



Rare earth element bioaccumulation and cerium anomalies in biota from the Eastern Canadian subarctic (Nunavik)



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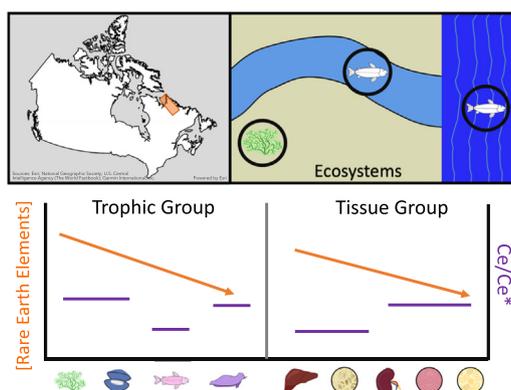
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HIGHLIGHTS

- Northern Canadian terrestrial and aquatic ecosystems follow a REE biodilution pattern.
- Vertebrate tissues presented highest REE bioaccumulation in the internal organs.
- Cerium anomalies are species- and tissue-specific.
- Baseline REE concentrations were established prior to mining development.
- Field study performed within a collaborative program with an Inuit community.

GRAPHICAL ABSTRACT



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ABSTRACT

Recent increases in the demand for rare earth elements (REE) have contributed to various countries' interest in exploration of their REE deposits, including within Canada. Current limited knowledge of REE distribution in undisturbed subarctic environments and their bioaccumulation within northern species is addressed through a collaborative community-based environmental monitoring program in Nunavik (Quebec, Canada). This study provides background REE values (lanthanides + yttrium) and investigates REE anomalies (i.e., deviations from standard pattern) across terrestrial, freshwater, and marine ecosystems in an area where a REE mining project is in development. Results are characteristic of a biodilution of REE, with the highest mean total REE concentrations (Σ REE) reported in sediments (10^2 nmol/g) and low trophic level organisms (i.e., biofilm, macroalgae, macroinvertebrates, common mussels, and reindeer lichens; 10^1 – 10^2 nmol/g), and the lowest mean concentrations in higher-level consumers (i.e., goose, ptarmigan, char, whitefish, cod, sculpin and seal; 10^{-2} – 10^1 nmol/g). The animal tissues are of importance to northern villages and analyses demonstrate a species-specific bioaccumulation of REE, with mean concentrations up to 40 times greater in liver compared to muscle, with bones and kidneys presenting intermediate concentrations and the lowest in blubber. Further, a tissue-specific fractionation was presented, with significant light REE (LREE) enrichment compared to heavy REE (HREE) in consumer livers (LREE/HREE $\approx 10^1$) and the most pronounced negative cerium (Ce) anomalies (<0.80) in liver and bones of fish species. These fractionation patterns, along with novel negative relationships presented between fish size (length, mass) and Ce anomalies suggest metabolic, ecological, and/or environmental influences on REE bioaccumulation and distribution within biota. Background concentration data will be

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useful in the establishment of REE guidelines; and the trends discussed support the use of Ce anomalies as biomarkers for REE processing in animal species, which requires further investigation to better understand their controlling factors.

1. Introduction

The rare earth elements (REE) are technologically critical elements with applications in various industries, especially for 'clean' technologies and electronics (Ng et al., 2011; Humphries, 2013; Natural Resources Canada, 2022). This group of 17 metals includes the lanthanides (La to Lu), yttrium and scandium (International Union of Pure and Applied Chemistry (IUPAC), 2005). The past couple of decades has shown an increase in the demand for REE (Haque et al., 2014) bringing with it a concern for their continuous availability (Alonso et al., 2012) and their increased release to the environment (Balaram, 2019; e.g., Tepe et al., 2014; Hatje et al., 2016). While China has been the ongoing primary producer of REE, representing 60 % of global production in 2021, Canada also hosts multiple (~20) REE deposits that altogether may contribute approximately 14 million tonnes of rare earth oxides to the market (Natural Resources Canada, 2022; U.S. Geological Survey (USGS), 2022). In Canada, mining activity has commenced at one of these locations, with the others in various stages of study (Natural Resources Canada, 2022). The main concerns with REE mining include the release of REE- and radioactive-dust to the atmosphere; the release of REE, associated radioactive material (i.e., U, Th, Ra, radionuclides) and heavy metals (e.g., Pb, Zn, Cd) from tailings or waste rock; the use of strong acids and other harsh chemicals during processing; and management of wastewaters (Weng et al., 2013; Liang et al., 2014; Huang et al., 2015).

Many REE deposits in Canada are in the more northern regions of the country, often in proximity to Indigenous communities (Yin et al., 2021). Ecosystems at northern latitudes ($\approx 50^{\circ}\text{N}$) face additional pressures from climate change, with permafrost thaw that may increase the mobility of metals to nearby waters (Vonk et al., 2015), and freeze-thaw events that could lead to greater leaching of metals from tailings (Costis et al., 2020). Local communities experience uncertainties related to the outcomes of these mining activities (Lockhart et al., 2015), as was the case for the Inuit community of Kangiqsualujjuaq upon discussion of the prospective Strange Lake REE mine in Nunavik (Gérin-Lajoie et al., 2018), which is currently in the pre-feasibility study stage. Collaboration between community members and researchers led to the development of a community-based environmental monitoring (CBEM) program in Kangiqsualujjuaq. Stemming from community interests, this program aimed to address concerns of REE mining projects and can now facilitate ongoing opportunities for long-term monitoring of local environments (Gérin-Lajoie et al., 2018).

