

Patterns and controls of rare earth element (REE) dynamics across a boreal stream network

Martin Škerlep^{a,b,*} , Hjalmar Laudon^a, Fredrik Lidman^a, Emma Engström^{c,d},
Iliia Rodushkin^{c,d} , Ryan A. Sponseller^b

^a Department of Forest Ecology and Management, Swedish University of Agricultural Sciences, Umeå, Sweden

^b Department of Ecology and Environmental Science, Umeå University, Umeå, Sweden

^c Division of Geosciences and Environmental Engineering, Luleå University of Technology, Luleå, Sweden

^d ALS Laboratory Group, ALS Scandinavia AB, Luleå, Sweden

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ABSTRACT

Increased demand for rare earth elements (REE) has resulted in their increased exploitation and the need to better understand their cycling in aquatic environments. Thus far much of the research in boreal areas focused on REE cycling in larger rivers, while relatively little is known regarding their mobilization in smaller headwater streams. Here we used the Krycklan Catchment Study in northern boreal Sweden to investigate how REE are mobilized from diverse boreal headwaters and how their catchment exports are influenced by processes such as weathering, hydrology, and complexation with other solutes. We found that wetland dominated headwaters were source limited and prone to dilution during high discharge, while forested headwaters had considerably higher total REE concentrations and were less affected by discharge fluctuations. Larger downstream catchments showed clear discharge driven seasonal patterns, with high concentrations during spring flood and low concentrations during base flow. While the proportion of mineral soils and water travel time in the catchment were important predictors of REE mobilization, complexation with organic matter appears to play a greater role in higher-order streams with higher pH and a larger contribution from deeper groundwater sources. Overall, we highlight the stark differences between REE cycling in the headwaters and in higher order streams, which can provide important information on the processes that mobilize REE from catchments.

1. Introduction

In recent decades, the global demand for rare earth elements (REE) has grown dramatically, due to their wide array of applications. Also known as ‘industrial vitamins’, REE are used in a range of fields, from the manufacturing of catalysts, metal alloys, magnets, batteries, and glass, to applications in clean energy technologies, medicine, and agriculture (Balaram, 2019; Haque et al., 2014; Tommasi et al., 2020). Indeed, the demand for REE has increased by 170 times since the 1950s and is projected to continue increasing by 5–8 % a year in upcoming decades (Dushyantha et al., 2020). Due to their high economic and developmental importance, REE deposits have also become increasingly important in the geopolitical perspective. For example, at present China controls >90 % of global REE supplies (Mancheri et al., 2019), which has resulted in exploration of extraction possibilities from other

geographical regions (Paulick and Machacek, 2017). Such efforts have concurrently increased societal interest in better understanding the environmental impacts of REE exploitation and the biogeochemical behaviors of REE in ecosystems (Gonzalez et al., 2014; Ramos et al., 2016).

REE are a chemically uniform group of elements consisting of lanthanoids (La–Lu) and two transition metals, scandium (Sc) and yttrium (Y). The lanthanoids consist of 15 elements with similar physicochemical characteristics and are loosely divided into light (LREE; La, Ce, Pr, Nd, Pm, Sm, Eu) and heavy (HREE; Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), based on how they interact with other elements and compounds. The natural abundance of REE decreases with increasing atomic number and generally follows the ‘Oddo–Harkins effect’, which suggests that elements with even atomic numbers are more abundant than those with odd numbers. Although their name suggests they are ‘rare’, most REE

Abbreviations: REE, Rare Earth Elements; DOC, Dissolved Organic Carbon; KCS, Krycklan Catchment Study; MTT, Mean Travel Time.

* Corresponding author.

E-mail address: skerlep.martin.uni@gmail.com (M. Škerlep).

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are actually relatively common in the Earth's crust, with abundances that are comparable to those of copper (Cu). The designation instead originates from their scarcity in mineral deposits, which makes them difficult to mine (Jordens et al., 2013).

Due to their diffuse geological presence and low concentrations in water, the fate of REE in the environment has received little attention when compared to, for example, most transition metals. Therefore, it is not surprising that relatively little is known about their biogeochemical cycling and distribution in natural environments. Due to their organophilic properties, REE have a strong affinity for dissolved organic matter (DOM) and have been found to accumulate in organic matter rich environments, such as minerogenic-wetlands and riparian zones (Arbuzov et al., 2018; Lidman et al., 2019). REE form stable complexes with organic and inorganic ligands in natural waters and are strongly depended on their complexation for transport across and throughout the terrestrial-aquatic continuum (Ingri et al., 2000; Klimpel and Bau, 2023; Köhler et al., 2014). It has been found that the majority of REE can be found in the colloidal fraction, especially in acidic ($\text{pH} < 7$) waters (Vasyukova et al., 2010). With increasing use and the potential for mining of REE in the boreal zone, we need to better understand of the fate and mobility of REE in catchments, as well as their baseline concentrations in streams.

The majority of research evaluating REE in boreal freshwaters has focused on their transport and fractionation in larger rivers, lakes, and estuaries (Andersson et al., 2006; Junqueira et al., 2024; Lafreniere et al., 2023; Vorobyev et al., 2019). On the other hand, less is known regarding the flux and biogeochemical cycling of REE in small boreal streams and/or across headwaters with variable catchment properties (Köhler et al., 2014). Boreal landscapes are characterized by a mosaic of coniferous forests, mires (wetlands), and lakes, which creates heterogeneity in organic matter storage and in the nature and arrangement of hydrological flow paths that drain organic and/or mineral soils (Peralta-Tapia et al., 2015). In this context, the large amounts of organic matter accumulated in boreal riparian soils can act as both a barrier and source of elements to streams and thus play an important role in controlling the export of organophilic elements from catchments (Lidman et al., 2017). Elevated concentrations of the REE lanthanum (La) in boreal streams have instead been linked to catchments draining mineral soils and to larger catchments with a higher proportion of groundwater inflow, while low concentrations are connected to catchments with high wetland cover (Köhler et al., 2014). Köhler et al. (2014) also found that La competes for organic ligand binding sites with Fe and Al, which can limit their mobilization from acidic soils if Fe and Al concentrations are elevated. Increases in pH further downstream lead to precipitation of Fe and Al (oxy)hydroxides, which can lead to co-precipitation of REE, while at the same time increasing the binding capacity to DOM (Neubauer et al., 2013). Collectively, these processes can create potentially contrasting and unpredictable REE behaviors from headwaters to larger streams and rivers.

