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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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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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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:

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

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

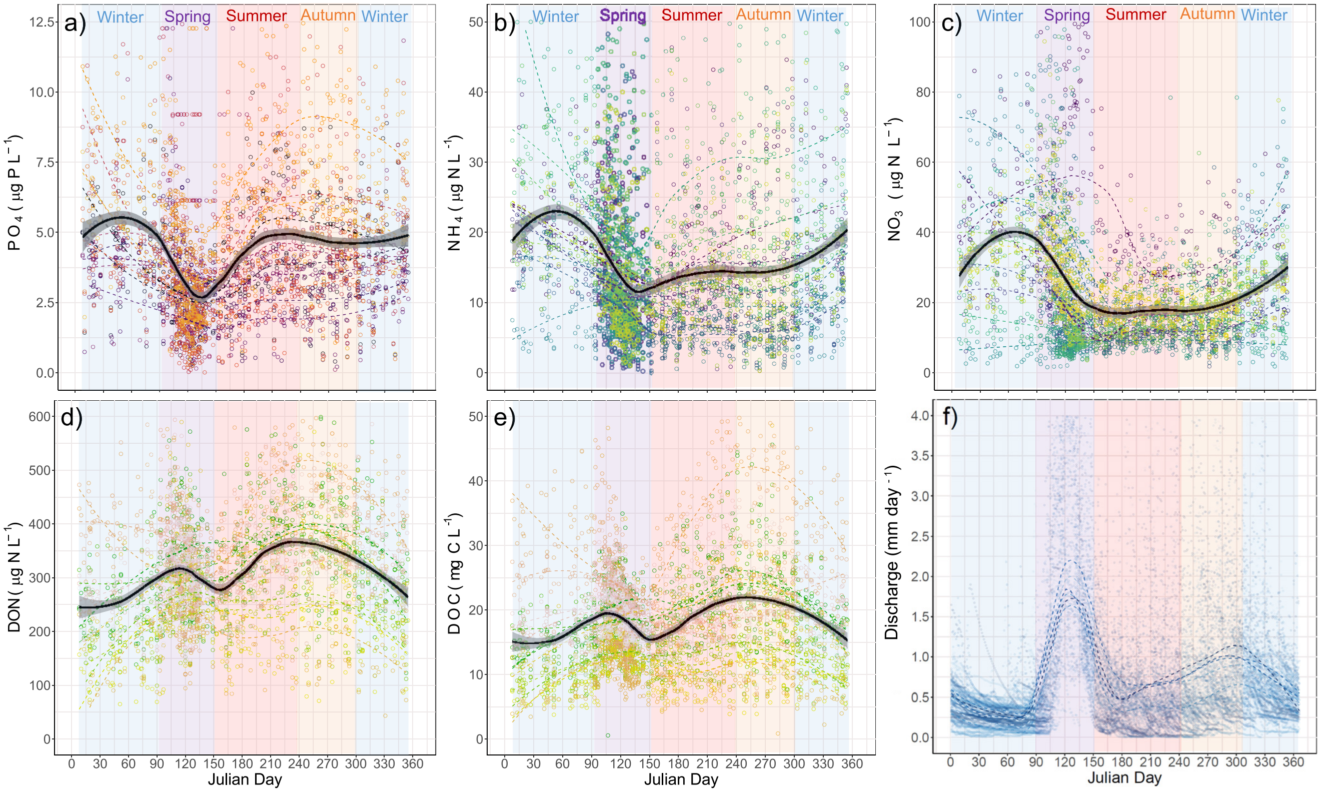

Figure 1. Intra-annual variability of organic and inorganic nutrients for the period 2008–2020 shown with locally weighted scatterplot smoothing (loess). (a) Phosphorus (P-PO_4), (b) ammonium (N-NH_4), (c) nitrate (N-NO_3), (d) dissolved organic nitrogen, (e) dissolved organic carbon, and (f) specific 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%).

