



Original Articles

Ce anomaly in hemiboreal headwater streams: An indicator of dominant groundwater flow paths through the catchment

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ABSTRACT

The water quality in headwater streams depends on the groundwater origin and its transport pathways before it eventually discharges as surface water. In this case study, we present the Ce anomaly of over 100 hemiboreal headwater streams in Sweden and discuss the potential of the Ce anomaly to define two stream end members as proxies for the stream origin. The data show a relation between topography and the Ce anomaly, with more negative values (−0.8 to −0.4) in hilly catchments with distinct slopes, defined as an oxidized groundwater end member. The second end member is dominated by groundwater discharge from reduced, organic-rich riparian and wetland soils (reduced groundwater) having small Ce anomalies (−0.3 to zero). Element concentrations show a wide range, depending on the end member of the stream. For example, redox elements (Fe, Mn, S and N) show concentrations up to five times in streams with small negative Ce anomalies (reduced groundwater) compared to the concentrations in streams with large negative Ce anomalies. While element concentrations (of the classic redox elements Fe, Mn, S, N) show seasonal variations due to a summer drought period and the resulting reduced conditions, the Ce anomaly is constant, offering an excellent indicator of the dominant groundwater flow paths regardless of seasonal variations.

1. Introduction

Headwater streams are critical in indicating natural and anthropogenic influences on geochemical processes (Bishop et al., 2008; Knorr, 2013; Meyer et al., 2007). Despite constituting up to 90 % of the total stream length in European river systems (Baatrup-Pedersen et al., 2018; Bishop et al., 2008; Ledesma et al., 2018), these headwater streams' chemistry has been systematically understudied (Pokrovsky et al., 2016a; Temnerud et al., 2010). This oversight is especially pronounced considering the dynamic interplay of land cover, land use, and hydrology, which defines unique geochemical signatures in boreal headwater streams due to the dynamic mixing of waters from spatially distinct catchment locations (Laudon et al., 2016; Löfgren et al., 2014). Different soil types in the boreal landscape generate groundwater of varying quality, discharging into streams and forming significant variations in surface water quality (Ledesma et al., 2013; Seibert et al., 2009). The connection between groundwater and surface water is essential for stream flow and stream chemistry (Erdbrügger et al., 2023). Especially in the boreal ecosystems, shallow groundwater is a source for different types of solutes to the headwater stream chemistry (Erdbrügger et al.,

2023; Jutebring Sterte et al., 2018; Laudon et al., 2011). Understanding variations in water quality is crucial, for example, in areas with forest biomass harvesting. Increasing demand for energy from forest biomass has put focus on the possible acidification effects of whole-tree harvesting (WTH) (Achat et al., 2015; de Jong et al., 2017; Thiffault et al., 2011), intended to be mitigated by wood ash application (WAA) (Azan et al., 2019; Ekvall et al., 2014; Norström et al., 2011; Pitman, 2006). To diminish the risks for adverse environmental impacts by WTH and subsequent WAA on soils and waters, the Swedish guidelines include restrictions on maximal allowable trace metal concentrations in the wood ash and define protection zones (10–15 m) along ditches, wetlands, streams and lakes where the application is forbidden (SFA, 2019).

This study assesses how the Ce anomaly (Eq. 1), a geochemical principle indicating Ce's relative enrichment or depletion compared to the remaining rare earth elements (REEs), can provide insights into oxidation pathways in a hemiboreal catchment.

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$$\delta Ce = \frac{\left(\frac{Ce}{Ce_N}\right)}{\frac{2}{3}\left(\frac{La}{La_N}\right) + \frac{1}{3}\left(\frac{Nd}{Nd_N}\right)} - 1 \quad (1)$$

Specifically, we investigate the Ce anomaly's relationship with redox-sensitive constituents and aim to establish its potential as a broader indicator for the redox state compared to the traditional Fe isotope composition (Beard et al., 2010; Conrad et al., 2019; Ingri et al., 2018). A negative Ce anomaly results from depletion relative to its neighbouring REEs, i.e., La and Pr. The principle of the Ce anomaly is based on its two oxidation states, Ce³⁺ and Ce⁴⁺, contrary to the other REEs, which occur solely in the oxidation state 3+ (Exception Eu²⁺). The Ce anomaly results from redox reactions, separating the Ce chemistry from that of other REEs during weathering and transport in the soil profile. Minerals containing REEs, including Ce, undergo weathering and release REEs into the soil water. The low ionisation potential of Ce³⁺ leads to a different behaviour than its neighbouring trivalent REEs (Seto and Akagi, 2008). When percolating porewater reaches the illuviated, Fe-rich B-horizon in podzols (Wiederhold et al., 2007), Ce³⁺ is adsorbed and subsequently oxidized to Ce⁴⁺ at Mn-Fe oxyhydroxide surfaces, producing a positive Ce anomaly in the solid phase of the soil (Feng, 2010; Ingri et al., 2000; Laveuf et al., 2012). This process is also known as oxidative scavenging (Bau, 1999; Davranche et al., 2005). Consequently, the soil water containing the remaining Ce³⁺ and REE displays a negative Ce anomaly, which percolates to the aquifer and eventually discharges as surface water. Within organic-rich soil layers, Ce³⁺ and other REE are complexed by organic matter (OM), which prevents oxidation (Davranche et al., 2008; 2005) and inhibits the development of a negative Ce anomaly in the soil water. A prior study of runoff from approximately 100 headwater streams in southern Sweden showed that it is possible to identify the redox state along the dominant groundwater flow paths and how organic soils affect these redox patterns (Conrad et al., 2019). The conclusions are based on evaluating the Fe isotope composition and the concentrations of redox-sensitive elements such as Fe, sulfate (SO₄²⁻) and nitrate (NO₃⁻), considering the concentration patterns for TOC, pH and ANC (Conrad et al., 2019). The Ce anomaly provides a more general indicator of the redox state (Pédrot et al., 2015) than the Fe isotope composition since the latter has a poor indicator value in runoff from organic soils due to Fe²⁺ complexation to OM and restricted oxidation of Fe²⁺ to Fe³⁺.

Prior studies have tested the possibility of using Ce anomaly as a tracer for aqueous solutions origin, movement and mixing (Davranche et al., 2016, 2011; Lawrence et al., 2006; Pourret et al., 2010; Smedley, 1991). Thus, several important aspects of the geochemistry of REE are well understood for groundwater (Smedley, 1991; Viers et al., 1997). A distinct Ce anomaly characterises REE patterns of deep groundwater, whereas organic-rich water from wetlands shows no or small Ce anomalies (Davranche et al., 2016, 2005; Gruau et al., 2004; Pourret et al., 2010). Further, data show relations between topography and Ce anomaly, with more negative values in hilly catchments with distinct slopes (Braun et al., 1998; Gruau et al., 2004; Pourret et al., 2010). The Ce anomaly detected in stream water, caused by oxidative scavenging (Bau, 1999; Davranche et al., 2005) in the soils, is reflected primarily by the total REE concentrations rather than those found in the dissolved phase. The reason is that colloids of Fe and Al hydroxides, flocculated humic substances and suspended particles are the most important carriers of REE in boreal streams (Åström et al., 2012). Stream water Fe originates from the soils via groundwater influx of dissolved Fe(II), which rapidly oxidizes to Fe(III) and forms nanoparticles and colloids due to hydrolysis and complexation with organic matter (Ekström et al., 2016; Sjöstedt et al., 2013). Similarly, Al enters the streams as Al³⁺, precipitating due to hydrolysis and complexation with organic matter (Löfgren et al., 2010; Löfgren and Cory, 2010; Sjöstedt et al., 2010).

By analyzing over 100 natural headwater streams in hemiboreal Sweden, this study aims to define two endmembers in the hemiboreal

landscape: (1) headwater streams dominated by oxic mineral soil profiles, for example podzols and (2) headwater streams dominated by organic-rich soils, for example histosols using the Ce anomaly. We define hemiboreal as climatic regions *Dfb*, *Dwb* and *Dsb* in the Köppen climate classification (Kottek et al., 2006), with long cold winters and warm summers. The region is defined by a mixed forest of coniferous and deciduous tree species. The resolution of soil, bedrock, and runoff maps is often too low to get detailed information on the catchment composition. Using the Ce anomaly as a more general indicator for catchment composition and redox state will improve the understanding of small-scale catchments. So far studies on the Ce anomaly are often limited to one catchment during a limited amount of sampling events. This is the first contribution representing a total area of approximately 67,000 km². The headwater streams catchment areas cover 4,800 km² and was sampled over three distinct seasons. Additionally, we assess how the concentrations of organic carbon (TOC) and pH vary with the Ce anomaly in the streams, potentially affecting the concentrations of REE, aluminium (Al), base cations (Ca²⁺, Mg²⁺) and some trace metals (Cu, Pb, Zn, Cd) due to varying levels of complexation and solubility.