In this study, we ask how the concentrations and exports of lanthanoids in boreal streams vary with catchment characteristics, change seasonally, and are influenced by hydrological processes. Our primary aim was to evaluate the main catchment sources of REE and determine how REEs are mobilized seasonally across catchments of differing sizes and land cover. To do this, we compiled five years of REE data in atmospheric deposition and from biweekly to monthly surface water samples at ten, nested streams within a 68 km² catchment. These streams thus vary dramatically in drainage area, but also in terms of the proportion of catchment covered by forests, wetlands, and sorted sediments, all of which may alter the dynamics of REE delivery to aquatic systems. We analyzed seasonal patterns of REE concentrations at each site, compared the ratio of atmospheric inputs to catchment exports, and explored hydrological drivers using concentration-discharge relationships (Godsey et al., 2009). Because we observed that general patterns are similar for all lanthanoids in these catchments, we present lanthanoids as a uniform group of elements and do not focus on the differences

between specific groups of lanthanoids or Eu and Ce anomalies.

2. Methods

2.1. Site description

The Krycklan Catchment Study (KCS) is located in Northern Sweden approximately 50 km from the city Umeå (64°14'N, 19°46'E). It is located in the boreal zone, with a cold temperate humid climate. The average yearly temperature was 2.0 °C (1981–2020), with the lowest temperatures in January (mean = -9.2 °C) and the highest in July (mean = 14.6 °C). Mean annual precipitation was 620 mm, of which ca 30 % comes as snowfall (Laudon et al., 2021). Over the last 40 years, the mean annual temperature has increased by 2.5 °C, with the biggest increases during the winter months. Although there has been no significant trend in annual precipitation, snow cover has been decreasing at a rate of ~0.5 days per year during the period (Laudon et al., 2021).

Bedrock at the site is dominated by migmatized meta-greywacke or paragneiss. In the upper part of the catchment, retreating ice from the last glaciation left behind till deposits and bare bedrock in exposed areas. Lower parts of the catchment, which were below the highest postglacial coastline, have higher proportions of glaciofluvial or fluvial silt and sand deposits. Nevertheless, the mineralogy of the Quaternary deposits is relatively similar across the KCS and is dominated by quartz, plagioclase, and K-feldspar, with smaller proportions of amphibolites, muscovite, and chlorite (Ledesma et al., 2013). Present-day land cover in the KCS is a mosaic of forests, peatlands, and lakes (Table 1). Forest covers the majority of the catchment (87 %) and mostly consists of Scots pine (63 %) and Norway spruce (26 %). Peatlands have developed in areas of lower topographic relief and are classified as oligotrophic minerogenic mires.

Within the KCS, several integrated catchments have been monitored and studied for several decades. For the purpose of this study, 10 sub-catchments were selected, that represent a range of sizes and catchment characteristics (Table 1). Coniferous forest covered C2, mire outlet C4 and lake outlet C5, represent different headwater types typical of the Fennoscandian boreal zone. At the KCS outlet, C16 is a higher-order stream, where deeper groundwater has an increasing effect on base-flow discharge and stream water chemistry (Laudon et al., 2021). Data for annual mean travel time (MTT) of water through each catchment was obtained from Sterte et al. (2021).

2.2. Sampling and analysis

As part of the KCS monitoring program, stream water sampling is performed several times per year (22 - 26) with more regular sampling during the spring freshet in April-May. Stream water grab samples were collected in acid-washed 250 ml high-density polyethylene bottles and stored cold. Atmospheric deposition samples were collected between 2002 and 2021 at the Svartberget field station in central parts of KCS, by pooling daily precipitation samples which were bulked and analyzed monthly (Supp. Fig. 1). In the laboratory, all samples were filtered (0.45 µm) and subsampled for different types of analysis. For analysis of REE and other metals samples were acidified with 5 % ultra-pure HNO₃ and analyzed in a commercial lab (ALS Scandinavia AB) using double focusing ICP-MS (ICP-SFMS) which offers low quantification limits (Rodushkin et al., 2005). For dissolved organic carbon (DOC) analysis, samples were stored cold and analyzed within 24–72 h after sampling via the combustion catalytic oxidation method on a Shimadzu TOC VCPH analyzer (Shimadzu, Duisburg, Germany). Further information regarding quality control and assurance can be found in the Supplementary material.

All statistical analysis was done in R studio version R 4.2.2. To test the strength and direction of association between REE and other elements, we used Spearman's rank correlation coefficients. Linear regression models were performed to determine the slope of the relationships

Table 1
Stream catchment characteristics in the Krycklan Catchment Study.

	Area	MTT	Lake	Forest	Mire	Open	Arable	Birch	Spruce	Pine	Till	Thin soils	Bedrock outcrop	Sorted sediments
	ha	yr.	%	%	%	%	%	%	%	%	%	%	%	%
C1	48	1.3	–	98	2	–	–	2	63	35	92	8	–	–
C2	12	0.8	–	100	–	–	–	–	36	64	84	16	–	–
C4	18	0.8	–	56	44	–	–	–	45	55	22	27	–	–
C5	65	0.8	6.4	54	40	–	–	12	26	62	40	5.5	–	–
C6	110	0.9	3.8	71	25	–	–	4	26	70	54	11	2.5	–
C7	47	1.1	–	82	18	–	–	1	35	64	65	15	–	–
C9	288	1.4	1.5	84	14	–	–	6	29	65	69	7	1.7	4
C13	700	1.4	0.7	88	10	0.2	0.6	8	25	68	61	9	1.3	16
C16	6790	2.3	1	87	9	1.1	1.9	10	26	63	51	7	1.2	30
C20	145	2.7	0	88	10	0	3	16	16	68	45	20	2	21

between REE and Q, and adjusted R^2 are presented where applicable.

