—given that our results also suggest a shift back toward less source-limited or even a constant behavior in 2018 when a severe summer drought hit the KCS (Gómez-Gener et al., 2020). It is worth noting that summer precipitation in this region is expected to be altered in the future, with longer periods without precipitation interspersed with large infrequent rain events (Teutschbein et al., 2018). Such changes to the hydrological regimes could potentially drive new patterns in solute supply.

4.4. Catchment Characteristics as the Ultimate Control Over *c*-*Q* Relationships

Catchment characteristics such as land-use, soil type, or drainage size can influence the complex interactions between hydrological and biogeochemical processes that underpin *c*-*Q* relationships (Thompson et al., 2011). Here, despite the general difference between organic and inorganic *c*-*Q* patterns, we found that the variation in *c*-*Q* slopes was related to catchment characteristics for nearly all solutes. Specifically, the spatial variation in organic and inorganic *c*-*Q* relationships was closely associated with the forest versus wetland proportion of each sub-catchment, as represented by PCA2. Even more interesting, these relationships persisted not only across organic and inorganic solutes but also for most seasons, and even as *c*-*Q* slopes changed over the longer time-period (i.e., for PO_4 and NH_4). For inorganic solutes, our results showed that *c*-*Q* regimes can vary among streams in the same network between source limitation and a constant pattern, depending on the degree of forest versus wetland cover, but these regimes rarely switch to transport limitation. In contrast, organic solute *c*-*Q* regimes can switch from a constant pattern to transport limited in response to gradients in the same land cover features, but almost never display source limitation. The mire-outlet stream was the only exception here since, as discussed above, extreme mire cover tends to push all solutes toward either source limitation or a constant pattern. Taken together, our results add new insights into the overwhelming influence of catchment properties on *c*-*Q* relationships (e.g., see Hashemi et al. (2020)) by adding evidence for multiple organic and inorganic solutes in a relatively remote, un-impacted boreal landscape. Such information is critical to predicting and managing potential climate-driven changes in the water quality of northern landscapes (Kincaid et al., 2020).

4.5. Implications for Aquatic Ecosystems

The stoichiometry of C, N, and P supplied to aquatic ecosystems can influence a wide range of processes, including rates of primary productivity and the strength of resource limitation (Elser et al., 2007; Sardans et al., 2012). Our results highlight clear seasonal patterns in the stoichiometry of C, N, and P supplied across land-water boundaries in the KCS. Such patterns reflect differences in the size of these resource pools on land, but also in the mechanisms and time-scales of their use and turnover. Similar to observations across Sweden (Teutschbein et al., 2017), NH_4, NO_3, and PO_4 concentrations in streams reach their annual maximum values during winter and minimum values during the growing season, ostensibly because plant and microbial demand for these nutrients is sufficient to deplete mobilizable pools during summer. By contrast, DON and DOC show the opposite seasonal pattern, which is partially linked to temperature-dependent rates of production in riparian soils, but also to seasonal changes in hydrology and water table height (Winterdahl et al., 2011). Consequently, DOC:DIN ratios in streams increased throughout the growing season, reaching the highest molar ratio in autumn, whereas DOC:PO_4 remained high throughout the growing season. In the KCS, this seasonal change in the stoichiometry of resource supply corresponds to predictable shifts in resource limitation of stream heterotrophic microbes—from strong carbon limitation during winter to greater degrees of N limitation during the summer growing season (Burrows et al., 2017).

Our results also indicate that abrupt changes in the stoichiometry of resource supply to streams can arise from solute-specific differences in hydrological mobilization (Figure 7). Across the KCS, *c*-*Q* regimes for the solutes

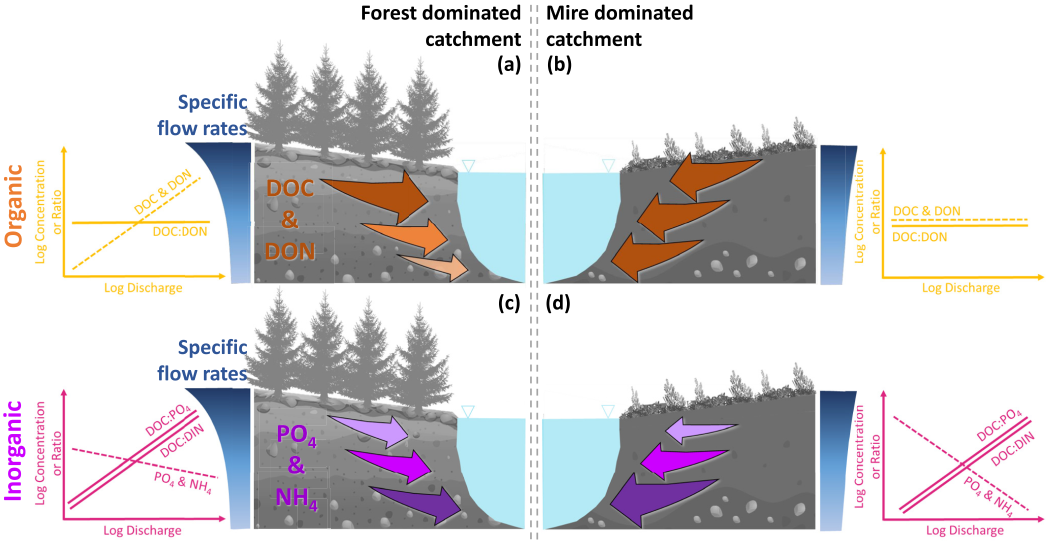

Figure 7. A conceptual diagram illustrating the dominant patterns of export behavior of (a, b) organic and (c, d) inorganic nutrients across headwaters dominated by forest cover (a, c) and headwaters with strong influence by mires (b, d). Color arrows represent fluxes of inorganic and organic solutes illustrating dominant transport pathways where color and arrow size is scaled. In right and left panels, concentration-discharge relationships are shown with dashed lines and the resulting ratio-discharge relationships are shown with solid lines to (based on Figures 3 and 4). Note that NO_3 is not depicted as it mostly showed a constant pattern and not related to catchment characteristic (Figures 3 and 4).

considered here were largely unique, arising from differences in the size and vertical distribution of subsurface storage pools, which together dictate how concentrations in the stream change as water tables fluctuate. When combined, these disparate *c*-*Q* relationships can generate strongly dynamic ratio-*Q* responses, particularly when considering resource pairs that have the most distinct subsurface storage and turnover patterns (Figure 7). Most notably, we find that the opposing mobilization patterns for organic versus inorganic solutes combine to create sharp increases in DOC:DIN and DOC:PO_4 ratios in streams during high flow events. These events likely supply aquatic ecosystems with far more organic energy than inorganic building blocks needed to support microbial metabolism. Thus, high flows potentially exacerbate the seasonal imbalance of energy versus nutrient supply to aquatic systems even though N and P deficits could be met to some degree by organic forms (Rulli et al., 2022). Such observations gain even more importance when considered in the context of general "browning trends" observed across northern aquatic systems (Kritzberg et al., 2020), "wetter autumns/winters" arising from altered precipitation patterns (Teutschbein et al., 2018), and the likelihood of more frequent flood events in the future (Vormoor et al., 2015), all of which may contribute to amplifying the supply of DOC and DON relative to inorganic nutrients across land-water boundaries. Conversely, an increasing frequency of summer drought in boreal landscapes could drive the opposite trends in streams, with reduced concentrations of DOC (Tiwari et al., 2022) coupled with elevated concentrations of reduced inorganic nutrients (Gómez-Gener et al., 2020).

5. Conclusions

Our results provide evidence that, despite being shaped by similar catchment features, the *c*-*Q* relationships for organic C and N differ fundamentally from inorganic nutrients, in terms of the direction of this relationship and its degree of seasonal variability. When integrated, these differences in individual solute response to hydrological change give rise to strong event- and seasonal-scale changes in the stoichiometry of resource supply to aquatic ecosystems. Given the critical interplay between the supply of resources from catchments and their demand in aquatic ecosystems, understanding the spatial-temporal variability of C, N, and P concentrations and ratio is key to predicting how northern streams and rivers may respond to ongoing and future environmental changes.

Data Availability Statement

The database used to support the findings of this study are openly available in Zenodo repository at https://doi.org/10.5281/zenodo.8093554 with description and steps to reproduce in Mosquera et al. (2023). Furthermore, all data can be accessed and download via the Krycklan Catchment Study repository at https://data.krycklan.se/ (Svartberget Research Station, 2023). All statistical analyses, as well as graphics were conducted using the freely available software R (R Core Team, 2022). Principal component analysis (PCA) was carried out by using the "vegan" package in R (Oksanen et al., 2019) and all Figure plots were performed in "ggplot" package in R (Wickham, 2016).

Acknowledgments
This work would not have been possible without the hard work and dedication of Krycklan Catchment Study students and field, lab, and database personnel, both past and present. In particular, we thank Johannes Tiwari, Kim Lindgren, Viktor Boström, and Abdulmajid Mahomoud for their invaluable assistance. All analysis have been conducted at the Biogeochemical Analyses Laboratory (BAL) at SLU. This work was funded by SITES: Vetenskapsrådet, Kempe Foundation: Kempestiftelserna, Swedish Research Council—Formas number 2018-02780 via the FORMAS—ERA-NET COFUND WATER JPI 2018 JOINT CALL CLOSING THE WATER CYCLE GAP—EU-COOPERATION—COFUND, Formas number 2018-00723 and FOMA: Swedish University of Agricultural Science.

References

Ali, G., Henry, W., Elliott, J., Penner, A., Haque, A., Ross, C., & Rabie, M. (2017). Phosphorus export dynamics and hydrobiogeochemical controls across gradients of scale, topography and human impact. *Hydrological Processes*, *31*(18), 3130–3145. https://doi.org/10.1002/hyp.11258

Basu, N. B., Destouni, G., Jawitz, J. W., Thompson, S. E., Loukinova, N. V., Darracq, A., et al. (2010). Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity. *Geophysical Research Letters*, *37*(23), 1–5. https://doi.org/10.1029/2010gl045168

Bieroza, M. Z., Heathwaite, A. L., Bechmann, M., Kyllmar, K., & Jordan, P. (2018). The concentration-discharge slope as a tool for water quality management. *Science of the Total Environment*, *630*, 738–749. https://doi.org/10.1016/j.scitotenv.2018.02.256

Bishop, K., Seibert, J., Köhler, S., & Laudon, H. (2004). Resolving the double paradox of rapidly mobilized old water with highly variable responses in runoff chemistry. *Hydrological Processes*, *18*(1), 185–189. https://doi.org/10.1002/hyp.5209

Blackburn, M., Ledesma, L. J., Näsholm, T., Laudon, H., & Sponseller, R. A. (2017). Evaluating hillslope and riparian contributions to dissolved nitrogen (N) export from a boreal forest catchment. *Journal of Geophysical Research: Biogeosciences*, *122*(2), 324–339. https://doi.org/10.1002/2016jg003535

Bowes, M. J., Jarvie, H. P., Halliday, S. J., Skeffington, R. A., Wade, A. J., Loewenthal, M., et al. (2015). Characterising phosphorus and nitrate inputs to a rural river using high-frequency concentration-flow relationships. *Science of the Total Environment*, *511*, 608–620. https://doi.org/10.1016/j.scitotenv.2014.12.086

Burrows, R. M., Laudon, H., McKie, B. G., & Sponseller, R. A. (2017). Seasonal resource limitation of heterotrophic biofilms in boreal streams. *Limnology and Oceanography*, *62*(1), 164–176. https://doi.org/10.1002/lno.10383

Cassidy, R., & Jordan, P. (2011). Limitations of instantaneous water quality sampling in surface-water catchments: Comparison with near-continuous phosphorus time-series data. *Journal of Hydrology*, *405*(1–2), 182–193. https://doi.org/10.1016/j.jhydrol.2011.05.020

Clark, J. M., Bottrell, S. H., Evans, C. D., Monteith, D. T., Bartlett, R., Rose, R., et al. (2010). The importance of the relationship between scale and process in understanding long-term DOC dynamics. *Science of the Total Environment*, *408*(13), 2768–2775. https://doi.org/10.1016/j.scitotenv.2010.02.046

Deininger, A., Kaste, Ø., Frigstad, H., & Austnes, K. (2020). Organic nitrogen steadily increasing in Norwegian rivers draining to the Skagerrak coast. *Scientific Reports*, *10*(1), 18451. https://doi.org/10.1038/s41598-020-75532-5

De Wit, H. A., Lepistö, A., Marttila, H., Wenng, H., Bechmann, M., Blicher-Mathiesen, G., et al. (2020). Land-use dominates climate controls on nitrogen and phosphorus export from managed and natural Nordic headwater catchments. *Hydrological Processes*, *34*(25), 4831–4850. https://doi.org/10.1002/hyp.13939

Ducharme, A. A., Casson, N. J., Higgins, S. N., & Friesen-Hughes, K. (2021). Hydrological and catchment controls on event-scale dissolved organic carbon dynamics in boreal headwater streams. *Hydrological Processes*, *35*(7), 1–12. https://doi.org/10.1002/hyp.14279

Duncan, J. M., Band, L. E., & Groffman, P. M. (2017). Variable nitrate concentration–discharge relationships in a forested watershed. *Hydrological Processes*, *31*(9), 1817–1824. https://doi.org/10.1002/hyp.11136

Dupas, R., Jomaa, S., Musolff, A., Borchardt, D., & Rode, M. (2016). Disentangling the influence of hydroclimatic patterns and agricultural management on river nitrate dynamics from sub-hourly to decadal time scales. *Science of the Total Environment*, *571*, 791–800. https://doi.org/10.1016/j.scitotenv.2016.07.053

Dupas, R., Musolff, A., Jawitz, J. W., Rao, P. S. C., Jäger, C. G., Fleckenstein, J. H., et al. (2017). Carbon and nutrient export regimes from headwater catchments to downstream reaches. *Biogeosciences*, *14*(18), 4391–4407. https://doi.org/10.5194/bg-14-4391-2017

Ebeling, P., Kumar, R., Weber, M., Knoll, L., Fleckenstein, J. H., & Musolff, A. (2021). Archetypes and controls of riverine nutrient export across German catchments. *Water Resources Research*, *57*(4), 1–29. https://doi.org/10.1029/2020wr028134

Elser, J., Bracken, M., Cleland, E., Gruner, D., Stanley, H., Hillebrand, H., et al. (2007). Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems. *Ecology Letters*, *10*(12), 1135–1142. https://doi.org/10.1111/j.1461-0248.2007.01113.x

Evans, C. D., Jones, T. G., Burden, A., Ostle, N., Zieliński, P., Cooper, M. D., et al. (2012). Acidity controls on dissolved organic carbon mobility in organic soils. *Global Change Biology*, *18*(11), 3317–3331. https://doi.org/10.1111/j.1365-2486.2012.02794.x

Fazekas, H. M., Wymore, A. S., & McDowell, W. H. (2020). Dissolved organic carbon and nitrate concentration-discharge behavior across scales: Land use, excursions, and misclassification. *Water Resources Research*, *56*(8), e2019WR027028. https://doi.org/10.1029/2019wr027028

Fork, M. L., Sponseller, R. A., & Hjalmar, L. (2020). Changing source-transport dynamics drive differential browning trends in a boreal stream network. *Water Resources Research*, *56*(2), e2019WR026336. https://doi.org/10.1029/2019wr026336

Francoeur, S. N. (2001). Meta-analysis of lotic nutrient amendment experiments: Detecting and quantifying subtle responses. *Journal of the North American Benthological Society*, *20*(3), 358–368. https://doi.org/10.2307/1468034

Gao, C., Li, W., Cui, L., Ma, Q., & Cai, J. (2021). Catchment landscape components alter relationships between discharge and stream water nutrient ratios in the Xitiao River Basin China. *Scientific Reports*, *11*(1), 1–15. https://doi.org/10.1038/s41598-021-89804-1

Gerber, S., & Brookshire, E. N. J. (2014). Scaling of physical constraints at the root-soil interface to macroscopic patterns of nutrient retention in ecosystems. *The American Naturalist*, *183*(3), 418–430. https://doi.org/10.1086/674907

Godsey, S., Kirchner, J., & Clow, D. (2009). Concentration-discharge relationship reflect chemostatic characteristics of US catchments. *Hydrological Processes*, *23*(13), 1844–1864. https://doi.org/10.1002/hyp.7315

Gómez-Gener, L., Anna, L., Laudon, H., & Sponseller, R. A. (2020). Drought alters the biogeochemistry of boreal stream networks. *Nature Communications*, *11*(1), 1795. https://doi.org/10.1038/s41467-020-15496-2

Gómez-Gener, L., Hotchkiss, E. R., Laudon, H., & Sponseller, R. A. (2021). Integrating discharge-concentration dynamics across carbon forms in a boreal landscape. *Water Resources Research*, *57*(8), e2020WR028806. https://doi.org/10.1029/2020wr028806

Gundale, M. J., Deluca, T. H., & Annika, N. (2011). Bryophytes attenuate anthropogenic nitrogen inputs in boreal forests. *Global Change Biology*, *17*(8), 2743–2753. https://doi.org/10.1111/j.1365-2486.2011.02407.x

Hashemi, F., Pohle, I., JohannesPullens, W. M., Tornbjerg, H., Kyllmar, K., Marttila, H., et al. (2020). Conceptual mini-catchment typologies for testing dominant controls of nutrient dynamics in three Nordic countries. *Water (Switzerland)*, *12*(6), 1–17. https://doi.org/10.3390/w12061776

Hasselquist, E. M., Lidberg, W., Sponseller, R. A., Ågren, A., & Laudon, H. (2018). Identifying and assessing the potential hydrological function of past artificial forest drainage. *Ambio*, *47*(5), 546–556. https://doi.org/10.1007/s13280-017-0984-9

Huser, B. J., Futter, M. N., Wang, R., & Fölster, J. (2018). Persistent and widespread long-term phosphorus declines in boreal lakes in Sweden. *Science of the Total Environment*, *613–614*, 240–249. https://doi.org/10.1016/j.scitotenv.2017.09.067

Huser, B. J., & Rydin, E. (2005). Phosphorus inactivation by aluminum in lakes Gårdsjön and Härsvatten sediment during the industrial acidification period in Sweden. *Canadian Journal of Fisheries and Aquatic Sciences*, *62*(8), 1702–1709. https://doi.org/10.1139/f05-083

Jutebring Sterte, E., Lidman, F., Lindborg, E., Sjöberg, Y., & Laudon, H. (2021). How catchment characteristics influence hydrological pathways and travel times in a boreal landscape. *Hydrology and Earth System Sciences*, *25*(4), 2133–2158. https://doi.org/10.5194/hess-25-2133-2021

Karlsen, R. H., Grabs, T., Bishop, K., Buffam, I., Laudon, H., & Seibert, J. (2016a). Landscape controls on spatiotemporal discharge variability in a boreal catchment. *Water Resources Research*, *52*(8), 6541–6556. https://doi.org/10.1002/2016wr019186

Karlsen, R. H., Seibert, J., Grabs, T., Laudon, H., Blomkvist, P., & Bishop, K. (2016b). The assumption of uniform specific discharge: Unsafe at any time? *Hydrological Processes*, *30*(21), 3978–3988. https://doi.org/10.1002/hyp.10877

Kincaid, D. W., Seybold, E. C., Adair, E. C., Bowden, W. B., Perdrial, J. N., Vaughan, M. C., & Schroth, A. W. (2020). Land use and season influence event-scale nitrate and soluble reactive phosphorus exports and export stoichiometry from headwater catchments. *Water Resources Research*, *56*(10), 1–20. https://doi.org/10.1029/2020wr027361

Kozii, N., Haahti, K., Tor-Ngern, P., Chi, J., Maher Hasselquist, E., Laudon, H., et al. (2020). Partitioning growing season water balance within a forested boreal catchment using sap flux, eddy covariance, and a process-based model. *Hydrology and Earth System Sciences*, *24*(6), 2999–3014. https://doi.org/10.5194/hess-24-2999-2020

Kritzberg, E. S., Hasselquist, E. M., Škerlep, M., Löfgren, S., Olsson, O., Stadmark, J., et al. (2020). Browning of freshwaters: Consequences to ecosystem services, underlying drivers, and potential mitigation measures. *Ambio*, *49*(2), 375–390. https://doi.org/10.1007/s13280-019-01227-5

Laudon, H., Berggren, M., Ågren, A., Buffam, I., Bishop, K., Grabs, T., et al. (2011). Patterns and dynamics of dissolved organic carbon (DOC) in boreal streams: The role of processes, connectivity, and scaling. *Ecosystems*, *14*(6), 880–893. https://doi.org/10.1007/s10021-011-9452-8

Laudon, H., Hasselquist, E. M., Peichl, M., Lindgren, K., Sponseller, R., Lidman, F., et al. (2021). Northern landscapes in transition: Evidence, approach and ways forward using the Krycklan catchment study. *Hydrological Processes*, *35*(4), 1–15. https://doi.org/10.1002/hyp.14170

Laudon, H., Ida, T., Ågren, A., Futter, M., Ottosson-Löfvenius, M., & Bishop, K. (2013). The Krycklan catchment study - A flagship infrastructure for hydrology, biogeochemistry, and climate Research in the boreal landscape. *Water Resources Research*, *49*(10), 7154–7158. https://doi.org/10.1002/wrcr.20520

Laudon, H., & Löfvenius, M. O. (2016). Adding snow to the picture – Providing complementary winter precipitation data to the Krycklan catchment study database. *Hydrological Processes*, *30*(13), 2413–2416. https://doi.org/10.1002/hyp.10753

Laudon, H., Sponseller, R. A., & Bishop, K. (2021). From legacy effects of acid deposition in boreal streams to future environmental threats. *Environmental Research Letters*, *16*(1), 015007. https://doi.org/10.1088/1748-9326/abd064

Ledesma, J. L., Futter, M. N., Blackburn, M., Lidman, F., Grabs, T., Sponseller, R. A., et al. (2018). Towards an improved conceptualization of riparian zones in boreal forest headwaters. *Ecosystems*, *21*(2), 297–315. https://doi.org/10.1007/s10021-017-0149-5

Lucas, R. W., Sponseller, R. A., Gundale, M. J., Stendahl, J., Fridman, J., Peter, H., & Laudon, H. (2016). Long-term declines in stream and river inorganic nitrogen (N) export correspond to forest change. *Ecological Applications*, *26*(2), 545–556. https://doi.org/10.1890/14-2413

Lupon, A., Denfeld, B. A., Laudon, H., Leach, J., & Sponseller, R. A. (2020). Discrete groundwater inflows influence patterns of nitrogen uptake in a boreal headwater stream. *Freshwater Science*, *39*(2), 228–240. https://doi.org/10.1086/708521

Marchetto, A. (2017). Mann-Kendall test, seasonal and regional Kendall tests. *R Statistical Program*, *10*.