As a complementing case study, we use the Ce anomaly to identify potential areas, where WAA could be suitable in the forested landscape. The efficiency of the protective zones (10–15 m) along streams, where no WAA is allowed, may differ among elements depending on their sensitivity to the physical-chemical environment. These protective zones are located mainly in organic-rich discharge areas, exhibiting substantial seasonal variations in redox state (Conrad et al., 2019; Laudon et al., 2016; Mitchell and Branfireun, 2005), TOC concentrations and pH (Clark et al., 2010; Ledesma et al., 2016). Hence, some elements may pass or dissolve in the protective zone due to, for example reduced conditions or low pH, while others may be attenuated there due to complexation or precipitation. Based on WAA, but probably relevant for other forestry measures like mineral fertilizer application, we hypothesize that the Ce anomaly can be used as an ecological indicator to identify catchments where a protective zone is useful.

2. Material and methods

This study was performed on data from 104 hemiboreal headwater streams in southeast Sweden (Conrad et al., 2019) (Fig. 1). The headwater streams were identified using a 'virtual hydrological network' generated from a 50 m × 50 m digital elevation model (Nisell et al., 2007). The object-oriented database contains water bodies, watersheds, their topological relations, data on flow accumulation and flow direction, and vector data on river reaches, lakes and contributing areas on a national scale (Löfgren et al., 2021). The headwater streams were then randomly selected whereas all streams are of first-order and fulfil the following criteria: (i) longer than 2.5 km; (ii) less than 5 % agricultural land; (iii) no urban areas and lakes; and (iv) within 500 m of a drivable road. Their catchments vary in size (95–725 ha), and due to the selection criteria, their composition is dominated by forests (48–100 %) and wetlands (0–44 %) on till with granite and gneiss in the bedrock (Hawkes et al., 2018). Forested land, including clear-cut areas and wetlands, dominate landscape features (Table S1). Each catchment area is based on a virtual hydrological network, VIVAN (Nisell et al., 2007), and digitalized by SLU, Uppsala. Using the catchment area polygons combined with height data of a 50x50m square grid digital elevation model from the Swedish Land Survey (Lantmäteriet). For each catchment, the average degree of the slope was calculated with the planar method of slope in ArcGISTM, where a vertical cliff has a slope of 90 degrees, and a flat surface has a slope of zero degrees (Table S1).

Based on the catchment slope, the topographic wetness index (TWI) was calculated for each stream catchment to quantify topographic control on the hydrological processes. The DEM of the catchment areas has been processed using SAGA GIS (Mattivi et al., 2019). The TWI describes the tendency of an area to accumulate water and is defined by the specific catchment area (SCA) and its slope angle (φ) assuming the

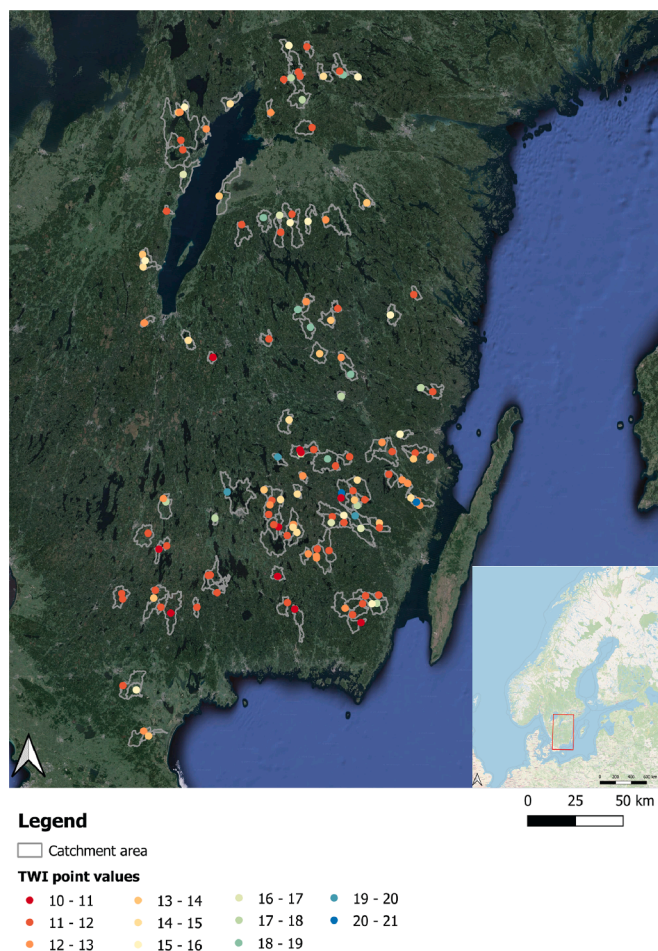


Fig. 1. Maps display the topographic wetness index point values for the sampling locations in southeast Sweden.

properties of the soil are uniform (Mattivi et al., 2019) (Eq. 2). The TWI is presented as the mean for the catchment and the sampling location (within 25 m²), (Fig. 1, Supplement Fig. 1).

$$TWI = \ln \left(\frac{SCA}{\tan \phi} \right) \quad (2)$$

The headwater streams were sampled during three sampling campaigns: (A) in summer (August/September 2016), (B) in late autumn (November/December 2016), and (C) in spring (March/April 2017) (Conrad et al., 2019a). During the sampling events, the groundwater table in shallow aquifers was lower than normal, and especially the summer sampling was performed during a period of exceptionally low groundwater tables (SGU, 2019). Therefore, in summer 65 headwater streams were not sampled due to drought and low discharge (Conrad et al., 2019). The water samples were collected using acid-cleaned, high-density polyethylene bottles previously rinsed with stream water. During the spring sampling in 2017, both unfiltered and filtered samples were collected. Filtering was performed with nitrocellulose filters (0.22 μm cut-off) mounted in polycarbonate filter holders. All samples were stored at 4 °C until further processing.

2.1. Analytical methods

Analyses of TOC, pH, SO₄²⁻, alkalinity/acidity and other ions (Ca²⁺, Mg²⁺, K⁺, Na⁺, Cl⁻ and NO₃⁻) needed for estimating acid neutralization capacity (ANC) were performed at the Department of Aquatic Sciences and Assessment, SLU and followed the procedures described in Löfgren

et al. (2014), (see Table 1 for a summary of the methods and analytical instrument used). The analytical methods are accredited by the Swedish Board for Accreditation and Conformity Assessment (<https://www.swedac.se>) and follow the Swedish standard pH, alkalinity/acidity and NO₃⁻ methods within one day of sampling. All observations were above the limits of detection.

Multi-elemental analysis of bulk water samples was carried out in a clean laboratory (Class 10,000) at ALS Scandinavia AB (Luleå, Sweden) on a Thermo Scientific ELEMENT2 inductively coupled plasma sector field mass spectrometer (ICP-SFMS) (Rodushkin et al., 2005; Rodushkin and Ruth, 1997) using internal In-standardization and external calibration (Jochum et al., 2005; Rodushkin et al., 2010). The presented REE data are verified using EBB-422 concentrations. REE concentration data were replicated with a standard deviation of 8.7 % (n = 9). We consider the methodology used for the REE results reliable based on replicating the EBB-422 data. Comparison with literature is difficult due to the REE's lack of reference values. All element concentrations discussed in this study can be found at <http://doi.org/10.5878/1cvt.c638>.