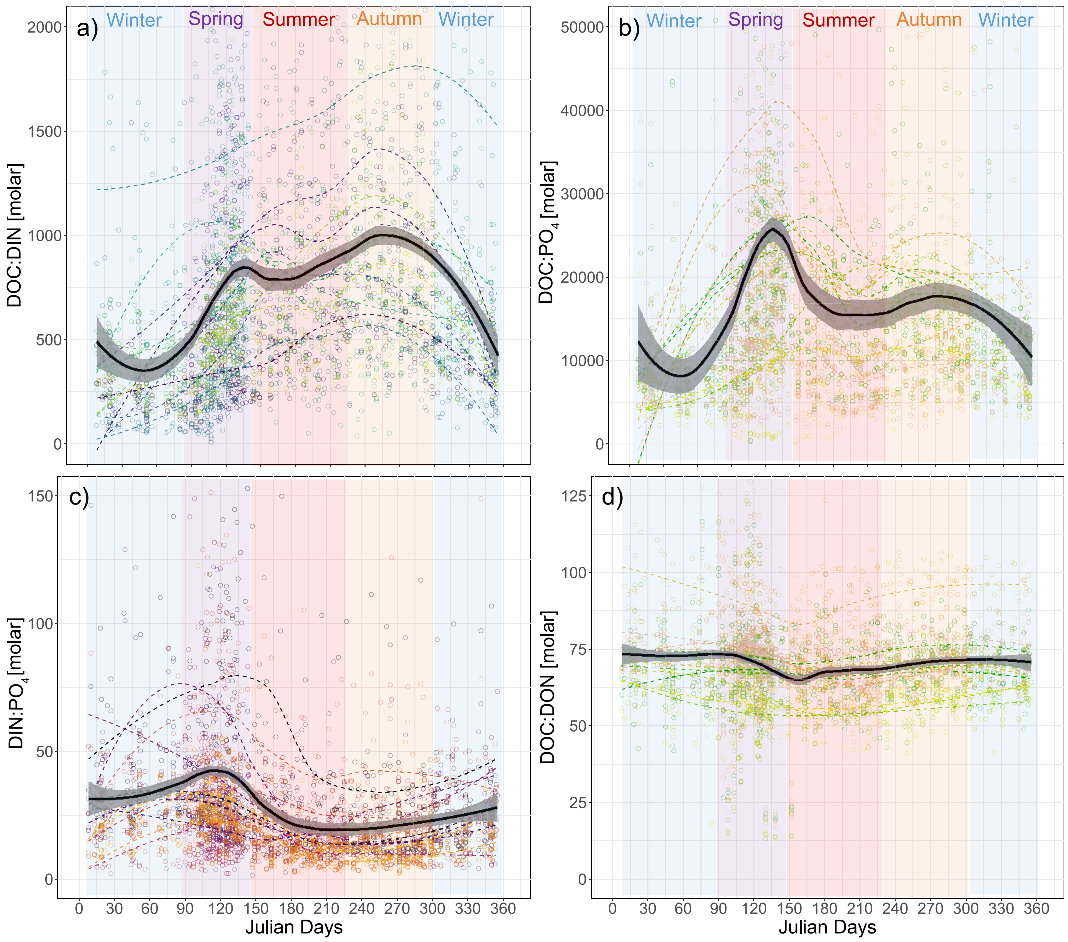

Figure 2. Intra-annual variability of nutrient ratios for the period 2008–2020 shown with locally weighted scatterplot smoothing (loess). (a) dissolved organic carbon (DOC):dissolved organic nitrogen, (b) DOC:Dissolved inorganic nitrogen (DIN), (c) DOC:PO_4, and (d) DIN:PO_4 for 12 headwater streams 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.