Mason, R. E., Craine, J. M., Lany, N. K., Jonard, M., Ollinger, S. V., Groffman, P. M., et al. (2022). Evidence, causes, and consequences of declining nitrogen availability in terrestrial ecosystems. *Science*, *376*(6590), eabh3767. https://doi.org/10.1126/science.abh3767

Moatar, F., Abbott, B. W., Minaudo, C., Curie, F., & Pinay, G. (2017). Elemental properties, hydrology, and biology interact to shape concentration-discharge curves for carbon, nutrients, sediment, and major ions. *Water Resources Research*, *53*(2), 1270–1287. https://doi.org/10.1002/2016wr019635

Monteith, D. T., Stoddard, J. L., Evans, C. D., De Wit, H. A., Forsius, M., Høgåsen, T., et al. (2007). Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature*, *450*(7169), 537–540. https://doi.org/10.1038/nature06316

Mosquera, V., Laudon, H., Blackburn, M., Maher Hasselquist, E., & Ryan, S. (2023). Nutrient concentration and discharge for streams of Krycklan catchment study (2008–2019) (version 1) [Dataset]. Zenodo. https://doi.org/10.5281/zenodo.8093554

Mosquera, V., Maher Hasselquist, E., Sponseller, R. A., & Laudon, H. (2022). Co-occurrence of browning and oligotrophication in a boreal stream network. *Limnology and Oceanography*, *67*(10), 2325–2339. https://doi.org/10.1002/lno.12205

Musolff, A., Fleckenstein, J. H., Rao, P. S. C., & Jawitz, J. W. (2017). Emergent archetype patterns of coupled hydrologic and biogeochemical responses in catchments. *Geophysical Research Letters*, *44*(9), 4143–4151. https://doi.org/10.1002/2017gl072630

Musolff, A., Schmidt, C., Selle, B., & JanFleckenstein, H. (2015). Catchment controls on solute export. *Advances in Water Resources*, *86*, 133–146. https://doi.org/10.1016/j.advwatres.2015.09.026

Oksanen, J., Blanchet, F. G., Friendly, M., Kindt, R., Legendre, P., McGlinn, D., et al. (2019). Vegan: Community ecology package (version 2.6.4). [R Package].

Peñuelas, J., Sardans, J., Rivas-Ubach, A., & Janssens, I. (2012). The human-induced imbalance between C, N and P in Earth' s life system. *Global Change Biology*, *18*(1), 3–6. https://doi.org/10.1111/j.1365-2486.2011.02568.x

Peralta-Tapia, A., Sponseller, R. A., Ågren, A., Tetzlaff, D., Soulsby, C., & Laudon, H. (2015). Scale-dependent groundwater contributions influence patterns of winter baseflow stream chemistry in boreal catchments. *Journal of Geophysical Research: Biogeosciences*, *120*(5), 847–858. https://doi.org/10.1002/2014jg002878

R Core Team. (2022). A language and environment for statistical computing (version 4.1.1).

Rose, L. A., Karwan, D. L., & Godsey, S. E. (2018). Concentration–discharge relationships describe solute and sediment mobilization, reaction, and transport at event and longer timescales. *Hydrological Processes*, *32*(18), 2829–2844. https://doi.org/10.1002/hyp.13235

Rulli, M. P., Bergström, A. K., Sponseller, R. A., & Berggren, M. (2022). Seasonal patterns in nutrient bioavailability in boreal headwater streams. *Limnology and Oceanography*, *1–15*(5), 1169–1183. https://doi.org/10.1002/lno.12064

Sardans, J., Rivas-Ubach, A., & Peñuelas, J. (2012). The elemental stoichiometry of aquatic and terrestrial ecosystems and its relationships with organismic lifestyle and ecosystem structure and function: A review and perspectives. *Biogeochemistry*, *111*(1–3), 1–39. https://doi.org/10.1007/s10533-011-9640-9

Schuldt, B., Buras, A., Arend, M., Vitasse, Y., Beierkuhnlein, C., Damm, A., et al. (2020). A first assessment of the impact of the extreme 2018 summer drought on central European forests. *Basic and Applied Ecology*, *45*, 86–103. https://doi.org/10.1016/j.baae.2020.04.003

Shousha, S., Maranger, R., & Lapierre, J. F. (2021). Different forms of carbon, nitrogen, and phosphorus influence ecosystem stoichiometry in a north temperate river across seasons and land uses. *Limnology and Oceanography*, *66*(12), 4285–4298. https://doi.org/10.1002/lno.11960

Sponseller, R. A., Blackburn, M., Nilsson, M. B., & Laudon, H. (2018). Headwater mires constitute a major source of nitrogen (N) to surface waters in the boreal landscape. *Ecosystems*, *21*(1), 31–44. https://doi.org/10.1007/s10021-017-0133-0

Stewart, B., Shanley, J. B., Kirchner, J. W., Norris, D., Adler, T., Bristol, C., et al. (2022). Streams as mirrors: Reading subsurface water chemistry from stream chemistry. *Water Resources Research*, *58*(1), 1–20. https://doi.org/10.1029/2021wr029931

Svartberget Research Station. (2023). Chemical variables - Stream from Krycklan [Dataset]. Swedish Infrastructure for Ecosystem Science (SITES). Retrieved from https://meta.fieldsites.se/objects/5BS1sf68_sxaYYQRgQ7IGqhl

Teutschbein, C., Grabs, T., Laudon, H., Karlsen, R. H., & Bishop, K. (2018). Simulating streamflow in ungauged basins under a changing climate: The importance of landscape characteristics. *Journal of Hydrology*, *561*(December 2016), 160–178. https://doi.org/10.1016/j.jhydrol.2018.03.060

Teutschbein, C., Sponseller, R. A., Grabs, T., Blackburn, M., Boyer, E. W., Hytteborn, J. K., & Bishop, K. (2017). Future riverine inorganic nitrogen load to the Baltic Sea from Sweden: An ensemble approach to assessing climate change effects. *Global Biogeochemical Cycles*, *31*(11), 1–28. https://doi.org/10.1002/2016gb005598

Thomas, Z., Abbott, B. W., Olivier, T., Baudry, J., & Pinay, G. (2016). Proximate and ultimate controls on carbon and nutrient dynamics of small agricultural catchments. *Biogeosciences*, *13*(6), 1863–1875. https://doi.org/10.5194/bg-13-1863-2016

Thompson, S. E., Basu, N. B., Lascurain, J., Aubeneau, A., & Rao, P. S. C. (2011). Relative dominance of hydrologic versus biogeochemical factors on solute export across impact gradients. *Water Resources Research*, *47*(7), 1–20. https://doi.org/10.1029/2010wr009605

Tiwari, T., Sponseller, R. A., & Laudon, H. (2022). The emerging role of drought as a regulator of dissolved organic carbon in boreal landscapes. *Nature Communications*, *13*(1), 1–11. https://doi.org/10.1038/s41467-022-32839-3

USEPA. (2000). Practical methods for data quality assessment.

Vaughan, M. C. H., Bowden, W. B., Shanley, J. B., Vermilyea, A., Sleeper, R., Gold, A. J., et al. (2017). High-frequency dissolved organic carbon and nitrate measurements reveal differences in storm hysteresis and loading in relation to land cover and seasonality. *Water Resources Research*, *53*(7), 5345–5363. https://doi.org/10.1002/2017wr020491

Vormoor, K., Lawrence, D., Heistermann, M., & Bronstert, A. (2015). Climate change impacts on the seasonality and generation processes of floods – Projections and uncertainties for catchments with mixed snowmelt/rainfall regimes. *Hydrology and Earth System Sciences*, *19*(2), 913–931. https://doi.org/10.5194/hess-19-913-2015

Wachholz, A., Dehaspe, J., Ebeling, P., Kumar, R., Musolff, A., Saavedra, F., et al. (2023). Stoichiometry on the edge—Humans induce strong imbalances of reactive C:N:P ratios in streams. *Environmental Research Letters*, *18*(4), 044016. https://doi.org/10.1088/1748-9326/acc3b1

Wickham, H. (2016). Ggplot: Elegant graphics for data analysis (version 3.4.2) [R Package]. Springer-Verlag.

Winterdahl, M., Futter, M., Köhler, S., Laudon, H., Seibert, J., & Bishop, K. (2011). Riparian soil temperature modification of the relationship between flow and dissolved organic carbon concentration in a boreal stream. *Water Resources Research*, *47*(8), 1–17. https://doi.org/10.1029/2010wr010235

Wymore, A. S., Fazekas, H. M., & McDowell, W. H. (2021). Quantifying the frequency of synchronous carbon and nitrogen export to the river network. *Biogeochemistry*, *152*(1), 1–12. https://doi.org/10.1007/s10533-020-00741-z

Zimmer, M. A., Pellerin, B., Burns, D. A., & Petrochenkov, G. (2019). Temporal variability in nitrate-discharge relationships in large rivers as revealed by high-frequency data. *Water Resources Research*, *55*(2), 973–989. https://doi.org/10.1029/2018wr023478

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Co-occurrence of browning and oligotrophication in a boreal stream network

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Abstract

The relative supply of carbon (C), nitrogen (N), and phosphorus (P) to freshwater ecosystems is of fundamental importance to aquatic productivity, nutrient cycling, and food web dynamics. In northern landscapes, ongoing climate change, as well as legacies from atmospheric deposition, have the potential to drive changes in how these elements are recycled on land and exported to streams. While it is well established that dissolved organic carbon (DOC) concentrations have increased in many high latitude streams, the simultaneous trends for N and P and the ratios among these resources, are not well documented. We used data from 13 sites in a boreal stream network to analyze decadal-scale changes in dissolved inorganic N (DIN), dissolved organic N (DON), and dissolved inorganic P (DIP) concentrations and partition these trends seasonally. We observed widespread declines for DIP and DIN in streams, regardless of catchment characteristics. DIN decline was strongest during the growing season, and together with increases in DOC/DON at several sites, suggests increasing N retention by plants and soil microbes across this landscape. By contrast, declines for DIP occurred primarily during late autumn and winter, indicating that key biogeochemical changes are also occurring during non-growing season. Linking these trends to increases in DOC concentration in streams revealed changes in the ratio of energy to nutrient supply for the majority of sites, becoming richer in carbon and poorer in limiting nutrients over time. Overall, our observations from this stream network point to ongoing oligotrophication, with possible consequences for aquatic ecosystems in boreal landscapes.

Carbon (C), nitrogen (N), and phosphorus (P) are major elements essential for the growth and reproduction of all organisms. In freshwater ecosystems, the concentration and stoichiometry of these elements can regulate aquatic productivity, nutrient cycling, secondary production, community composition, and food web dynamics (Elser et al. 2000; Eimers et al. 2009; Taylor and Townsend 2010). Long-term trends in the concentrations of these resources in streams and lakes are thus a significant concern in environmental research, mostly from the standpoint of anthropogenic nutrient enrichment and the obvious impacts of eutrophication (Smith and Schindler 2009). Yet, understanding these trends is also important at high latitudes, where direct anthropogenic inputs of nutrients are often low, but rapid, ongoing environmental changes may nonetheless alter the fate of these elements in landscapes, with important consequences for aquatic ecosystems.

Several environmental changes at high latitudes can directly or indirectly influence C, N, and P cycling and retention on land and thus the export to streams and lakes. For example, observed trends in declining atmospheric deposition for some regions directly reduce nutrient inputs to ecosystems (Isles et al. 2018), but can also alter soil chemistry and processes in ways that indirectly influence nutrient retention and loss (e.g., by enhancing microbial mineralization of soil organic matter due to reductions in soil acidity; Rosi-Marshall et al. 2016). In addition, rapid climate warming at high latitudes, together with elevated atmospheric CO_2, is linked to increased plant growth (i.e., "greening"; Piao et al. 2020), which in turn increases the sequestration of limiting nutrients on land (Craine et al. 2018), while potentially leading to greater soil dissolved organic carbon (DOC) production (Finstad et al. 2016). Furthermore, climate change is also altering seasonal attributes at high latitudes, including longer

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plant growing seasons (Barichivich et al. 2013), wetter autumns, and warmer winters (Teutschbein et al. 2015), all of which have consequences for the timing and magnitude of resource uptake, production, and mobilization in soils. Finally, in northern Fennoscandia, these environmental changes co-occur with widespread forest management, which over the last century has also promoted greater tree biomass production and thus nutrient storage in plant biomass and soils (Lucas et al. 2016).

There is clear evidence that these collective changes are altering stream and lake chemistry in northern landscapes. Perhaps the most well-documented change is the increase in DOC concentrations (Monteith et al. 2007; De Wit et al. 2016; Fork et al. 2020), which is part of a general "browning" trend that is most likely connected to acid deposition recovery and vegetation change (Asmala et al. 2019; Kritzberg et al. 2020). By contrast, several studies in the boreal region suggest that surface waters are becoming more nutrient-poor over time. Here, observed long-term declines in inorganic N in streams and rivers have been attributed to land cover change (Sarkkola et al. 2012), declining N deposition (Deininger et al. 2020), and interactions between land management and climate warming (Lucas et al. 2016). More recently, attention has also been drawn to declines in inorganic P in Canadian (Eimers et al. 2009) and Nordic rivers and lakes (Huser et al. 2018; de Wit et al. 2020), which may similarly arise from changes in climate, recovery from acid deposition, land-use transitions and from emergent geochemical sinks (e.g., increase in Aluminum sinks) (Huser and Rydin 2005). Despite these observations, the relative influence of various catchment properties, soil characteristics, and climate drivers on trends in boreal stream nutrient chemistry remains poorly resolved. In addition, studies to date have not explored simultaneous trends in C, N, and P to assess whether or not these are synchronous at seasonal and interannual scales and thus potentially operate under a shared set of drivers. In this context, differences in the direction and magnitude of trends across resources may signify shifts in aquatic nutrient limitation via changing N : P (Isles et al. 2018) as well as a growing imbalance in the supply of organic energy vs. nutrients (e.g., DOC : inorganic N). These shifts and imbalances could constrain the growth of aquatic heterotrophs (Taylor and Townsend 2010) and regulate aquatic productivity (Stetler et al. 2021).

In this paper, we ask how C, N, and P chemistry in a boreal stream network has changed over the last decade, how different catchment characteristics influence these trends, and how such changes influence the stoichiometric balance of dissolved resources. To answer these questions, we used long-term water quality records from 13 sites within the Krycklan Catchment Study (KCS) located in boreal Sweden (Laudon et al. 2021*b*). Specifically, we characterized trends of inorganic and organic N and inorganic P from 2008 to 2020 and partitioned these seasonally to assess whether there are time windows when a directional change in nutrient chemistry is particularly strong or weak. We then used regression approaches to explore how variation in the strength of trends among sites is related to catchment characteristics, including differences in forest and wetland land cover. Further, we addressed changes in N and P chemistry in light of other chemical trends linked to the recovery from atmospheric deposition in the catchment (e.g., sulfate; Laudon et al. 2021*a*). Finally, we integrated nutrient data with ongoing increases in DOC concentration in KCS streams (Fork et al. 2020) to explore changes in the ratio of energy to nutrient supply from soils to aquatic ecosystems in this landscape.

Methods

Site description

This study was conducted within the Krycklan Catchment Study (KCS), a long-term research and monitoring watershed located in the boreal zone of northern Sweden (64°14′N, 19°46′E) approximately 60 km from the Baltic Sea coast. The 68-km^2 catchment is composed of 13 intensively monitored sub-catchments ranging over three orders of magnitude in size, from 12 to over 1900 ha (see Laudon et al. 2013 for further details about site description). The climate is typical of the northern boreal zone, characterized as a cold temperate humid type with short and cool summers followed by long dark winters. The 30-year mean annual air temperature (1986–2015) is 2.1°C with the highest mean monthly temperature occurring in July and the lowest in January (+ 14.6 and −8.6°C, respectively; Kozii et al. 2020). The area is affected by general warming as mean annual temperature has increased by 2.5°C in the last 40 years, most rapidly during late autumn and winter months (Laudon et al. 2021*b*). For the period of study (2008–2020), mean annual temperature increased by 0.02°C yr^{-1}. The average snow cover is 167 d yr^{-1}, typically from late October to early May, but has been declining at a rate of ~ 0.5 d yr^{-1} (Laudon and Löfvenius 2016). Total annual precipitation averages around 614 mm yr^{-1} of which approximately 35–50% falls as snow and 311 mm becomes runoff (Laudon et al. 2013). The hydrologic regime is characterized by high flow during the spring snowmelt (April–May), which accounts for 40–60% of the annual discharge. For the period of our analysis (2008–2019), there is no evidence of directional changes in annual discharge in the KCS. However, trend analysis on monthly discharge suggests significant declining trends for two sites, as well as non-significant declining trend for the rest. If analyzed seasonally, spring discharge (April and May) has increased significantly over this time period at five sites with non-significant changes at the other seven; no other seasons show discharge trend (Supplementary Table S1).

The KCS is primarily covered by forest (87%) and is dominated by Scots Pine (*Pinus sylvestris*; 63% cover) found mostly on the dry uplands, Norway Spruce (*Picea abies*; 26%) in wetter low-lying areas, and deciduous trees (~ 10%), primarily birch (*Betula* spp.). The understory is dominated by ericaceous shrubs, mostly bilberry (*Vaccinium myrtillus*) and lingonberry (*Vaccinium vitis-idaea*) with extensive cover of mosses dominated by *Hylocomium splendens* and *Pleurozium schreberi*. When divided by sub-catchments, the KCS presents a land cover gradient ranging from 54% to almost 100% forest cover, from 0% to almost 50% cover by *Sphagnum*-dominated wetlands (acid, oligotrophic, and minerogenic mires), and from 0% to more than 5% of humic lake cover. This landscape is underlain by quaternary deposits dominated by till soils (51%) that vary in thickness from a few centimeters to tens of meters, and sorted sediments (30%) (Laudon et al. 2013). In the lower catchment, large deposits of postglacial sediments are found as a result of a post-glacial river delta which covered an esker that followed the Vindeln River (Ledesma et al. 2013; Tiwari et al. 2014). Approximately 25% of the KCS has been protected from forest management since 1922, mostly in the central sub-catchments of the KCS area. Most of the other sub-catchments have been subject to some recent forest management including patches of second- and third-generation forests.

Sample collection and analytical methods

We compiled data for dissolved organic carbon (DOC), total dissolved nitrogen (TDN), nitrate (NO_3^-) ammonium (NH_4^+), and phosphate or soluble reactive phosphorus (PO_4^{3-}), sulfate (SO_4^{2-}), pH, and discharge from the KCS regular monitoring program for streams during the period between 2008 and 2020. The sampling regime is flow weighted, meaning that during spring flood samples are collected as frequently as twice per week, during the terrestrial growing season sampling occurs every 2 weeks, and during winter base-flow sampling occurs once per month. We analyzed data from 13 streams in the KCS, where 11 of these had data for the entire period, ranging from 262 to 311 observations per stream. For the other two streams (C14 and C15) the monitoring program started in 2012, and thus included data from fewer years, or 144 and 133 observations, respectively. For DOC, the monitoring program started in 2003 for the 13 sites, thus we took advantage of this longer period, having 478–408 observations per stream. Furthermore, at Site 12, discharge measurements could not be used due to inaccuracies in field measurements.

All samples were collected in acid-washed high-density polyethylene bottles, filtered in the lab (0.45 μm Millipore) within 24–48 h. Samples for DOC, TDN, SO_4, and pH were refrigerated (+ 4°C) and analyzed within 10 d after field collection. Finally, filtered subsamples were frozen (−20°C) immediately after subsampling and stored for later analysis of NO_3-N, NH_4-N, and PO_4-P. The analytical methods for DOC, TDN, NO_3^-, and NH_4^+ have been described in detail by Blackburn et al. (2017). Dissolved inorganic nitrogen (DIN) was calculated as the sum of NO_3 (including nitrite) and NH_4 and dissolved organic nitrogen (DON) was calculated as the difference between TDN and DIN. PO_4^{3-} was accounted as the dissolved inorganic phosphorus (DIP) and was analyzed on a Seal Analytical Autoanalyzer 3 HR using method G-297-03. SO_4-S was measured by liquid chromatography. This database includes values reported as "below detection level (BDL)" for PO_4, NH_4, and NO_3. Rates of BDL occurrence were similar across sites and accounted < 5% of observations for PO_4, < 2% for NH_4, and less < 1% for NO_3. This small proportion of BDL is influenced by the low detection limits (DL) of the analytical method (0.4, 0.3, and 0.4 $\mu g\ L^{-1}$, for PO_4, NH_4, and NO_3, respectively). Moreover, our statistical method is not biased by BDL observations because it compares values and determines which is the larger (Hirsch et al. 1982); thus we applied a conventional substitution method for all such occurrences (DL/2).