2.2. Ce anomaly and pH-sensitivity

The Ce anomaly is defined as δCe (Lidman et al., 2019) and was calculated for each stream and each sampling occasion according to Equation (1).

where Ce, La and Nd are the measured concentrations and the normalization (index N) is based on data from Swedish till (Öhlander et al., 1996), which is almost identical to the upper continental crust (Rudnick and Gao, 2003). Neodymium is used in the calculation instead of praseodymium (Pr), as the analytical precision for Nd is more accurate than for Pr. We use the delta notation for the anomaly, traditionally used in isotopic systems, as it emphasises the similarities between isotope fractionation and lanthanide fractionation (Lidman et al., 2019). Further, this introduces the subtraction of 1 into the equation as it is more consistent with the convention of describing anomalies as negative or positive. Earlier publications would describe the anomaly as negative if the result is <1 and positive if the result is >1. On the other hand, the delta notation will result in negative numbers if the anomaly is negative, which is more logical and consistent, making interpretations and discussions easier to follow (Lidman et al., 2019).

Table 1

Summary of the analytical methods carried out at SLU and ALS Scandinavia AB in collaboration with LTU.

		Method, Instrument
SLU	TOC	Swedish Standard SS-EN 1484 1st ed. Water samples not conserved. Preparation treatment with HCL and CO ₂ expulsion. The sample is subsequently combusted and produced CO ₂ is measured using an NDIR detector. Instrument (since January 2007): Shimadzu TOC-VCPH with TNM-1 module and automatic sample changer ASI-V.
	pH	Swedish Standard SS-EN ISO 10523:2012 (modified). The analysis is made at 25 °C, calibration range 4–7. Instruments: sample changer Metrohm 856
	SO ₄ ²⁻	SS-EN ISO 10304-1 1st ed. (modified). Instrument: Metrohm 881 Compact IC pro with Sample changer 858 Professional Sample Processor with automatic filter
	Alkalinity/acidity	SS-EN ISO 9963-2:1994 (modified). Titration to pH 5.6. Instruments: Metrohm 855 Robotic Titrator with combination electrode. Samples are weighed.
	Ca ²⁺ , Mg ²⁺ , K ⁺ , Na ⁺ , Cl ⁻ , SO ₄ ²⁻ , NH ₄ ⁺ , NO ₃ ⁻	ICP-MS, SS-EN ISO 17294-2:2005 Instrument: Agilent
ALS	70+ elements	ICP-SFMS, multi element analysis

The stream water pH-sensitivity was estimated based on the sigmoid relation between pH measured at equilibrium with the carbon dioxide concentration in air (380 ppm CO₂) and buffer capacity, with a theoretical inflexion point of pH = 5.6 in natural waters (Löfgren et al., 2017; Stumm and Morgan, 1996). To obtain a continuous pH-sensitivity distribution with positive numbers ≤1, Equation (2) was used.

$$pH - sensitivity = \frac{1}{(|pH - 5.6| + 1)} \quad (2)$$

The datasets generated and/or analysed during the current study are available in the Swedish National Data Service repository.

The dataset is published under <http://doi.org/10.5878/1cvt.c638>.

3. Results and discussion

All element concentrations are based on unfiltered waters. During spring sampling, filtered and unfiltered element concentrations were compared, and a negligible difference was observed between these two sample types. The here-discussed elements are, on average, 96 ± 3 % in the “dissolved” phase (Conrad, 2016), including fine nanoparticles and fine colloids (smaller than 0.22 μm) (Gottselig et al., 2017). This aligns with previous studies of headwater streams, which showed that the difference between filtered and total concentrations is negligible (Laudon et al., 2004; Neubauer et al., 2013a). However, these operationally defined “dissolved” phases primarily represent nanoparticles and fine colloids (0.66–300 nm), which in European streams constitute between 2 ± 5 % (Si) and 53 ± 21 % (Fe; mean ± SD) of the total concentrations of a wide range of elements. Up to 99 % of Fe, 95 % of Al and 92 % of org C were found to be associated with nanoparticles and fine colloids in the organic-rich, acidic northern European streams (Gottselig et al., 2017).

The stream waters were sampled close to their springs, where at normal groundwater levels surface water could be expected to emerge. Therefore, we assume that the REE surface water concentrations reflect the most essential soil processes and that the main REE fraction is sorbed on nanoparticles and colloids.

The pH varied between 4.0 to a maximum of 8.1, with an average pH of 5.5 and a standard deviation of 0.9, while the alkalinity/acidity ranged from −0.3 to 3.8 meq/L, with an average value of 0.2 meq/L and a standard deviation of 0.5 meq/L (Table 2). These metrics provide insights into the buffering capacity of the ecosystem, offering information crucial for understanding how the system may respond to changes in external factors. The range suggests a spectrum of acidity and alkalinity, while the standard deviation underscores the degree of pH fluctuation, which may influence ecological processes.

The Ce anomaly ranged between −0.74 and −0.01, with an average of −0.27 and a standard deviation of 0.15 for all stations across all seasons. At a single sample location, the Ce anomaly has negligible seasonal differences (average standard deviation 0.028).

An overview of the discussed element concentration can be found in Table 2; As, Fe, Mn, Pb, Sr and Zn showed higher values during the summer sampling than during late autumn and spring, whereas Al, Cd and Mg showed elevated concentrations in late autumn.

3.1. Topography, redox state, and the origin of runoff as indicated by the Ce anomaly

Each sampling location’s REE pattern looked almost identical during the three sampling seasons, indicating underlying processes forming these patterns, rather than seasonal variations in flow patterns. At some locations, differences in the concentration were observed between different seasons, exemplified by Streams 32 and 42 in Fig. 2.

Compared to the late autumn and spring surveys, some streams showed deviating REE element concentrations in summer due to drought and low flow conditions. The variation in REE concentrations

Table 2 Minimum, maximum, and average concentrations of the discussed elements and element ratios (including their standard deviations) of the headwater streams during summer, late autumn and spring.

	pH	pH –sensitivity	Alk./Acid meq/L	ANC meq/L	TOC mM	SO ₄ ²⁻ meq/L	NO ₃ ⁻ μg/L	NH ₄ ⁺ μg/L	Al μM	As nM	Cd nM	Fe μM	Mg μM	Mn μM	Pb nM	Rb nM	Sr nM	Zn nM	∑REE nM	Ce anomaly	Rb/Sr	
Summer (n = 37)																						
Min	4.5	0.3	-0.1	0.10	0.2	0.0	4.4	2.0	0.4	1.0	0.0	1	21	0.1	0.0	5	102	4	1.9	-0.65	0.01	
Max	7.6	1.0	2.6	2.70	12.5	1.2	378.6	1038	57.7	37.1	0.5	651	151	12.5	25.2	145	2123	1129	366	-0.04	0.26	
Average	6.0	0.5	0.4	0.50	2.5	0.1	62.3	108.1	14.5	9.5	0.2	84	73	2.3	3.8	30	475	92	82.4	-0.25	0.08	
Standarddev	0.9	0.2	0.7	0.61	2.3	0.2	90.5	200.4	14.5	7.9	0.1	119	33	3.1	4.9	27	389	180	99.8	0.14	0.06	
Late autumn (n = 97)																						
Min	4.0	0.3	-0.3	-0.04	0.5	0.1	4.0	5.3	1.5	0.3	0.04	0	5	0.0	0.0	1	31	1	5.2	-0.74	0.01	
Max	7.4	1.0	1.0	1.11	5.3	3.0	4731.0	262.0	80.7	13.3	2.16	87	221	5.9	10.9	78	1420	829	422	-0.06	0.42	
Average	5.2	0.6	0.0	0.21	2.4	0.4	339.2	26.0	22.8	5.1	0.53	18	81	1.4	2.7	26	463	137	98.5	-0.27	0.07	
Standarddev	0.8	0.2	0.2	0.20	1.1	0.4	764.3	36.4	15.9	2.5	0.35	15	36	1.2	2.3	1.3	239	103	100	0.15	0.07	
Spring (n = 97)																						
Min	4.1	0.3	-0.3	0.02	0.5	0.0	1.0	3.0	0.1	1.2	0.03	0	19	0.0	0.0	4	75	2	0.9	-0.74	0.01	
Max	8.1	1.0	3.8	3.84	6.1	0.7	1481.0	252.2	57.4	18.8	1.57	98	148	7.8	9.7	119	888	638	733	-0.01	0.45	
Average	5.4	0.6	0.1	0.30	2.1	0.2	151.5	25.5	19.1	4.8	0.37	18	60	0.9	2.4	24	340	91	100	-0.26	0.09	
Standarddev	0.9	0.2	0.5	0.44	1.1	0.1	268.7	32.4	13.0	2.6	0.22	15	24	1.1	1.9	1.3	169	75	113	0.15	0.09	
Total average	5.5	0.5	0.2	0.33	2.3	0.2	215.4	38.9	18.8	6.5	0.37	40	71.1	1.5	3.0	26	426	107	96.0	-0.3	0.1	
Stddev	0.9	0.2	0.5	0.42	1.5	0.3	534.9	90.5	14.4	4.3	0.23	50	31.0	1.8	3.0	17	265	119	106	0.1	0.1	