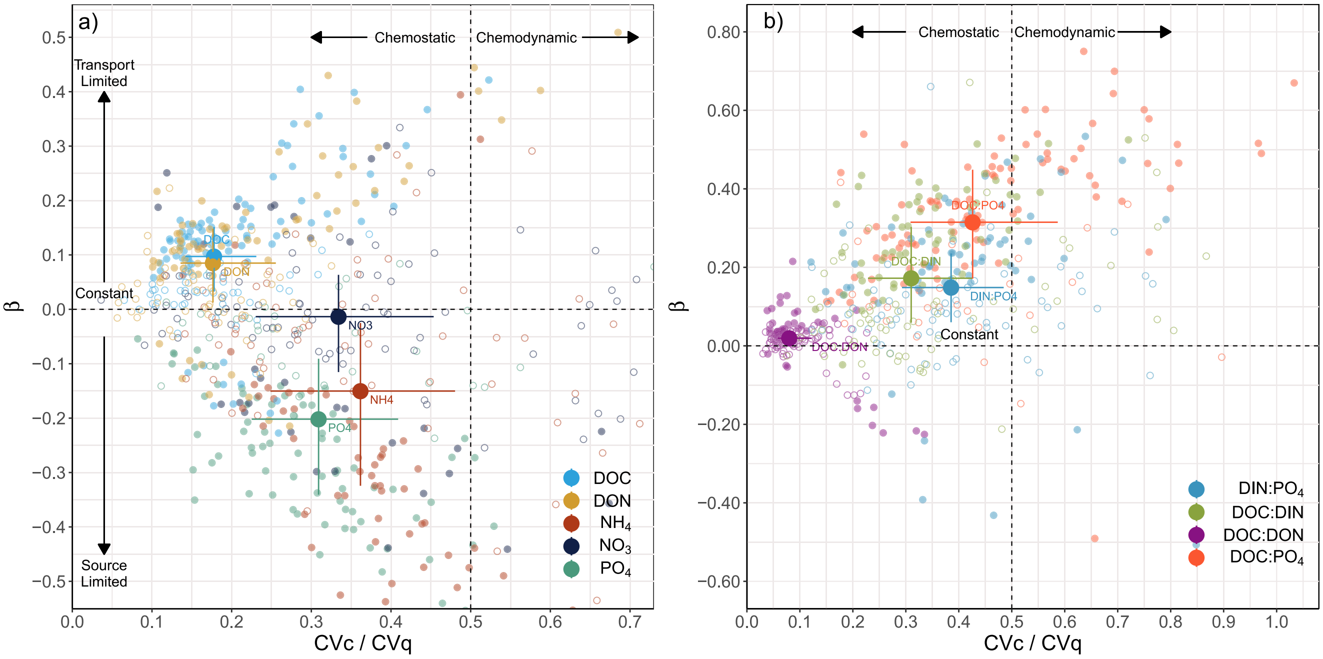

Figure 3. Slope of the linear regression relationship (β) of concentration and ratio versus the coefficient of variation (CV) of concentration divided by the CV of discharge. (a) Slope of the linear log(concentration)-log(discharge) relationships (β) of PO_4, NH_4, NO_3, dissolved organic nitrogen (DON), 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%

