

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 CO₂, 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. 2021b). 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. 2021a). 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-km² 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. 2021b). 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 Vindel 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 $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and $\text{PO}_4\text{-P}$. 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. $\text{SO}_4\text{-S}$ 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 $\mu\text{g L}^{-1}$, 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 (Pohler 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 km²) 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 observed 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 $-0.5 \mu\text{g P L}^{-1} \text{ yr}^{-1}$ between sites, averaging a decrease of -5.4% annually (SD ± 1.6). DIN declines ranged from -1.8 to $-3.6 \mu\text{g N L}^{-1} \text{ yr}^{-1}$ between sites and averaging -7.1% annually (SE ± 1.6).

DIN in the mire outlet stream (C4) was dominated by NH₄, which accounted for 68% (SD ± 6) of the inorganic pool. By contrast, NO₃ 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 NO₃ and NH₄ decreased over the study period ($p < 0.05$) in all the streams (11 of 13 with statistical significance for NO₃ and 13 of 13 for NH₄) (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 NO₃ or for NH₄ 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 NH₄/NO₃ ratios far less than 1 and were notably dominated by NO₃. 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 $\pm 5\%$, 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% ($-12.4 \mu\text{g N L}^{-1} \text{ yr}^{-1}$) in the lake outlet (C5) to a decline of only -1.9% annually ($-8.0 \mu\text{g N L}^{-1} \text{ yr}^{-1}$) 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 $+0.37 \text{ mg C L}^{-1} \text{ yr}^{-1}$ averaging an increase of 1.2% annually (SD ± 0.56). Streams draining the lake, the mire, and