Limited data is available regarding the distribution and bioaccumulation of REE in undisturbed northern ecosystems. As northern communities experience increased pressures from mining development and climate change (AMAP, 2016), it is important to understand the background levels of REE in these environments, which will allow for accurate comparisons in the future. Of particular interest are the species expected to serve as biomonitors, such as benthic invertebrates (e.g., Cairns and Pratt, 1993; Bonada et al., 2006) and lichens (Leonardo et al., 2011; Abas, 2021), which can reflect levels of metals in the aquatic environment and atmosphere, respectively (Holt and Miller, 2010) and are the prey of many consumers, acting as entry points to food webs (Naeth and Wilkinson, 2008). Additionally important is the study of traditional species consumed by local communities to provide a database from which REE health guidelines may be derived, as they are not yet established by national governments. In terms of REE accumulation trends, field studies to date suggest that ecosystems may demonstrate a biodilution of REE along the trophic chain (Amyot et al., 2017). However, few

studies provide bioaccumulation data across multiple ecosystems or ranges of trophic levels (e.g., MacMillan et al., 2017). Additionally, the light REE (LREE) and heavy REE (HREE), classified by their relative atomic weights, are typically not present in equal concentrations; instead, an enrichment of LREE is common and has been reported in both marine (reviewed by Piarulli et al., 2021) and freshwater environments (Amyot et al., 2017). Certain studies have reported inter-species variations in the magnitude of their bioaccumulation (Li et al., 2016; Wang et al., 2019), with some further enrichment in LREE relative to the seawater (Akagi and Edanami, 2017). Investigating the fractionation of REE may provide greater insight on REE behaviour in the environment and throughout ecosystems.

Studies on the REE accumulation in distinct animal tissues from natural environments are uncommon, typically focused on aquatic species, and often limited to muscle or whole-body values. Where investigated, vertebrate animal organs involved in detoxification, such as the liver (MacMillan et al., 2017) and kidneys (Squadrone et al., 2020), have shown a greater accumulation of REE than muscles. Further, there has been some evidence of differential accumulation (LREE versus HREE) between body compartments (Schwabe et al., 2012; Belyanovskaya, 2019). Northern communities traditionally consume animal organs in addition to the flesh (Egeland et al., 2013), and experience a higher level of concern over food security than in other regions of Canada (Leblanc-Laurendeau, 2020). It is therefore important that various tissues are considered in the monitoring of REE to better understand their biodistribution and internalization in animal species, as current knowledge suggests the processes involved may be related to factors such as solubility, matrix pH, biological function, uptake mechanisms of the various tissues (Wells and Wells, 2012; Belyanovskaya, 2019) and potential sequestration of bioavailable REE (Evans, 1990; Cardon et al., 2019).

Though REE generally display similar biogeochemical behaviours due to similar atomic masses, ionic radii, electron configuration, and trivalent charges (Gonzalez et al., 2014; Van Gosen et al., 2017), deviations from this trend exist. Normalized REE patterns, by comparison to standard concentrations, highlight enrichments or depletions (i.e., anomalies) of elements in relation to their neighbours on the periodic table (Lawrence and Kamber, 2006; Piper and Bau, 2013; Tostevin, 2021). The redox chemistry of certain REE can affect their fate: for instance, cerium (Ce) can be oxidized to the 4+ state, which is less soluble than its 3+ state, and europium (Eu) can be reduced to the 2+ state (Manini, 2017). Recent REE studies on biota have noted the appearance of anomalies in various species, such as in fruits (Squadrone et al., 2019), bivalve soft tissues (Akagi and Edanami, 2017), and whole fish (Wang et al., 2019). Typically, anomalies in waters and sediments have been thought to reflect the matrices' source, weathering, among other processes, and could be used to track changes in geochemistry (Akagi and Masuda, 1998; Lawrence and Kamber, 2006; Benabdelkader et al., 2019; Tostevin, 2021) or anthropogenic inputs (Bau and Dulski, 1996). However, studies have yet to provide detailed insight into the cause of this varied REE fractionation in biota, and there are inconsistent values across these limited studies, highlighting the need for a greater database. Investigations into anomalies in biota may allow for better understanding of REE behaviour in ecosystems, environmental control factors, or biological processes (Li et al., 2016; MacMillan et al., 2017; Wang et al., 2019).

Through a CBEM program within the northeastern region of Nunavik, this study aims to provide insight into: (1) the background levels of REE in northern ecosystems prior to anthropogenic disturbance from REE mining; (2) the inter- and intra-species bioaccumulation of REE in traditional

food species; and (3) the fractionation of REE within biota through exploratory analyses of Ce anomalies and their possible control variables.

2. Methods

2.1. Study sites

Field locations were in Nunavik, Quebec, Canada (Fig. S1) with a focus on sites utilized by the community of Kangiqsualujjuaq for hunting and fishing. The study area extends from Lake Brisson in the south, located near the forecasted REE mine site (Boisjoly et al., 2015), northward to the coastal region of the Ungava Bay. Other than the community of Kangiqsualujjuaq with a population of 956 as of 2021 (Statistics Canada, 2022), no known significant anthropogenic activity is present in the study area. Further, sampling sites are primarily concentrated within the George River basin (GRB) and Koroc River basin, two major river systems that cover drainage areas of 41,700 km² (Laycock, 2020) and 4050 km² (Bunn et al., 1989), respectively. Within the Southeastern Churchill Province of the Canadian Shield, the watersheds are in a transition zone with boreal forests to treed shrublands and primarily discontinuous permafrost in the southwest; tundra and more continuous permafrost to the northeast (Allard et al., 2012; Brackley, 2019).