Data analysis and statistical methods

We analyzed nutrient and sulfate concentration and molar ratios for overall significant monotonic time series trends by performing a non-parametric Seasonal Mann–Kendall test with seasons as the blocking variable using the "rkt" package (Marchetto 2017) in freely available software R (R Core Team 2020). The Seasonal Mann–Kendall is well suited to distinguish between random fluctuations and monotonic trends and is applicable to data sets with seasonality. It is not biased by missing values or values reported as "below detection limit" and requires no assumption of normality (Hirsch and Slack 1984). Specifically, we determined the Seasonal Kendall slope (unit yr^{-1}), an extension of the Theil Sen slope, to estimate the magnitude of statistically significant trends. If the Seasonal Kendall slope is positive it means that the variable consistently increases and if it is negative the variable decreases, yet, does not imply a linear regression (Hirsch et al. 1982). The seasons were determined using the World Meteorological Organization (WMO) standard definition based on air temperature measured at Svartberget Field Station located in the center of the KCS (Laudon et al. 2013). Accordingly, spring begins when air temperature reaches above 0°C for five consecutive days and the maximum temperature is still below 20°C. Summer begins when the 5-day mean temperature rises above 10°C for 10 consecutive days. Autumn starts when the mean daily temperature falls below 10°C and the minimum temperature is below 0°C, and winter starts when the daily mean temperature is below 0°C for five consecutive days. To further understand the seasonal differences in the trends we used the Seasonal Mann–Kendall to test for trends of the different seasons and individual months using the median of samples collected within each month or season (Hirsch et al. 1982).

To assess whether concentration trends were an effect of dynamics, changes, or trends in discharge, we performed a partial Mann–Kendall test (PMK) using the "trend" package in R (Pohlert 2020), incorporating discharge as a covariate and allowing the correction for the relationship (Libiseller and Grimvall 2002), both for the entire period and for spring months (April–May). The PMK, however, is designed to estimate the statistical significance of trends and does not include a direct estimate of their magnitude. Therefore, the PMK was particularly useful to address the potential influence of changes in stream discharge on trends in concentration. Before performing a PMK, the correlation between discharge and concentration must be found. We then used Spearman's rank correlation to determine the strength of the relationship between discharge and concentration (Pohlert 2020). To capture and illustrate the general pattern of nutrient concentration and molar ratio over time, a locally weighted scatterplot smoothing (loess) fitting curve was applied using the "ggplot" package in R (Wickham 2009). Furthermore, Seasonal Kendall slopes were used to estimate the percentage change in the mean quantity (trend/mean, % yr^{-1}) of concentration and molar ratio per year (Huser et al. 2018; Deininger et al. 2020) and were also used to correlate the decline with the period mean concentration for each stream using ordinary least-squared regression (lm package) in R.

To identify the drivers behind the significant trends, we first conducted a principal component analysis (PCA) of sub-catchment characteristics using the "vegan" package in R (Oksanen 2015) with standardized parameters. The sub-catchment characteristics used in the PCA are the ones reported in Laudon et al. (2013), in addition to ditch density ($km\ km^2$) for each sub-catchment (Hasselquist et al. 2018) and presented in Supplementary Table S3. Ditches reflect historical efforts to drain forested wetlands and peatlands to increase forest production. We included ditch density due to its impact on hydrology and consequently nutrients dynamics (Hasselquist et al. 2018). We used multiple linear regression analysis to assess the relationship between the magnitude of the Theil Sen slope and the integrated catchment characteristics (i.e., PC1, PC2, and PC3 scores) for each site. Similarly, we used ordinary least-squares regression to test the relationships between sulfate, pH, and nutrients (i.e., DIP due to adsorption mechanisms), which may influence the observe trends. These regressions were done using the lm package with the step procedure in R. All the graphics of this study were produced using the R package "ggplot2" (Wickham 2009).

Results

Annual decline of inorganic nutrients is widespread in streams with different catchment characteristics

Over this 13-year period (2008–2020), all KCS streams ($n = 13$) showed statistically significant ($p < 0.05$) declines in DIP concentration and almost all (11 out of 13 streams) showed a statistically significant decline in DIN concentrations (Fig. 1a,b; Table 1). The other two streams also showed a negative trend but with no statistical significance ($p > 0.05$). Although concentration and discharge were correlated for DIP (10 out of 12 streams) and DIN (9 out of 12 streams), when discharge was corrected for, the significant concentration trends remained (Supplementary Table S2). The overall magnitude of concentration trends varied between DIN and DIP and among sub-catchments, but was broadly similar as an annual percentage. Specifically, the annual magnitude of DIP decrease (Seasonal Kendall slope estimator) ranged from −0.1 to −0.5 $\mu g\ P\ L^{-1}\ yr^{-1}$ between sites, averaging a decrease of −5.4% annually (SD ± 1.6). DIN declines ranged from −1.8 to −3.6 $\mu g\ N\ L^{-1}\ yr^{-1}$ between sites and averaging −7.1% annually (SE ± 1.6).

DIN in the mire outlet stream (C4) was dominated by NH_4, which accounted for 68% (SD ± 6) of the inorganic pool. By contrast, NO_3 was the dominant fraction of DIN in seven of the 13 sub-catchments (64–79% of DIN), whereas these two forms were essentially co-equal in the remaining sites. Both NO_3 and NH_4 decreased over the study period ($p < 0.05$) in all the streams (11 of 13 with statistical significance for NO_3 and 13 of 13 for NH_4) (Table 1). Overall, streams with higher annual average concentrations of DIN and DIP generally showed the largest relative declines during this period of record (Fig. 2a,b). Yet, this pattern did not hold true for NO_3 or for NH_4 by themselves (Fig. 2c,d). Both the sub-catchment subject to extensive ditching (C1; Hasselquist et al. 2018) and the sub-catchment influenced by higher percentage of alluvial deposits (Ledesma et al. 2013) and greater cover by open and arable lands (C15), had NH_4/NO_3 ratios far less than 1 and were notably dominated by NO_3. Specifically, the mean DIN for C1 was almost twofold higher than the rest of the streams and more than three times higher than the other forested catchment (C2). The inclusion of these sites obscured the relationship between Mean DIN and DIN Seasonal Kendall slope (Figs. 2, 4).

Total dissolved N (TDN) concentrations also showed a significant decline ($p < 0.05$) in almost all streams (11 of 13) and a non-statistically significant decline for the other two streams (Table 1). DON, which on average represented 88% of TDN, dominated the dissolved N pool (SD ± 5%, ranging from 77% to 98%). Statistically significant declining trends in DON concentrations were only observed in 7 out of 13 streams, while the other six streams also showed a negative trend but with no statistical significance (Fig. 1c; Table 1). The annual percent change was lower than that observed for inorganic N, averaging −2.6% (SD ± 0.84) per year. Specifically, DON concentrations in stream water ranged from a declining trend of −3.3% (−12.4 $\mu g\ N\ L^{-1}\ yr^{-1}$) in the lake outlet (C5) to a decline of only −1.9% annually (−8.0 $\mu g\ N\ L^{-1}\ yr^{-1}$) from the mire outlet. Contrary to N and P trends, and as already established by Fork, et.al (2020) for the period from 2003 to 2018, DOC concentrations increased in most of the KCS streams. For the period of 2003–2020, 9 out of 13 streams had statistically significant ($p < 0.05$) increase of DOC (Fig. 1d), ranging from + 0.09 to + 0.37 $mg\ C\ L^{-1}\ yr^{-1}$ averaging an increase of 1.2% annually (SD ± 0.56). Streams draining the lake, the mire, and

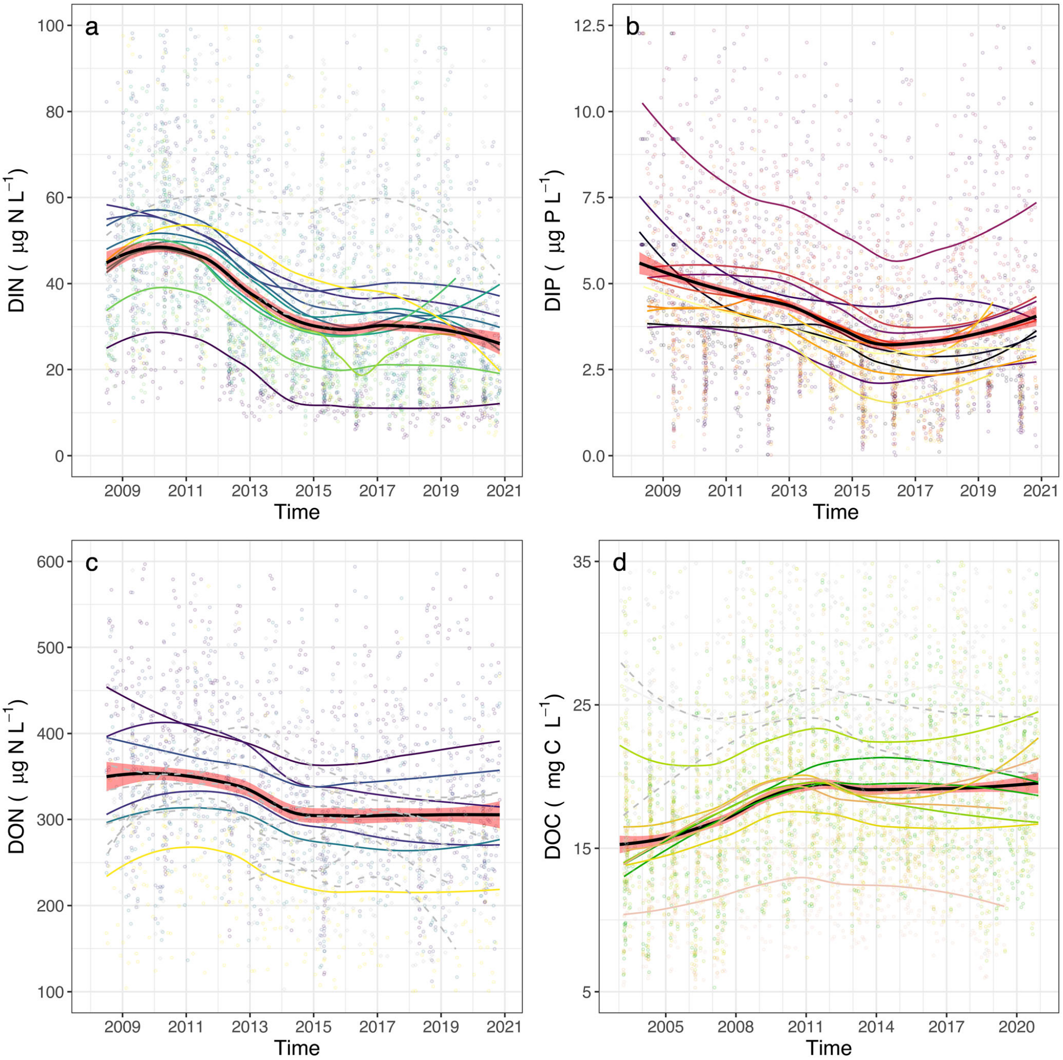

Fig. 1. Time series of organic and inorganic nutrients for the period 2008–2020 shown with locally weighted scatterplot smoothing (loess). (**a**) Dissolved inorganic nitrogen (DIN), (**b**) dissolved inorganic phosphorus (DIP), (**c**) dissolved organic nitrogen (DON) (C14 and C15 have data from 2012 to 2020), and (**d**) dissolved organic carbon (DOC) for 13 streams of the KCS (all streams have data from 2003 to 2020). Statistically significant trends (seasonal Mann–Kendall test) per stream are shown in solid lines, streams with no significant trend are shown with gray dashed lines, and the mean trend for all rivers combined is shown in black line with ± 1 SE in shaded red.

the entire KCS (C16) showed a positive Seasonal Kendall slope estimator but these were not statistically significant (Table 1). Finally, across sites, there was no significant correlation between the Seasonal Kendall slope for DIN and DIP decline and the slopes that describe DOC increases ($n = 13$, $r^2 = 0.10$ and $r^2 = 0.002$, $p > 0.05$ for DIN and DIP, respectively).

Different seasons are important for driving inorganic nitrogen and phosphorus declining trends

While both DIN and DIP concentrations show declines for most of the KCS sub-catchments at annual scales, a more detailed assessment using the Seasonal Kendall test revealed distinct seasons during which most of this long-term change

Table 1. Trends 2008–2020 of stream concentration. Significance levels are indicated by * $p < 0.05$ and ** $p < 0.01$), non-significant trends by "ns" and data not available by "n.a." Upward and downward trends are indicated by Seasonal Kendall slope estimator.

	KCS stream concentration (μg N L^{-1} yr^{-1})						
Catchment ID	**TDN**	**DIN**	**NO_3**	**NH_4**	**DON**	**DIP**	**DOC†,‡**
C1	−0.34 ns	−0.26 ns	−0.4 ns	**−0.4****	−1.3 ns	**−0.2****	**0.4****
C2	−0.84 ns	**−2.0****	**−0.8****	**−0.9****	−0.6 ns	**−0.3****	**0.3****
C4	**−8.1***	**−2.7****	**−1.1****	**−1.4****	**−6.7***	**−0.3****	0.1 ns
C5	**−12.4****	**−2.8****	**−0.9****	**−1.9****	**−11.1****	**−0.2****	0.1 ns
C6	**−9.9****	**−3.7****	**−1.5****	**−2.0****	**−6.5****	**−0.2****	**0.1***
C7	**−6.9****	**−2.7****	**−1.3****	**−1.2****	**−4.7***	**−0.5****	**0.2***
C9	**−7.0****	**−2.6****	**−0.9****	**−1.5****	**−5.7****	**−0.2****	**0.1***
C10	**−6.1***	**−2.7****	**−0.9****	**−1.5****	**−4.1***	**−0.2****	**0.2***
C12	**−4.7***	**−3.0****	**−1.0****	**−1.6****	−2.5 ns	**−0.1****	**0.2***
C13	**−4.5***	**−2.6****	**−0.9****	**−1.6****	−1.9 ns	**−0.3****	**0.3****
C14§	**−7.2****	**−2.6***	**−1.5****	**−1.3***	−2.9 ns	**−0.3****	0.05 ns
C15§	**−5.2****	−1.5 ns	−0.2 ns	**−1.4****	−3.4 ns	**−0.3****	**0.1***
C16	**−8.9****	**−3.0****	**−1.3****	**−1.5****	**−6.2****	**−0.4****	0.05 ns

†Data available from 2003 to 2020.
‡Concentrations are in (mg C L^{-1} yr^{-1}).
§Data available from 2012 to 2019.

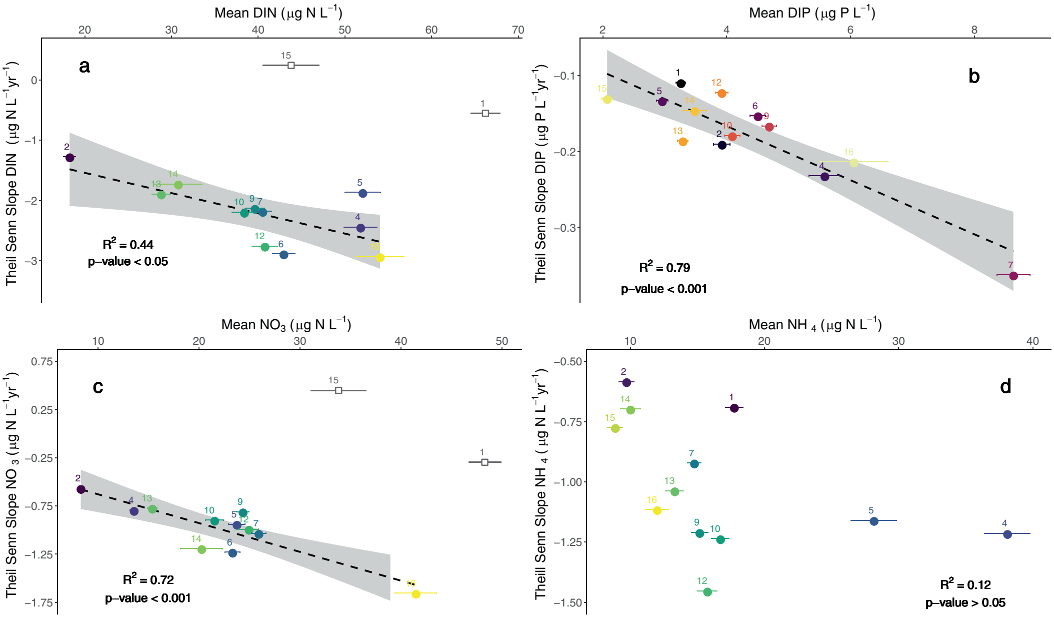

Fig. 2. Relationship between mean (error bars are ± SE) for the period of 2008–2020 of (**a**) DIP concentration vs. DIP Seasonal Kendall slope, (**b**) DIN concentration vs. DIN Seasonal Kendall slope, (**c**) NO_3 concentration vs. NO_3 Seasonal Kendall slope, and (**d**) NH_4 vs. NH_4 Seasonal Kendall slope for all streams. Streams with significant ($p < 0.05$) long-term trends are shown in colored circles, non-significant ($p > 0.05$) in light gray symbols; open square represents the site that is directly influenced by alluvial deposits; open triangle is the catchment within the KCS that has been extensively drained. Black dashed line represents the linear regression with ± 1 SE (in gray). The regression line for DIN (**b**) is based only on the closed symbols (indicated by asterisk). The numbers shown are the ID for each stream and the full description of catchment characteristics is given in Supplementary Table S1.

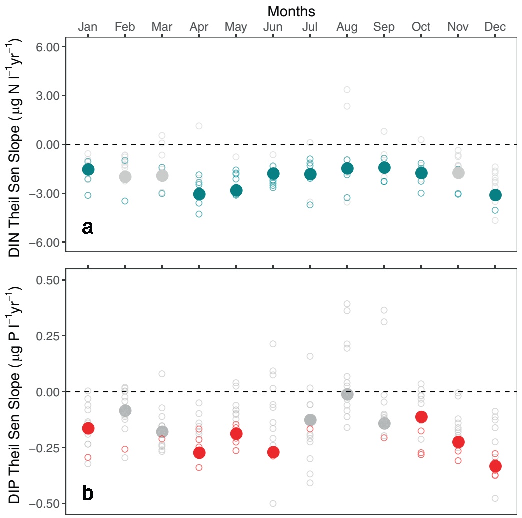

Fig. 3. Seasonal Kendall test for inorganic nutrients in stream waters. (**a**) DIN Seasonal Kendall test and (**b**) DIP Seasonal Kendal test. Pooled Theil Sen slope is shown with filled circles and site-specific Theil Sen slope is shown with hollow circles. Streams with non-significant monthly declines ($p > 0.05$) are shown in light gray. Note that the scales in *y*-axis show different magnitudes of decline.

occurred. For example, the pooled significant ($p < 0.05$) decline for DIN trends was dominated by changes during the open water season (April–October), but declines were also observed during winter months (Fig. 3a). By comparison, significant declines ($p < 0.05$) for DIP occurred during spring (April–June), as well as from autumn to early winter (October–January; Fig. 3b), both periods that begin with relatively elevated stream discharge. Specifically for spring months (April–May), discharge increased significantly in five streams and non-significantly in other seven (Supplementary Table S1), yet, when discharge is accounted for as co-variate in the trend analysis, declining trends both for DIN and DIP also remain (Supplementary Table S2).

Seasonal Kendall tests showed variation among sub-catchments in terms of the seasonality of these trends. For example, streams draining the lake (C5) and the mire (C4) did not show a decline in DIN concentrations during growing season, but rather a strong decline at spring flood (April and May), and then again later in the year (October and November, respectively). Likewise, the stream draining a forested headwater sub-catchment (C1) did not show a decline in DIP concentration during spring, but showed a strong decline during winter. Even with this variation among individual sites, the majority followed the overall seasonal trend for both DIP (8 of 13) and DIN (6 of 11, excluding C1 and C15, which did not show overall statistically significant decline for DIN).

Differentiated drivers of the declining trends of inorganic nitrogen and phosphorus

PCA analysis of catchment characteristic metrics explained 33% of the variation on axis 1, 25% of the variation on axis 2%, and 12% of the variation on axis 3 (Fig. 4d). PCA1 describes tree volume (m^3 ha^{-1}); stand age (year), ditch density (km km^2) and quaternary deposits made up of till (%). PCA2 is associated with large-scale, landscape factors like mire vs. forest cover, whereas PCA3 describes forest characteristics, specifically between spruce and pine (%). At annual time scales, the magnitude of DIN concentration decline across KCS streams was not correlated with any of these integrated catchment characteristics (i.e., PC1, PC2, or PC3). However, analysis on seasonal declines indicates that the magnitude of summer DIN change (Seasonal Kendall slope) was positively correlated to the catchment characteristics as represented by PC1 and PC2 (Fig. 4a–c). Specifically, our analysis suggests that DIN declines during summer were weakest for sub-catchments that had both higher forest cover (%) and greater tree volume (m^3 ha^{-1}) (i.e., larger relative forest cover and greater total biomass per area unit), higher stand age (year), higher ditch density (km km^2), and more quaternary till deposits (%). For this test, we did not consider the stream draining directly from the lake due to the potential for within-lake processes to drive stream chemistry, or sites affected by the esker, where summer low flow conditions are driven by contributions from deeper groundwater sources (Tiwari et al. 2014) (i.e., C16). By comparison, sub-catchments with less forest cover (%) and less sorted sediments (%), showed stronger absolute DIN declines. However, it is worth noting that the score of PC1 for catchment characteristics is also inversely correlated with the overall mean DIN concentration across sites, such that sub-catchments with greater tree volume (m^3 ha^{-1}), higher stand age (year), higher ditch density (km km^2), and more till (%) had lower mean concentrations of DIN (Supplementary Fig. S1). Furthermore, neither the magnitude of DIP decline nor the mean DIP concentration among streams in the KCS network were correlated with differences in integrated catchment characteristics, whether this was assessed annually or within seasons. Finally, while we observed declines in SO_4-S across the KCS (Supplementary Fig. S3), the magnitude of these trends was also unrelated to DIP trends for the different streams. Similarly, we observed no statistically significant trend ($p > 0.05$) for pH in any of the streams in the KCS during this period, nor were trends in DIP correlated with the average pH across sites.