2.3. Discharge modelling

Discharge exerts a strong control on stream solute concentrations in both small and large catchments and the relationships between concentration and flow can inform on solute storage patterns in soils. Discharge (Q) was measured at the outlet of each sub-catchment where samples were also collected for water chemistry (Karlsen et al., 2016). Automatic water-level observations from pressure loggers were used to estimate stage (depth) at each site. Manual water-level measurements were made to calibrate the automatic data, and stage-Q relationships were calculated for each catchment outlet using manual flow gauging. For missing data, in particular during winter from stations without heated weirs, values were gap-filled using a semidistributed hydrological model (Karlsen et al., 2019). From the modeled daily discharge values, we calculated the REE fluxes for each stream by linearly interpolating daily concentrations between measured values and multiplying by daily discharge. Yearly per area REE exports were calculated by dividing yearly exports by catchment area. To estimate the amount of catchment exports that come from atmospheric deposition versus weathering, the ratio between deposition and exports was calculated.

To assess the influence of discharge on REE concentrations, we evaluated concentration-discharge relationships by calculating the slope (β) of the $\log c - \log Q$ relationship and the ratio of the coefficients of variation between concentration and discharge (CV_c/CV_Q) (Musolff et al., 2015). 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 represents the slope of the log transformed c-Q relationship. Additionally, the coefficient of variation is the standard deviation (σ) of a variable normalized by its mean (μ). The metric is the ratio as follows:

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

The c-Q relationships responses of the β slope were classified in the following ways: (i) positive β slope signifies transport limitation, (ii) negative β slope signifies source limitation, and (iii) a “flat” β slope ($\beta \approx 0$) signifies a constant concentration response to changes in discharge (Musolff et al., 2017). The coefficients of variation between concentration and discharge (CV_c/CV_Q) were used to characterize whether export regimes are chemostatic or chemodynamic. According to (Musolff et al., 2017), chemodynamic refers to solutes that vary strongly and independently from discharge ($CV_c/CV_Q > 0.5$), whereas chemostasis refers to situations where solute concentrations are less variable than discharge ($CV_c/CV_Q < 0.5$).

3. Results

3.1. REE concentrations in streams

Concentrations of REE in streams followed the ‘Oddo–Harkins effect’, where elements with even numbers of electrons are more abundant than their odd-numbered neighbors in the periodic table (Fig. 1A). Expectedly, concentrations of lanthanoids also decreased with increasing atomic number from La-Lu. The proportions of different REE

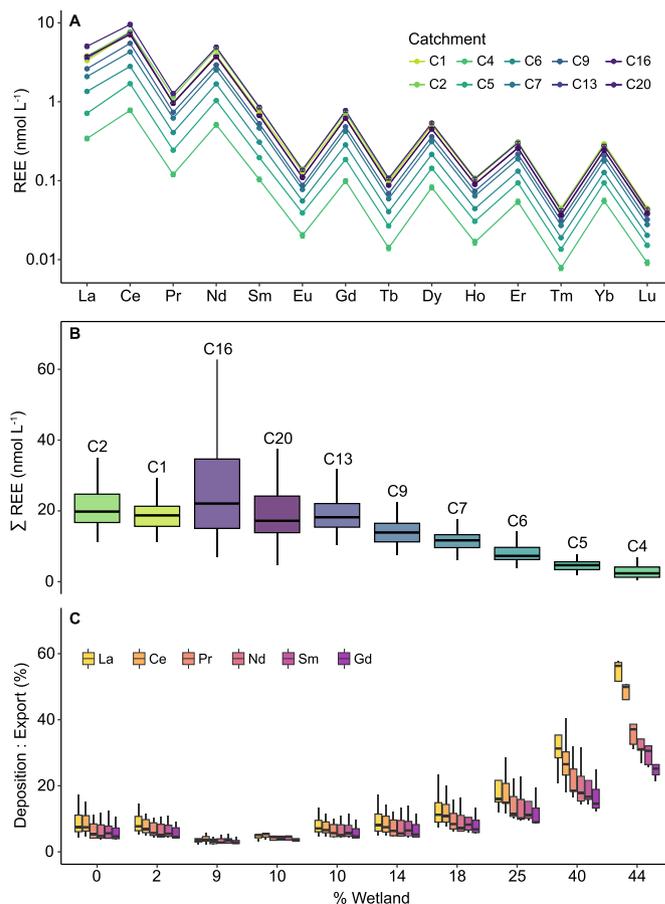


Fig. 1. Mean stream REE concentrations (A), total REE concentrations (B) and the percent of yearly stream exports that come as deposition (C) for each catchment. Since several REE were below detection limit in the deposition samples, only the REE with $<10\%$ below detection limit (BDL) values are plotted (BDL values are replaced by $\frac{1}{2}$ detection limit). On the x-axes of panels B and C, catchments are sorted by percent wetland cover and are plotted in the same order in B and C. Boxplots represent median values with first and third quartile, and whiskers represent data distribution limits. Note that the y-axis of panel A is log scaled.

varied slightly across catchments and seasonally, with HREE enrichment in most small streams and LREE enrichment at the outlet of KCS (Supp. Fig. 2). At the outlet, LREE enrichment was most pronounced during high discharge events, while proportions remained consistent throughout the year in headwaters. Despite this, the general trends and variation were very similar for all REE, which are therefore presented as the total sum of REE. Compared to Fe and Al, molar concentrations of REE were 4–6 orders of magnitude lower in respective streams and mean total REE concentrations ranged from 4.7 to 36.2 nmol L⁻¹ (Supp. Table 1).