2.2. Sampling methods

Field sampling took place from June – August of 2017 to 2019 and 2021, except for ptarmigans which were collected in March of 2018. Field equipment and sampling containers were acid-washed (glassware: 45 % HNO₃, 5 % HCl; plasticware: 10 % HCl) and rinsed with ultrapure water (Milli-Q, 18.2 MΩcm) prior to collection. Sampling was performed using gloves changed between sites, where applicable.

The above-ground plant segments were cut from lichen ($n = 62$) of genus *Cladonia*, presumed to be reindeer lichen (*Cladonia rangiferina*) and kept in resealable plastic bags. Lichen sampling aimed to acquire specimens from a wide range across the GRB, including near the forecasted Strange Lake REE mine for environmental monitoring as this genus is consumed by various terrestrial herbivores (e.g., *Rangifer tarandus*) and can act as a biomonitor for the atmosphere (Naeth and Wilkinson, 2008; Abas, 2021). No pre-analysis rinsing of lichen was done as to obtain concentrations representative of those to which wildlife would be exposed (MacMillan et al., 2017). Sediment samples ($n = 18$) were taken 3 m from the shore where the water depth was between 0.3 m and 0.5 m. Two sites were within the mainstream and one in a small tributary (approximate length < 10 km) of the George River. Triplicates from two depths at each site (0–5 cm and 5–10 cm) were collected using a hand-corer with a 5 cm diameter tubing and stored in double-wrapped plastic bags. Riverbanks often had steep slopes and were comprised of rocky material, leading to a limited access of sediment deposition zones. Biofilm samples ($n = 4$) were collected (similar to Chételat et al., 2018) at the three sediment stations in triplicate by brushing multiple (~5) rocks for each replicate with a toothbrush and placed into a Whirl-Pak sample bag with site water. Benthic invertebrates were sampled from a tributary of the George River following a protocol for rocky riverbeds presented in Moisan (2017). A D-frame net (600 μm) was used to collect individuals after brushing rocks located 0.5 m upstream, or taken directly from under rocks in the riverbed. The net was rinsed with site water and specimen were kept in sample containers with water. Identification was completed using an identification key for freshwater benthic macroinvertebrates. The individuals (no depuration) were sorted by taxonomic group and size, forming four pooled samples ($n = 4$): one stonefly group (*Plecoptera*: 2 individuals), one mayfly group (*Ephemeroptera*: 5 individuals), and two caddisfly groups (*Trichoptera*: 4 small individuals; 3 adult individuals). Macroalgae of genus *Alaria* sp. ($n = 3$) and common mussels (*Mytilus edulis*, $n = 10$) were collected by hand from the coastal estuarine region of Kangiqsualujjuaq, George River, and stored in sealed plastic bags. Mussels (no depuration) were 3.4 to 6.7 cm in length.

The fish (Arctic char, *Salvelinus alpinus*, $n = 34$; whitefish, *Coregonus clupeaformis*, $n = 40$; Arctic sculpin, *Myoxocephalus scorpioides*, $n = 7$; Arctic cod, *Boreogadus saida*, $n = 2$), seal (bearded seal, *Erignathus barbatus*, $n = 2$; ringed seal, *Pusa hispida*, $n = 7$), ptarmigan ($n = 18$, presumed to be rock ptarmigan, *Lagopus muta* and willow ptarmigan, *Lagopus lagopus*), and Canada goose (*Branta canadensis*, $n = 3$) specimens were collected through the CBEM program, where participation and knowledge of Inuit hunters from Kangiqsualujjuaq were essential. Hunters were financially compensated and were provided with sampling kits and protocols to log data. Fish were caught using a gill net, seals were hunted with rifles, and ptarmigans and geese were hunted with a pellet gun or a 22-calibre lead gun. The animal species sampled were selected to represent the diet of the local Inuit population (Table 1), as well as different environments and trophic levels to give a general overview of the study area. Fish were within the size range of 26 cm to 66 cm, with an average (\pm standard deviation) of 48 ± 8.7 cm in total length. Seals had total lengths of 39 cm to 171 cm and varied blubber thicknesses of 1.0 to 5.5 cm, where measured in the field. There were 2 male bearded seals, and 4 female and 3 male ringed seals. Sizes of ptarmigans ranged from 500 g to 592 g, where measured. The geese included one adult female and two goslings.

2.3. Laboratory methods

Samples were frozen prior to laboratory analysis (-20 °C). Laboratory tools were acid-washed (10 % HCl) and rinsed with ultrapure water (Milli-Q). The workstation was covered in plastic wrap and changed between specimens. The animal samples were prepared by removing external sections and identifying and sampling the clean, internal tissues (0.3–20 g). Subsamples of interest were muscle, liver, kidney, and opercula from fish; muscle, liver, kidney, blubber, and jawbone from seal; crop and gizzard contents, muscle, liver, and kidney from ptarmigans; muscle, liver, and gizzard wall from geese; and soft tissue from mussels. The ptarmigan crop contents were considered their own taxonomic group throughout the study as they display a direct link between producer and consumer within the food

Table 1

Sample size (n) and details about the consumption of each species and tissue type by the Inuit community of Kangiqsualujjuaq. (*) Groups include two species. (–) Indicates an unknown field. Consumption data provided by José Gérin-Lajoie, personal communication, and validated by Eleonora Townley.