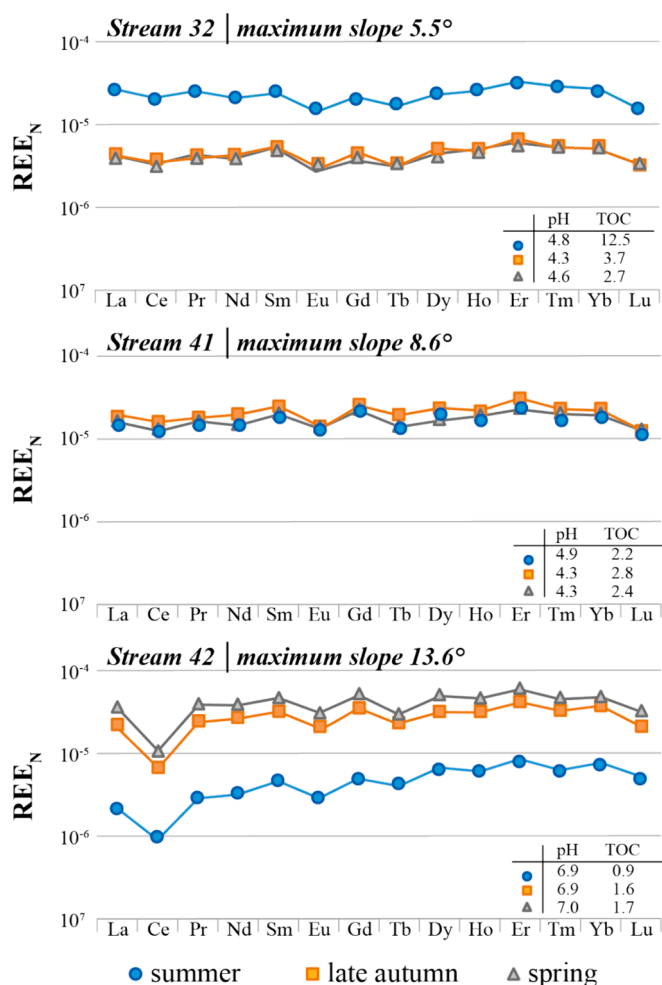


Fig. 2. Swedish till normalized rare earth element (REE) patterns of unfiltered waters for stations 32, 41 and 42. Each graph includes a table with the pH, TOC (mM) and δCe during the three sampling occasions. While the normalized REE_N concentrations between summer, late autumn and spring show differences at some stations, the REE_N patterns and the Ce anomalies are consistent throughout the sampling events.

between summer, late autumn, and spring varied between different types of headwater streams, but the shapes of the normalised REE_N concentration patterns were stable between the sampling surveys (Fig. 2). Iron isotope ratios, sulfate, and nitrate concentrations from these three surveys (Conrad et al., 2019) were used to show that the soils were reduced during summer along the main groundwater flow paths, the source of stream water runoff. Similar reduced conditions were observed in northern Sweden, linked to a drought in the summer of 2018 (Gómez-Gener et al., 2020). Fig. 3 shows the impact of seasonal redox changes on the Fe isotope composition, the sulfate concentration, and the nitrogen ion speciation versus the Ce anomaly, which seems to complement the other variables for assessing the redox state and the origin of infiltration and water solutes in boreal headwater streams. During summer, dominated by an influx of reduced groundwater as indicated by the Fe isotope composition, the Ce anomaly was above -0.4 , and the concentrations of sulfate and nitrate were low, while ammonium was high. Negative Fe isotope ratios display reduced groundwater discharge from mainly anoxic, moist, organic-rich mineral soils (Mitchell and Branfireun, 2005).

The varying redox status between seasons is complemented by the REE_N concentrations, indicating three principally different biogeochemical patterns (Fig. 2) in the studied catchments. Based on data from stream 32, high TOC concentrations during the summer drought (12.5

mg L^{-1}) indicate a strong influence by runoff from organic-rich and reduced riparian soils and wetlands, increasing the normalized REE_N concentrations and keeping the negative Ce anomaly close to zero (-0.15 in summer). During the following late autumn and spring surveys, decreasing TOC concentrations (3.7 and 2.7 mg L^{-1} , respectively) and a slight decrease in Ce anomaly (-0.19 and -0.17) indicate less influence by organic-rich soils and very restricted changes in redox. Similar patterns were found by Dia et al. (Dia et al., 2000) in reduced groundwater in wetlands. Stream 41, which is a clear water stream with comparable low TOC concentrations (2.2 – 2.8 mg L^{-1}), exhibits low variation between the surveys in TOC and REE_N concentrations (Fig. 2) as well as in Ce anomaly (-0.15 , -0.17 and -0.15). This indicates dominating groundwater flow paths through constantly reduced soils, for example highly decomposed peat or anoxic mineral soils, presumably histosols. Stream 42 shows a similar picture to stream 41, with lower TOC (0.9 – 1.7 mg L^{-1}) and REE_N concentrations, especially low during summer (Fig. 2). However, compared to streams 32 and 41, stream 42 exhibited tangible negative Ce anomalies (-0.65 , -0.73 , -0.72) at all three surveys, indicating strong influence by groundwater discharge from oxidized and Fe-rich mineral soils, presumably podzols, not only during summer baseflow but also during seasons with high runoff.

Summarising, the data distribution allows us to define two source endmembers; the *reduced groundwater* has a Ce anomaly between -0.3 and zero ($n = 77$). In contrast, the *oxidized groundwater* has a Ce anomaly between -0.8 and -0.4 ($n = 18$) in the hemiboreal headwater streams of this study. In the interval -0.3 to -0.4 ($n = 9$), the variation in stream water chemistry indicates a relatively even influence by *oxidized and reduced groundwater*, causing uncertainties in the end-member classification.

Correlating the average Ce anomaly with the mean slope, average catchment TWI, and single point TWI shows a moderate negative correlation between the average Ce anomaly and the average slope. (Table 3). The negative correlation shows that headwater streams with a more negative Ce anomaly drained more hilly catchments, suggesting that the Ce anomaly also reflects this landscape feature. The mean slope of the catchments ranged from 0.5 to 7 degrees, i.e., 1 to 10 m elevation on 100 m . The headwater streams 32, 41 and 42 (Fig. 2) represent a topographic gradient with a mean slope and standard deviation of $1.2^\circ \pm 0.9^\circ$, $2.3^\circ \pm 1.6^\circ$ and $3.4^\circ \pm 2.2^\circ$, respectively. The correlation between the average slope of the catchments and the average Ce anomaly is -0.5 , with small differences between the seasons (summer: -0.47 , late autumn: -0.52 , winter: -0.47). Data from the Swedish Geological Survey (SGU, Table S1) show that the catchment of stream 32 is 80% covered by glacial till and 20% by peat. Very shallow soils and bare bedrock dominate the other two catchments on 70 – 75% of the area, and glacial till is on the remaining parts. Both TWIs showed a weak correlation, 0.34 and -0.37 , during summer, while the correlations were negligible in late autumn and spring. The TWI uses topography to identify where surface water, such as streams and rivers, can be found; it gives no information on travel time through the soil. We suggest that the average slope of the catchment displays a better parameter for assessing travel time through soil profiles and, therefore, the potential to develop a negative Ce anomaly.