Across streams, concentrations of REE varied widely and were well correlated with catchment characteristics. The highest average concentrations were found at C16, the outlet of the KCS (Fig. 1A; Supp. Table 1). Concentrations were also relatively high in small streams with a high percentage of coniferous forest (C1, C2) and in streams with higher proportions of sorted sediments in their catchments (C13, C20). In comparison, concentrations were comparatively low in streams draining mire (C4) and lake (C5, C6) dominated catchments (Fig. 1B). The proportion of forest and sorted sediments in the catchments were the two variables that best predicted the concentrations of REE in the streams (Fig. 1). Sorted sediments are only found in the lower part of the KCS (C13, C16, C20), while till soils dominate upper parts of the catchment (Table 1).

3.2. Correlations between REE and other elements

Complexation with DOC prevents REE from precipitating from solution and thereby increases their concentrations and transport in streams. REE were thus positively correlated with DOC within all streams except for C5 and C6, which are the lake outlet and the site downstream of the lake outlet (Fig. 2). Yet, the strength and slopes of the correlation between REE and DOC varied notably across streams and was steepest and strongest furthest down in the KCS at C16 (slope = 0.038, R² = 0.82). By comparison, at C4, REE and DOC were correlated, but with a far shallower slope (slope = 0.0016; R² = 0.64).

In addition to DOC, Fe and Al (oxy)hydroxides can also be important binding sites for REE and facilitate their transport in streams, but Fe and Al might also compete with REE for binding sites on organic colloids. Both Fe and Al correlated positively with REE, although the strength of the correlation varied across catchments (Fig. 2). The relationship between REE and Fe was strongest in the stream with the mire dominated catchment (C4; R² = 0.96), while for Al, the relationship was strongest at C4 (R² = 0.88) plus the two catchments with higher proportions of

sorted sediments C16 (R² = 0.88) and C20 (R² = 0.87). pH correlated negatively with REE only at sites C9, C16, and C20 all in the lower parts of the KCS, while it was positive in headwaters with high wetland cover (C4–C6) and showed no correlation in headwaters with forest cover.

Base cations and Si, common tracers of mineral weathering, correlated negatively with REE at C16, which suggests that a general increase in weathering products does not directly affect REE concentrations at the KCS outlet. Finally, REE and U correlated strongly positively in all catchments, suggesting they are weathered simultaneously throughout the KCS and transported by similar mechanisms.

REE concentrations exhibited distinct seasonal variation but these patterns varied among catchments (Fig. 3). Accordingly, in most smaller catchments (C1 - C7) concentrations were highest during the summer and early autumn months (Jul-Oct) and were generally lowest during the spring flood period from April-May. For C20, contrary to other smaller catchments, concentrations were higher in early spring (Apr) and were low during the winter months. In the two intermediate-sized catchments (C9 & C13), stream REE concentrations did not show clear seasonal patterns that could be directly related to any of the upstream headwater catchments. Finally, at the outlet of the KCS (C16), and in contrast to most upstream catchments, REE concentrations were highest during the spring snowmelt flood (Apr-May) and were lower during the winter and summer – early autumn period.

The correlation between log(REE) and log(Q) varied widely among catchments (Fig. 4; Supp. Fig. 3). In the two small coniferous forest dominated streams (C1 & C2), REE concentrations did not correlate with discharge (Fig. 3). By contrast, in the mire (C4) and lake (C5 & C6) dominated catchments, REE showed a strong negative correlation with discharge. Finally, in the two catchments with higher proportions of sorted sediment, C16 and C20, REE concentrations followed the seasonal patterns in discharge and showed a strong positive correlation with log(Q).

Seasonal patterns and hydrological influences on REE at the catchment outlet C16 and in C20 contrasted strongly with the smaller streams higher up in the catchment. This was most evident from the relationship between β -slope (log(c)/log(Q)) and the coefficients of variation between concentration and discharge (CV_c/CV_Q). The small mire and lake dominated catchments (C4 & C5) had a negative β -slope, suggesting that the REE concentrations in these streams were source limited and diluted during periods of higher discharge. In contrast, the largest catchment in this study (C16) was clearly transport limited (β -slope > 0), which suggests hydrological connectivity, rather than abundance and availability in catchment sources were limiting factors for stream REE

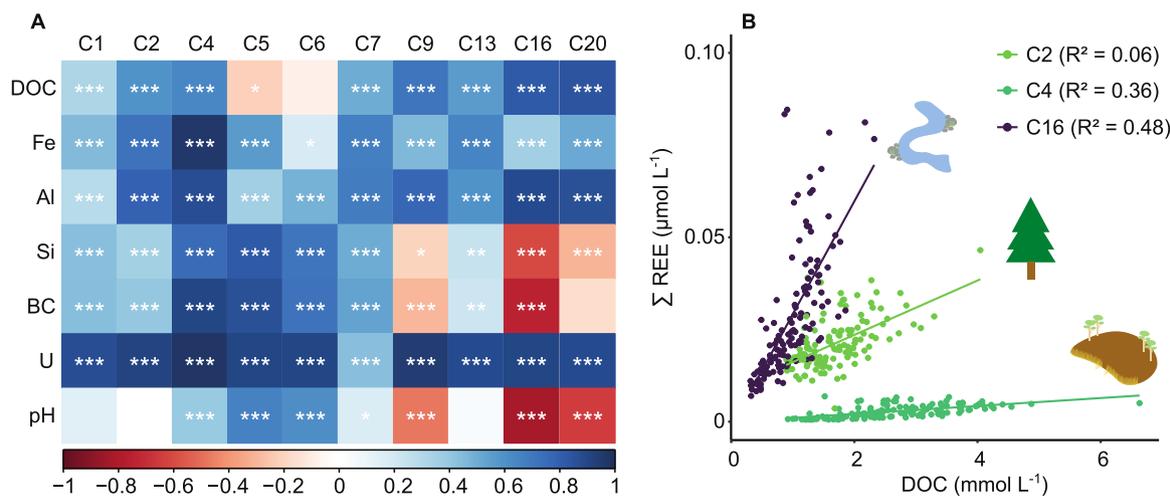


Fig. 2. Correlation between the sum of REE and other water chemistry variables in different streams (A). In panel (B), are the linear relationships (lines) between total REE and DOC in the three representative streams; forest dominated (C2), wetland dominated (C4), and higher order downstream location (C16). Colors in the correlation matrix represent Spearman's rank coefficients and symbols show significance levels (<0.05, <0.01, <0.001) of the relationship.