Sample group		n	Consumed or not
Algae (<i>Alaria</i> sp.)	NA	3	Yes, middle section
Common Mussel	Whole, soft	10	Yes
Canada Goose	Muscle	3	Yes
	Liver	3	Yes
Ptarmigan*	Gizzard wall	2	Yes
	Thigh muscle	18	Yes
	Breast muscle	10	Yes
	Liver	18	Yes
	Kidney	11	Yes
	Crop contents	11	No
	Gizzard contents	12	No
Arctic Char	Muscle	34	Yes
	Liver	23	Yes
	Bone	24	Boiled in fish chowder
Whitefish	Muscle	40	Yes
	Liver	39	Yes
	Kidney	24	No
	Bone	17	Boiled in fish chowder
Arctic Cod	Muscle	2	Yes
	Liver	2	–
Arctic Sculpin	Muscle	7	Yes
	Liver	7	Yes
	Kidney	7	No
	Bone	3	–
Seal*	Muscle	9	Yes
	Liver	9	Yes
	Kidney	2	Yes
	Blubber	6	Yes
	Bone	3	Boiled in stew

web. The material itself was largely undigested and consisted of willow buds, berries, branches, twigs, and fibrous material.

Samples were lyophilised for at least 24 h and homogenized with a glass mortar and pestle, except for bones, which were simply crushed using a hammer on the exterior of the sample bag to avoid contamination. From each sample, between 10 and 15 mg of material was digested (similar to [Khadra et al., 2019](#); [Charette et al., 2021](#)) in pre-washed (HNO₃ 45 %, HCl 5 %) Teflon vials by equal volumes (0.25 mL) of HCl (OmniTrace Ultra, EMD Millipore) and HNO₃ (OmniTrace Ultra, EMD Millipore) in a pressure cooker (50X-120 V, All American) at 15–20 PSI for 3 h. Once cooled, 0.25 mL of hydrogen peroxide (30 % H₂O₂, OPTIMA grade, Fisher Scientific) was added to each sample and left to react overnight. Samples from 2021 were instead digested by 0.6 mL HNO₃ (trace-metal grade, Fischer Scientific) purified by sub-boiling (DST-1000, Savillex), with 0.25 mL H₂O₂ (30 %) and 0.15 mL HCl (trace-metal grade, Fisher Scientific) added after pressure cooking under the same conditions. Finally, all samples were transferred to trace-metal free vials and diluted with ultrapure water (Milli-Q) for analysis.

A total of 16 REE [lanthanum (¹³⁹La), cerium (¹⁴⁰Ce), praseodymium (¹⁴¹Pr), neodymium (¹⁴⁶Nd), samarium (¹⁴⁷Sm), europium (¹⁵¹Eu, ¹⁵³Eu), gadolinium (¹⁵⁷Gd), terbium (¹⁵⁹Tb), dysprosium (¹⁶³Dy), holmium (¹⁶⁵Ho), erbium (¹⁶⁶Er), thulium (¹⁶⁹Tm), ytterbium (¹⁷⁴Yb), lutetium (¹⁷⁵Lu); excluding promethium (Pm); including yttrium (⁸⁹Y) and scandium (⁴⁵Sc)], were analyzed by inductively coupled plasma mass spectrometry (ICP-MS/MS, 8900 Triple Quadrupole, Agilent Technologies) at Université de Montréal (Montreal, QC, Canada). BCR-668 (Mussel Tissue), BCR-670 (Aquatic Plant), and SLRS-6 (River Water; National Research Council Canada) certified reference materials were used to test for analysis accuracy. The recovery for reference materials (Table S1) varied between analyses with averages of 94 ± 16 % for LREE and 88 ± 14 % for HREE. Blanks and standards were treated identically to samples and were run approximately every 10 samples to assure accuracy was maintained. Germanium (⁷⁴Ge), rhenium (¹⁸⁵Re) and iridium (¹⁹¹Ir) were used as internal standards. Results were compared to detection limits (DL) that were calculated as three times the standard deviation of approximately 10 analytical blanks and concentrations were only reported where greater than the DL. Element DL (Table S2) ranged on average from 0.0004 to 0.003 µg/L across all analyses.

The detection frequencies of REE (>DL) were dependent on the matrix (Table S3), with 100 % detectability across individual REE for sediment, biofilm, benthic invertebrates, algae and mussel; 100 % detectability of LREE and 50–100 % detectability of HREE for lichens; and varied detectability for vertebrates (0–100 %). Metal concentrations in digestion blanks were subtracted from sample concentrations when detected. Total REE concentrations (ΣREE) were calculated as the sum of individual REE, when concentrations were detected, as all individual REE demonstrated a strong correlation (Table S4; R² = 0.77 to 1.00). The sum includes Y as it had a strong positive linear relationship to the lanthanides by Pearson's correlation coefficients (R² = 0.88 to 0.99), but excludes Sc due to analytical interferences.

2.4. Statistical methods

All statistical tests were performed in RStudio (4.0.1). Q-Q plots and Shapiro-Wilk normality tests were completed to check for normality of sample groups; values were log₁₀-transformed to improve normality where required. Levene's test was used to check for equal variances of sample groups. Analysis of variance (ANOVA) with Tukey's HSD post-hoc test was performed on data where normality, homogeneity of variance and equal sample size assumptions were met, otherwise a Welch's ANOVA with games-Howell post-hoc test was performed. The two-sided *t*-test was employed to determine where anomalies were present (≠ 1). The significance level (α) was set at 0.05 for each test. The benthic invertebrates were combined into a single taxonomic group to perform statistical tests as ANOVA requires *n* > 2. Linear model analyses were performed using the 'lm' function. R-squared values and regression lines were reported

where the model was significant (α = 0.01). Further investigation into model validity was conducted through evaluation of residuals and coefficient significance values.