Declining trends are affecting the stream nutrient balance over time

Given declining trends in DIP and DIN, together with increasing trends for DOC, we found that the ratios between C : N and C : P increased over time in almost all the streams in the KCS. Specifically, 11 of 13 streams showed a significant increase ($p < 0.05$) in the DOC : DIN ratio (Fig. 5a) and 12 of

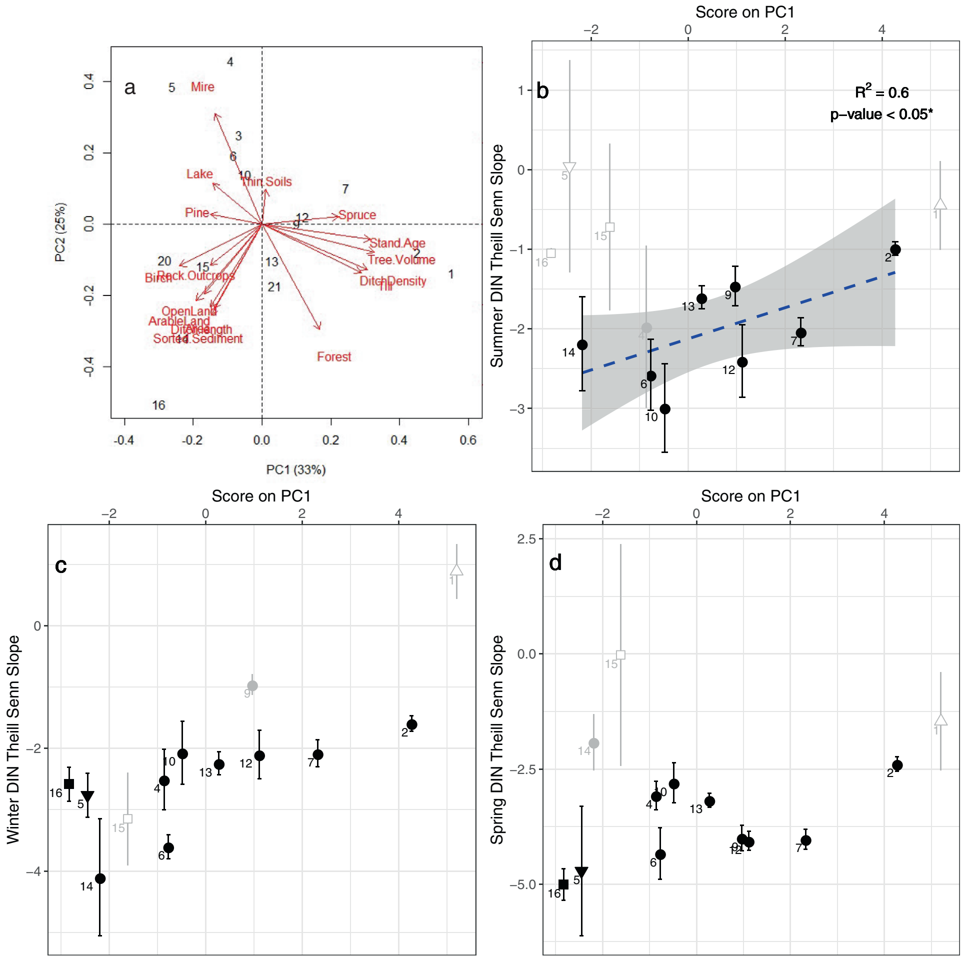

Fig. 4. Relationship between PCA scores of catchment characteristics and seasonal Theil Sen slope; streams with significant ($p < 0.05$) relationships are shown in black, non-significant ($p > 0.05$) in light gray squares (mean ± 1 SE of monthly Theil Sen slope for a given stream for the season). (**a**) Principal component analysis (PCA) of catchment characteristics for KCS, linear regression of PCA1 vs. (**b**) summer DIN Theil Sen slope, (**c**) winter DIN Theil Sen slope, and (**d**) spring DIN Theil Sen slope. Circles represent sites draining glacial till soils; the triangle is a catchment within the KCS that drains the lake; squares are two sites being influence directly and indirectly by the esker within the KCS. In panels (**b**) and (**c**), blue dotted line is the linear regression with ± 1 SE (in gray). The regression line for summer DIN (**b**) is based only on the closed symbols (indicated by asterisk). In panels (**b–d**), R^2 and p value are from multiple linear regression of PC1 and PC2 vs. seasonal Theil Sen slope, but for simplicity, only PCA1 vs. the Theil Sen slope is plotted. The numbers shown are the ID for each stream; the full description of catchment characteristics is given in Supplementary Table S1.

13 streams showed a significant increase ($p < 0.05$) in the DOC : DIP ratio (Fig. 5b). It is worth noting the two streams that did not have statistically significant increases of DOC : DIN ratio also did not show significant decreases for DIN (Tables 1 and 2). As expected, we also found high variability in the magnitude of increase in ratios among subcatchments (Table 2). On average DOC : DIN ratios significantly ($p < 0.05$) increased annually 5.9% (SD ± 1.9), ranging from 3.1% in the stream draining the entire KCS (C16) to 9.8% in the stream draining a 100% forest coverage subcatchment (C2). DOC : DIP annual increase on average was of 3.5% (SD ± 1.5), ranging from an increase of 1.5% at the stream draining a forested catchment (C10) to 5.9% at the stream draining the entire KCS (C16). Furthermore, none of the streams in the KCS had a statistically significant trend of DOC : DON ratio ($p < 0.05$) (Table 2), nevertheless 11 of

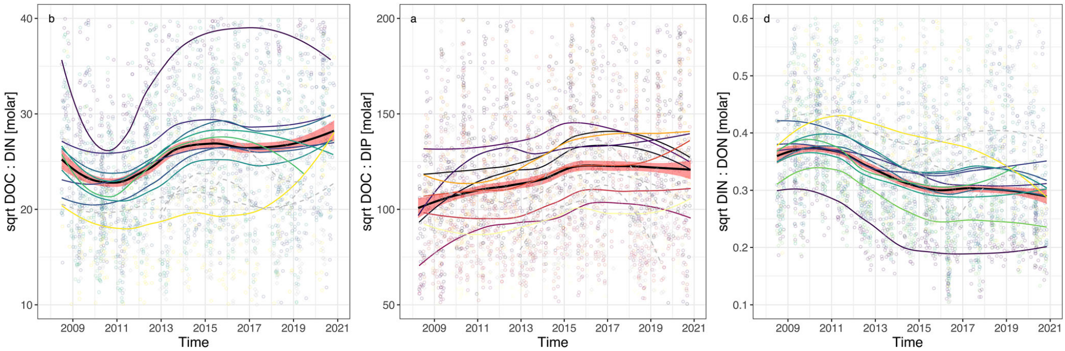

Fig. 5. Time series of molar ratios for the 13 streams of the KCS for the period of 2008–2020 shown with loess smoothing. Time series of (**a**) DOC : DIN ratio, (**b**) DOC : DIP ratio, and (**c**) DIN : DON ratio (C14 and C15 have data from 2012 to 2020). Trends of individual streams with significant trend are shown in colored solid lines, while streams with no significant trend are shown in gray dashed lines. The trend for all streams combined is shown in solid black (mean ± 1 SE in red).

13 streams showed a non-significant increasing trend. The Seasonal Mann–Kendall analysis also indicated a significant declining trend of DIN : DON ratio for 11 of the 13 streams ($p < 0.001$). Lastly, the DIN : DIP ratio showed a statistical significant decline ($p < 0.05$) for only five of the 13 streams (Table 2). Yet, for these sites, the strongest declines were observed during the summer growing season (Supplementary Fig. S2).

Discussion

Multiple ongoing environmental changes operating across high latitude landscapes have the potential to alter water quality, including the concentrations and stoichiometry of organic matter and nutrients. Here, we report widespread declines in stream DIN, DON, and DIP concentrations, which co-occur with increases in DOC concentration across a boreal stream network. Collectively, these trends suggest an overall pattern of oligotrophication across this landscape, and underpin significant changes in the stoichiometry of resource supply (DOC : DIN; DOC : DIP, DIN : DIP) to streams, which likely have consequences for aquatic communities and ecosystems (Jeppesen et al. 2002; Van De Waal et al. 2010). Further, even though the mechanisms that regulate N and P mineralization and immobilization in soils can differ in fundamental ways (Neff et al. 2000) we found declining trends both for

Table 2. Trends 2008–2020 of molar ratio for individual streams. Significance levels are indicated by * $p < 0.05$) and ** $p < 0.01$), non-significant trends by “ns” and data not available by “n.a.” Upward and downward trends are indicated by Seasonal Kendall slope estimator.

	Element ratios in streams (mol L^{-1} yr^{-1})				
Catchment ID	DOC : DIN	DOC : DIP	DOC : DON	DIN : DIP	DIN : DON
C1	4.3 ns	**621.4****	−0.12 ns	**1.5****	−0.004 ns
C2	**156.1****	**944.5****	0.05 ns	**−0.6****	**−0.006****
C4	**48.5****	**720.2****	0.34 ns	−0.2 ns	**−0.006****
C5	**26.8****	**877.6****	0.27 ns	**1.1****	**−0.005***
C6	**39.0****	**275.9***	0.03 ns	**−0.8****	**−0.010****
C7	**42.2****	**538.7****	0.11 ns	−0.1 ns	**−0.007****
C9	**28.7****	**305.3****	0.18 ns	−0.2 ns	**−0.007****
C10	**58.3****	**291.0***	0.07 ns	**−0.7****	**−0.008****
C12	**48.2****	228.6 ns	−0.24 ns	**−0.9***	**−0.010****
C13	**85.8****	**923.3****	0.05 ns	**−0.3***	**−0.007****
C14†	**44.7****	**514.1***	0.61 ns	−0.5 ns	**−0.009****
C15†	11.5 ns	**926.8***	0.83 ns	1.4 ns	0.003 ns
C16	**12.7****	**572.9****	0.24 ns	0.3 ns	**−0.009****

†Data available from 2012 to 2019.

DIN and DIP in nearly all study streams, which occur regardless of catchment characteristics and independent of hydrological change. However, despite such similarities, the seasons within which declining trends were most pronounced differed between DIN and DIP, suggesting different sets of biogeochemical controls are acting on these nutrients. Overall, given the spatial extent of observed changes, we suggest that decadal-scale trends in nutrient concentrations are most likely shaped by drivers operating at broader spatial scales, including ongoing climate changes and the legacy of atmospheric deposition (Laudon et al. 2021*a*).

Role of climatic variability

Longer and warmer growing season

The decline of DIN concentration was strongest throughout the growing season, which has been dramatically affected by climate warming. Indeed, this region has undergone an overall warming pattern for at least the last 30 years, leading to longer and warmer growing seasons, confirmed by an increase in mean summer temperature, a greater number of growing degrees days, and a shift toward earlier snowmelt (Lucas et al. 2016; Laudon et al. 2021*b*). By upregulating plant and soil processes, these climate changes could be responsible for a general tightening of the terrestrial N cycle (e.g., Craine et al. 2018), leading to reduced export to aquatic systems. For example, similar declines in riverine N in northern Sweden have been linked to greater N accumulation in soils and forest biomass, both of which have steadily increased over the last decades (Lucas et al. 2016; Craine et al. 2018). Furthermore, as observed for headwater catchments in Canada (Creed and Beall 2009), our multiple regression analysis with catchment characteristics suggests that it is not the forested catchments, but rather those with higher peat (mire) coverage that had the strongest DIN declines in stream. This pattern could mean that N cycling in peatlands has been more responsive to recent environmental changes than adjacent forests. However, this relationship could also be spurious and affected by the relatively short time scale considered here, as longer records from forested catchments in Sweden show DIN declines over the last few decades (Lucas et al. 2016), and studies elsewhere indicate that such declines may operate on the scale of centuries (Bernal et al. 2012). Similarly, given that the percentage change in DIN per year was similar across these sites, variation in absolute declines may simply result from differences in average concentration. Accordingly, correlations between the Sen slope for DIN and catchment structure likely reflect the role of mires as comparatively strong DIN sources to outlet streams (arising from deep peat layers, Laudon and Sponseller 2018). By comparison, DIN concentrations in the most forested catchments are already so low that the magnitude of absolute decline is small. Either way, our observations suggest that decline in stream DIN reflects a tightening of the N cycle owing to elevated rates of biological activity in the terrestrial landscape (Hu et al. 2014). Furthermore, consistent with this hypothesis, DON concentrations have also declined, and the DOC : DON ratio has increased for more than half of the sites, indicating a general increase in the efficiency by which N is recycled and retained in catchment soils (Wymore et al. 2021) and suggesting that the DOM pool is experiencing fundamental changes (Rodríguez-Cardona et al. 2022).

Warmer winters and wetter autumns

Our results also highlighted declines for DIN but more notably for DIP during autumn and winter, when rates of biological activity in the surrounding catchment should be relatively low. However, these are seasons that are also currently being altered by climate change (Laudon et al. 2021*b*). In fact some of the most significant longer-term hydro-climatic changes in the KCS (1981–2010) are observed during autumn and winter, including a clear warming trend, a delay in the onset of snow cover by $\sim 0.5\ \mathrm{d\,yr^{-1}}$ over the last 40 years (Laudon and Löfvenius 2016), and increases in late winter discharge (March; Laudon and Sponseller 2018). These changes in winter conditions could influence stream chemistry through physical, biological, and geochemical mechanisms. For example, wetter conditions in autumn/winter (e.g., Vormoor et al. 2015) could drive observed declines in winter DIN and DIP concentration simply by dilution. Yet, for the period considered here, we observed decreases in winter discharge, suggesting that declines in DIP and DIN are not a dilution signal, and must be driven by other processes. Declining nutrient trends during spring (April–May) could reflect dilution as almost all sites exhibited increases in discharge during this time window, but this hydrological change was not sufficient to account for the solute trends, indicating that other mechanisms are operating. Multiple biogeochemical processes in catchments and near-stream soils could underlie these observations. For example, the emergence of thinner snow packs and accelerated freeze–thaw cycles throughout may have negative consequences for microbial communities and processes in near-stream soils (Campbell and Laudon 2019), leading to reductions in N and P mineralization and thus declines in supply to streams. Further, in the autumn months, changes of in-stream uptake such as higher heterotrophic uptake rates due to colonization of new inputs of detritus coupled with a decrease of in-stream nitrification may be happening, resulting in net uptake of NO_3 and PO_4 (Mulholland 2004; Sebestyen et al. 2014). It is worth noting that although biological activity could be influencing the declining trends in autumn/winter months, it seems that it is not driven by the land cover characteristics of the catchments (O'Brien et al. 2013). Finally, wetter conditions during the non-growing season could elevate water tables, activating shallower layers of riparian soils and thereby promoting geochemical processes that remove DIP. Specifically, these upper soil horizons are more organic rich and acidic (Ledesma et al. 2018), and in some cases also have higher concentrations of aluminum (Al) and iron (Fe) (Lidman et al. 2017).

Activating more surficial soil pathways could therefore enhance phosphate sorption (Giesler et al. 2005) and thereby reduce mobilization to streams. This same mechanism could also explain the declines observed during May and June where the water tables are highest and the declines in DIP are even stronger. These various mechanisms are not mutually exclusive and resolving their potential influences will require additional work. Regardless, our results indicate that recent and ongoing changes in winter conditions are altering the exchange of key nutrients between boreal soils and streams.

Legacy effects of atmospheric deposition

While changing climate conditions can influence catchment nutrient cycles through effects on biology and hydrology, these changes often co-occur with a recovery from historical atmospheric deposition, which may also influence nutrient trends. However, the legacy of N deposition does not seem to, by itself, explain the decline of DIN concentration in northern Swedish streams (Lucas et al. 2016), in contrast to studies that have reported this connection for lakes and streams elsewhere (Kothawala et al. 2011; Isles et al. 2018; Kaste et al. 2020). For the KCS, this mechanism seems unlikely for several reasons. First, atmospheric N deposition is comparatively low in the region (Gundale et al. 2011; Isles et al. 2018), well below suggested thresholds of deposition required to support significant leaching in streams (e.g., 10 $\mathrm{kg\,N\,ha^{-1}\ yr^{-1}}$; Dise and Wright 1995). Similarly, while N deposition has declined by twofold over that last 25 years, levels have never been notably elevated, peaking at around 2.5 $\mathrm{kg\,N\,ha^{-1}\ yr^{-1}}$ in 1980 and dropping to $\sim 1\ \mathrm{kg\,N\,ha^{-1}\ yr^{-1}}$ in 2020 (Laudon et al. 2021*a*). Given the critical role of N as a limiting nutrient in Fennoscandian landscapes (Högberg et al. 2017), these levels of deposition are unlikely to drive a surplus in the plant–soil system. Finally, while some studies have explicitly linked reductions in N deposited by snow to changes in stream chemistry during spring (e.g., Kothawala et al. 2011), empirical evidence during snowmelt in the KCS suggests that inorganic N is rapidly taken up by mosses and soils before reaching streams (Petrone et al. 2007; Forsum et al. 2008). Therefore, it seems more likely that the observed declines in stream DIN are closely linked to catchment processes that are altered by ongoing climate trends (Kaste et al. 2020).

By comparison, it is less clear whether and how recovery from atmospheric deposition is influencing trends in stream DIP. For example, it is possible that declines in DIP reflect an increase in P adsorption as the catchment recovers from sulfate deposition, which peaked in the late 1970s (Laudon et al. 2021*a*). We observed widespread declines in stream S-$\mathrm{SO_4}$ across the KCS (Supplementary Fig. S3), which could decrease the competition between sulfate and P in soil adsorption processes, specifically those involving aluminum (Al) and iron (Fe), thus elevating the P-binding capacity of soils (Geelhoed et al. 1997). However, it is important to note that we were not able to correlate the magnitudes of DIP and $\mathrm{SO_4}$ trends across the different sub-catchments. Alternatively, adsorption rates could be enhanced by acidic conditions in organic soils (Giesler et al. 2005), where lower pH can increase P adsorption (McDowell et al. 2002). And although it is well documented that northern Sweden never reached a state of chronic acidification (Bishop et al. 2000), the KCS sub-catchments remain naturally acidic throughout the year (pH range from 4.4 to 6.6) and pH does not show any statistically significant recovery trend ($p > 0.05$) for the period. However, there is still a discrepancy among studies on the relationship between pH, P sorption, and declines in surface water P concentration as both positive (Baker et al. 2015) and negative (McDowell et al. 2002) relationships have been reported in acidic solutions. In the end, a combination of lower rates of biological mineralization, increased activation of Al and Fe sinks, and reduced competition with sulfate for adsorption (McDowell et al. 2002; Giesler et al. 2005) could all have an impact on P retention in soils, with consequences for DIP supply to streams. Clearly, further empirical studies are needed to resolve which of these alternatives are most important and identify the linkages between soil P cycling and stream chemistry. This is particularly important during winter, as this is a time when DIP trends are strongest—and a time that is projected to change most in the future (Teutschbein et al. 2015).

Ecosystem implications

The widespread decline in DIP and DIN, concurrent with the increase of DOC in almost all sites in the KCS has fundamentally changed the stoichiometry of resource supply to streams. Firstly, for some streams, the N : P molar ratio is decreasing, suggesting that N is declining faster than P, as observed in lakes across this region (Isles et al. 2018). While this change in DIN : DIP is not as widespread in the network, if analyzed by season, we see that the strongest declines occur during the most important time of the year for aquatic productivity (July–September; Supplementary Fig. S2). Given the role of N as a limiting nutrient in lakes (Isles et al. 2020) and streams (Burrows et al. 2021) in this region, these trends point to a strengthening of N deficiency which could lead to declines in aquatic productivity in these ecosystems. Furthermore, decreasing trends in DIN : DON ratios suggest that biological N demand in these streams and lakes may need to be increasingly met by organic forms. While there is evidence that browning trends can be linked to increased availability of nutrients to support aquatic productivity (Bergström and Karlsson 2019), it is not clear whether and how organic N may compensate for losses of DIN in these ecosystems. Estimates of DON bioavailability in this region indicate that ca. 20–25% of this pool is biologically reactive (Soares et al. 2017), but the implications of increasing reliance on this as an N source for aquatic processes and communities may depend on environmental conditions (Wymore et al. 2015) and remain poorly understood. For that matter, several KCS sites are also showing declines in DON, which collectively suggests that these already N-limited ecosystems are receiving less and less of this critical resource.

Finally, we found the strongest trend in the balance between the supply of organic energy vs. nutrients, with DOC : DIN and DOC : DIP ratios increasing in the majority of the streams. While these changes could reflect the direct influence of increasing DOC on these nutrient pools via upregulated immobilization (sensu Taylor and Townsend 2010), we did not observe any obvious relationship in the magnitudes of nutrient decline and DOC increase across sites in the KCS. The potential for direct causal links between trends in DOC and inorganic nutrients deserves more attention. Currently, however, our results point toward independent sets of drivers acting on all three solutes, with DOC likely regulated by SO_4 decline (Fork et al. 2020), DIN linked to biological processes in the catchment, and P likely connected to geochemical changes in near-stream soils. Regardless of these mechanisms, the observed imbalance in energy vs. nutrient supply could have long-term effects on the oligotrophication process (i.e., decline of nutrients and ecosystem productivity) in KCS streams, since most are becoming richer in organic carbon but poorer in inorganic nutrients. Several studies have demonstrated the importance of interactions among N, P, and DOC stream water concentrations in freshwater systems (Francoeur 2001; Elser et al. 2007; Bechtold et al. 2012; Peñuelas et al. 2012) where there are strong ecological and biogeochemical connections among these elements (Dodds et al. 2004). For example, declines in inorganic N and P could influence C cycling in streams either by limiting or co-limiting nutrients for primary production (Burrows et al. 2021) and heterotrophic respiration (Burrows et al. 2015) and/or by altering how these nutrients facilitate litter decomposition (Maranger et al. 2018).