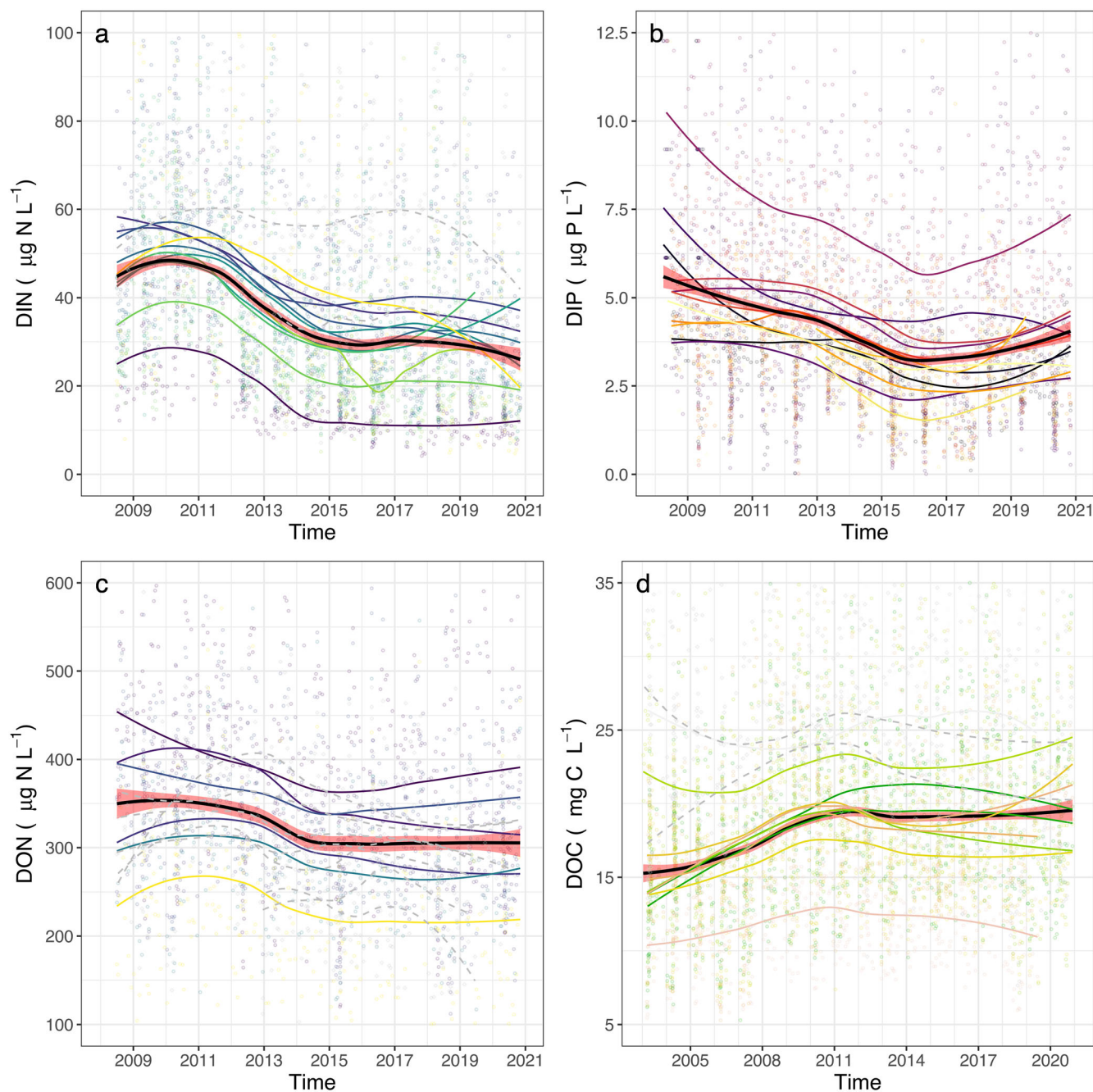


Fig. 1. Time series of organic and inorganic nutrients for the period 2008–2020 shown with locally weighted scatterplot smoothing (loess). **(a)** Dissolved inorganic nitrogen (DIN), **(b)** dissolved inorganic phosphorus (DIP), **(c)** dissolved organic nitrogen (DON) (C14 and C15 have data from 2012 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.