2.5. Data analysis

REE concentrations are presented in nanomoles per gram on a dry weight basis (nmol/g dw) and often presented as the mean ± SD. The LREE included La – Gd and Yb – Lu plus Y were considered HREE ([Voncken, 2016](#); [Van Gosen et al., 2017](#)). Biomagnification factors (BMF) for ptarmigans were calculated according to: $BMF = [REE]_{tissue} / [REE]_{crop\ contents}$ using wet weights (ww). For anomaly calculations, individual REE concentrations were normalized, REE_N, using the Post-Archean Australian Shale standard values of [Pourmand et al. \(2012\)](#). Ce anomalies (Ce/Ce*) were calculated using various equations ([Akagi and Masuda, 1998](#); [Slack et al., 2004](#); [Lawrence and Kamber, 2006](#); [Tostevin, 2021](#)). All calculation results were similar, with average anomaly values within 10 % of each other across all samples. Therefore, equation $Ce/Ce^* = Ce_N / (La_N^{0.667} \times Nd_N^{0.333})$ as mentioned in [Slack et al. \(2004\)](#) was selected based on its slightly stronger linear correlations (R²) during statistical analyses. Anomaly values <1 signify the sample has a negative anomaly, while values >1 signify a positive anomaly is present. Two whitefish muscle samples were removed from anomaly analyses due to their low REE concentrations causing oversensitivity, and consequently, inaccuracies in ratio calculations.

3. Results

3.1. Concentrations of REE in ecosystems

A large variation in REE concentrations was seen among the biota and sediments studied ([Fig. 1](#); [Table 2](#)). Average individual REE concentrations decreased in % of total REE concentration (Table S5) according to the following, where recovered: Ce > La > Nd > Y > Pr > Sm ≈ Eu > Gd > Er ≈ Dy > Yb > Tb ≈ Ho ≈ Tm ≈ Lu, with the LREE accounting for 81 ± 18 % of total REE. The vertebrate animals typically had undetected HREE, except for Y, which was among the most highly detected elements in all samples (Table S3). Further, calculation of LREE/HREE ratios ([Table 2](#)) demonstrated an LREE enrichment across all taxonomic groups with averages ranging from 2.5 to 68. Additional details regarding REE concentrations (e.g., mg/kg), ratios, and anomalies are provided in Supplementary Information (Table S6).

As expected, some of the highest concentrations of REE were seen in the sediments with concentrations of 716.3 ± 338.3 nmol/g. Additionally, each ecosystem presented the strongest bioaccumulation of REE in the lowest taxonomic groups. For terrestrial system ([Fig. 1A](#)), this included lichens (17.07 ± 35.05 nmol/g) and the ptarmigan crop contents (0.57 ± 0.74 nmol/g). Further, an approximate 10-fold decrease in REE concentration was seen between the ptarmigan muscles and their diet (i.e., crop contents). Within the freshwater ecosystem ([Fig. 1B](#)), a strong REE bioaccumulation was presented for biofilm (753.4 ± 95.22 nmol/g) and benthic invertebrates (90.01 ± 74.32 nmol/g). Freshwater fish muscles had mean REE concentrations on the order of 10⁻¹ nmol/g, which were significantly less than the riverine invertebrates and biofilm by about 100-times and 1000-times, respectively. For marine species ([Fig. 1C](#)) with significant ANOVA, a similar pattern was displayed by a decrease in average REE concentration by multiple orders of magnitude from algae (123.2 ± 76.83 nmol/g) and invertebrates (70.95 ± 19.58 nmol/g) into Arctic sculpin muscles (10⁻¹ nmol/g), and further by an additional 10-fold decrease into the ringed seal muscles (10⁻² nmol/g).

3.2. Bioaccumulation of REE in animal tissues

Animal tissues demonstrated greater REE accumulation in the liver than the muscle ([Fig. 2](#)), up to about 40-times greater by group mean comparison. Bones typically had REE in the middle of the range for tissues, with