The SGU soil classification system classifies the land cover as bedrock if the soil layer is less than 0.5 m . The soil is classified as peat if this soil type exceeds a depth of 0.5 m . Hence, the REE_N patterns and Ce anomaly in headwater stream 32 reflect the conditions in a relatively flat catchment with a large proportion of peat, from which the discharge seems to originate during drought. The other two headwater streams' catchments have a slightly hilly topography dominated by shallow soils and bare bedrock. According to the Swedish Land Cover Data (SMD), the catchment of stream 41 has 2% wetlands, while the catchment of stream 42 has none (Table S1). These catchments are probably dominated by discharge from lateral groundwater flow paths in extensive areas with shallow soils. However, the Ce anomaly in headwater stream 41 suggests

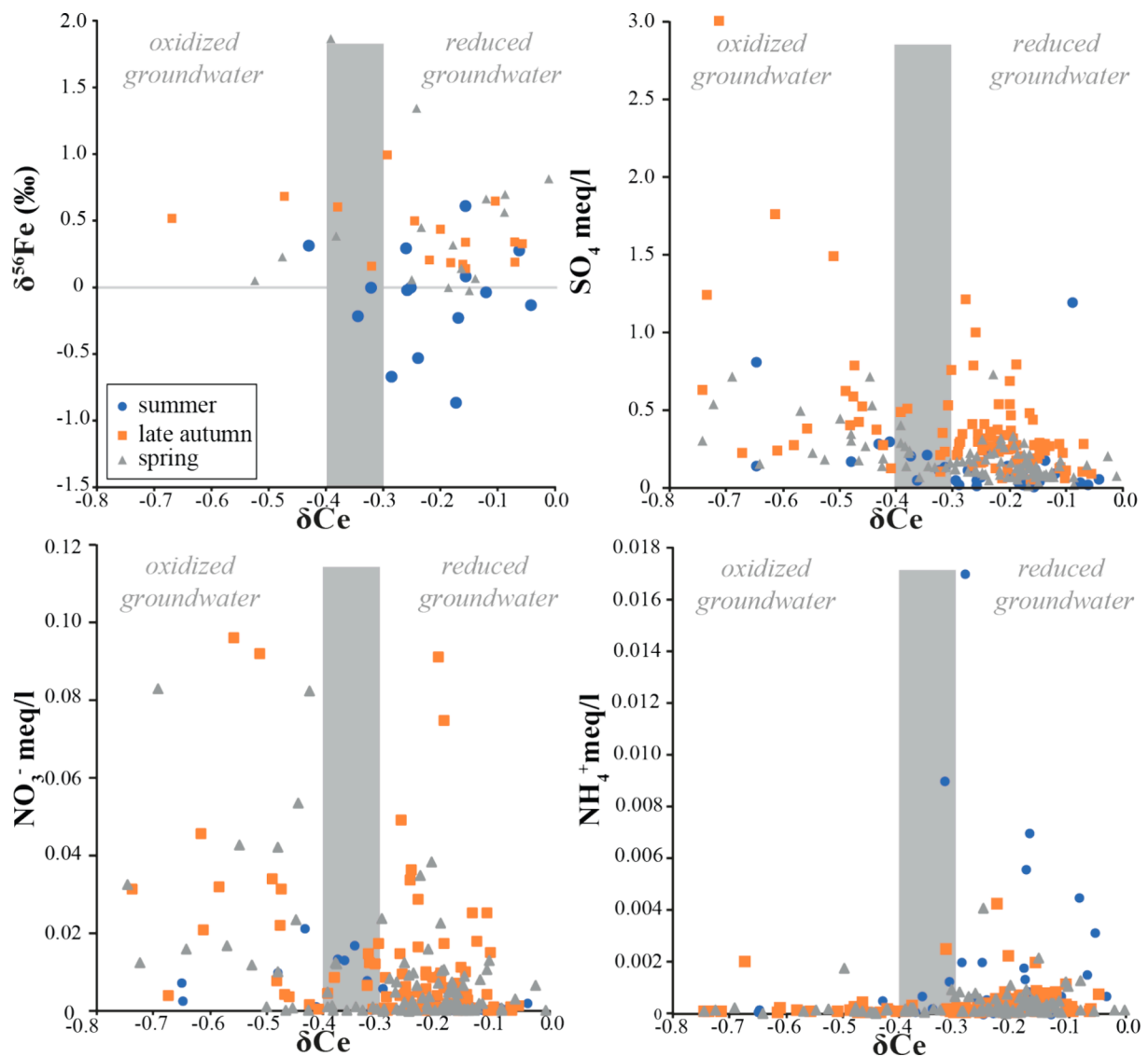


Fig. 3. Iron isotope ratios, sulphate, and nitrogen ion speciation versus the Ce anomaly (δCe) in the hemiboreal headwater streams during the three sampling surveys (summer, late autumn, and spring). The grey shaded area displays the shift from reduced (acidic) to oxidized (circumneutral) headwaters at a δCe range from -0.4 to -0.3 . Based on earlier findings, the graph Fe isotope ratios versus δCe excludes data from streams 7, 13, 52, 61, 68, and 78 (Conrad et al., 2019). Within these streams, Fe-OC complexes with a positive Fe isotope ratio restrict Fe isotope variations and the formation of clear trends caused by oxidation (Conrad et al., 2019).

Table 3

Correlation coefficient between the Ce anomaly and catchment properties. δCe_A : Ce anomaly in summer, δCe_B : Ce anomaly in late autumn, δCe_C : Ce anomaly in spring, $\delta\text{Ce}_{Average}$: Average Ce anomaly of summer, late autumn and spring.

	Slope mean	TWI catchment mean	TWI single point	δCe_A	δCe_B	δCe_C	$\delta\text{Ce}_{Average}$
Slope mean	1						
TWI catchment mean (n = 103)	-0.267	1					
TWI single point (n = 103)	0.206	-0.041	1				
δCe_A (n = 37)	-0.470	0.341	-0.376	1			
δCe_B (n = 97)	-0.522	0.189	-0.144	0.720	1		
δCe_C (n = 97)	-0.470	0.154	-0.166	0.792	0.913	1	
$\delta\text{Ce}_{Average}$ (n = 103)	-0.501	0.168	-0.179	0.886	0.961	0.975	1

that the groundwater passes through an organic-rich riparian zone with reduced conditions before entering the stream. Another possibility might be the wetland area in the catchment of stream 41, which is contributing towards a reduced environment before entering the stream. In contrast, the riparian zone must have been oxidized in headwater stream 42, reflecting discharge through primarily mineral soils that are poor in OM.

3.2. Acidity and OM concentrations related to the Ce anomaly

The average concentrations of TOC (2.3 ± 1.5 mM) and pH-sensitivity (0.5 ± 0.2) showed slight variation between the seasons. At the same time, alkalinity/acidity (0.2 ± 0.5 meq/L) and pH (5.5 ± 0.9) were tangibly higher during the summer base flow (alkalinity/acidity (0.4 ± 0.7 meq/L) and pH (6.0 ± 0.9), Table 1 and Fig. 4). The measured

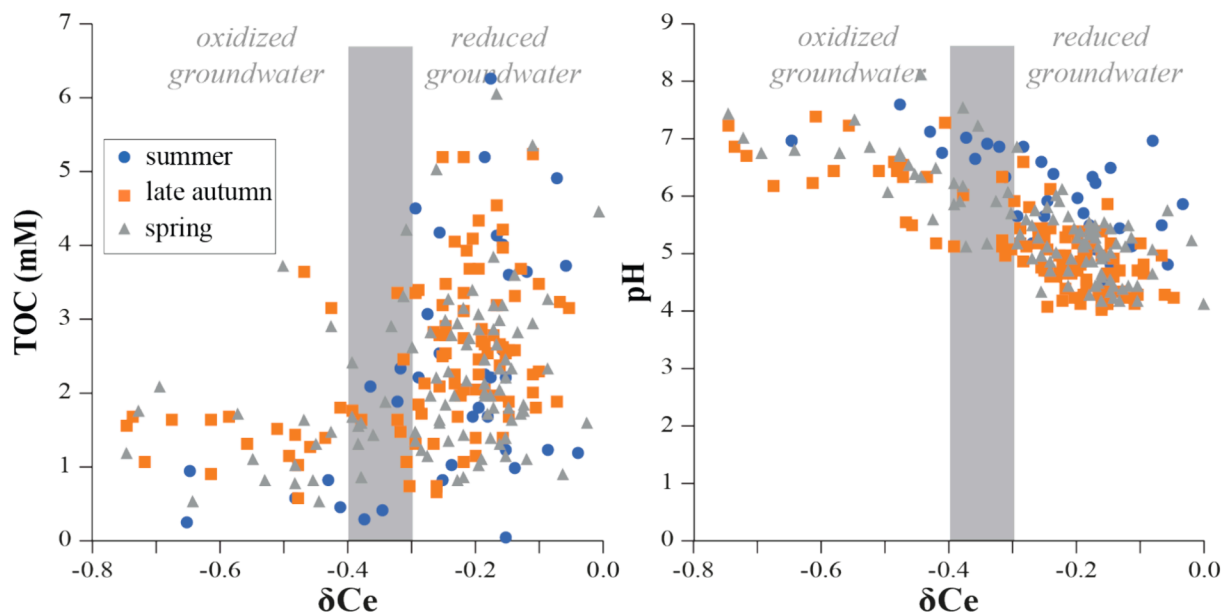


Fig. 4. Samples with a small negative Ce anomaly (δCe) had a wide range of TOC concentrations as well as low pH. Samples with a larger negative Ce anomaly had low TOC concentrations and a high pH. The data points can be divided into two groups at a Ce anomaly between -0.4 to -0.3 . (Note: Station 100C sampling has been excluded from the alkalinity/acidity versus Ce-anomaly plot (-0.44 ; 3.82).