Conclusion

Widespread increases in nutrient inputs to aquatic ecosystems are responsible for a litany of unwanted water quality outcomes (i.e., eutrophication) and thus rightfully receive much attention from scientists and managers alike. Yet, for large parts of the global north, water chemistry trends are often not directly shaped by anthropogenic nutrient loading, but instead are more subtly altered by catchment responses to environmental change operating at larger scales (Davis et al. 2013). While these aquatic systems may be far removed from population centers, they nonetheless provide important ecosystem services, including the support of economically and culturally important food webs. Our 13-year dataset provides insight into the how ongoing environment change at high latitudes, including climate warming and the legacy of atmospheric deposition, may modify the supply of key elements essential for the growth and reproduction of aquatic organisms. There is clearly uncertainty regarding the proximate mechanisms driving these trends, and further research into the soil processes that mediate connections between northern streams to their catchments is needed. Despite these limitations, our results show clear declines in inorganic nutrient concentrations that are concurrent with increases in DOC across this boreal stream network. Compared to our relatively deep understanding of the eutrophication process, we know little about how oligotrophication may alter aquatic communities and ecosystems, and even less about how concurrent increases in DOC supply may mediate such responses. Our observations raise the strong potential for declines in autotrophic productivity in these systems, but may also signal the emergence of compensatory processes, including greater use of organic nutrients and/or upregulated rates of nitrogen fixation. Either way, the future of these northern rivers and the food webs they support seems to hinge on how they respond to an environment that is poorer in inorganic nutrients and richer in dissolved organic matter.

Data availability statement

All data are available for download from the KCS database (https://data.krycklan.se/).

References

Asmala, E., J. Carstensen, and A. Raike. 2019. Multiple anthropogenic drivers behind upward trends in organic carbon concentrations in boreal Rivers. Environ. Res. Lett. **14**: 124018. doi:10.1088/1748-9326/ab4fa9

Baker, S. R., S. A. Watmough, and M. Catherine Eimers. 2015. Phosphorus forms and response to changes in PH in acid-sensitive soils on the Precambrian shield. Can. J. Soil Sci. **95**: 95–108. doi:10.4141/cjss-2014-035

Barichivich, J., K. R. Briffa, R. B. Myneni, T. J. Osborn, T. M. Melvin, P. Ciais, S. Piao, and C. Tucker. 2013. Large-scale variations in the vegetation growing season and annual cycle of atmospheric CO2 at high northern latitudes from 1950 to 2011. Glob. Chang. Biol. **19**: 3167–3183. doi:10.1111/gcb.12283

Bechtold, H. A., A. M. Marcarelli, C. V. Baxter, and R. S. Inouye. 2012. Effects of N, P, and organic carbon on stream biofilm nutrient limitation and uptake in a semi-arid watershed. Limnol. Oceanogr. **57**: 1544–1554. doi:10.4319/lo.2012.57.5.1544

Bergström, A.-K., and J. Karlsson. 2019. Light and nutrient control phytoplankton biomass responses to global change in Northern Lakes. Glob. Chang. Biol. **25**: 2021–2029. doi:10.1111/gcb.14623

Bernal, S., L. O. Hedin, G. E. Likens, S. Gerber, and D. C. Buso. 2012. Complex response of the Forest nitrogen cycle to climate change. PNAS **109**: 3406–3411. doi:10.1073/pnas.112144810

Bishop, K. H., H. Laudon, and S. Kohler. 2000. Separating the natural and anthropogenic components of spring flood PH decline: A method for areas that are not chronically acidified anthropogenic nitrate. Water Resource Res. **36**: 1873–1884. doi:10.1029/2000WR900030

Blackburn, M., J. L. J. Ledesma, T. Näsholm, H. Laudon, and R. A. Sponseller. 2017. Evaluating hillslope and riparian contributions to dissolved nitrogen (N) export from a boreal Forest catchment. J. Geophys. Res. Biogeo. **122**: 324–339. doi:10.1002/2016JG003535

Burrows, R. M., E. R. Hotchkiss, M. Jonsson, H. Laudon, B. G. Mckie, and R. A. Sponseller. 2015. Nitrogen limitation of heterotrophic biofilms in boreal streams. Freshwater Biol. **60**: 1237–1251. doi:10.1111/fwb.12549

Burrows, R. M., M. Jonsson, E. Fältström, J. Andersson, and R. A. Sponseller. 2021. Interactive effects of light and nutrients on stream algal growth modified by forest management in boreal landscapes. Forest Ecol. Manage. **492**: 119212. doi:10.1016/j.foreco.2021.119212

Campbell, J. L., and H. Laudon. 2019. Carbon response to changing winter conditions in northern regions: Current understanding and emerging research needs. Environ. Rev. **27**: 545–566. doi:10.1139/er-2018-0097

Craine, J. M., and others. 2018. Isotopic evidence for oligotrophication of terrestrial ecosystems. Nature Ecol. Evol. **2**: 1735–1744. doi:10.1038/s41559-018-0694-0

Creed, I. F., and F. D. Beall. 2009. Distributed topographic indicators for predicting nitrogen export from headwater catchments. Water Resour. Res. **45**: 1–12. doi:10.1029/2008WR007285

Davis, J. M., C. V. Baxter, E. J. Rosi-Marshall, J. L. Pierce, and B. T. Crosby. 2013. Anticipating stream ecosystem responses to climate change: Toward predictions that incorporate effects via land-water linkages. Ecosystems **16**: 909–922. doi:10.1007/s10021-013-9653-4

Deininger, A., H. F. Kaste, and K. Austnes. 2020. Organic nitrogen steadily increasing in Norwegian Rivers draining to the Skagerrak coast. Sci. Rep. **10**: 1–9. doi:10.1038/s41598-020-755232-5

Dise, N. B., and R. F. Wright. 1995. Nitrogen leaching from European forests in relation to nitrogen deposition. For. Ecol. Manage. **71**: 153–161. doi:10.1016/0378-1127(94)06092-W

Dodds, W. K., and others. 2004. Carbon and nitrogen stoichiometry and nitrogen cycling rates in streams. Ecosyst. Ecol. **140**: 458–467. doi:10.1007/s00442-004-1599-y

Eimers, M. C., S. A. Watmough, A. M. Paterson, P. J. Dillon, and H. Yao. 2009. Long-term declines in phosphorus export from forested catchments in South-Central Ontario. Can. J. Fish. Aquat. Sci. **66**: 1682–1692. doi:10.1139/F09-101

Elser, J. J., and others. 2000. Nutritional constraints in terrestrial and freshwater food webs. Nature **408**: 578–580. doi:10.1038/35046058

Elser, J., and others. 2007. Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems. Ecol. Lett. **10**: 1135–1142. doi:10.1111/j.1461-0248.2007.01113.x

Finstad, A. G., T. Andersen, S. Larsen, K. Tominaga, S. Blumentrath, H. A. De Wit, H. Tømmervik, and D. O. Hessen. 2016. From greening to Browning: Catchment vegetation development and reduced S-deposition promote organic carbon load on decadal time scales in Nordic Lakes. Sci. Rep. **6**: 1–8. doi:10.1038/srep31944

Fork, M. L., R. A. Sponseller, and H. Laudon. 2020. Changing source-transport dynamics drive differential browning trends in a boreal stream network. Water Resour. Res. **56**: e2019WR026336. doi:10.1029/2019WR026336

Forsum, Å., H. Laudon, and A. Nordin. 2008. Nitrogen uptake by *Hylocomium splendens* during snowmelt in a boreal Forest. Ecoscience **15**: 315–319. doi:10.2980/15-3-3174

Francoeur, S. N. 2001. Meta-analysis of lotic nutrient amendment experiments: Detecting and quantifying subtle responses. Am. Benthol. Soc **20**: 358–368. doi:10.2307/1468034

Geelhoed, J. S., T. Hiemstra, and W. H. Van Riemsdijk. 1997. Phosphate and sulfate adsorption on goethite: Single anion and competitive adsorption. Geochim. Cosmochim. Acta **61**: 2389–2396. doi:10.1016/S0016-7037(97)00096-3

Giesler, R., T. Andersson, L. Lövgren, and P. Persson. 2005. Phosphate sorption in aluminum- and iron-rich humus soils. Soil Sci. Soc. Am. J. **69**: 77–86. doi:10.2136/sssaj2005.0077a

Gundale, M. J., T. H. Deluca, and A. Nordin. 2011. Bryophytes attenuate anthropogenic nitrogen inputs in boreal forests. Glob. Chang. Biol. **17**: 2743–2753. doi:10.1111/j.1365-2486.2011.02407.x

Hasselquist, E. M., W. Lidberg, R. A. Sponseller, A. Ågren, and H. Laudon. 2018. Identifying and assessing the potential hydrological function of past artificial Forest drainage. Ambio **47**: 546–556. doi:10.1007/s13280-017-0984-9

Hirsch, R. M., J. R. Slack, and R. A. Smith. 1982. Techniques of trend analysis for monthly water quality data. Water Resour. Res. **18**: 107–121. doi:10.1029/WR018i001p00107

Hirsch, R. M., and J. R. Slack. 1984. A nonparametric trend test for seasonal data with serial dependence. Water Resour. Res. **20**: 727–732. doi:10.1029/WR020i006p00727

Högberg, P., T. Näsholm, O. Franklin, and M. N. Högberg. 2017. Tamm review: On the nature of the nitrogen limitation to plant growth in Fennoscandian boreal forests. For. Ecol. Manage. **403**: 161–185. doi:10.1016/j.foreco.2017.04.045

Hu, Y.-L., E.-R. Yan, W.-J. Choi, F. Salifu, Z. Xiao Tan, C. Chen, D.-H. Zeng, and S. X. Chang. 2014. Soil nitrification and foliar Δ15N declined with stand age in trembling Aspen and Jack pine forests in Northern Alberta, Canada. Plant and Soil **376**: 399–409. doi:10.1007/s11104-013-1994-4

Huser, B. J., and E. Rydin. 2005. Phosphorus inactivation by aluminum in lakes Gårdsjön and Härsvatten sediment during the industrial acidification period in Sweden. Can. J. Fish. Aquat. Sci. **62**: 1702–1709. doi:10.1139/f05-083

Huser, B. J., M. N. Futter, R. Wang, and J. Fölster. 2018. Persistent and widespread long-term phosphorus declines in Boreal Lakes in Sweden. Sci. Total Environ. **613–614**: 240–249. doi:10.1016/j.scitotenv.2017.09.067

Isles, P. D. F., I. F. Creed, and A. K. Bergström. 2018. Recent synchronous declines in DIN:TP in Swedish Lakes. Global Biogeochem. Cycles **32**: 208–225. doi:10.1002/2017GB005722

Isles, P. D. F., A. Jonsson, I. F. Creed, and A. K. Bergström. 2020. Does Browning affect the identity of limiting nutrients in lakes? Aquat. Sci. **82**: 1–14. doi:10.1007/s00027-020-00718-y

Jeppesen, E., J. P. Jensen, and M. Sondergaard. 2002. Response of phytoplankton, zooplankton and fish to re-oligotrophication: An 11 year study of 23 Danish lakes. Aquat. Ecosyst. Health Manage. **5**: 31–43. doi:10.1080/14634980260199945

Kaste, Ø., K. Austnes, and H. A. de Wit. 2020. Streamwater responses to reduced nitrogen deposition at four small upland catchments in Norway. Ambio **49**: 1759–1770. doi:10.1007/s13280-020-01347-3

Kothawala, D. N., S. A. Watmough, M. N. Futter, L. Zhang, and P. J. Dillon. 2011. Stream nitrate responds rapidly to decreasing nitrate deposition. Ecosystems **14**: 274–286. doi:10.1007/s10021-011-9422-1

Kozii, N., and others. 2020. Partitioning growing season water balance within a forested boreal catchment using sap flux, eddy covariance, and a process-based model. Hydrol. Earth Syst. Sci. **24**: 2999–3014. doi:10.5194/hess-24-2999-2020

Kritzberg, E. S., E. M. Hasselquist, M. Škerlep, S. Löfgren, O. Olsson, J. Stadmark, S. Valinia, L. A. Hansson, and H. Laudon. 2020. Browning of freshwaters: Consequences to ecosystem services, underlying drivers, and potential mitigation measures. Ambio **49**: 375–390. doi:10.1007/s13280-019-01227-5

Laudon, H., I. Taberman, A. Ågren, M. Futter, M. Ottosson-Löfvenius, and K. Bishop. 2013. The Krycklan catchment study - A flagship infrastructure for hydrology, biogeochemistry, and climate research in the boreal landscape. Water Resour. Res. **49**: 7154–7158. doi:10.1002/wrcr.20520

Laudon, H., and M. O. Löfvenius. 2016. Adding snow to the picture – providing complementary winter precipitation data to the Krycklan catchment study database. Hydrol. Process. **30**: 2413–2416. doi:10.1002/hyp.10753

Laudon, H., and R. A. Sponseller. 2018. How landscape organization and scale shape catchment hydrology and biogeochemistry: Insights from a long-term catchment study. Wiley Interdiscip. Rev. Water **5**: e1265. doi:10.1002/wat2.1265

Laudon, H., R. A. Sponseller, and K. Bishop. 2021*a*. From legacy effects of acid deposition in boreal streams to future environmental threats. Environ. Res. Lett. **16**: 15007. doi:10.1088/1748-9326/abd064

Laudon, H., and others. 2021*b*. Northern landscapes in transition: Evidence, approach and ways forward using the Krycklan catchment study. Hydrol. Process. **35**: 1–15. doi:10.1002/hyp.14170

Ledesma, J. L. J., T. Grabs, M. N. Futter, K. H. Bishop, H. Laudon, and S. J. Köhler. 2013. Riparian zone control on base cation concentration in boreal streams. Biogeosciences **10**: 3849–3868. doi:10.5194/bg-10-3849-2013

Ledesma, J. L. J., M. N. Futter, M. Blackburn, F. Lidman, T. Grabs, R. A. Sponseller, H. Laudon, K. H. Bishop, and S. J. Köhler. 2018. Towards an improved conceptualization of riparian zones in boreal forest headwaters. Ecosystems **21**: 297–315. doi:10.1007/s10021-017-0149-5

Libiseller, C., and A. Grimvall. 2002. Performance of partial Mann-Kendall tests for trend detection in the presence of covariates. Environmetrics **13**: 71–84. doi:10.1002/env.507

Lidman, F., Å. Boily, H. Laudon, and S. Köhler. 2017. From soil water to surface water – how the riparian zone controls the transport of major and trace elements from a boreal forest to a stream. Biogeosciences. **14**: 3001–3014. doi:10.5194/bg-14-3001-2017

Lucas, R. W., R. A. Sponseller, M. J. Gundale, J. Stendahl, J. Fridman, P. Högberg, and H. Laudon. 2016. Long-term declines in stream and river inorganic nitrogen (N) export correspond to forest change. Ecol. Appl. **26**: 545–556. doi:10.1890/14-2413

Maranger, R., S. E. Jones, and J. B. Cotner. 2018. Stoichiometry of carbon, nitrogen, and phosphorus through the freshwater pipe. Limnol. Oceanogr. Lett. **3**: 89–101. doi:10.1002/lol2.10080

Marchetto, A. 2017. rkt: Mann-Kendall test, Seasonal and Regional Kendall tests.

McDowell, R. W., P. C. Brookes, N. Mahieu, P. R. Poulton, A. E. Johnston, and A. N. Sharpley. 2002. The effect of soil acidity on potentially mobile phosphorus in a grassland soil. J. Agric. Sci. **139**: 27–36. doi:10.1017/S0021859602002307

Monteith, D. T., and others. 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature **450**: 537–540. doi:10.1038/nature06316

Mulholland, P. J. 2004. The importance of in-stream uptake for regulating stream concentrations and outputs of N and P from a forested watershed: Evidence from long-term chemistry records for Walker Branch Watershed. Biogeochemistry **70**: 403–426. doi:10.1007/s10533-004-0364-y

Neff, J. C., S. E. Hobbie, and P. M. Vitousek. 2000. Nutrient and mineralogical control on dissolved organic C, N and P fluxes and stoichiometry in Hawaiian soils. Biogeochemistry **51**: 283–302. doi:10.1023/A:1006414517212

O'Brien, H. D., M. Catherine Eimers, S. A. Watmough, and N. J. Casson. 2013. Spatial and temporal patterns in total phosphorus in South-Central Ontario streams: The role of wetlands and past disturbance. Can. J. Fish. Aquat. Sci. **70**: 766–774. doi:10.1139/cjfas-2012-0474

Oksanen, J. 2015. Multivariate analysis of ecological communities in R: Vegan tutorial.

Peñuelas, J., J. Sardans, A. Rivas-Ubach, and I. Janssens. 2012. The human-induced imbalance between C, N and P in Earth's life system. Glob. Chang. Biol. **18**: 3–6. doi:10.1111/j.1365-2486.2011.02568.x

Petrone, K., I. Buffam, and H. Laudon. 2007. Hydrologic and biotic control of nitrogen export during snowmelt: A combined conservative and reactive tracer approach. Water Resour. Res. **43**: 1–13. doi:10.1029/2006WR005286

Piao, S., and others. 2020. Characteristics, drivers and feedbacks of global greening. Nature Rev. Earth Environ. **1**: 14–27. doi:10.1038/s43017-019-0001-x

Pohlert, T. 2020. Trend: Non-parametric trend tests and change-point detection. 1–18.

R Core Team. 2020. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria.

Rodríguez-Cardona, B. M., and others. 2022. Shifting stoichiometry: Long-term trends in stream-dissolved organic matter reveal altered C:N ratios due to history of atmospheric acid deposition. Glob. Chang. Biol. **28**: 98–114. doi:10.1111/gcb.15965

Rosi-Marshall, E. J., E. S. Bernhardt, D. C. Buso, C. T. Driscoll, and G. E. Likens. 2016. Acid rain mitigation experiment shifts a forested watershed from a net sink to a net source of nitrogen. Proc. Natl. Acad. Sci. USA **113**: 7580–7583. doi:10.1073/pnas.1607287113

Sarkkola, S., and others. 2012. Trends in concentrations and export of nitrogen in boreal forest streams. Boreal Environ. Res. **17**: 85–101.

Sebestyen, S. D., J. B. Shanley, E. W. Boyer, C. Kendall, and D. H. Doctor. 2014. Coupled hydrological and biogeochemical processes controlling variability of nitrogen species in streamflow during autumn in an upland Forest. Water Resour. Res. **50**: 1569–1591. doi:10.1002/2013WR013670

Smith, V. H., and D. W. Schindler. 2009. Eutrophication science: Where do we go from here? Trends Ecol. Evol. **24**: 201–207. doi:10.1016/j.tree.2008.11.009

Soares, A. R. A., A. K. Bergstrom, R. A. Sponseller, J. M. Moberg, R. Giesler, E. S. Kritzberg, M. Jansson, and M. Berggren. 2017. New insights on resource stoichiometry: Assessing availability of carbon, nitrogen, and phosphorus to bacterioplankton. Biogeosciences **14**: 1527–1539. doi:10.5194/bg-14-1527-2017

Stetler, J. T., L. B. Knoll, C. T. Driscoll, and K. C. Rose. 2021. Lake Browning generates a spatiotemporal mismatch between dissolved organic carbon and limiting nutrients. Limnol. Oceanogr. Lett. **10**: 182–191. doi:10.1002/lol2.10194

Taylor, P. G., and A. R. Townsend. 2010. Stoichiometric control of organic carbon-nitrate relationships from soils to the sea. Nature **464**: 1178–1181. doi:10.1038/nature08985

Teutschbein, C., T. Grabs, R. H. Karlsen, H. Laudon, and K. Bishop. 2015. Hydrological response to changing climate conditions: Spatial streamflow variability in the boreal region. Water Resour. Res. **51**: 9425–9446. doi:10.1002/2015WR017337

Tiwari, T., H. Laudon, K. Beven, and A. M. Ågren. 2014. Downstream changes in DOC: Inferring contributions in the face of model uncertainties. Water Resour. Res. **50**: 514–525. doi:10.1002/2013WR014275

Van De Waal, D. B., A. M. Verschoor, J. M. H. Verspagen, E. Van Donk, and J. Huisman. 2010. Climate-driven changes in the ecological stoichiometry of aquatic ecosystems. Front. Ecol. Environ. **8**: 145–152. doi:10.1890/080178

Vormoor, K., D. Lawrence, M. Heistermann, and A. Bronstert. 2015. Climate change impacts on the seasonality and generation processes of floods – projections and uncertainties for catchments with mixed snowmelt/rainfall regimes. Hydrol. Earth Syst. Sci. **19**: 913–931. doi:10.5194/hess-19-913-2015

Wickham, H. 2009. Ggplot2: Elegant graphics for data analysis. Springer.

Wit, H. A., and others. 2020. Land-use dominates climate controls on nitrogen and phosphorus export from managed and natural Nordic headwater catchments. Hydrol. Process. **34**: 4831–4850. doi:10.1002/hyp.13939

de Wit, H., and others. 2016. Current Browning of surface waters will be further promoted by wetter climate. Environ. Sci. Technol. Lett. **3**: 430–435. doi:10.1021/acs.estlett.6b00396

Wymore, A. S., B. Rodríguez-Cardona, and W. H. McDowell. 2015. Direct response of dissolved organic nitrogen to nitrate availability in headwater streams. Biogeochemistry **126**: 1–10. doi:10.1007/s10533-015-0153-9

Wymore, A. S., and others. 2021. Gradients of anthropogenic nutrient enrichment alter N composition and DOM stoichiometry in freshwater ecosystems. Global Biogeochem. Cycles **35**: 1–11. doi:10.1029/2021GB006953

Conflict of Interest

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RESEARCH ARTICLE

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Biochar as a potential tool to mitigate nutrient exports from managed boreal forest: A laboratory and field experiment

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Abstract

Forest management in drained forested peatlands can negatively affect water quality due to the increase in exports of organic matter and nutrients. Therefore, new methods to alleviate this impact are needed. In laboratory conditions, biochar has been shown to be a strong sorbent of organic and inorganic nutrients due to its high surface area and ion-exchange capacity. However, evidence of the adsorption capacity in field conditions is lacking. Here, we studied the water purification performance of two different biochar feedstocks (wood- and garden residue-based) in a 10-day laboratory experiment where we incubated biochar with runoff water collected from drainage ditches in clear-cut peatland forests. We measured changes in pH and concentrations of inorganic phosphorus (PO_4), total dissolved nitrogen (TDN), and dissolved organic carbon (DOC). The biochar with the best adsorbent capacity in the laboratory experiment was then tested in field conditions in a replicated catchment-scale experiment, where both clear-cutting and ditch cleaning were performed. We determined the nutrient concentration of water at the inlet and outlet of biochar filters placed in outflow ditches of four catchments. We found that under laboratory conditions wood-based biochar efficiently adsorbed TDN and DOC, however, it released PO_4. Furthermore, we found that the biochar filters reduced TDN and DOC concentration in field conditions. However, the percentage decrease in concentration was dependent on the initial concentrations of nutrients in the water and could be considered low. Moreover, we found that the biochar in the filters increased in TN content over the course of the experiment. This suggests that a wood-based biochar filter has the potential to be a water protection tool for reducing the export of nutrients from catchments with high nutrient concentration. And that the biochar from the ditches could be applied back to the regenerating forest catchment as a potential soil amendment, closing the nutrient cycle.