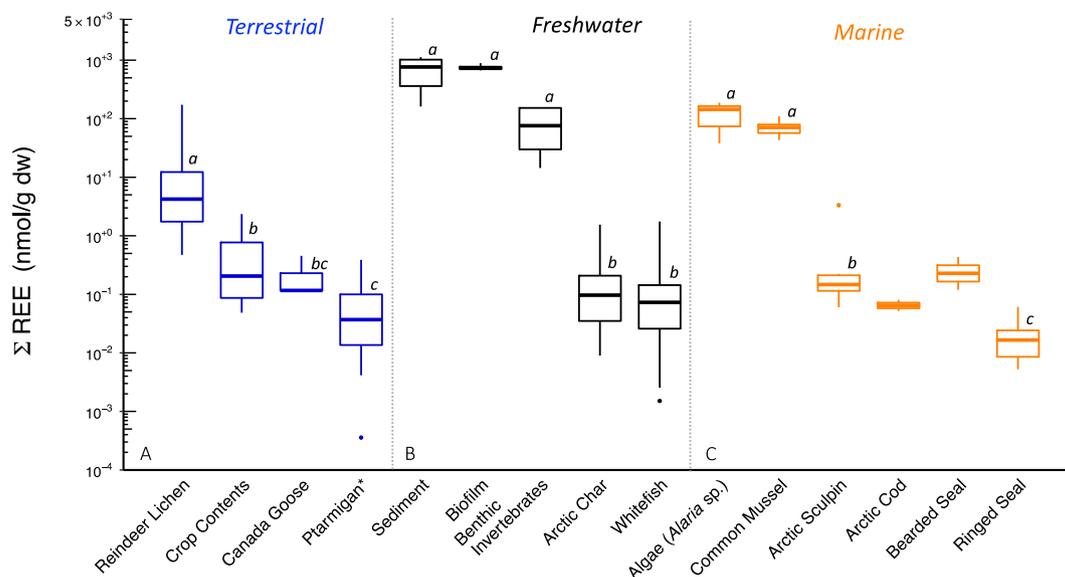


Fig. 1. Concentrations of total REE by taxonomic group (log₁₀-scaled axis, nmol/g dw) organized by ecosystem. Muscle tissue concentrations presented for the animal samples. Different letters represent significantly different means across all taxonomic groups where *n* > 2. *Ptarmigan group comprised of both species. Boxplots show 1st and 3rd quartiles as box boundaries, whiskers reaching the maximum and minimum, the median as a bold middle line, and any outliers as individual points. (For interpretation of the references to color the reader is referred to the web version of this article).

Table 2

Mean values with (standard deviations) for total REE concentration (ΣREE, nmol/g dw), Ce anomaly (Ce/Ce*), the ratio of light to heavy REE (LREE/HREE), and biomagnification factor (BMF). (*) where two species were combined in a single sample group. (†) where sample consisted of the digestive tract contents. NA where no data was available. Muscle Th. and Br. refer to thigh and breast muscle, respectively.

Sample group	ΣREE nmol/g	Ce/Ce*	LREE/HREE	BMF
Sediment	716.29 (338.27)	0.93 (0.06)	7.4 (1.9)	
Lichen	17.07 (35.05)	1.01 (0.11)	6.8 (2.0)	
Biofilm	753.42 (95.22)	0.95 (0.03)	6.4 (0.9)	
Algae	123.22 (76.83)	0.88 (0.07)	7.7 (1.0)	
Benthic Invertebrates	90.01 (74.32)	0.86 (0.04)	12.9 (5.1)	
Common Mussels	70.95 (19.58)	0.81 (0.04)	8.2 (0.7)	
Canada Goose				
Liver	7.32 (9.75)	0.83 (0.03)	19.8 (21.7)	
Muscle	0.23 (0.20)	1.07 (0.32)	13.6 (9.7)	
Gizzard	0.11 (0.04)	0.93 (0.15)	4.6 (0.5)	
Ptarmigan*				
Crop†	0.57 (0.74)	0.72 (0.17)	16.6 (8.7)	
Gizzard†	18.04 (28.82)	1.02 (0.43)	8.7 (7.1)	170 (338)
Liver	1.80 (2.10)	0.72 (0.10)	67.6 (96.7)	10.6 (12.0)
Muscle Th.	0.08 (0.11)	1.50 (0.64)	5.6 (5.0)	0.24 (0.26)
Muscle Br.	0.05 (0.06)	1.09 (0.19)	5.7 (NA)	0.10 (0.19)
Kidney	0.06 (0.05)	1.20 (0.45)	4.3 (2.8)	0.24 (0.33)
Whitefish				
Liver	2.58 (2.07)	0.52 (0.04)	28.5 (15.7)	
Muscle	0.16 (0.29)	0.82 (0.25)	4.2 (3.3)	
Bone	0.83 (0.41)	0.64 (0.06)	4.9 (1.8)	
Kidney	1.65 (1.00)	0.85 (0.18)	9.3 (1.8)	
Arctic Char				
Liver	9.32 (9.34)	0.47 (0.07)	26.9 (17.6)	
Muscle	0.23 (0.34)	0.89 (0.16)	6.6 (3.9)	
Bone	2.59 (1.56)	0.51 (0.18)	3.1 (0.9)	
Arctic Cod				
Liver	0.42 (0.33)	0.75 (0.00)	26.1 (17.6)	
Muscle	0.07 (0.02)	1.08 (0.17)	2.5 (NA)	
Arctic Sculpin				
Liver	0.80 (0.55)	0.73 (0.05)	9.2 (4.8)	
Muscle	0.60 (1.21)	1.06 (0.28)	9.4 (9.3)	
Bone	1.16 (1.15)	0.74 (0.17)	2.9 (2.1)	
Kidney	3.54 (4.72)	0.89 (0.10)	6.8 (3.0)	
Bearded seal				
Liver	3.59 (3.79)	0.88 (0.01)	37.9 (12.4)	
Muscle	0.28 (0.22)	0.87 (0.20)	3.6 (2.8)	
Blubber	0.06 (0.07)	1.02 (NA)	6.6 (NA)	
Kidney	0.77 (NA)	1.05 (NA)	5.9 (NA)	
Ringed Seal				
Liver	1.04 (1.23)	0.90 (0.08)	27.9 (17.8)	
Muscle	0.02 (0.02)	1.31 (NA)	2.6 (2.5)	
Blubber	0.02 (0.01)	1.13 (NA)	NA	
Bone	0.12 (0.14)	1.05 (0.20)	4.1 (1.3)	
Kidney	0.43 (NA)	1.01 (NA)	7.6 (NA)	