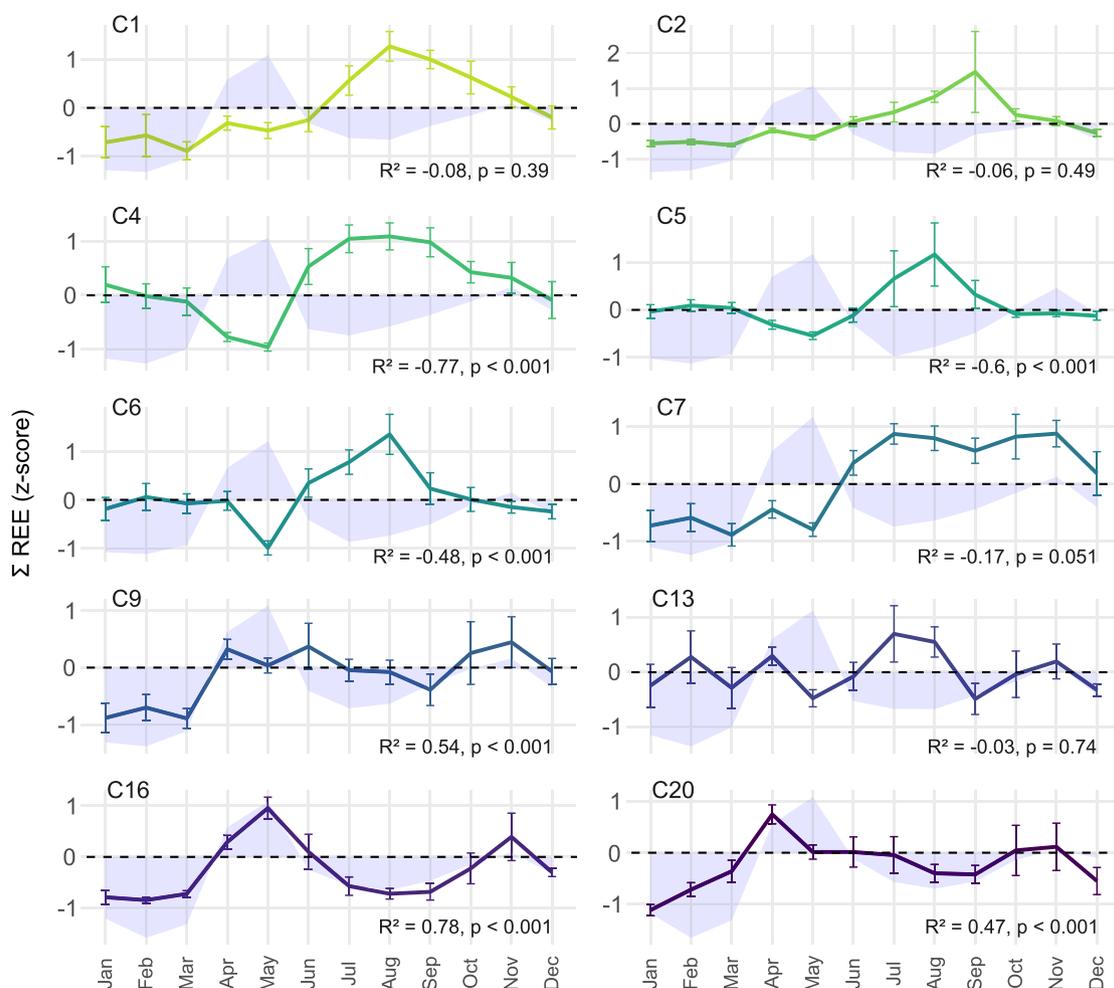


Fig. 3. Seasonal changes in REE concentrations for each catchment (monthly means; error bars represent standard error). Blue shaded area represents mean logarithm discharge values ($\log(Q)$) for each month and the R^2 and p values are derived from the linear relationship between $\log(\text{REE})$ and $\log(Q)$. Both total REE and discharge are normalized to units of standard deviation (z-score) at each site, to allow for better comparison. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

concentrations (Fig. 4). For the rest of the catchments, REE showed a constant response to variations in discharge (β -slope ≈ 0), which suggests that discharge has a limited impact on stream concentrations. In addition, stream REE dynamics were closer to chemodynamic in catchments C4, C5, C16, and C20 (i.e., $CV_C/CV_Q > 0.5$), whereas they behaved chemostatically in the rest of the catchments (i.e., $CV_C/CV_Q < 0.5$).

3.3. Catchment exports

Yearly catchment exports of REE ranged from 0.2 to 768 mol catchment⁻¹ year⁻¹, generally increasing with catchment size. Catchments also differed in the amount of REE exported per area (Supp. Table 3), with the highest exports coming in streams of the lower parts of the KCS in C16 and C20, where exports were 11 and 7.9 $\mu\text{mol m}^{-2} \text{y}^{-1}$, respectively. On the other hand, per area exports were lowest in catchments with higher proportions of wetlands and lakes, like C4 and C5, where exports were 0.88 and 1.7 $\mu\text{mol m}^{-2} \text{y}^{-1}$. Mean transit time (MTT) through the catchment was a good predictor for the relative amount of REE exported, especially when accounting for the proportion of mineral soils in each catchment. A linear model including MTT and proportions of mineral soils (MTT + mineral cover) could predict 84 % of the variation in per area REE exports amongst the catchments (Supp. Fig. 4) and could be expressed as:

$$\text{REE export} = 0.029\text{MTT} + 0.0009 (\% \text{ mineral cover}) - 0.058$$

At the KCS outlet (C16), exports showed strong seasonal variation, with the majority of annual exports (53 %) coming during April and May. On the other hand, only 6 % of all annual exports came during the winter season (Dec-Mar). This largely reflects the runoff during different seasons.