KEYWORDS

biochar, dissolved organic carbon, forest management, nitrogen, nutrient adsorption, phosphorus, water quality

1 | INTRODUCTION

In Sweden, 15% of peatland areas are influenced by forestry (Vasander et al., 2003) and are thus affected by forest management activities such as clear-cutting harvest followed by ditch cleaning. Clear-cutting and ditch cleaning in drained forested peatlands often deteriorates water quality due to the increased export of organic matter, nutrients, and suspended solids (Joensuu et al., 2002; Kaila et al., 2014; Nieminen et al., 2017; Nieminen & Penttilä, 2004). Specifically, increased concentrations of dissolved organic matter (DOC) and nutrients such as nitrogen (N) and phosphorus (P) to downstream freshwater ecosystems could lead to notorious alterations of streams and lakes such as brownification (Kritzberg et al., 2020; Monteith et al., 2007) and eutrophication accompanied with algae blooms (Smith & Schindler, 2009).

Large areas of drained peatlands will soon reach harvest age in Sweden and Finland (Hytönen et al., 2020), increasing the risk of diffuse pollution in the near future. At present, a wide range of technologies and methods for safeguarding water resources have been used to mitigate nutrient export loads to watercourses, including sedimentation ponds and peatland buffer areas. However, these are either expensive, require large areas, or are rather inefficient in reducing dissolved nutrients export loads, especially outside the growing season (Hynninen et al., 2011; Liljaniemi et al., 2003). Consequently, new scalable tools are needed to counteract the negative effects of forest management on water quality. A promising solution to reduce nutrient exports is adsorption-based purification of runoff water using biochar has been proposed (Saarela et al., 2020). Biochar is a carbon-rich product made from any type of organic material (feedstock) by pyrolysis where the organic matter is heated at 300–800°C under low oxygen concentrations (Lehmann & Joseph, 2012). Biochar has been shown to be an effective nutrient adsorbent (Laird et al., 2010) due to its porous structure, large specific surface area, and high cation and anion exchange capacity (Ahmad et al., 2014; Gwenzi et al., 2017). Furthermore, it is also well established that the application of biochar to soils can promote soil fertility, which ultimately may enhance plant growth (Barrow, 2012; Jeffery et al., 2011). Hence, suggesting a potential circular system where nutrients successfully captured by biochar could then be applied back to forests, adding to the soil carbon stocks, and serving as a source of nutrition to trees that enhances growth (Palviainen et al., 2020).

The adsorption capacity of biochar varies with the properties of the feedstock, the pyrolysis temperature, and other manufacturing parameters (Liu et al., 2020; Zhang et al., 2020). A number of feedstocks including agricultural residues, wood biomass, manure, and solid waste have been utilized to produce biochar. Likewise, new biochar feedstocks, such as municipal garden residues, are currently reaching the market. However, the effectiveness of novel biochar feedstocks in the remediation of organic and inorganic contaminants is still uncertain (Ahmad et al., 2014). Furthermore, less attention has been focused on testing biochar as adsorbents for nutrient removal in an aqueous solution, with the available literature largely derived from laboratory experiments (Gwenzi et al., 2017). Nevertheless, existing experiments with biochar from novel feedstocks (e.g., rice straw) show different potentials in removing pollutants from water and soil environments (Luo et al., 2019). Therefore, understanding their potential and risk outside controlled experiments is a fundamental question that needs to be answered before we can apply this method as a mitigation tool for diffuse pollution from forestry.

The effectiveness of biochar in the purification of peatland runoff water has several challenges, specifically in field conditions. Biochar absorption capacity increases when the initial nutrient concentration is high, as for example in wastewater (Zhang et al., 2020) or agricultural runoff (Laird et al., 2010). Although nutrient concentration increases after clear-cutting, the concentration of solutes remains low in comparison, at least in a Nordic context (Palviainen et al., 2014). Furthermore, discharge, nutrients, and DOC concentrations vary across weather conditions and seasons in peatland forests (Mattsson et al., 2015), creating unstable conditions with high water volume and fluctuating nutrient concentrations. Unfortunately, few studies have addressed the use of biochar in water protection in peatland forests (Kakaei Lafdani et al., 2020, 2021; Saarela et al., 2020), and to our knowledge, there are no studies that have tested the biochar adsorption capacity in on-site field conditions. Therefore, in order to upscale this technology it is important to understand the effectiveness and limitations of this method in a field context.

In this study, we studied biochar as a water purification method both in controlled conditions and in field conditions. The study was conducted in two different phases; initially, we (a) evaluated the adsorption capacity of two different types of biochars (i.e., wood- and garden residue-based) and (b) assessed the effect of initial nutrient concentration on the adsorption capacity of these biochars. Subsequently, the biochar feedstock that presented the best adsorption capacity in the controlled laboratory environment was tested in field conditions. Here, we (c) tested the biochar adsorption capacity in the field under fluctuating solute concentrations, temperatures, and flowing water and (d) examined the role of average inflow solute concentration (i.e., outflow from managed catchments with different catchment characteristics) on the adsorption capacity. Changes in water pH, total dissolved nitrogen (TDN), phosphate (PO_4), and dissolved organic carbon (DOC) concentrations were measured throughout both experiments, as well as changes in total organic carbon (Tot-C), total nitrogen (Tot-N), and total phosphorus (Tot-P) in the biochars.

2 | MATERIALS AND METHODS

2.1 | Study site

Both phases were conducted in the Trollberget Experimental Area (TEA), an experimental study site established in 2018 to test best practices for forestry management and develop new methods to mitigate negative effects on freshwater ecosystems (Laudon et al., 2021). The ~60 ha site is located in the boreal zone of northern Sweden (64°14′ N, 19°46′ E), approximately 60 km from the Baltic Sea coast (Figure 1). The climate is typical for the northern boreal zone, characterized as a cold temperate humid type with short and cool summers followed by long dark winters. The 30-year mean annual air temperature (1986–2015) is +2.1°C with the highest mean monthly temperature occurring in July and the lowest in January (+14.6°C and −8.6°C, respectively; Kozii et al., 2020). Snow usually covers the ground from the end of October to late April. The total annual precipitation averages 614 mm $year^{-1}$ of which approximately 35%–50% falls as snow and 311 mm becomes runoff (Laudon et al., 2013). At the TEA, a replicated catchment-scale approach has been established, with four side-by-side comparison catchments (Figure 1) with two treatments (clear-cut with or without ditch cleaning). Ditches were dug during the 1930s with the goal of draining forested peatlands to increase forest production (Hånell & Päivänen, 2012). To function as intended, ditches may require periodic maintenance or the cleaning out of vegetation, eroded soils, or other debris, which lowers the water table and consequently changes the nutrient dynamics on the site (Hasselquist et al., 2018; Laurén et al., 2021). The study catchments have an average size of 10 ha, an average tree volume prior to clear-cut of 270 m^3 ha^{-1}, and a ditch density of 166 ± 40 m ha^{-1}. In addition, for all catchments a weir has been installed in

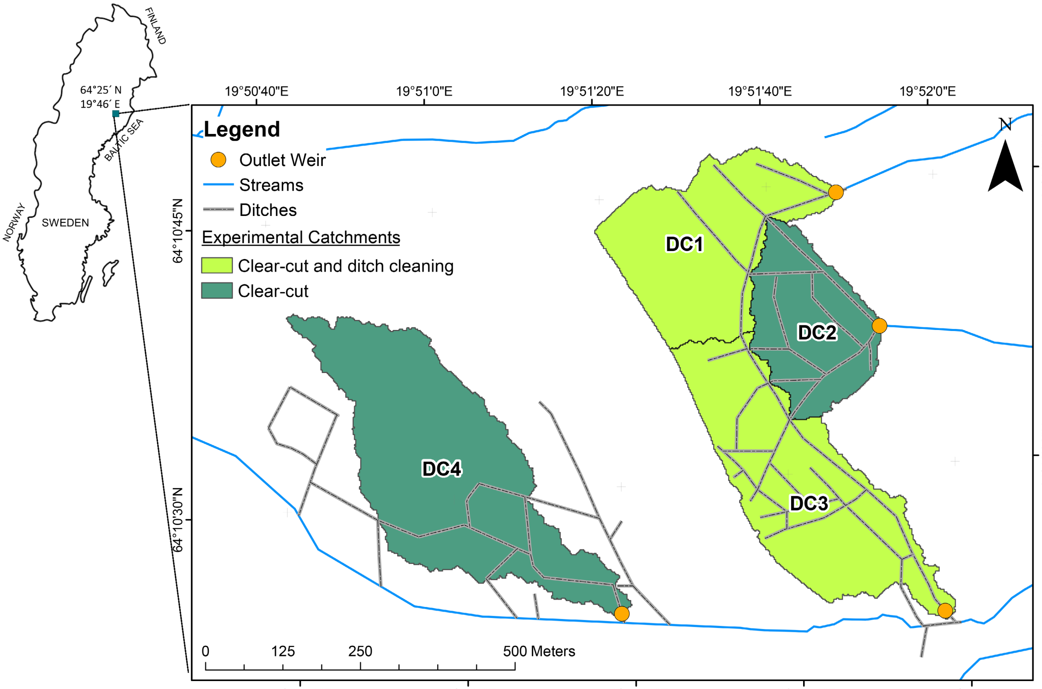

FIGURE 1 Trollberget Experimental Area (TEA) is located in northern Sweden (left). The green areas are different treatment catchments; grey lines mark the ditch networks, and the orange circles are the locations of the biochar filters and water quality monitoring sites (outlet weirs) Map lines delineate study areas and do not necessarily depict accepted national boundaries. Map lines delineate study areas and do not necessarily depict accepted national boundaries.

the outlet ditch for water sampling and discharge measurements. In summer 2020, all four catchments were clear-cut using standard forestry practice and tree stems and branches were removed from the site (i.e., DC1, DC2, DC3, and DC4; Figure 1). In September 2021, two of the four catchments were ditch-cleaned using a 20-ton crawling excavator in DC1 and DC3, whereas the ditches were left uncleaned in DC2 and DC4 (see Laudon et al., 2021 for further details about the catchments).

2.2 | Experimental setup

2.2.1 | Experiment 1: Biochar adsorption potential in a laboratory experiment

In the laboratory phase, we tested for adsorption capacity of two different biochars, both produced by slow pyrolysis at high temperature (i.e., 600°C), known to increase the adsorption capacity (Yao et al., 2012). The wood-based biochar was produced by a local company (Vindekol AB, Vindeln Sweden) and manufactured primarily from the wood and bark of *Pinus sylvestris*, and a small portion of *Picea abies* and *Betula pendula* (hereafter referred to as "wood" feedstock; Gundale et al., 2016). The garden residue-based biochar was made from municipal garden residues, primarily shrubs and branches (hereafter referred to as "garden" feedstock) provided by a municipal company (Telge, Södertälje, Sweden). We sieved both biochar types to 4–10 mm to homogenize the material and to exclude the effect of various particle sizes of biochar in the adsorption process (Saarela et al., 2020); afterward, the biochar was dried for 12 h at 60°C. We collected 100 g of biochar from each feedstock to analyze for difference in C, N, and P contents in the biochar.

We conducted the laboratory incubation using the two biochars described above, with two different doses (3 and 12 g) to determine the effect of biochar dose on the adsorption rate and capacity and two different initial nutrient concentration in the water. Each treatment was replicated four times. In order to get two different initial nutrient concentration in water for the laboratory experiment, we collected samples from ditches draining two catchments with different landscape characteristics; one water source was a former forested, clear-cut catchment and the other was a drained peatland 1 km from TEA. After collection, the water samples were refrigerated and transported to the laboratory, upon which it was frozen until further processing. Due to a delay in the garden residue biochar delivery, the collection of runoff water was done in two different sampling occasions, May and August 2021, unfortunately resulting in slightly different initial concentrations between the wood and garden residue experimental setup. In both catchments, the average initial nutrient concentration was slightly higher in May (e.g., $6 \pm 0.5\,\mu\mathrm{g\,L^{-1}}$ PO_4, $1 \pm 0.01\,\mathrm{mg\,L^{-1}}$ TDN and $50 \pm 0.2\,\mathrm{mg\,L^{-1}}$ DOC) than in August (e.g., $4 \pm 0.3\,\mu\mathrm{g\,L^{-1}}$ PO_4, $0.5 \pm 0.02\,\mathrm{mg\,L^{-1}}$ TDN, and $30 \pm 0.2\,\mathrm{mg\,L^{-1}}$ DOC). Upon the start of the experiment, water was thawed, allowed to stabilize at room temperature (+20°C), standardized mixed among replicates, and kept at constant temperature throughout the experiment. We then added either 3 or 12 g biochar into 2000 mL glass jars, with four replications of each biochar dose for the two different water types. In addition, four glass jars contained only water without biochar as blank controls. Thereafter, 1500 mL of water from the field site was added to each jar and 35 mL of water was taken to measure the initial element concentration in each jar. Jars were covered with aluminum foil and placed on a platform shaker at 105 rpm for 10 days. Subsequently, 35 mL of water was sampled from each jar at the following time points: 1, 2.33, 5.5, 25, 28, 46, 49, 70, 145, 169, 196, and 215 h from the beginning of the experiment (Saarela et al., 2020). After sampling, water was filtered (0.45 μm Millipore) immediately after collection and stored in acid-washed high-density polyethylene (HDPE) bottles. Samples for DOC and TDN were refrigerated (+4°C) and analyzed within 3 days after collection. Samples for PO_4-P were frozen (−20°C) immediately after subsampling and stored for later analysis.

DOC, TDN, and PO_4 concentration change in water was measured to determine the adsorption of nutrients onto the biochar, calculated as follows (Saarela et al., 2020):

$$\mathrm{Ads}_t = \frac{\left(C_{\mathrm{ini}} V_{\mathrm{ini}} - C_t V_t\right) - \sum_{k=\mathrm{ini}}^{t} \left(C_k V_{\mathrm{sample}}\right)}{m_{\mathrm{biochar}}},$$

where Ads_t is the cumulative adsorption of the nutrient ($\mathrm{mg\,g^{-1}}$ biochar), C_{ini} is the initial concentration of the nutrient ($\mathrm{mg\,L^{-1}}$ or $\mu\mathrm{g\,L^{-1}}$), V_{ini} is the water initial volume (L), C_t is the concentration of the nutrient in time t ($\mathrm{mg\,L^{-1}}$ or $\mu\mathrm{g\,L^{-1}}$), V_t is water volume at time t, C_k is the concentration of the nutrient in previous sampling occasion at time k, V_{sample} is the volume of water sample in each sampling occasion (35 mL), and m_{biochar} is the biochar mass (g). Moreover, cumulative adsorption was calculated for each time step during the experiment.

2.2.2 | Experiment 2: Biochar adsorption potential in field conditions

After evaluating the biochar feedstock for nutrient adsorption in the laboratory, the biochar that adsorbed the most nutrients was chosen to upscale the experiment to field conditions. The biochar was placed in jute sacks (Granngården AB, Malmö, Sweden) and placed in the ditches that drain the four experimental catchments (i.e., DC1, DC2, DC3, and DC4, $n = 4$). We expected different solute concentration in the runoff from the catchments with ditch cleaning and the catchments without ditch cleaning (Nieminen et al., 2018), therefore testing the effectiveness of biochar adsorption with different nutrient concentrations in field conditions. Sacks were filled with approximately 100 L of biochar and 4–5 sacks, depending on flow and geomorphology, were placed in each catchment outlet aimed to direct the ditch water flow through the biochar and to avoid bypass flow around and under the sacks. Water sampling points in the ditch were established at the weir above the biochar (inlet) and ~1 m below the biochar (outlet). Water samples were taken daily for the first 2 weeks after ditch cleaning operations (September 27–October 10) and twice a week until ditch water froze (November 3). All samples were collected in acid-washed high-density polyethylene (HDPE) bottles, filtered in the laboratory (0.45 μm Millipore) within 24–48 hours, and stored as described before for further analysis.

2.3 | Laboratory analyses

In both experiments, water quality variables were measured to determine the nutrient recovery from the runoff water. DOC and TDN concentrations were determined using the combustion catalytic oxidation method on a Shimadzu TOC VCPH analyzer (Shimadzu, Duisburg, Germany; Blackburn et al., 2017). PO_4^{3-} was accounted as the dissolved inorganic phosphorus (DIP) and was quantified colorimetrically using a Seal Analytical Autoanalyzer 3 HR and following method G-297-03 (SEAL Analytical, 2023). Water pH was measured with a pH meter (Mettler Toledo MP220). In addition, the C, N, and P concentrations in the biochars were analyzed using a Leco TruMac CN analyzer.

2.4 | Statistical analyses

All statistical analyses were conducted in R (R Core Team, 2022) and significance levels were set at $p < 0.05$ for all tests. Response variables for both experiments consisted of dissolved nutrient concentration in water ($\mathrm{mg\,L^{-1}}$ TDN and DOC and $\mu\mathrm{g\,L^{-1}}$ PO_4-P) and available nutrient concentration in biochar (% of Tot-C and Tot-N, and $\mathrm{mg\,kg^{-1}}$ of Tot-P). Water quality data in the laboratory experiment were first evaluated for assumption of normality and data were logarithmic transformed when necessary to meet this assumption. First, a two-way multivariate analysis of variance (MANOVA) was used to test the effect of biochar, initial nutrient concentration in water, dose, and their interactions on dissolved nutrient concentration in water. Wilk's Lambda was used in the MANOVA to assess the significance of these main factors. Afterward, data were analyzed using a one-way analysis of variance (ANOVA), and where significance was found, Tukey's Honestly Significant Differences (HSD) post hoc comparison was used to explore differences among means in the *agricolae package* (Mendiburu, 2020). Furthermore, pH data from the laboratory experiment and Tot-N, Tot-C, and Tot-P extracted from the biochar from both experiments could not be transformed to meet the normality assumption; thus, these variables were instead analyzed with a Kruskal–Wallis nonparametric rank sum test and using Fisher's least significant difference (LSD) for the post hoc nonparametric test in the *agricolae package* (Mendiburu, 2020).

For the field experiment, we used a linear mixed-effect model (LMM) to analyze differences in the concentration of PO_4, DOC, and TDN between the inlet and the outlet. The analysis was performed using lme model from the *nlme package* (Pinheiro et al., 2022). The LMM provided a nonparametric approach to explain variability in the response variables by fixed effects (factors that were included in the study design) and random effects, which accounted for factors that were not part of the study design, but possibly affected variability in the concentration of PO_4, DOC, and TDN between the inlet and the outlet. The fixed effects considered in this study were the biochar treatment (inlet–outlet) and sampling time (i.e., day number); the random effects included were catchment ID and sampling time to account for repeated measures.

3 | RESULTS

3.1 | Laboratory experiment: Biochar adsorption potential in a controlled environment

The initial concentration of total C, N, and P in the two biochars showed significant ($p < 0.05$) differences (Figure 2). The garden residue biochar had higher concentrations of N (0.5 ± 0.01%) and P (1288.6 ± 4.1 $\mathrm{mg\,kg^{-1}}$), but lower concentration of C (73.2 ± 2.4%) compared with the wood biochar (0.09 ± 0.003% of N, 55.5 ± 11.5 $\mathrm{mg\,kg^{-1}}$ of P and 85.7 ± 0.5% of C).

In the laboratory experiment, the results of the multivariate analysis of variance showed that there was a statistically significant effect of biochar feedstock ($p < 0.01$) and initial nutrient concentration ($p < 0.01$) on the combined nutrient variables (PO_4, TDN, and DOC).

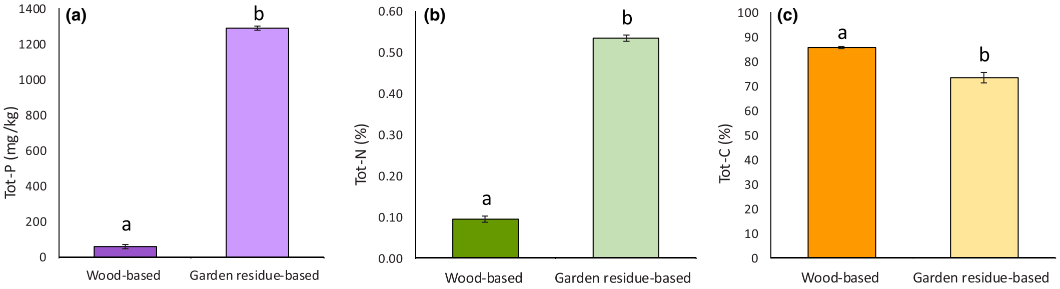

FIGURE 2 P (a), N (b), and C (c) concentrations in wood and garden residue biochar. Letters indicate significant differences between nutrient concentrations of the different biochars ($p < 0.05$, $n = 4$).