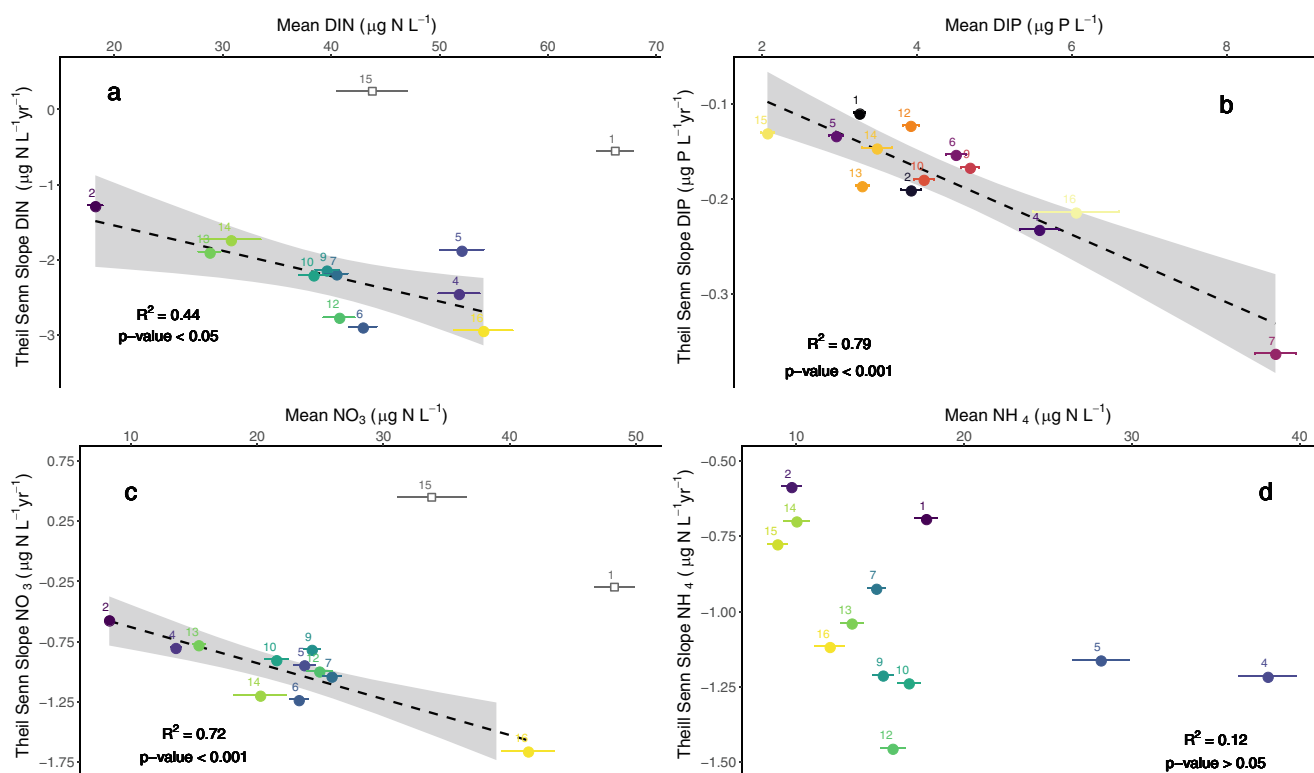
the entire KCS (C16) showed a positive Seasonal Kendall slope estimator but these were not statistically significant (Table 1). Finally, across sites, there was no significant correlation between the Seasonal Kendall slope for DIN and DIP decline and the slopes that describe DOC increases ($n = 13$,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