data lie within comparable hemiboreal and boreal streams of other studies (Ekström et al., 2016; Kritzberg and Ekström, 2012; Laudon et al., 2011; Löfgren et al., 2014; Pokrovsky and Schott, 2002; Wallin et al., 2014). The large amount of data (Fig. 4) allows us to distinguish the two groundwater endmembers, oxidized and reduced, specifically their different behaviour of TOC, alkalinity/acidity, pH, and pH sensitivity. Generally, *oxidized groundwaters* have lower TOC concentrations and, thereby, more alkaline waters with higher pH. In contrast, *reduced groundwater* has higher TOC concentrations, restricting the bicarbonate alkalinity and creating lower pH (Table 2). Due to higher alkalinity, the pH sensitivity of *oxidized groundwater* is tangibly lower than in streams with *reduced groundwater*. The relatively large number of observations of pH-sensitive streams in the -0.1 to 0.1 meq/L alkalinity/acidity range (Fig. 5) agrees well with earlier findings in headwater streams of

southern Sweden (Löfgren et al., 2017). The number of observations for the most pH-sensitive streams (pH-sensitivity > 0.6) is equally distributed (31–40 %) between the seasons.

Total organic carbon, alkalinity/acidity, pH, and pH-sensitivity combined with the Ce anomaly strengthen the definition of two source endmembers for the stream water. These data show a defined shift from acidic to circumneutral headwater streams at a Ce anomaly from -0.4 to -0.3 . The *oxidized groundwater* streams are well-buffered and show a low pH sensitivity. The two groundwater endmembers could also be identified as catchments dominated by mineral-rich soils, for example, podzol or organic-rich soils, for example, histosols. A significant Ce anomaly can be developed in catchments with podzol domination due to comparable little organic-rich layers in the soil profile (up to 10 cm) (WRB, 2022). In catchments with no or minor Ce anomalies, histosols

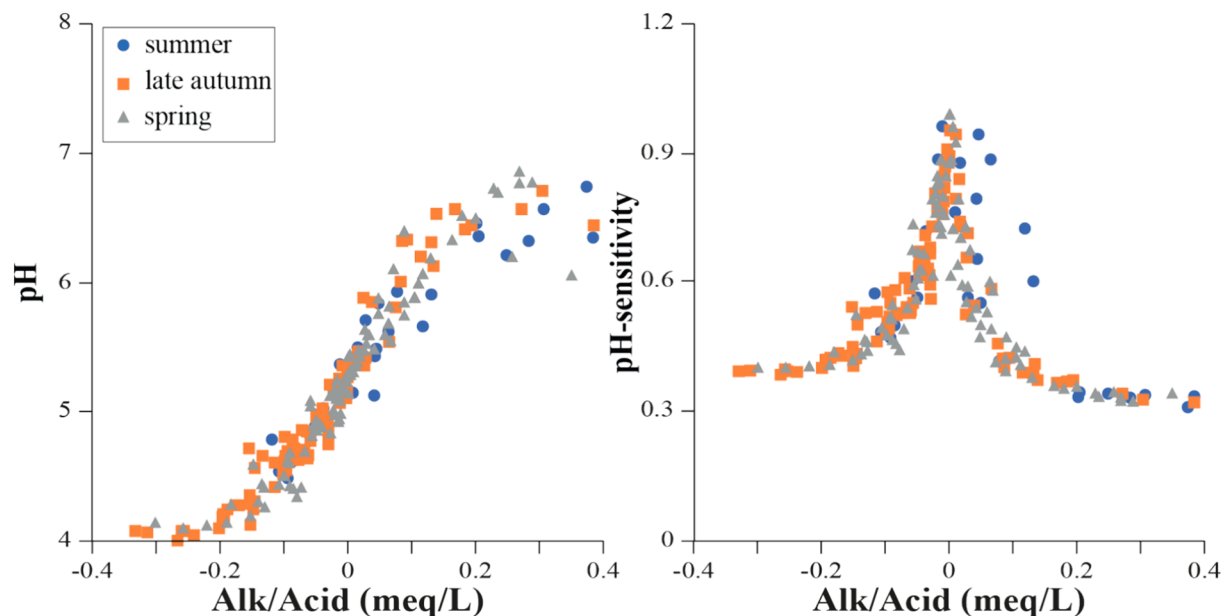


Fig. 5. Relationship between pH and pH-sensitivity and alkalinity/acidity in the range $-0.4 < \text{Alk/Acid} < 0.4$ meq/L during the sampling events.

might be the dominating soil type, these soils consist of a minimum of 40 cm of organic layers, which start in the upper 40 cm of the soil profiles⁸⁵. Identifying the dominant soil type using the Ce anomaly opens new possibilities, as the resolution of soil maps is often too low on a headwater stream level. The negative relation between the Ce anomaly and the average slope in a catchment (Table 3) suggests that the distinct negative Ce anomalies are typically found in catchments with a distinct topography. The average slope of these catchments is generally steeper, which indicates vertical percolation of groundwater through mineral soils in the recharge areas and lateral transport downhill before entering the headwater streams through primarily oxidized soils in the discharge areas.

These data support the importance of topography in the development of the Ce-anomaly (Braun et al., 1998; Gruau et al., 2004; Pourret et al., 2010), indicating that one endmember in our catchments is dominated by an influx of *oxidized groundwater*, dominated by mineral soils for example podzol. The second endmember is dominated by acidic headwater streams with a small negative Ce anomaly, highly pH-sensitive and high TOC concentrations, typical for streams with the influx of *reduced groundwater* from organic-rich soils (Neubauer et al., 2013b). These soils are typically found in wetlands (Davranche et al., 2011; Lidman et al., 2014) but are common in the riparian zone (Bishop et al., 1994; Ledesma et al., 2018; Pokrovsky et al., 2016b). Riparian zones are characterized by wetter conditions than up-slope areas of a catchment (Anderson et al., 2015) and can react rapidly to changing groundwater levels (Bishop et al., 2004). This second end-member source is dominated by groundwater discharge from *reduced groundwater*, dominated by organic-rich soils for example histosols.

3.3. Element composition related to the Ce anomaly

Reduced groundwater streams generally showed a wide variation of element concentrations (Fig. 6, Table 2). We observed up to seven times higher concentrations in headwater streams fed by such groundwater compared with those clearwater streams fed by more alkaline and *oxidized groundwater*. In the latter streams, element concentrations were up to twice as high compared with the former streams.

Elements liberated by weathering, such as Ca^{2+} , Mg^{2+} , and Sr^{2+} , showed higher concentrations in streams fed by *oxidized groundwater* than in streams fed by *reduced groundwater*. The higher elevation in these catchments suggests groundwater travel through mineral-rich soils by lateral transport. The presence of these elements in stream water depends mainly on catchment composition and land use (Potasznik and Szymczyk, 2015), these elements are released to the streams by weathering primarily silicate-rich rocks (Tipper et al., 2006) in the study area. The formed bicarbonate ions keep the cations mobile (Zetterberg et al., 2013), which are transported conservatively along the groundwater flow paths.