The fraction of exports that could be accounted for by annual atmospheric deposition also varied strongly across catchments. In this context, REE deposition relative to export from the catchments was low ($< 10\%$ of ΣREE) for the majority of catchments. However, for the mire (C4) and lake (C5) dominated catchments, deposition accounted for a considerably higher proportion of catchment exports (13–53 %; Fig. 1C; Supp. Fig. 1), suggesting that this is an important REE source for catchments with a low proportion of mineral sources. Notably, La and Ce deposition represented $\sim 50\%$ of total exports at C4 and the proportions of deposition to exports were generally higher for lighter REE (Fig. 1C; Supp. Table 3).

4. Discussion

Past research on riverine REE cycling, has mainly focused on larger rivers, while less attention has been given to headwater streams and understanding how REE are mobilized from soils to streams. In the KCS,

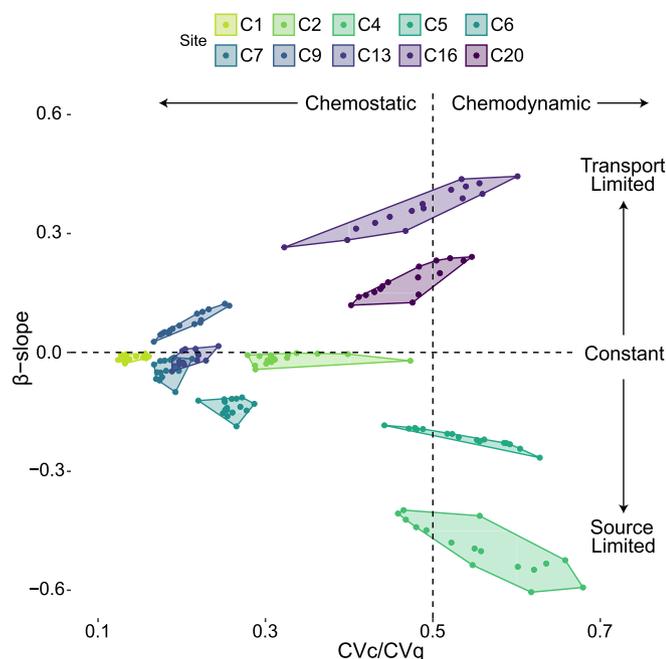


Fig. 4. Slope of the linear concentration and discharge relationships (β) versus the average coefficients of REE variation divided by the average coefficient of variation in discharge (CV_c/CV_q). Each point represents the mean for each REE at each site and the polygons represent the distribution of the REE at each site.

REE concentrations reported here were comparable to other boreal streams with high DOC concentrations (Andersson et al., 2006; Pokrovsky and Schott, 2002; Pokrovsky et al., 2006). On the other hand, REE concentrations were considerably higher when compared to headwaters elsewhere with lower DOC concentrations (Larsen et al., 2021; Stille et al., 2006), but substantially lower than in streams draining highly acidic soils or those subject to acid mine draining (Oliás et al., 2018; Åström et al., 2010). Overall, our results highlight strong landscape heterogeneity, not only in terms of stream REE concentrations but also in terms of the seasonal export dynamics and their relationship with flow. In addition, our results suggest there are differences in REE mobilization processes along the river network, which are dependent on both land cover and catchment size.

4.1. Landscape patterns in REE concentrations

We observed up to 8-fold variation in total REE concentrations across KCS streams which could be linked to differences in catchment structure and water travel time. First, concentrations of all REE in streams were negatively correlated to the proportion of wetlands and lakes in the surrounding catchment. Such a pattern is not surprising as catchments with a high proportion of wetland and lake cover have a lower proportion of mineral soils, which are the major source of REE in these systems. In addition to source limitation, REE are known to accumulate in wetlands, which can further decrease their flux to streams (Arbuzov et al., 2018). For example, Lidman et al. (2013) observed that uranium U, an element strongly correlated with REE in the KCS, was transported to mires from surrounding mineral soils but accumulated in peat along the edges of mires. Since REE have similar organophilic properties, it is reasonable to assume that they also accumulate in peat and are therefore retained in mires. Looking across a wide range of weathering-derived metals in stream water from KCS it has been shown that the mires consistently suppress stream water concentrations and the strength of the impact is related to the affinity for organic matter for the different metals (Lidman et al., 2014). Indeed, accumulation of REE in peat has been reported elsewhere and is mainly associated with complexation to

organic molecules, rather than mineral formation in wetlands (Arbuzov et al., 2018). Thus, the considerably lower REE concentrations in the mire outlet stream (C4), compared to the nearby forested catchment C2, likely reflect both the lower proportion of mineral weathering and REE accumulation within the mire.

REE dynamics across other catchments reflect stronger influences of mineral soils. For example, forest dominated headwater catchments C1 and C2 showed relatively high REE concentrations, which are likely weathered in upslope mineral soils and transported to the stream via the riparian zone. Organic matter rich riparian zones in boreal landscapes have been shown to accumulate REE and exert control over organophilic metal concentrations in streams of (Lidman et al., 2017). In comparison to wetland-dominated catchments, these catchments provide a mineral source of REE, ample organic matter to facilitate weathering (via organic acids), and sufficient DOC to facilitate the transport of REE across land-water boundaries. As expected, streams with mixed catchments (both forest and mire) showed intermediate stream REE concentrations, reflecting the combined chemical signals from distinct headwater units. Finally, in the lower parts of the KCS, sorted sediments provide additional mineral sources of REE. These catchments also have considerably longer water transit times, which increases mineral contact and can lead to higher concentrations of weathering products (Sterte et al., 2021). Increased groundwater-mineral contact and thereby increased mineral weathering, have been shown to lead to higher concentrations of weathering products such as base cations K, Mg, and Ca (Klaminder et al., 2011; Sterte et al., 2021). Our findings suggest that REE concentrations in streams are similarly dependent on mineral sources within their catchments and the transit time of water within the catchment.