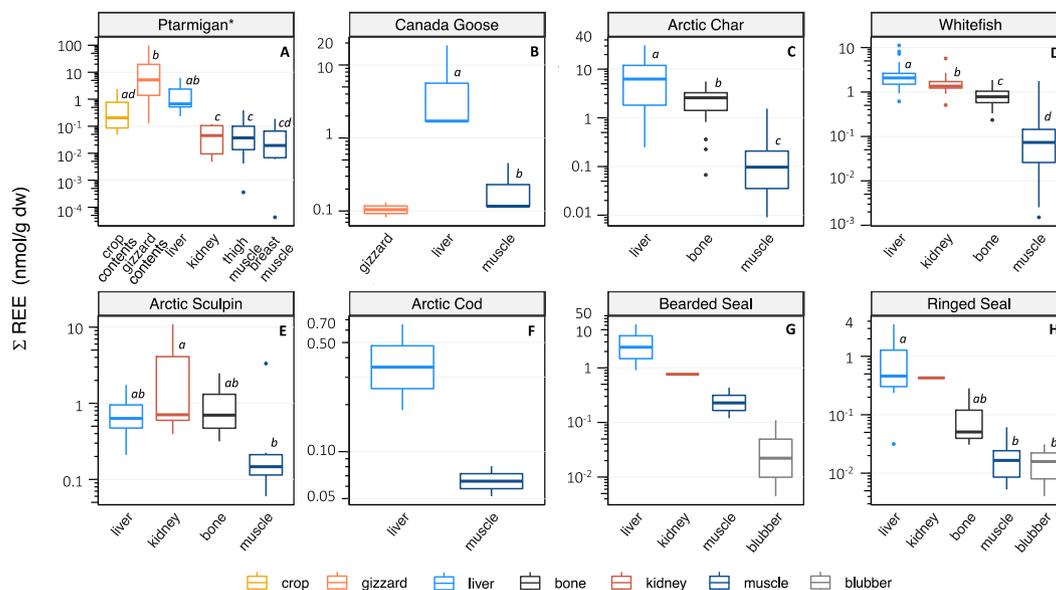


Fig. 2. Concentrations of total REE in various animal tissues (\log_{10} -scaled axis, nmol/g dw). Seal group comprised of bearded and ringed seals. Different letters represent significantly different means within each animal group. Hare samples not shown as $n = 1$ for each tissue type. (For interpretation of the references to color the reader is referred to the web version of this article).

REE values up to 10-times their respective muscle concentrations. Kidney REE concentrations were more variable among species, as they displayed the lowest average bioaccumulation among ptarmigan tissues, while the aquatic animals had REE values 3- to 20-times greater in kidneys than their respective muscle concentrations. The strong LREE bioaccumulation presented herein (Table 2) was especially notable for vertebrate livers, which frequently displayed average LREE/HREE values 10-fold the ratios of other tissues studied. Additionally, the digestive tract contents from ptarmigans were also analyzed, and the partially digested gizzard contents presented REE values at least 10-times greater than the REE accumulated in the internal organs.

BMF values were calculated for the ptarmigan tissues (Table 2) as a direct relationship between consumer and diet was made through analysis of their crop contents. Though values were highly variable (max/

min $\geq 10^2$), even within a single tissue type, the thigh and breast muscle BMF reflected a biodilution of REE in ptarmigans, with BMF values of 0.24 ± 0.26 and 0.10 ± 0.19 , respectively. The suspected biodilution of REE was also supported by the kidney BMF, with an average below 1. However, the ptarmigan liver tissues did not follow the same pattern: instead, 72 % of individuals showed a magnification of REE with an average BMF of 10.6 ± 12.0 .

3.3. Cerium anomalies in ecosystems

Ce/Ce* results for each taxonomic group were presented in Fig. 3, with values that span from 0.23 to 2.2 across all biota and sediment (Table S6). The lower taxonomic groups and sediments displayed Ce/Ce* values near to 1.0, or representative of geogenic background concentrations, and

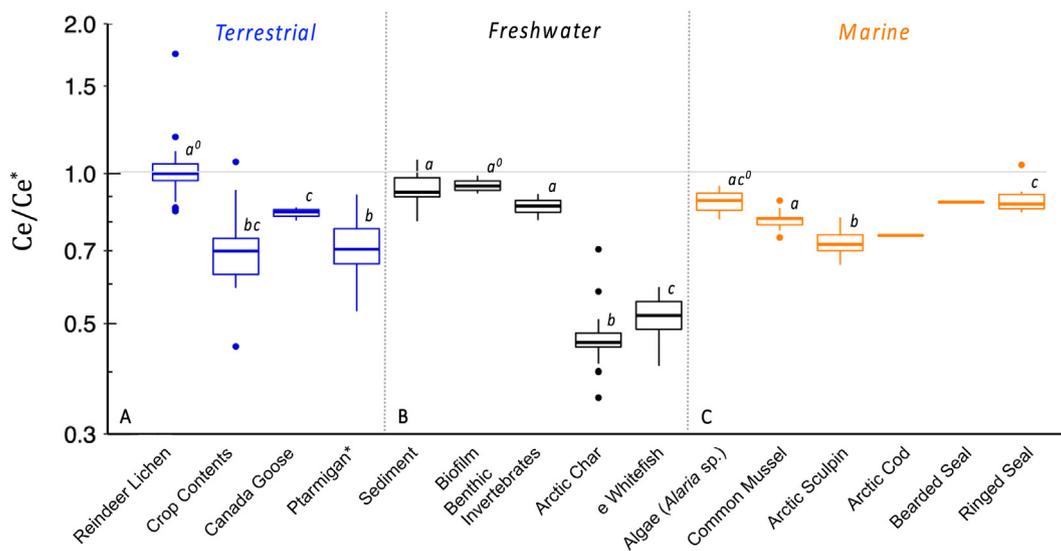


Fig. 3. Ce anomalies by taxonomic group across ecosystems (\log_{10} -scaled). Significantly different means within each ecosystem denoted by different letters. Group means not significantly different from 1.0 denoted by superscript "0". Anomaly values from the liver tissues were used for the animal groups. (For interpretation of the references to color the reader is referred to the web version of this article).