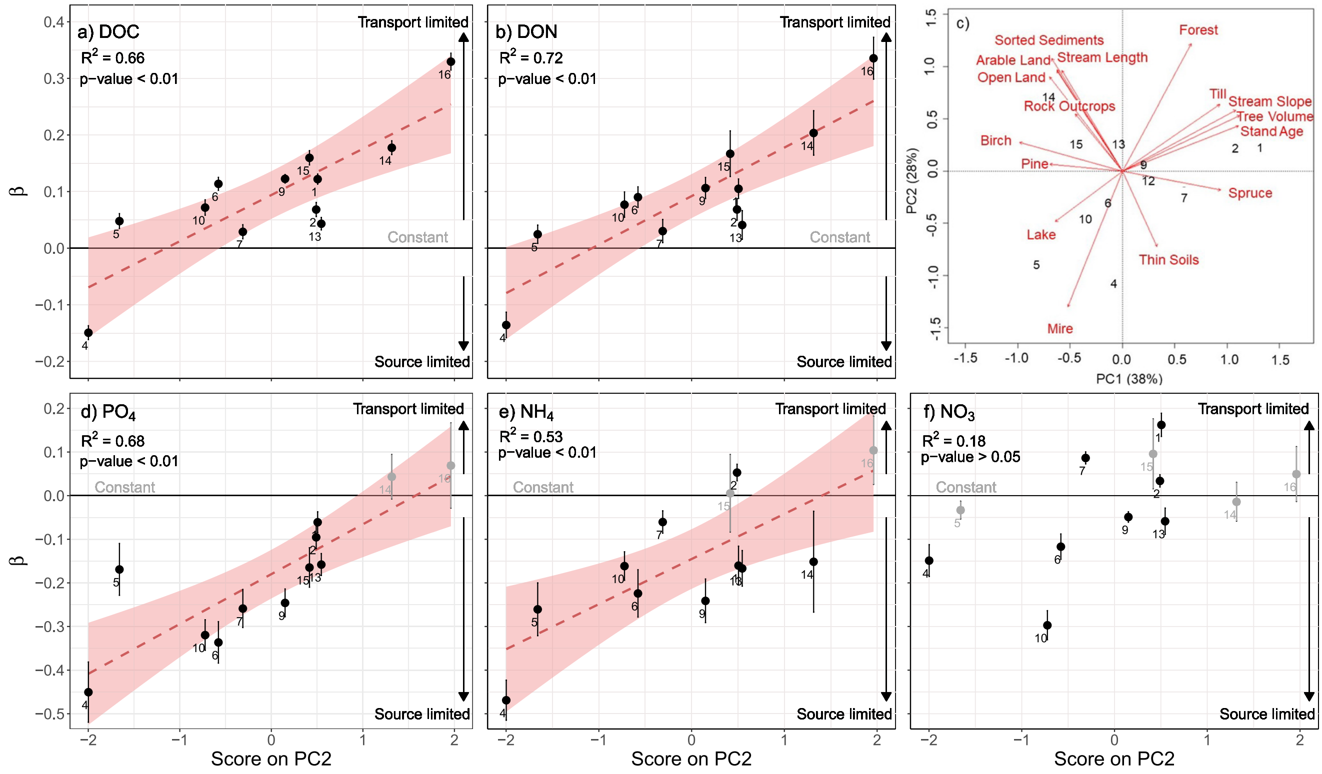

Figure 4. Relationship between principal component analysis (PCA) scores of catchment characteristics and *c*-*Q* relationships (β); streams with significant β ($p < 0.05$) are shown in black circles, non-significant ($p > 0.05$) in light gray, (overall inter-annual ±1 SE β for a given stream). Linear 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