4.2. Correlations with REE and other solutes

In DOC rich surface waters, REE mobilization and transport are strongly dependent on complexation with colloidal carriers such as organic matter, ferric hydroxides, and mixed organo-metallic colloids (Ingri et al., 2000; Pokrovsky and Schott, 2002). This leads to correlations between DOC, Al, Fe, and REE in surface waters and although correlation does not necessarily mean causation, these relationships between elements can inform us about processes such as catchment mobilization and stream processing. While REE generally correlated positively with DOC, DOC concentrations alone could not predict REE concentrations amongst our different catchments. For example, stream DOC concentrations were high in wetland dominated catchments, but the lack of a mineral source means REE concentrations were lower than in streams that had both a mineral source and where DOC concentrations were high enough to facilitate the transport of REE. Further downstream the potential for complexation with DOC increases as pH rises and competition for binding sites with elements such as H, Fe, and Al declines (Neubauer et al., 2013). Since REE are mostly bound to the organic matter components of Fe-OM complexes, precipitation of Fe does not directly affect REE transport in streams (Tadayon et al., 2024). Indirectly, however, precipitation of Fe and Al might decrease the competition for binding sites on DOC, allowing more room for REE. Through geochemical modeling, Köhler et al. (2014) found that La in boreal streams was almost exclusively bound to organic matter and that binding to ferrihydrite was negligible. They further found that La was mobilized together with U throughout the catchment. The strong correlation between REE and U in the present study corroborates those findings within our stream water dataset and suggests that REE and U are mobilized from the same sources, likely by binding strongly to organic colloids.

The lake outlet C5, was the only stream where REE correlated negatively with DOC while correlating positively with Fe and Al. This stream has higher Fe concentrations than the rest of the catchments and decoupling between Fe and DOC cycles has been reported at this site previously (Škerlep et al., 2023). Small boreal lakes have been observed

to behave similarly to wetlands when it comes to metal exports (Lidman et al., 2014), with REE being clearly source-limited in such catchments. The negative correlation between REE and DOC reported here may be related to the fact that considerable amounts of DOC are processed biotically and abiotically in the lake, while REE concentrations are mainly controlled by hydrology.

In global rivers, REE generally correlate negatively with pH, which was suggested to be caused by the correlation between pH and DOC (Ingri et al., 2000), rather than increased mobilization in more acidic soils. Within the KCS stream network, the influence of pH on REE concentrations varied widely among catchments, and negative relationships were only observed in three streams with sorted sediments in their catchments. These were also the streams where REE correlated negatively with Si and base cations, which are typical products of mineral weathering and can be indicative of deeper groundwater contribution to streams (Klaminder et al., 2011). This is also consistent with the longer MTT in these catchments (Table 1). Negative correlations with pH, Si, and base cations and at the same time strong positive correlations with Al and DOC, suggest that REE in these streams originated from shallower organic rich soil horizons, rather than from deeper groundwater. That is in line with Ingri et al. (2000), who suggested that organic-rich colloids, transported to the river from shallow soils during high discharge events, are the main carriers of REE in boreal rivers. At higher pH values (6), REE were observed to bind to smaller organic colloids, as compared to lower pH (4) conditions, when REE were complexed in larger, less mobile organic aggregates (Tadayon et al., 2024). This pattern suggests that REE should be more mobile at downstream sites with higher pH. It is important to note that this study focused on REE in the dissolved fraction (based on 0.45 μm filtering), meaning larger organic aggregates and associated REE were omitted from the samples. Previous research in boreal rivers found that REE were mainly transported in the colloidal phase, with a considerable amount of REE also found in the particulate (> 0.22 μm) phase (Andersson et al., 2006; Ingri et al., 2000; Vasyukova et al., 2010). The main carrier phases in the aforementioned studies were a large Fe-rich colloidal phase and a smaller C-rich colloidal phase. Fe-rich colloids are present mainly in downstream sites in the KCS and are largely absent from the acidic headwaters (Neubauer et al., 2013). The effects of pH on REE concentrations thus seem to be mostly related to the changes in REE binding capacity to organic colloids across the pH range of a boreal stream network. Precipitation of small Fe colloids in higher order streams further frees up organic colloid binding sites and increases the mobility of REE. While these findings shed light on possible REE mobilization processes, future investigation of catchment soils and the ratios between different REE will hopefully provide more detail on what mobilizes REE in different boreal catchments and how they fractionate within the streams.

4.3. Seasonal and hydrologically driven patterns in REE

Distinct seasonal patterns in REE concentrations were observed in the KCS and varied largely between catchments. The seasonal differences between catchments highlight the heterogeneity within the boreal landscape that is missed when only looking at downstream sites. For example, at the outlet of the KCS (C16), seasonal patterns match those of boreal rivers Kalix and Ob, which have considerably larger catchment areas (24,000 and 260,000 km^2) than the 68 km^2 of C16 (Andersson et al., 2006; Vorobyev et al., 2019). These rivers show a clear REE concentration increase during spring flood and low concentrations during winter and summer baseflow. Interestingly, this seasonal pattern was unlike those observed across the majority of headwaters, suggesting that different drivers emerge to regulate REE supply to streams across spatial scales. Collectively, our findings show large variation in seasonal/discharge REE patterns within the mesoscale KCS basin and highlight the importance of understanding discharge driven source contribution across different land uses and catchment sizes. Examining the importance of spatial scale river chemistry, Tiwari et al. (2017)

suggested that conservative mixing and increasing contributions from deep groundwater conceal headwater signals in boreal catchments larger than $\sim 10 \text{ km}^2$, while continued increases in deep groundwater contributions and instream processing further shape chemical signals in catchments larger than $\sim 70 \text{ km}^2$. These scale-dependent processes seem to in part explain the variation in REE between catchments within the KCS.