Specifically, the wood biochar significantly ($p < 0.05$) decreased the concentrations of TDN and DOC of the ditch water, while the garden residue biochar did not significantly decrease ($p > 0.05$) the TDN concentration and even released DOC ($p < 0.05$) to the ditch water. Conversely, both the wood and garden residue biochars increased ($p < 0.05$) the PO_4 in the water (Figure 3). By the end of the experiment, the higher dose (i.e., 12 g) of wood biochar significantly decreased ($p < 0.05$) the concentration of DOC and TDN in ditch water (Figure 3b,c,f,g), on average by 8% and 15%, respectively. A lower dose of wood biochar (i.e., 3 g) significantly reduced the TDN concentration when the initial N concentration was higher (Figure 3b); however, it did not significantly affect ($p > 0.05$) the concentration of other elements in the water (Figure 3c,e–g). Here, the reduction in TDN concentration was slightly higher when the initial N concentration in water was higher and for DOC the stronger decrease occurred when the initial C concentration in the water was lower. The higher dose (i.e., 12 g) of garden residue biochar adsorbed C and reduced the concentration of DOC ($p > 0.05$) by 17% in ditch water when the initial C concentration was higher (Figure 3k) but significantly released DOC when the initial C concentration was lower (Figure 3o). Neither doses of garden residue biochar significantly changed the concentration of TDN (Figure 3j,n). In addition, the higher dose of the wood biochar released PO_4 into the water, significantly increasing ($p < 0.05$) the concentration of PO_4 from 2.2 to 11 μg P L^{-1} when the initial P concentration in the ditch water was higher (Figure 3a). Likewise, the garden residue biochar released P into the ditch water and increased ($p < 0.05$) the concentration of PO_4 by 111 and by 289 μg P L^{-1} when the initial concentration of P was low and high, respectively. It is worth highlighting that the increase in PO_4 concentration in water was much higher from the garden residue biochar compared with the wood biochar. Finally, the addition of both wood and garden residue biochar increased ($p < 0.05$) the pH of the ditch water, for both high and low doses. Yet again, the garden residue biochar had a larger effect, increasing pH from 5.0 to 7.0, with the lower biochar dose and up to 8.0 with the higher dose of biochar (Figure 3l,p). The wood biochar reached pH of 5.5 and 5.8 with the higher biochar dose, respectively (Figure 3d,h).

Regarding temporal responses to biochar addition in the laboratory experiment, our results show that, for all elements, with a higher initial solute concentration in water and the addition of a lower wood biochar dose, the cumulative adsorption is higher, being the highest 2.5 mg C g $biochar^{-1}$, 0.05 mg N g $biochar^{-1}$ and 1.1 μg P g $biochar^{-1}$, for DOC, TDN and PO_4, respectively (Figure 4). However, for PO_4 and in some time steps for TDN, solutes were released from biochar to the water when we added a high wood biochar dose and the initial concentration was higher. Both for the wood and garden residue biochar, the cumulative adsorption of DOC was higher when the lower dose was added, reaching the peak adsorption at 145 h after the start of the experiment for the wood biochar (Figure 4c,f) and at 169 for the garden residue biochar (Figure 4i). For the garden residue biochar, the release of all solutes happened at some or multiple points with all treatments, showing a strong release pattern for PO_4 and TDN when the initial solute concentration was higher and for DOC when the initial C concentration was lower. Specifically, the garden residue biochar released between 9.2 and 29.8 μg P g $biochar^{-1}$ of PO_4, between 0.01 and 0.05 mg N g $biochar^{-1}$ of TDN, and between 0.1 and 2.7 mg C g $biochar^{-1}$ for DOC. Furthermore, both the wood and garden biochar adsorbed and released N when the initial N concentration was lower. Note that unfortunately, due to sampling difficulties, we did not have a high initial concentration for TDN when the garden residue biochar was tested.

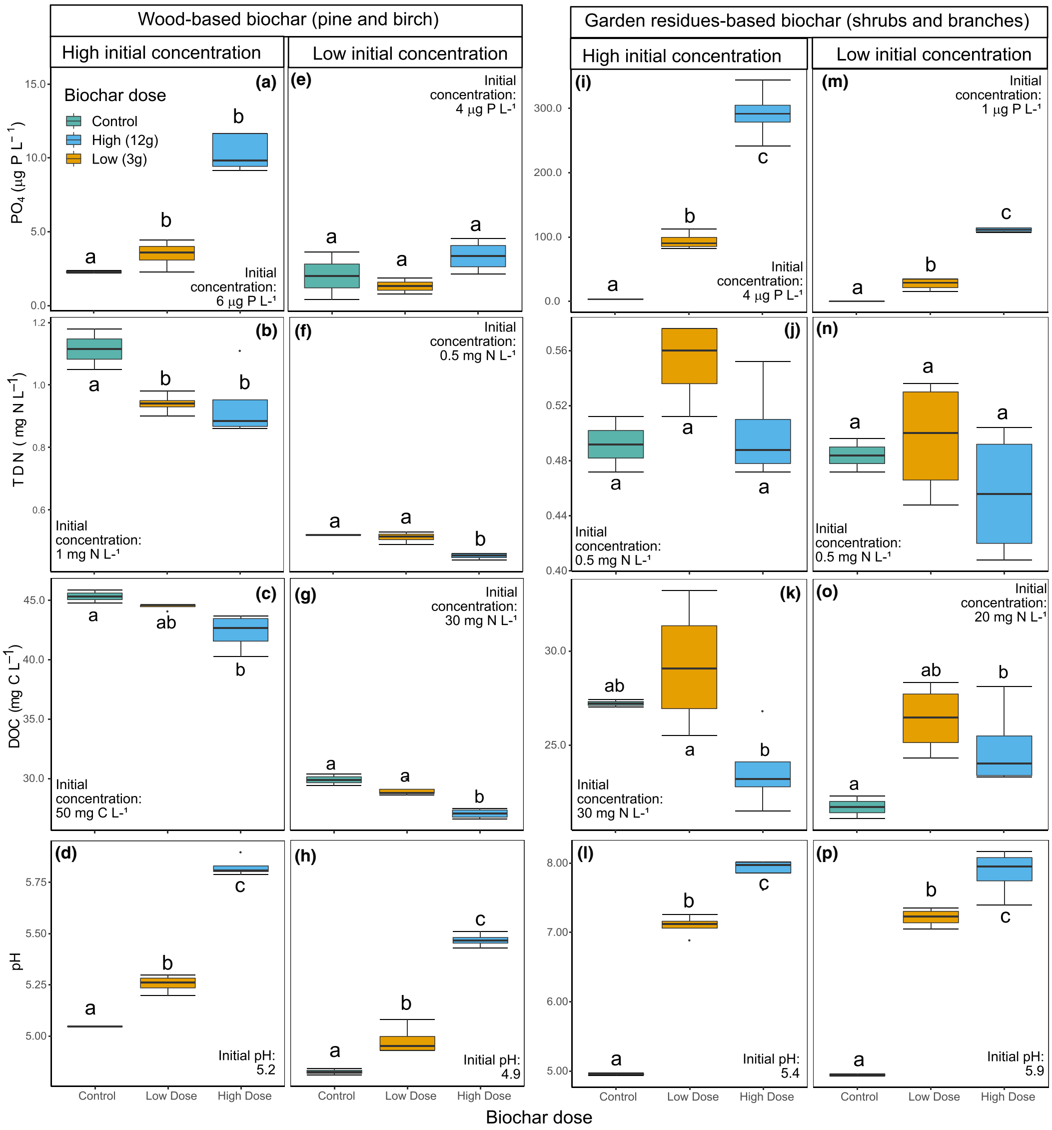

FIGURE 3 Effect of different doses of two different biochar feedstock in water with low and high solute concentration in laboratory conditions. Wood biochar (a–h) in higher initial solute concentration (a–d) and lower initial solute concentration (e–h) and garden residue biochar (i–p) in higher initial solute concentration (i–l) and lower initial solute concentration (m–p). Letters indicate significant differences between biochar doses ($p < 0.05$). Colors represent the different biochar doses added (control = 0 g, low = 3 g, high = 12 g). The solid line in box plots is the median value, box extents are the interquartile range (IQR), and whiskers show the minimum and maximum data points. Note that the scales for the *y*-axes show different magnitudes of concentrations.

Overall, the wood biochar demonstrated the highest potential to adsorb nutrients from stream water, specifically, for TDN and DOC removal. Our results also showed that the adsorption capacity increased when the initial nutrient concentration in water was higher. In contrast, nutrient release from the garden biochar into the stream water was higher (i.e., PO_4 and DOC). These differences justified the use of wood biochar for the second experiment, where biochar was tested at the catchment level in the field.

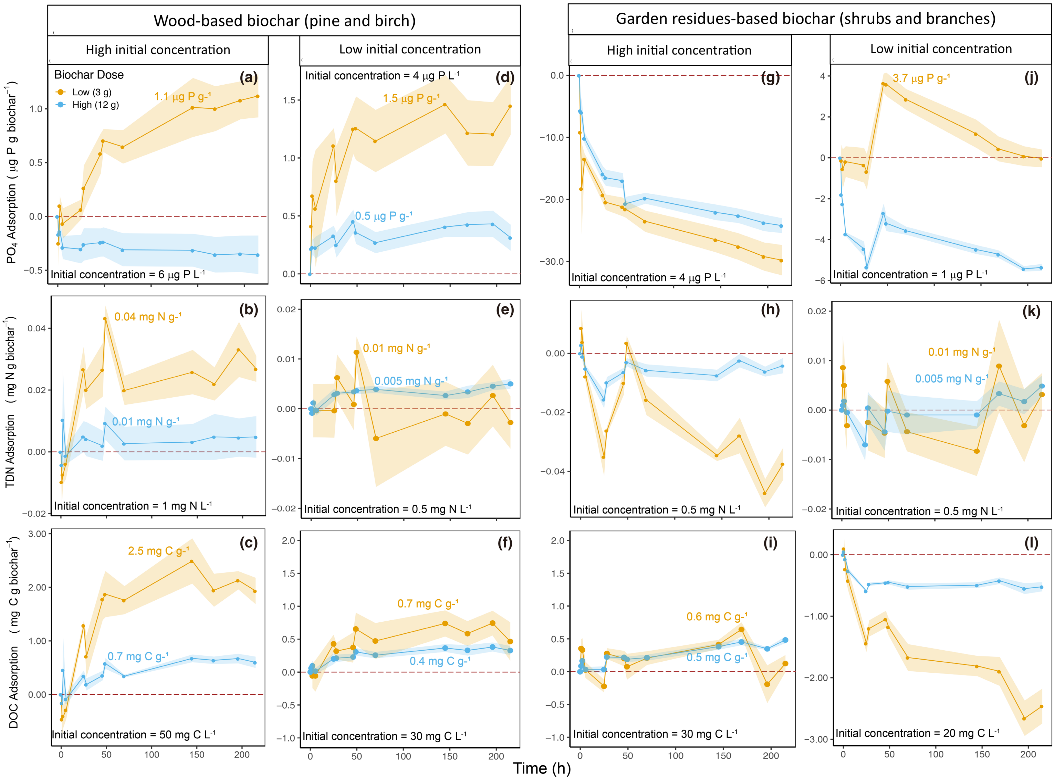

FIGURE 4 Cumulative adsorption by two doses of two biochar feedstock in the laboratory experiment that included water with low and high solute concentrations. The left side of the figure includes adsorption in wood biochar (a–f) in higher initial solute concentration (a–c) and lower initial solute concentration (d–f) and (g–l). The right side of the figure shows adsorption in garden residue biochar in higher initial solute concentration (g–i) and lower initial solute concentration (j–l). Colored numbers indicate the time step and highest adsorption capacity. Colored circles represent the average between replicates and shadowed area is the standard error. Values over zero indicate adsorption, while values below zero indicate release.

3.2 | Field experiment: Biochar adsorption potential in field conditions

The efficiency of wood biochar to remove DOC and TDN in the field was dependent on the initial concentration of the incoming water ($p < 0.05$), suggesting that the higher the concentration of DOC and TDN in the inlet, the higher the removal. Experimental catchment DC4 had the highest inlet concentration of TDN ($2.6\,\mathrm{mg\,N\,L^{-1}}$) and DOC ($95.6\,\mathrm{mg\,C\,L^{-1}}$) and was the only site where the water collected at the outlet (downstream) of the biochar filter had a significantly lower mean concentration ($p < 0.05$, Table 1) compared with the inlet (Figure 5b,c). For DC4, the mean percent of removal over the length of the experiment was 7% for TDN and 6% for DOC, with a maximum removal of 20% and 15%, respectively. In DC1-3, sites with lower inlet solute concentrations, the biochar did not significantly reduce TDN or DOC. Furthermore, there was no statistical difference ($p > 0.05$) between the inlet and outlet concentration for PO_4 in any of the experimental catchments; thus, the biochar filter did not remove PO_4. In fact, at DC4, there was an average increase in PO_4 concentration after the biochar filter of 2.4% (Table 1). Finally, the biochar filters did not significantly change the water pH ($p > 0.05$) in any of the experimental catchments, remaining on average acidic (i.e., 4–5).

Furthermore, we analyzed the nutrient content of the wood biochar before and after the field experiment (Figure 6) and found that the N content of the biochar had increased ($p > 0.05$) from 0.1% (±0.01) before the biochar filters were placed in ditches to 0.14% (±0.03) after they had been in ditches for 2 months, with no statistical difference between catchments ($p > 0.05$). Thus, there was an average increase of 45% in the N content of the biochar.

TABLE 1 Average inlet concentration of PO4, TDN, and DOC for all experimental catchments at TEA.

	Mean inlet concentration ± SE	Mean outlet concentration ± SE	Mean removal	*p*-value
PO_4	**($\mu g\,P\,L^{-1}$)**	**($\mu g\,P\,L^{-1}$)**	**(%)**	
DC1	17.9 ± 1.3	17.5 ± 1.4	−2	n.s.
DC2	31.7 ± 3.1	30.8 ± 3.3	−3	n.s.
DC3	12.5 ± 1.1	11.6 ± 1.2	−7	n.s.
DC4	10.7 ± 0.8	11.0 ± 0.9	+2	n.s.
TDN	**($mg\,N\,L^{-1}$)**	**($mg\,N\,L^{-1}$)**	**(%)**	
DC1	0.9 ± 0.04	0.9 ± 0.04	0	n.s.
DC2	1.9 ± 0.08	1.8 ± 0.08	−1	n.s.
DC3	1.3 ± 0.06	1.3 ± 0.05	−2	n.s.
DC4	2.6 ± 0.03	2.4 ± 0.02	−7	**<0.01**
DOC	**($mg\,C\,L^{-1}$)**	**($mg\,C\,L^{-1}$)**	**(%)**	
DC1	35.3 ± 1.0	34.9 ± 1.1	−1	n.s.
DC2	69.0 ± 1.6	68.0 ± 1.2	−1	n.s.
DC3	41.5 ± 1.3	40.8 ± 1.2	−2	n.s.
DC4	95.6 ± 1.4	89.7 ± 1.7	−6	**<0.01**

Note: Percent removal is calculated in each time step and averaged. Negative values represent removal and positive values represent release. *p*-value is based on linear mixed-effect model for PO4, DOC, and TDN. The bold values show the significance level, $p < 0.01$.

However, the percent of C and P in the biochar did not change over the course of the field experiment ($p > 0.05$).

4 | DISCUSSION

We tested different feedstocks of biochars, both in the laboratory and in the field conditions as a method to reduce nutrient exports to water courses from managed forested catchments. Forest management activities such as clear-cut, commonly occur across high-latitude landscapes and typically affect DOC, N, and P exports affecting trends of brownification and eutrophication downstream.

4.1 | Adsorption capacity of two feedstock biochars in a controlled environment

Our results from the controlled laboratory experiment showed that higher doses of wood biochar effectively adsorbed TDN and DOC, although with lower cumulative adsorption, and released PO_4. The garden residue biochar also released PO_4 and was not efficient in the adsorption of any nutrient. Our results support previous studies, where feedstock is one of the key parameters controlling the adsorption properties (Ahmad et al., 2014) and nutrient adsorption capacity (Gai et al., 2014). The reduction in DOC and TDN concentration in solution could be explained by a wood biochar with large specific surface area, high porosity, and active sites on the adsorbent surface interacting with the arriving organic molecules from DOC and the organic part of TDN (i.e., dissolved organic nitrogen DON) (Lee et al., 2018). TDN reduction can also be explained by the capacity of the biochar to adsorb ammonium (NH_4^+) and nitrate (NO_3^-), as TDN is a combined measure of the inorganic (i.e., NH_4^+ and NO_3^-) and the organic fraction of N (i.e., DON). Specifically, biochars are known to be an effective adsorbent for NH_4 (Yin et al., 2017) because of its negative surface charges due to carboxylate and phenolate groups (Liang et al., 2006), which enhances the ability to adsorb and retain cations (Gai et al., 2014; Novak et al., 2009). However, the NO_3^- adsorption capacity of biochar is less clear, with comparable studies showing somewhat opposite effects, such as 2 out of 13 biochars absorbing NO_3 (Yao et al., 2012), none of the biochar types being able to adsorb NO_3 (Hollister et al., 2013) or even release of $NO_3^-$from the biochar to solution (Gai et al., 2014). Nevertheless, Kakaei Lafdani et al. (2021) found NO_3^- adsorption by wood biochar from clear-cut boreal forest runoff, arguing that the discrepancy in results could be explained by pyrolysis conditions and different initial N concentrations (Gundale & DeLuca, 2006). Furthermore, our results showed that for both biochar feedstocks, PO_4^{3-} was not only not adsorbed, but showed a net release back to the water. This may be attributed to the solubilization of ash residue enriched with P, given that the pyrolysis temperature for the preparation of both biochar samples was lower than the required 700–800°C temperature for P volatilization

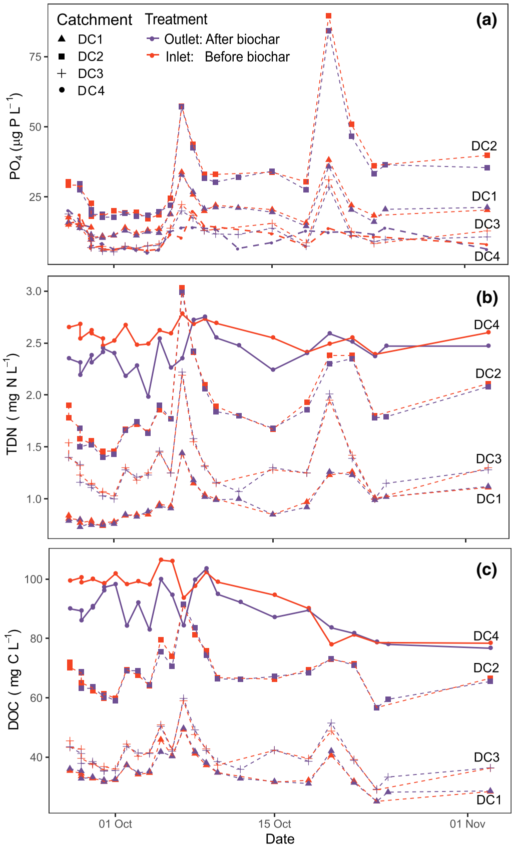

FIGURE 5 Nutrient concentrations of water from the inlet and outlet of the biochar filter for each experimental catchment. Solid lines represent a significant difference between inlet (red) and outlet (purple) over time of the experimental catchments according to the LMM ($p < 0.5$). The dotted lines represent non-significant relationships. Shape of the points identifies catchments, where circle is DC4, triangle DC1, square DC2, and cross DC3.

(Deluca et al., 2015). However, Yao et al. (2011) did find the removal of PO_4^{3-} from aqueous solution by biochar converted from anaerobically digested sugar beet. Both types of biochar used in our study, in higher and lower doses, increased pH significantly, turning the solution basic, and therefore, potentially improving further the adsorption of organic nutrients into the biochar (Ahmad et al., 2014) by increasing the net negative charge on the surface due to the dissociation of phenolic-OH group (Xu et al., 2011).

The laboratory experiment also showed that wood biochar has the potential to mitigate the environmental impact of forestry by removing organic C and N from runoff waters. Specifically, the reduction in DOC is gaining more importance in boreal freshwater ecosystems due to an ongoing brownification trend, with implications to the structure and function of aquatic ecosystems (Kritzberg et al., 2020). Furthermore, the reduction in N export would decrease the risk of eutrophication of freshwater ecosystems, as N and P are the main limiting elements to regulate aquatic productivity and accompanied algal bloom (Smith & Schindler, 2009). However, we also found that the novel garden residue biochar has the potential to increase the concentration of P in solution, consequently becoming a risk to freshwater ecosystems, by increasing the concentration of a main limiting nutrient (P) that could trigger eutrophication processes in receiving waterways. Therefore, to upscale a specific novel feedstock to field conditions as a mitigation tool for nutrient leaching from anthropogenic activities it is of utmost importance to consider an array of possible collateral effects.

4.2 | Biochar to adsorb nutrients in field conditions

In the field experiment, we found that our biochar filter was only effective at the removal of TDN and DOC when there was a high initial solute concentration. This is likely due to an increase in adsorption in response to the increased N availability in the water which improves the adsorption of nitrogen compounds onto biochar surfaces (Saarela et al., 2020). These results are consistent with our laboratory experiment results and results obtained by others (Kakaei Lafdani et al., 2021; Saarela et al., 2020), where in controlled environments, the higher adsorption rate was found when the solute initial concentration in water was higher. Yet, even in the catchment with the higher solute concentration, the percentage of N removed was low (7%) compared with other studies, where the biochar was shown to reduce 58% of the TN concentration (Kakaei Lafdani et al., 2020). Or, even compared with the increase in DOC and TN after clear-cut (i.e., an average increase of 42% ± 8 and 56% ± 12, respectively) in our study sites (Laudon et al., 2023). However, the observed low adsorption capacity might be an artifact of our filter setup, particularly when compared with other configurations such as horizontally oriented columns with longer residence time (Kakaei Lafdani et al., 2020). Moreover, contrary to our results in the laboratory experiment, the biochar filters did not change the pH of the water flow in any of the experimental catchments. This discrepancy suggests that a biochar filter design with a longer residence time could be beneficial in enhancing pH levels and increasing nutrient adsorption capacity.