Catchment ID	KCS stream concentration ($\mu\text{g N L}^{-1} \text{ yr}^{-1}$)						
	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 ($\text{mg C L}^{-1} \text{ yr}^{-1}$).[§]Data available from 2012 to 2019.**Fig. 2.** Relationship between mean (error bars are \pm 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) NO₃ concentration vs. NO₃ Seasonal Kendall slope, and (d) NH₄ vs. NH₄ 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.

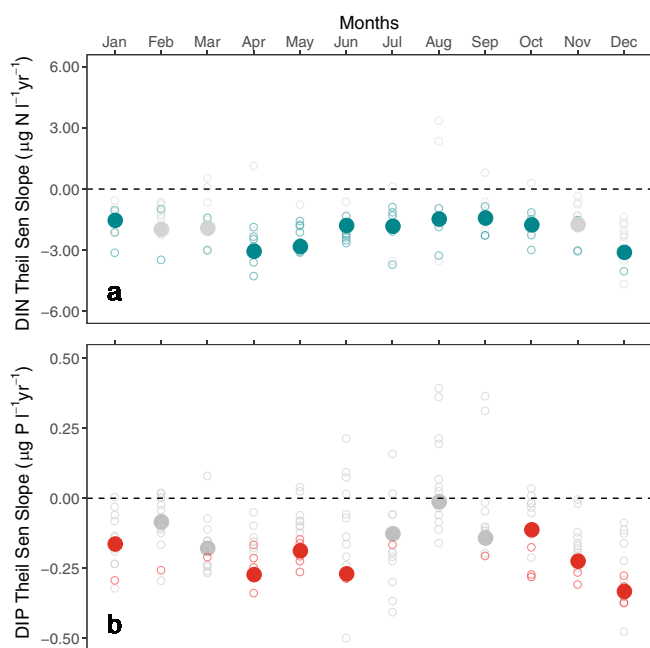


Fig. 3. Seasonal Kendall test for inorganic nutrients in stream waters. **(a)** DIN Seasonal Kendall test and **(b)** DIP Seasonal Kendall test. Pooled Theil Sen slope is shown with filled circles and site-specific Theil Sen slope is shown with hollow circles. Streams with non-significant monthly declines ($p > 0.05$) 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 ($\text{m}^3 \text{ha}^{-1}$); 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 ($\text{m}^3 \text{ha}^{-1}$) (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 ($\text{m}^3 \text{ha}^{-1}$), 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 $\text{SO}_4\text{-S}$ 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