At the catchment outlet (C16), discharge exerted a strong positive control on seasonal variation in REE concentrations. Again, these patterns were not unique to REE, but agree with previous findings for other organophilic metals and DOC at the site (Björkvald et al., 2008). Surprisingly, the strong REE mobilization during spring flood was only reflected in another stream with sorted sediments in its catchment, which suggests that REE mobilization in catchments with sorted sediments markedly changes the contribution to lower parts of the KCS. Since different layers of the catchment are connected to the stream during different hydrological conditions, we might speculate on the catchment sources of REE, based on how concentrations respond to changes in discharge. If deeper groundwater were the main source of REE during spring flood, one would expect that concentrations would be more similar to those during winter baseflow when deeper older water feeds the stream. This was not the case at the catchment outlet C16, where concentrations were low during baseflow and highest during spring flood. However, considering the importance of REE complexation with OM, it is likely that during base flow the lack of OM binding sites limits the transports of REE in the catchments. On the other hand, during spring flood, the mixing of deeper mineral rich groundwater and DOC rich surface runoff provide both a mineral source of REE and DOC for complexation. This together with the reduced competition for binding sites with Al and Fe leads to high concentrations of REE at the catchment outlet.

As previously mentioned, most headwater streams in the upper part of the KCS did not reflect seasonal and hydrological patterns observed in the lower part of the KCS. In forested headwaters, concentrations peaked during late summer and autumn months and did not show any correlation with seasonal discharge patterns. Riparian soils have a profound impact on forested headwater streams and have been shown to accumulate high concentrations of REE throughout the soil profile (Lidman et al., 2017). Reductive dissolution of Fe-(oxy)-hydroxides and release of the associated REE could explain the high concentrations in the warmer months when redox potential is presumably low (Köhler et al., 2014). In addition, higher turnover of organic matter and higher weathering rates during summer and early autumn could cause higher rates of REE mobilization in riparian soils. Since dissolved REE concentrations are high throughout the riparian soil profile (Lidman et al., 2017), seasonally changing groundwater flow paths through the riparian soils likely play a smaller role on stream REE concentrations.

REE in streams draining wetland and lake dominated headwaters correlated negatively with discharge and were clearly source limited. This led to low REE concentrations during spring flood when overland flow, limited contact with mineral soils, and shorter water transit times have a diluting effect on solutes in the stream. The same response has been observed for DOC and other metals at C4 (Björkvald et al., 2008; Cory et al., 2006) as well as in wetland dominated catchments in other boreal regions (Clark et al., 2007; Eimers et al., 2008).

4.4. Understanding catchment mass-balance of REE

Exports varied across the catchment, with total REE exports naturally increasing with increasing catchment size and discharge. Yearly exports per area ($\text{mol REE area}^{-1} \text{ year}^{-1}$) were 1.8 and 10-times higher at C16 than in the forest and mire headwater catchments, respectively. This suggests that catchments with till forest soils and mires cannot account for the total REE exports downstream and that an additional high REE source must contribute to the outlet of the KCS. Part of the increased exports could be explained by increased mineral contact time, which

increases weathering rates and was a strong predictor of REE exports from the catchments. As with most other elements, the majority of REE exports come during the prominent spring flood period, owing to the disproportionately high discharge (Björkvald et al., 2008; Ågren et al., 2007). At the outlet of the KCS, 53 % of all exports came during April and May, with 41 % exported during the open water seasons (summer and autumn), and only 6 % during the winter baseflow period (Dec-Mar).

Although atmospheric deposition generally represented a small proportion of stream REE exports, it could be a considerable source of REE in catchments with higher proportions of wetlands and lakes, where the contribution from mineral weathering is limited (Aubert et al., 2006; Fagel et al., 2014). In the present study, atmospheric deposition accounted for up to 50 % of catchment exports in the mire dominated C4 while contributing <10 % in catchments with higher proportions of mineral soils. In catchments with significant wetland cover, the ratio between deposition and export was higher for lighter lanthanoids (La & Ce; Fig. 1), which results from their increased relative proportions in precipitation as compared to the local bedrock. Our findings suggest that although changing atmospheric REE deposition would have a minor effect on most boreal catchments, it could lead to drastic changes in REE cycling in catchments with low proportions of mineral soils, where deposition represents a significant proportion of stream REE exports.

5. Conclusions

This study shows that while REE concentrations and seasonal variation might be similar in higher order streams and large boreal rivers, there is large variation when it comes to headwater streams. Wetland dominated headwaters were source limited and prone to dilution during high discharge, while forested headwaters had considerably higher REE concentrations and were less affected by changes in discharge. Larger downstream catchments showed clear discharge driven seasonal patterns, with high concentrations during spring flood and low concentrations during base flow. While it is well recognized that organic matter is essential for mobilizing REE, we show that hydrology strongly affects stream REE concentrations at downstream sites. Our data further demonstrate the importance of complexation with DOC to keep REE in solution, especially in higher order streams with higher pH and inputs of deeper groundwater. In this study, we showed that to understand REE concentrations and exports from a mesoscale stream network, we need to elucidate how water travels through catchments and from what sources REE can be mobilized. Higher proportions of mineral soils and longer travel times through the catchment result in higher REE exports, while complexation with DOC ensures REE remain in solution even in higher order streams. Future research looking at the fractionation of different REE within boreal catchments can inform us about weathering rates and other processes linked to environmental change within the boreal landscape.

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CRedit authorship contribution statement

Martin Škerlep: Writing – original draft, Visualization, Software, Methodology, Formal analysis, Conceptualization. **Hjalmar Laudon:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization. **Fredrik Lidman:** Writing – review & editing, Conceptualization. **Emma Engström:** Resources, Project administration, Methodology, Investigation. **Iliia Rodushkin:** Resources, Methodology, Investigation. **Ryan A. Sponseller:** Conceptualization, Funding

acquisition, Project administration, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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Data availability

Data will be made available on request.

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