Redox-sensitive elements such as Mn and Fe showed seven- and five-times higher concentrations in streams fed by *reduced groundwaters*. These elements originate from sources within the catchment, for example, podzols (Ekström et al., 2016), and are sensitive to redox changes. Different studies showed the importance of redox conditions on the mobility of Fe in experiments, mesocosm studies and in-situ measurements (Conrad et al., 2019; Ekström et al., 2016; Knorr, 2013; Todorova et al., 2005). In anoxic waters, Fe^{2+} and Mn^{2+} are the dominating species (Stumm and Lee, 1960; Stumm and Sulzberger, 1992) and

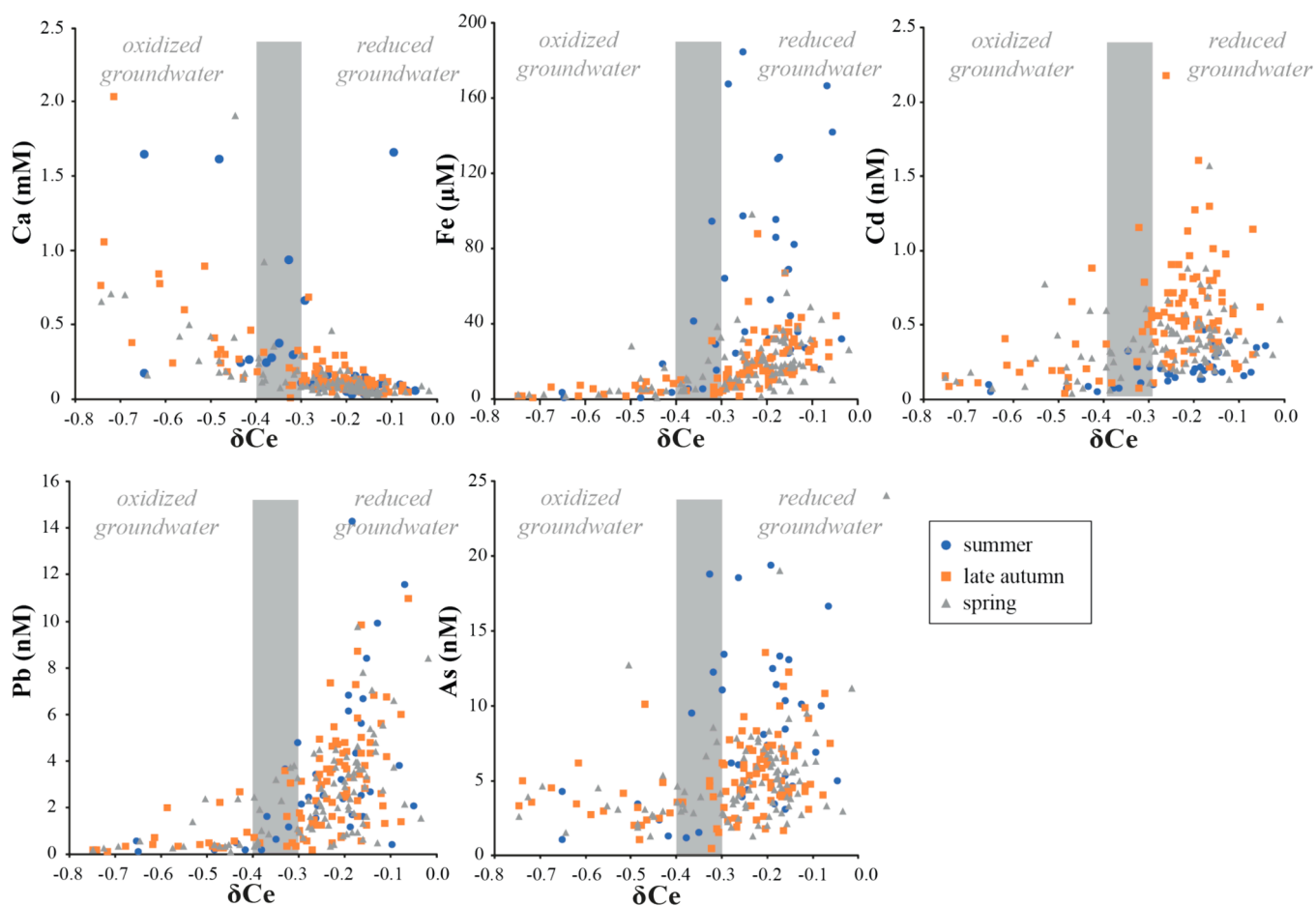


Fig. 6. Selection of element concentrations versus the Ce anomaly (δCe) with the defined source areas of the stream water. Streams with a small negative Ce anomaly generally showed a wide variation of trace element concentrations with the maximum measured values.

reducing conditions in catchment soils leads to high Fe concentrations in surface waters (Kritzberg and Ekström, 2012). The measured high Fe concentrations reflect an influx of Fe^{2+} from well-buffered, *reduced groundwaters*. We observed the highest concentrations during summer drought. Fe isotope data from these streams verified strong reducing conditions in the catchments during summer (Fig. 3). In contrast, Fe isotope data suggest a higher groundwater table and flushing of the surface near soil horizons during late autumn and spring (Conrad et al., 2019). High TOC concentrations restrict the oxidation of Fe^{2+} to Fe^{3+} by complexation with OM; this complexation is strongly pH-dependent. At pH 4, 100 % is complexed, whereas at pH 7, just 10 % is complexed (Lofts et al., 2008). For anions such as AsO_4^{3-} and PO_4^{3-} , coprecipitation with Fe-OM complexes and FeO(OH) is the main mechanism restricting transport in oxic and circumneutral pH locations along the flow paths. Therefore, concentrations of these anions, detected in our study as As and P, follow the same pattern as Fe, with high concentrations in streams with a reduced groundwater source and low values in streams with *oxidized groundwater* source.

Element mobility of Al, Zn, and Cd depends on the pH along the groundwater flow paths, and they had low concentrations in streams fed by well-buffered, *oxidized groundwaters* and about twice as high in streams fed by more acidic, *reduced groundwater*. The mobile forms of Al are primarily organic complexes laterally transported from uphill or formed in the riparian zone by reactions with inorganic Al (Löfgren and Cory, 2010). The pH in the streams favours Al to occur in solid form as Al hydroxides and organic complexes (Sjöstedt et al., 2010). Aluminium strongly correlates to TOC in the headwater streams (Table S2), suggesting that the metals are bound to OM. Aluminium, as well as Ca and Fe, was found to be in the same colloidal size fraction (0.66 nm to 20 nm) as organic C (Gottselig et al., 2017), supporting our hypothesis that organic-rich colloids are an important carrier phase in the “dissolved phase” from the upper soil horizon into the streams. Zn and Cd depend primarily on pH but pe may have some retarding effect, even though they do not belong to the redox elements. As these streams are fed by *reduced groundwater*, these elements may be arrested in sulfide rich soils, for example, ZnS and CdS.

Pb and Cu have higher concentrations in streams with *reduced groundwater* as a source. Already at low pH (≈ 5) these elements tend to sorb on surfaces; they have been shown to have a high affinity to OM (Tipping et al., 2003) and Fe(OH) (Gustafsson et al., 2011), which

overall increases the mobility of these elements. The main source of Pb is a consequence of the historically high anthropogenic deposition, which dominates upper soil layers (Brännvall et al., 2001; Klaminder et al., 2006) and it has been shown that in these types of streams, it is transported mainly bound to OM (Wällstedt et al., 2017).

The ratio between light and heavy REE (LREE/HREE) showed a loss of LREE during transport in headwater streams fed by *oxidized groundwater* (Fig. 7). We observe a strong correlation between Al and the REE, suggesting weathering and transport mechanisms following similar geochemical patterns. The correlation between Fe and the REE to OM is less distinct in the streams compared to Al. Fe-Al-OC colloids are likely formed during the podzolization process and this mobile colloidal soil phase transports organic and inorganic compounds to the headwater streams. Aluminium and Fe show two groups of data, like TOC. Headwater streams fed by *oxidized groundwater*, show lower concentrations than organic-rich headwater streams fed by *reduced groundwater*. This is supported by recent findings showing a higher release of trace metals from organic-rich histosols (Tittel et al., 2022). This is also shown by the Rb/Sr ratios, which are higher in headwater streams with a *reduced groundwater* source reflecting the input of organic-rich waters (Wortberg et al., 2017).

Further, the average element concentrations can be categorized by seasonal impacts (Table 2). Cadmium, Zn, and SO_4^{2-} showed low concentrations during the summer drought compared to late autumn and spring, suggesting sulfate reduction and precipitation of sulfide minerals (CdS and ZnS). Contrary, As, Fe, Mg, Mn, Pb and Rb showed high concentrations during the summer drought and lower during the other seasons. Aluminium and Sr do not show seasonal-dependent variations in their concentrations. Our data show that the redox elements and those bound to redox complexes are influenced by the low groundwater level during the summer 2016 (Conrad et al., 2019).