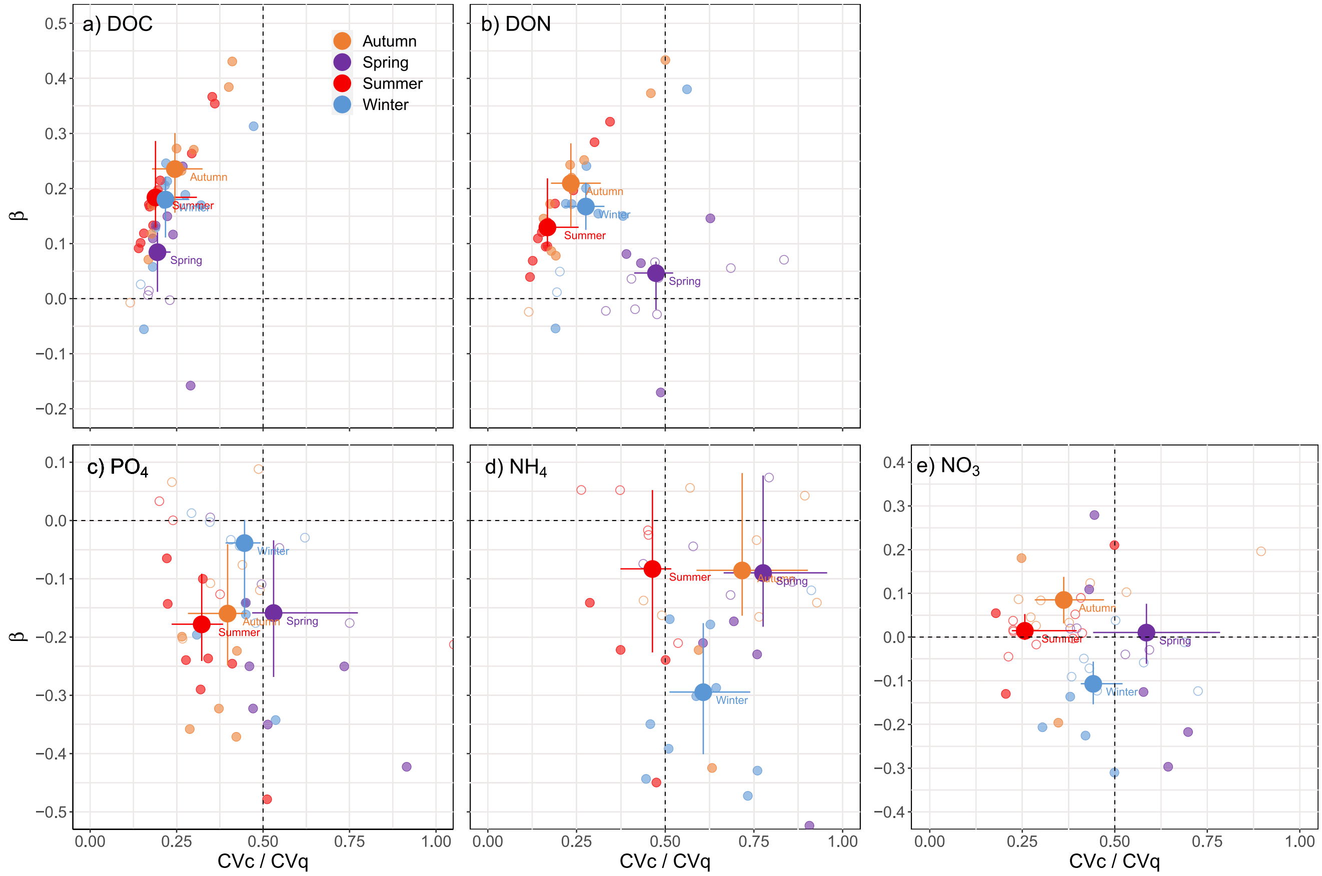

Figure 5. Slope of the linear log(concentration)-log(discharge) relationships (*β*) versus the coefficient of variation for (a) dissolved organic carbon, (b) dissolved organic nitrogen, (c)PO_4, (d) NH_4, and (e) NO_3 for winter, spring, summer, and autumn. Points are colored by season and show *c*-*Q* 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)