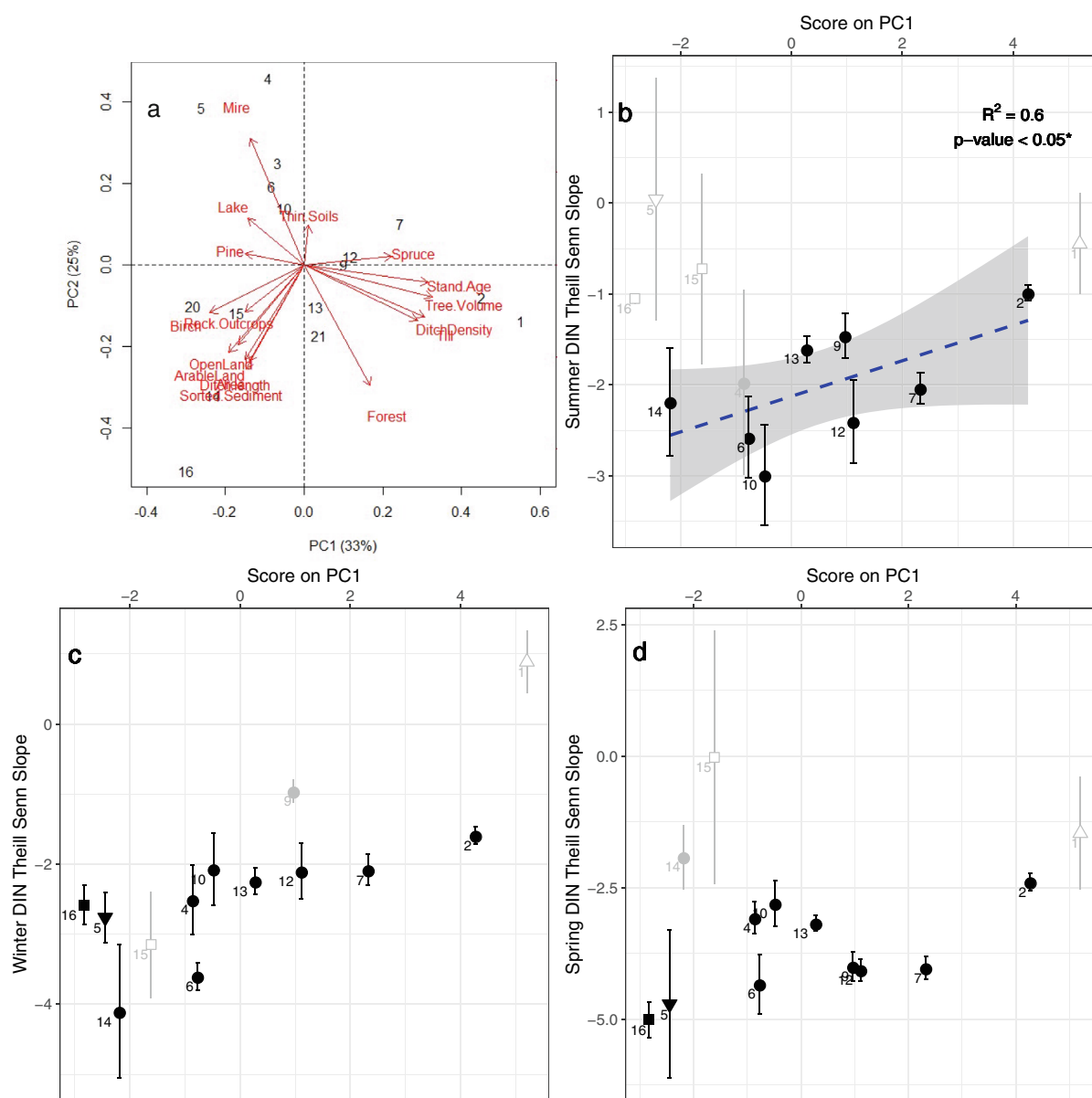


Fig. 4. Relationship between PCA scores of catchment characteristics and seasonal Theil Sen slope; streams with significant ($p < 0.05$) relationships are shown in black, non-significant ($p > 0.05$) in light gray squares (mean ± 1 SE of monthly Theil Sen slope for a given stream for the season). **(a)** 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 sub-catchments (Table 2). On average DOC : DIN ratios significantly ($p < 0.05$) increased annually 5.9% ($SD \pm 1.9$), ranging

from 3.1% in the stream draining the entire KCS (C16) to 9.8% in the stream draining a 100% forest coverage sub-catchment (C2). DOC : DIP annual increase on average was of 3.5% ($SD \pm 1.5$), 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

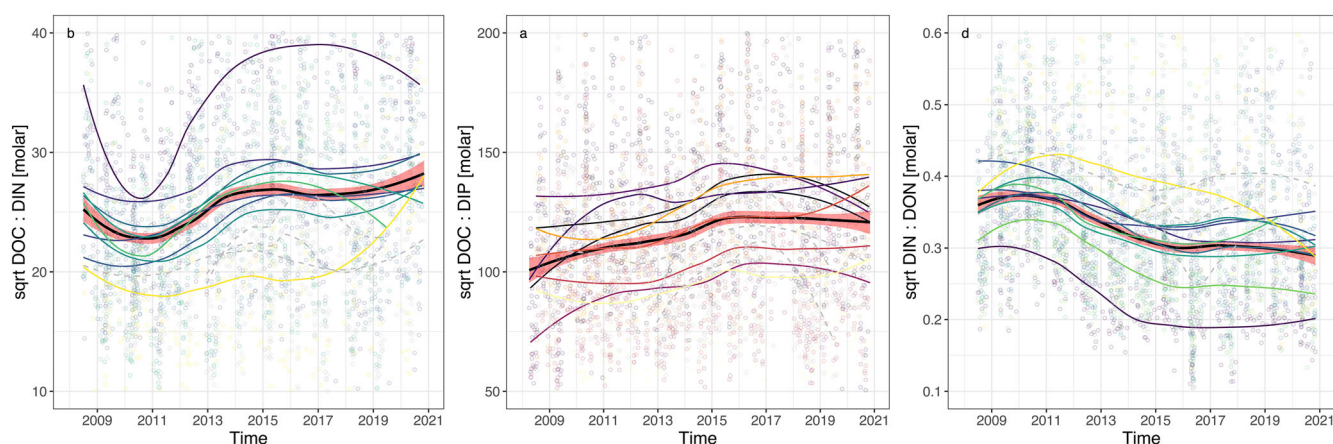


Fig. 5. Time series of molar ratios for the 13 streams of the KCS for the period of 2008–2020 shown with loess smoothing. Time series of (a) DOC : DIN ratio, (b) DOC : DIP ratio, and (c) DIN : DON ratio (C14 and C15 have data from 2012 to 2020). Trends of individual streams with significant trend are 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 \pm 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.

Catchment ID	Element ratios in streams ($\text{mol L}^{-1} \text{yr}^{-1}$)				
	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. 2021a).

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. 2021b). 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. 2021b). 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 $\sim 0.5 \text{ d yr}^{-1}$ 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^{3-} (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 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 kg N ha⁻¹ yr⁻¹ in 1980 and dropping to ~1 kg N ha⁻¹ yr⁻¹ in 2020 (Laudon et al. 2021a). 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 (Petroni 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. 2021a). We observed widespread declines in stream S-SO₄ 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 SO₄ 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 SO₄ 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/>).

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Conflict of Interest

The authors declare that they have no conflict of interest.

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