3.4. Stream water Ce anomaly may guide the localization of wood ash application

Knowledge of the stream water's origin is essential in predicting the export capacity for small streams. Especially the mobilisation and export of trace elements (As, Cu, Cr, Ni, Pb) from *reduced groundwater* with low pH and high OC concentration is an important factor for the downstream water quality, assuming that accumulated trace elements will become

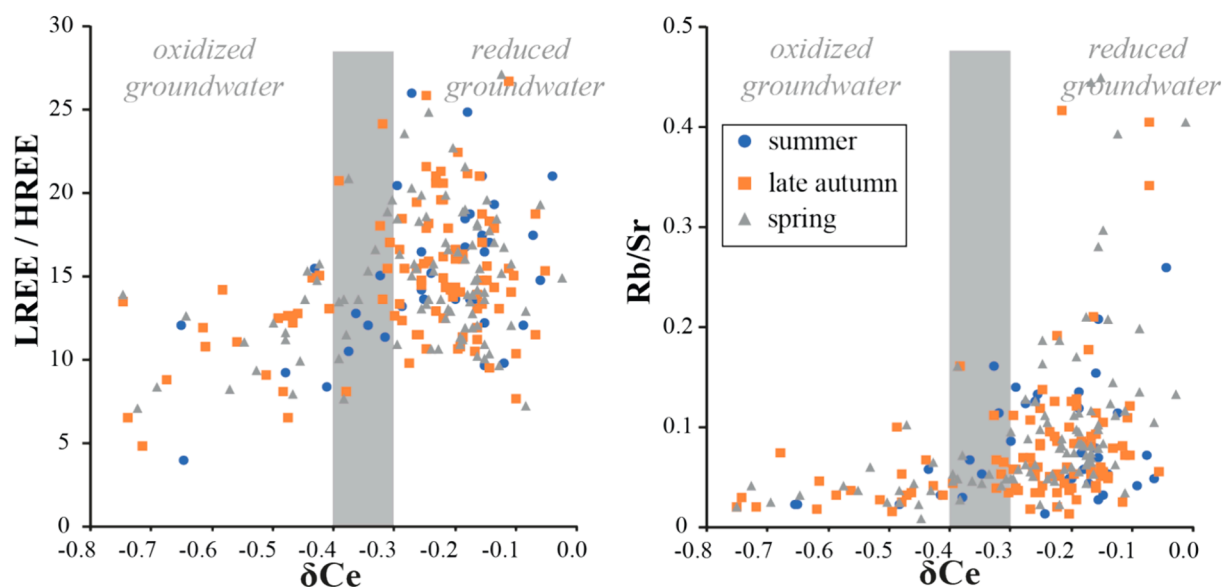


Fig. 7. Light rare earth elements/heavy rare earth element ratio (LREE/HREE) and Rb/Sr ratios versus the Ce anomaly (δCe) with the defined source areas of the stream water. The ratios can be used as indicators for the source end member. LREE are lost during the transport in headwater streams fed by *oxidized groundwater*, whereas an increased Rb/Sr ratio indicates the transport of *reduced groundwaters* through organic-rich soil layers.

more mobile in the future (Wällstedt et al., 2017). Here, we show that the Ce anomaly as a single tool can be used to estimate the risks for increased export of such elements since it indicates the effects of landscape and groundwater flow paths on the runoff chemistry. We also suggest that the Ce anomaly can be used to discuss and locate suitable areas for wood ash application (WAA) after whole-tree harvest (WTH). There is no general agreement on how WTH and WAA would influence the acidity and trace metal concentrations in headwater streams draining catchments of different topography and groundwater origin (Ågren and Löfgren, 2012; Löfgren et al., 2017). Therefore, simple methods and guidelines for identifying catchments sensitive to WTH and relevant WAA use are needed.

The effect of WAA is highly variable, as the ash composition, the applied amount, the catchment composition, and the reaction time vary. Overall, wood ash is highly alkaline and has high concentrations of base cations. These base cations can compensate for the losses caused by WTH and avoid nutrient depletion in soils and streams. The Swedish landscape types are patchily distributed and show varying landscape types. The buffering capacity of a headwater stream is defined by the different land cover (Buffam et al., 2007) and manages the influence of acidification by WTH and the influence of base addition by WAA. The pH sensitivity identifies stream catchments, sensitive to acidification and alkalinisation (Löfgren et al., 2017). The Ce anomaly may be used as a complementing tool to assess the physicochemical status of the groundwater discharge, which creates the stream water runoff and to identify catchments that are more suitable for WAA than others.

Waters from streams with a Ce anomaly between -0.4 and -0.8 are primarily fed by groundwater with large contact with the mineral soil, for example, podzol profiles, and enough contact time through the soil profile. The groundwater is less acidic and increases the acid neutralisation capacity of the recipient streams (Giesler et al., 2002; Löfgren et al., 2017; Löfgren and Cory, 2010; Pellerin et al., 2002). Wood ash applied in these areas releases cations and anions with a long travel time through the soils, implying a slow transport to the stream and an increase of its buffer capacity over a more extended period. On the other hand, waters in headwater streams with a Ce anomaly between -0.3 and zero are generally more acidic and are fed by groundwater moving through the histosols (Löfgren and Cory, 2010) before they discharge into the stream. The pH sensitivity of these waters is high compared to headwaters dominated by an influx of groundwater with a long travel time through the soil profile in the up-slope catchment (Fig. 5).

For WAA, Swedish authorities aim to increase the pH in the stream water and minimise the risk of increasing the concentrations of toxic metals (Davranche et al., 2005). For the primarily pH-dependent metals (Al, Zn, Cd, etc.), there is no conflict between these two goals if the WAA is carried out in the riparian zone, which is the most efficient way to increase pH (Löfgren and Cory, 2010). However, for those metals that primarily are weathered/solubilized in the recharge areas and laterally transported downhill due to, for example, reduced conditions (Fe, Mn) or complexed to organic ligands (Cu, Pb, etc.) (Lydersen et al., 2002), WAA in uphill source areas would be preferred since it is potentially more efficient in limiting the downhill metal transport and thereby the risk of trace metal contamination of the stream. Besides identifying catchments suitable for WAA and depending on water quality problems (pH and/or toxic metal contamination), the Ce anomaly may also be used to identify where WAA would be most profitable in the catchment. By identifying the Ce anomaly along a headwater stream it would be possible to identify the area with the largest Ce anomaly, therefore offering places with mineral soils suitable for WAA.

4. Conclusions

This study shows that the Ce anomaly is an indicator of the stream water origin, showing relations to topography, with more negative values (-0.8 to -0.4) in hilly catchments with distinct slopes discharging oxidized groundwater from mineral soils, for example,

podzols. In less hilly catchments, dominated by groundwater discharge from reduced, organic-rich riparian and wetland soils (or histosols) less negative Ce anomalies are found (-0.3 to zero). Excluding weathering elements (for example Ca, Al), most element concentrations are tangibly higher in streams with small negative Ce anomalies (reduced groundwater) compared to the concentrations in streams with large negative Ce anomalies (oxidized groundwater). The element mobility of the classic redox elements (for example Fe, Mn, S, N), acidity (pH), organic matter, and others showed seasonal variations, while the Ce anomaly was constant, offering an excellent indicator for identifying the dominant groundwater flow paths regardless of seasonal variations. The Ce-anomaly is a useful tool for identifying catchments where protective zones may be profitable, restricting potentially negative water chemical effects of forestry measures for example wood ash return. The Ce anomaly has the potential to be an applicable tool in other temperate and boreal regions with similar hydrology, geomorphology, soil types etc., but further research is needed to generalize this.

CRediT authorship contribution statement

Sarah Conrad: Writing – original draft, Funding acquisition, Conceptualization. **Stefan Löfgren:** Writing – original draft, Funding acquisition. **Johan Ingri:** Writing – original draft.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Sarah Conrad reports financial support was provided by Bio4Energy. Stefan Löfgren reports financial support was provided by Swedish Energy Agency. Stefan Löfgren reports financial support was provided by Swedish Agency for Marine and Water Management. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All data is available under <http://doi.org/10.5878/lcvt.c638>.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ecolind.2024.112491>.

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