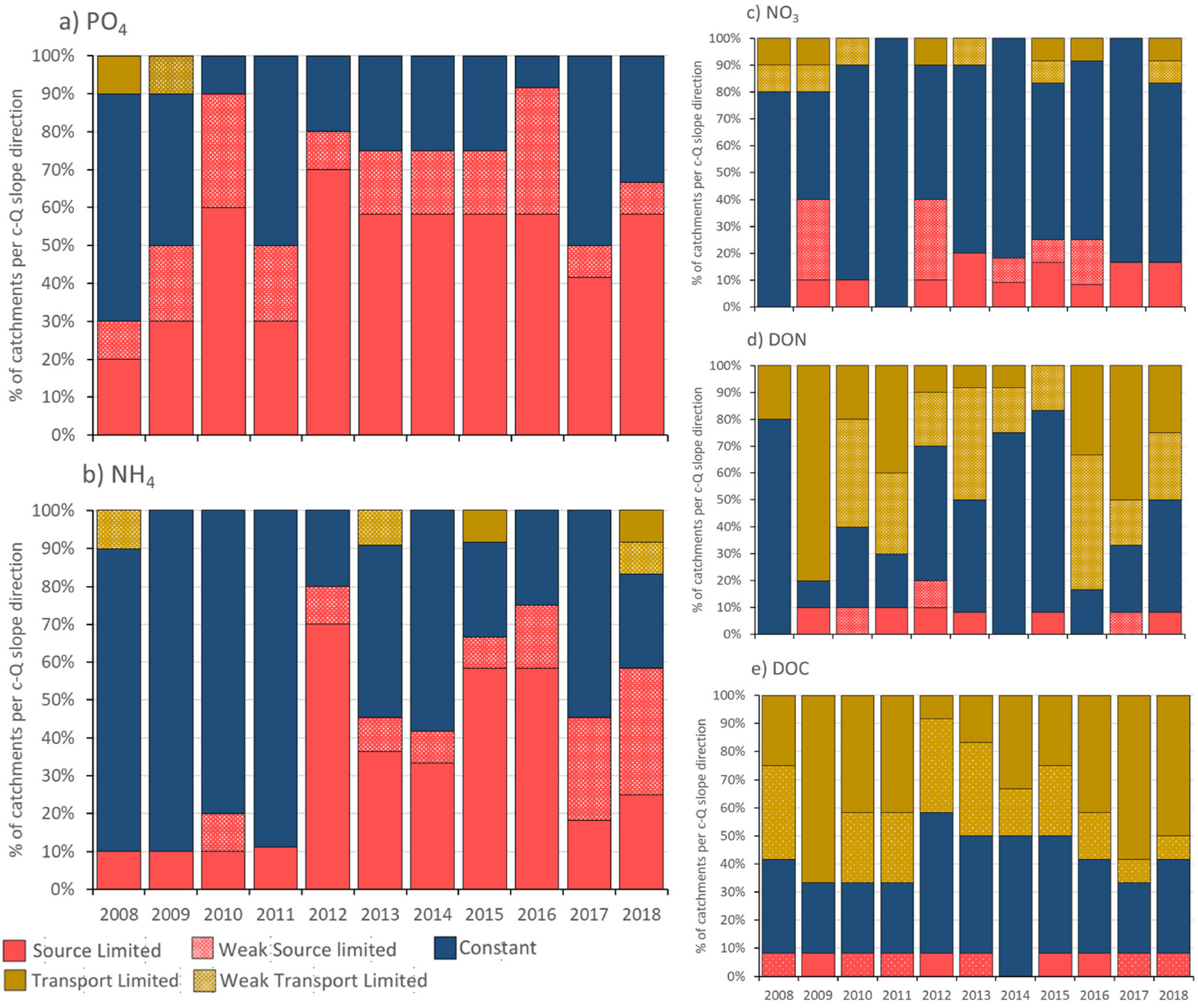

Figure 6. Percentage of sub-catchments *c-Q* archetypes for the following solutes: (a) PO_4 and (b) NH_4 responses across the study period (2008–2018). Constant pattern is presented in blue, transport limited (positive slope) in yellow, weak transport limited (positive slope with low r^2) in dotted yellow, 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

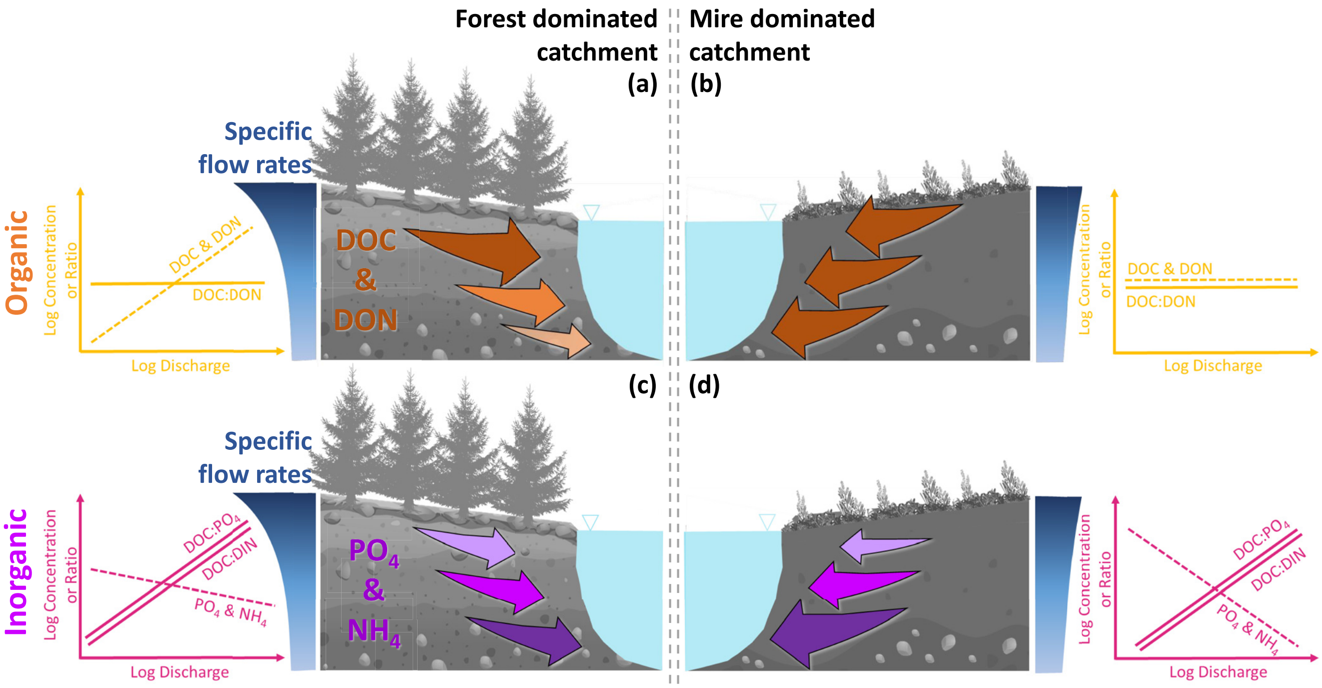

Figure 7. A conceptual diagram illustrating the dominant patterns of export behavior of (a, b) organic and (c, d) inorganic nutrients across headwaters dominated by forest cover (a, c) and headwaters with strong influence by mires (b, d). Color arrows represent fluxes of inorganic and organic solutes 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).

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