Finally, our results agree with other studies that establish the potential of wood biochar as a water protection

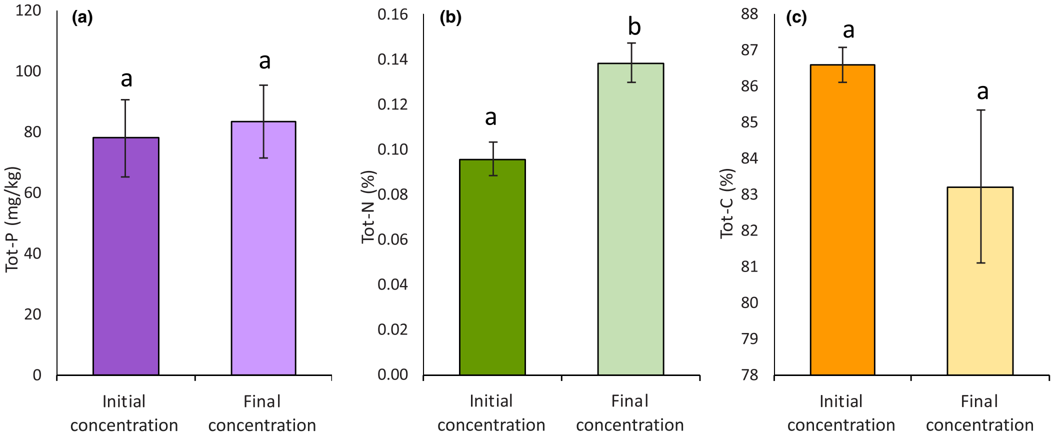

FIGURE 6 Concentration of P (a), N (b), and C (c) of the wood biochar before and after exposure to runoff water. Different letters indicate significant differences between nutrient concentrations in the biochar ($p < 0.05$).

tool, specifically for the retention of soluble nutrients (Lee et al., 2018; Zhang et al., 2020). However, using the wood biochar on-site with a simple setup for the removal of C, N, and P from runoff water in managed peatland forests could be challenging if the initial solute concentration leaching from the catchment is not high enough and discharge fluctuates over time. Yet, further efforts could be directed toward designing a better biochar filter with longer residence times. Ultimately, our study supports previous findings that a biochar filter in field conditions could be a feasible method for purifying runoff water with elevated nutrient concentration (Kaetzl et al., 2019; Perez-Mercado et al., 2019), with the potential for the most benefit in remediation of forestry outflows with higher nutrient concentrations or in agricultural and wastewater outflows with considerably higher concentrations. However, further development is needed to optimize the system and achieve greater reduction in dissolved nutrients.

4.3 | Closing the nutrient cycle

It is well established that biochar addition to soils can promote soil fertility and improve soil properties, which ultimately may enhance the growth of plants and trees (Biederman & Harpole, 2013; Jeffery et al., 2011; Palviainen et al., 2020). Pingree et al. (2022) suggests that the increase in plant growth in boreal environments after biochar addition is likely due to direct nutrient supply from biochar, hence a higher biochar nutrient content could be beneficial. Our results showed that the biochar N content increased significantly after 2 months of functioning as adsorption-based water purification. Therefore, by filtering ditch water, the biochar has the potential to become a soil amendment in boreal ecosystems with widespread terrestrial N limitation (Högberg et al., 2017); as nutrients (i.e., N) adsorbed onto the biochar are easily available for plants when placed in soil (Taghizadeh-Toosi et al., 2012). This would promote a closed nutrient cycle in boreal forest management, where nutrients leached from the catchment due to forest management activities such as clear-cut could be reincorporated to soils in the catchment and enhance forest productivity (Gundale et al., 2016). In summary, undesirable contaminants in aquatic ecosystems (i.e., C and N) can be transformed into desirable nutrients in the forest system, which could be used to promote growth and therefore C capture. Nevertheless, even though our field results revealed that our biochar filter reduces TDN and DOC concentration from outflows, the percentage decrease is dependent on initial concentrations of nutrients in water and could be considered low. Therefore, further research is needed to design an improved biochar filter to mitigate the impact of forest management on boreal aquatic ecosystems. Finally, although not suited for use in cleaning ditch water, the garden residue biochar used in the laboratory experiment could also present potential as a soil amendment, since it has relatively high levels of N and P as well as released PO_4, TDN, and DOC back to the solution. Yet, more research should be done to establish the desorption capacity of garden residue biochar in soils.

AUTHOR CONTRIBUTIONS

Virginia Mosquera: Conceptualization; data curation; formal analysis; funding acquisition; methodology; project administration; visualization; writing – original draft; writing – review and editing. **Michael Gundale:**

Conceptualization; funding acquisition; writing – review and editing. **Marjo Palviainen:** Conceptualization; funding acquisition; methodology; writing – review and editing. **Annamari Laurén:** Conceptualization; funding acquisition; methodology; writing – review and editing. **Hjalmar Laudon:** Conceptualization; funding acquisition; writing – review and editing. **Eliza Maher Hasselquist:** Conceptualization; funding acquisition; methodology; project administration; visualization; writing – original draft; writing – review and editing.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interests.

DATA AVAILABILITY STATEMENT

Data on laboratory and field experiment can be available upon request to the authors.

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REFERENCES

Ahmad, M., Rajapaksha, A. U., Lim, J. E., Zhang, M., Bolan, N., Mohan, D., Meththika, V., Lee, S. S., & Ok, Y. S. (2014). Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere*, *99*, 19–33. https://doi.org/10.1016/j.chemosphere.2013.10.071

Barrow, C. J. (2012). Biochar: Potential for countering land degradation and for improving agriculture. *Applied Geography*, *34*, 21–28. https://doi.org/10.1016/j.apgeog.2011.09.008

Biederman, L. A., & Harpole, W. S. (2013). Biochar and its effects on plant productivity and nutrient cycling: A meta-analysis. *GCB Bioenergy*, *5*(2), 202–214. https://doi.org/10.1111/gcbb.12037

Blackburn, M., Ledesma, J. L. J., Näsholm, T., Laudon, H., & Sponseller, R. A. (2017). Evaluating hillslope and riparian contributions to dissolved nitrogen (N) export from a boreal forest catchment. *Journal of Geophysical Research: Biogeosciences*, *122*(2), 324–339. https://doi.org/10.1002/2016JG003535

Deluca, T. H., Gundale, M. J., MacKensie, D., & Jones, D. (2015). Biochar effects on soil nutrient transformations. Chapter 18. In *Biochar for environmental management: Science and technology* (2nd ed.). Routledge. https://www.researchgate.net/publication/302558326

Gai, X., Wang, H., Liu, J., Zhai, L., Liu, S., Ren, T., & Liu, H. (2014). Effects of feedstock and pyrolysis temperature on biochar adsorption of ammonium and nitrate. *PLoS One*, *9*(12), 1–19. https://doi.org/10.1371/journal.pone.0113888

Gundale, M. J., & DeLuca, T. H. (2006). Temperature and source material influence ecological attributes of ponderosa pine and Douglas-fir charcoal. *Forest Ecology and Management*, *231*(1–3), 86–93. https://doi.org/10.1016/j.foreco.2006.05.004

Gundale, M. J., Nilsson, M. C., Pluchon, N., & Wardle, D. A. (2016). The effect of biochar management on soil and plant community properties in a boreal forest. *GCB Bioenergy*, *8*(4), 777–789. https://doi.org/10.1111/gcbb.12274

Gwenzi, W., Chaukura, N., Noubactep, C., & Mukome, F. N. D. (2017). Biochar-based water treatment systems as a potential low-cost and sustainable technology for clean water provision. *Journal of Environmental Management*, *197*, 732–749. https://doi.org/10.1016/j.jenvman.2017.03.087

Hånell, B., & Päivänen, J. (2012). *Peatland ecology and forestry: A sound approach*. Department of Forest Ecology, University of Helsinki.

Hasselquist, E. M., Lidberg, W., Sponseller, R. A., Ågren, A., & Laudon, H. (2018). Identifying and assessing the potential hydrological function of past artificial forest drainage. *Ambio*, *47*(5), 546–556. https://doi.org/10.1007/s13280-017-0984-9

Högberg, P., Näsholm, T., Franklin, O., & Högberg, M. N. (2017). Tamm review: On the nature of the nitrogen limitation to plant growth in Fennoscandian boreal forests. *Forest Ecology and Management*, *403*, 161–185. https://doi.org/10.1016/j.foreco.2017.04.045

Hollister, C. C., Bisogni, J. J., & Lehmann, J. (2013). Ammonium, nitrate, and phosphate sorption to and solute leaching from biochars prepared from corn stover (*Zea mays* L.) and oak wood (*Quercus* spp.). *Journal of Environmental Quality*, *42*(1), 137–144. https://doi.org/10.2134/jeq2012.0033

Hynninen, A., Sarkkola, S., Laurén, A., Koivusalo, H., & Nieminen, M. (2011). Capacity of riparian buffer areas to reduce ammonium export originating from ditch network maintenance areas in peatlands drained for forestry. *Boreal Environment Research*, *16*(5), 430–440.

Hytönen, J., Hökkä, H., & Saarinen, M. (2020). The effect of planting, seeding and soil preparation on the regeneration success of Scots pine (*Pinus sylvestris* L.) on drained peatlands – 10-year results. *Forestry Studies*, *72*(1), 91–106. https://doi.org/10.2478/fsmu-2020-0008

Jeffery, S., Verheijen, F. G. A., van der Velde, M., & Bastos, A. C. (2011). A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis.

Agriculture, Ecosystems and Environment, *144*(1), 175–187. https://doi.org/10.1016/j.agee.2011.08.015

Joensuu, S., Ahti, E., & Vuollekoski, M. (2002). Effects of ditch network maintenance on the chemistry of run-off water from peatland forests. *Scandinavian Journal of Forest Research*, *17*(3), 238–247. https://doi.org/10.1080/028275802753742909

Kaetzl, K., Lübken, M., Uzun, G., Gehring, T., Nettmann, E., Stenchly, K., & Wichern, M. (2019). On-farm wastewater treatment using biochar from local agroresidues reduces pathogens from irrigation water for safer food production in developing countries. *Science of the Total Environment*, *682*, 601–610. https://doi.org/10.1016/j.scitotenv.2019.05.142

Kaila, A., Sarkkola, S., Laurén, A., Ukonmaanaho, L., Koivusalo, H., Xiao, L., O´Driscoll, C., Asam, Z., Tervahauta, A., & Nieminen, M. (2014). Phosphorus export from drained scots pine mires after clear-felling and bioenergy harvesting. *Forest Ecology and Management*, *325*, 99–107. https://doi.org/10.1016/j.foreco.2014.03.025

Kakaei Lafdani, E., Laurén, A., Cvetkovic, J., Pumpanen, J., Saarela, T., & Palviainen, M. (2021). Nitrogen recovery from clear-cut Forest runoff using biochar: Adsorption–desorption dynamics affected by water nitrogen concentration. *Water, Air, and Soil Pollution*, *232*(10), 1–15. https://doi.org/10.1007/s11270-021-05366-y

Kakaei Lafdani, E., Saarela, T., Laurén, A., Pumpanen, J., & Palviainen, M. (2020). Purification of forest clear-cut runoff water using biochar: A meso-scale laboratory column experiment. *Water (Switzerland)*, *12*(2), 478. https://doi.org/10.3390/w12020478

Kozii, N., Haahti, K., Tor-Ngern, P., Chi, J., Maher Hasselquist, E., Laudon, H., Launuaunensasa, S., Oren, R., Peichl, M., Wallerman, J., & Hasselquist, N. J. (2020). Partitioning growing season water balance within a forested boreal catchment using sap flux, eddy covariance, and a process-based model. *Hydrology and Earth System Sciences*, *24*(6), 2999–3014. https://doi.org/10.5194/hess-24-2999-2020

Kritzberg, E. S., Hasselquist, E. M., Škerlep, M., Löfgren, S., Olsson, O., Stadmark, J., Valinia, S., Hansson, L. A., & Laudon, H. (2020). Browning of freshwaters: Consequences to ecosystem services, underlying drivers, and potential mitigation measures. *Ambio*, *49*(2), 375–390. https://doi.org/10.1007/s13280-019-01227-5

Laird, D., Fleming, P., Wang, B., Horton, R., & Karlen, D. (2010). Biochar impact on nutrient leaching from a Midwestern agricultural soil. *Geoderma*, *158*(3–4), 436–442. https://doi.org/10.1016/j.geoderma.2010.05.012

Laudon, H., Hasselquist, E. M., Peichl, M., Lindgren, K., Sponseller, R., Lidman, F., Kuglerová, L., Hasselquist, N. J., Bishop, K., Nilsson, M., & Ågren, A. M. (2021). Northern landscapes in transition: Evidence, approach and ways forward using the Krycklan Catchment Study. *Hydrological Processes*, *35*(4), 1–15. https://doi.org/10.1002/hyp.14170

Laudon, H., Mosquera, V., Eklöf, K., Järveoja, J., Karimi, S., Krasnova, A., Peichl, M., Pinkwart, A., Tong, C. H. M., Wallin, M., Zannella, A., & Hasselquist, E. M. (2023). Consequences of rewetting and ditch cleaning on hydrology, water quality and greenhouse gas balance in a drained northern landscape. *Scientific Reports*, *13*, 20218. https://doi.org/10.1038/s41598-023-47528-4

Laudon, H., Taberman, I., Ågren, A., Futter, M., Ottosson-Löfvenius, M., & Bishop, K. (2013). The Krycklan Catchment Study – A flagship infrastructure for hydrology, biogeochemistry, and climate research in the boreal landscape. *Water Resources Research*, *49*(10), 7154–7158. https://doi.org/10.1002/wrcr.20520

Laurén, A., Palviainen, M., Iñaki, U., Nieminen, M., Launiainen, S., Leppä, K., Laiho, R., & Hökkä, H. (2021). Drainage and stand growth response in peatland forests—Description, testing, and application of mechanistic peatland simulator susi. *Forests*, *12*(3), 293. https://doi.org/10.3390/f12030293

Lee, D. J., Cheng, Y. L., Wong, R. J., & Wang, X. D. (2018). Adsorption removal of natural organic matters in waters using biochar. *Bioresource Technology*, *260*(April), 413–416. https://doi.org/10.1016/j.biortech.2018.04.016

Lehmann, J., & Joseph, S. (2012). *Biochar for environmental management – Science and technology*. MBG Book.

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., … Neves, E. G. (2006). Black carbon increases cation exchange capacity in soils. *Soil Science Society of America Journal*, *70*(5), 1719–1730. https://doi.org/10.2136/sssaj2005.0383

Liljaniemi, P., Vuori, K. M., Tossavainen, T., Kotanen, J., Haapanen, M., Lepistö, A., & Kenttämies, K. (2003). Effectiveness of constructed overland flow areas in decreasing diffuse pollution from forest drainages. *Environmental Management*, *32*, 602–613. https://doi.org/10.1007/s00267-003-2927-4

Liu, J., Jiang, S., Chen, D., Dai, G., Wei, D., & Shu, Y. (2020). Activation of persulfate with biochar for degradation of bisphenol A in soil. *Chemical Engineering Journal*, *381*(August 2019), 122637. https://doi.org/10.1016/j.cej.2019.122637

Luoa, L., Wanga, G., Shib, G., Zhanga, M., Zhanga, J., Hea, J., Xiaoa, Y., Tiana, D., Zhanga, Y., Denga, S., Zhouc, W., Lanc, T., & Deng, O. (2019). The characterization of biochars derived from rice straw and swine manure, and their potential and risk in N and P removal from water. *Journal of Environmental Management*, *245*(May), 1–7. https://doi.org/10.1016/j.jenvman.2019.05.072

Mattsson, T., Kortelainen, P., Räike, A., Lepistö, A., & Thomas, D. N. (2015). Spatial and temporal variability of organic C and N concentrations and export from 30 boreal rivers induced by land use and climate. *Science of the Total Environment*, *508*, 145–154. https://doi.org/10.1016/j.scitotenv.2014.11.091

Mendiburu, F. D., & Yaseen, M. (2020). agricolae: Statistical procedures for agricultural research. R package version 1.4.0. https://myaseen208.github.io/agricolae/https://cran.r-project.org/package=agricolae

Monteith, D. T., Stoddard, J. L., Evans, C. D., De Wit, H. A., Forsius, M., Høgåsen, T., … Vesely, J. (2007). Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature*, *450*(7169), 537–540. https://doi.org/10.1038/nature06316

Nieminen, M., Piirainen, S., Sikström, U., Löfgren, S., Marttila, H., Sarkkola, S., Laurén, A., & Finér, L. (2018). Ditch network maintenance in peat-dominated boreal forests: Review and analysis of water quality management options. *Ambio*, *47*(5), 535–545. https://doi.org/10.1007/s13280-018-1047-6

Nieminen, M., Piirainen, S., Sikström, U., Löfgren, S., Marttila, H., Sarkkola, S., & Finér, L. (2018). Ditch network maintenance in peat-dominated boreal forests: Review and analysis of water quality management options. *Ambio*, *47*(5), 535–545. https://doi.org/10.1007/s13280-018-1047-6

Nieminen, M., Sarkkola, S., & Laurén, A. (2017). Impacts of forest harvesting on nutrient, sediment and dissolved organic carbon exports from drained peatlands: A literature review, synthesis and suggestions for the future. *Forest Ecology and Management*, *392*, 13–20. https://doi.org/10.1016/j.foreco.2017.02.046

Novak, J. M., Lima, I., Xing, B., Gaskin, J. W., Steiner, C., Das, K. C., Ahmedna, M., Rehrah, D., Watts, D. W., Busscher, W. J., & Schomberg, H. (2009). Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. *Annals of Environmental Science*, *3*, 195–206.

Palviainen, M., Aaltonen, H., Laurén, A., Köster, K., Berninger, F., Ojala, A., & Pumpanen, J. (2020). Biochar amendment increases tree growth in nutrient-poor, young Scots pine stands in Finland. *Forest Ecology and Management*, *474*(May), 118362. https://doi.org/10.1016/j.foreco.2020.118362

Palviainen, M., Finér, L., Laurén, A., Launiainen, S., Piirainen, S., Mattsson, T., & Starr, M. (2014). Nitrogen, phosphorus, carbon, and suspended solids loads from forest clear-cutting and site preparation: Long-term paired catchment studies from eastern Finland. *Ambio*, *43*, 218–233. https://doi.org/10.1007/s13280-013-0439-x

Perez-Mercado, L. F., Lalander, C., Joel, A., Ottoson, J., Dalahmeh, S., & Vinnerås, B. (2019). Biochar filters as an on-farm treatment to reduce pathogens when irrigating with wastewater-polluted sources. *Journal of Environmental Management*, *248*(June), 109295. https://doi.org/10.1016/j.jenvman.2019.109295

Pingree, M. R. A., Kardol, P., Nilsson, M. C., Wardle, D. A., Maaroufi, N. I., & Gundale, M. J. (2022). No evidence that conifer biochar impacts soil functioning by serving as microbial refugia in boreal soils. *GCB Bioenergy*, *14*, 972–988. https://doi.org/10.1111/gcbb.12978

Pinheiro, J., Bates, D., DebRoy, S., Sarkar, D., & R Core Team. (2018). nlme: Linear and nonlinear mixed effects models. R package version 3.1–131.1. https://CRAN.R-project.org/package=nlme

R Core Team. (2022). *R: A language and environment for statistical computing*. R Foundation for Statistical Computing. https://www.R-project.org/

Saarela, T., Kakaei Lafdani, E., Laurén, A., Pumpanen, J., & Palviainen, M. (2020). Biochar as adsorbent in purification of clear-cut forest runoff water: Adsorption rate and adsorption capacity. *Biochar*, *2*(2), 227–237. https://doi.org/10.1007/s42773-020-00049-z

SEAL Analytical. (2023). *Method G-297-03 for determination of phosphate in seawater and low level water* [Unpublished method]. https://www.seal-analytical.com/Methods/AutoAnalyzer-Methods/AutoAnalyzer-Multi-test-Methods

Smith, V. H., & Schindler, D. W. (2009). Eutrophication science: Where do we go from here? *Trends in Ecology and Evolution*, *24*(4), 201–207. https://doi.org/10.1016/j.tree.2008.11.009

Taghizadeh-Toosi, A., Clough, T. J., Sherlock, R. R., & Condron, L. M. (2012). Biochar adsorbed ammonia is bioavailable. *Plant and Soil*, *350*(1–2), 57–69. https://doi.org/10.1007/s11104-011-0870-3

Vasander, H., Tuittila, E. S., Lode, E., Lundin, L., Ilomets, M., Sallantaus, T., Heikkilä, R., Pitkänen, M. L., & Laine, J. (2003). Status and restoration of peatlands in northern Europe. *Wetlands Ecology and Management*, *11*, 51–63. https://doi.org/10.1023/A:1022061622602

Xu, R. K., Xiao, S. C., Yuan, J. H., & Zhao, A. Z. (2011). Adsorption of methyl violet from aqueous solutions by the biochars derived from crop residues. *Bioresource Technology*, *102*(22), 10293–10298. https://doi.org/10.1016/j.biortech.2011.08.089

Yao, Y., Gao, B., Inyang, M., Zimmerman, A. R., Cao, X., Pullammanappallil, P., & Yang, L. (2011). Removal of phosphate from aqueous solution by biochar derived from anaerobically digested sugar beet tailings. *Journal of Hazardous Materials*, *190*(1–3), 501–507. https://doi.org/10.1016/j.jhazmat.2011.03.083

Yao, Y., Gao, B., Zhang, M., Inyang, M., & Zimmerman, A. R. (2012). Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. *Chemosphere*, *89*(11), 1467–1471. https://doi.org/10.1016/j.chemosphere.2012.06.002

Yin, Q., Zhang, B., Wang, R., & Zhao, Z. (2017). Biochar as an adsorbent for inorganic nitrogen and phosphorus removal from water: A review. *Environmental Science and Pollution Research*, *24*(34), 26297–26309. https://doi.org/10.1007/s11356-017-0338-y

Zhang, M., Song, G., Gelardi, D. L., Huang, L., Khan, E., Mašek, O., Parikh, S. P., & Ok, Y. S. (2020). Evaluating biochar and its modifications for the removal of ammonium, nitrate, and phosphate in water. *Water Research*, *186*, 116303. https://doi.org/10.1016/j.watres.2020.116303

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This thesis explores the simultaneous supply of C, N and P from boreal catchments to freshwater ecosystems, how this natural supply is disrupted by forest management activities and a way to mitigate disturbances using over ten years of water quality data and field experiments. The results highlight that, given the critical interplay between the supply from catchments and demand in aquatic ecosystems, understanding the variability and controls over C, N, and P exports is central to water quality management.

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