higher-level taxonomic groups often had significant negative anomalies ($Ce/Ce^* \leq 0.8$), suggesting a possible biotransformation of Ce. For example, in the freshwater environment, biofilms had Ce/Ce^* values that are not significantly different from 1.0 (i.e., no anomaly). Meanwhile, slight negative anomalies of 0.86 ± 0.04 were developed in benthic invertebrates, followed by stronger negative anomalies in the whitefish and Arctic char (liver) of 0.52 ± 0.04 and 0.47 ± 0.07 , respectively. For marine species, this development in negative Ce anomalies was presented from algae and mussel into the fish species but was unexpectedly interrupted by more elevated Ce/Ce^* values in seals. Similarly, within the terrestrial ecosystem, lichens presented no anomaly on average, while significant negative anomalies were seen within vertebrates (Ce/Ce^* averages < 0.85). However, no significant difference was noted in the anomaly values between ptarmigan crop contents and the liver (Fig. 3A).

3.4. Cerium anomalies in animal tissues

Significant differences in Ce anomaly between vertebrate animal tissues within a species were also detected (Fig. 4). There was a general trend of near 1.0 Ce/Ce^* values in muscle, and more negative Ce anomaly in the livers with mean values that range from 0.47 in Arctic char to 0.90 in seals. While bone and kidney tissues did not consistently differ significantly from the other tissues, they tended to have anomaly values that were in the approximate range between the muscle and liver. Further investigation into Ce anomalies across the four fish species demonstrated for the first time that Ce/Ce^* could be explained in part by fish size. The total length had a significant relationship to the \log_{10} -transformed Ce anomaly values (Fig. 5) in bone ($R^2 = 0.37$), kidney ($R^2 = 0.25$), and liver (R^2 of 0.23). The total mass (\log_{10} -transformed) also had a significant relationship to Ce anomalies (Fig. S2) in bone ($R^2 = 0.34$), kidney (R^2 of 0.14), and liver (R^2 of 0.24). No significant relationships were found for Ce/Ce^* values of muscle tissues in fish, noting that the detection of REE in muscle tissues was analytically challenging due to low REE concentrations. These relationships therefore suggest a stronger and more negative Ce anomaly for fish species that were larger in size, which in general follow the trend of decreasing total length: Arctic char > Arctic cod > whitefish > Arctic sculpin.

4. Discussion

4.1. Distribution of REE in ecosystems and animal tissues

The REE concentrations presented herein provide background values for use in future studies, especially within subarctic Canadian

environments. Certain taxonomic groups displayed large concentration ranges (i.e., across multiple orders of magnitude), which may be explained by two factors. First, in the case of reindeer lichens, sampling occurred over a large area of the GRB, with sites up to 200 km away from each other and therefore concentrations encompass some regional variability and different influences. Second, in the case of the vertebrate muscles, this can likely be explained in part by the very low REE concentrations present (often near DL), causing total REE concentrations to be sensitive to small differences. Overall, higher concentrations of REE were presented in biofilm, algae, and other low trophic level taxonomic groups, with lower concentrations in species from higher trophic levels (i.e., vertebrate animals). These findings are characteristics of a trophic dilution, or biominification, and has been previously proposed in studies that acquired REE concentrations for specimens at different food web positions (MacMillan et al., 2017; Amyot et al., 2017; Squadrone et al., 2019). This pattern may suggest that humans would experience a lower exposure to REE in consumption of high-level consumers, relative to species from lower food web positions.

Sediments of the GRB had a range of values from 161.8 to 1126 nmol/g (Table S6), similar to those found in the literature for remote, undisturbed locations (e.g., Amyot et al., 2017; MacMillan et al., 2019). For example, freshwater sediments of Northern Quebec had Σ REE concentrations of 71–185 $\mu\text{g/g dw}$ (Romero-Freire et al., 2019) (present study: 22.2–155 $\mu\text{g/g}$). In general, while REE are considered non-essential elements (Goecke et al., 2017), vegetative species have consistently demonstrated an ability to bioaccumulate to a high degree compared to their environment and high-level organisms (Campbell et al., 2005). REE concentrations of GRB lichens are comparable to fruticose lichens and moss from the Hudson Bay region of eastern Nunavik (MacMillan et al., 2017), which displayed Σ REE concentrations of 41.5 ± 81.4 nmol/g (dw, geometric mean \pm SD). As for the biofilm samples, their equally elevated concentrations are thought to be due to the presence of sediment particles that can be naturally associated with this matrix; no biofilm analyses were found in REE literature. Goecke et al. (2017) reported a bioaccumulation of lanthanides (up to 7.61 mg/kg dw) in brown algae off the Chilean coast, and to a lesser extent also in red algae. Concentrations were 2-fold greater in regions with significant mining activity, with climate factors thought to contribute additional inter-site variability. While concentrations of up to 10^2 mg/kg dw REE in algae (var. marine species) have been presented by studies across Europe, Asia and South America (reviewed by Goecke et al., 2017), the current study presented the first reports of REE analyses in Canadian macroalgae (16.9 ± 10.6 mg/kg), to the authors' knowledge.

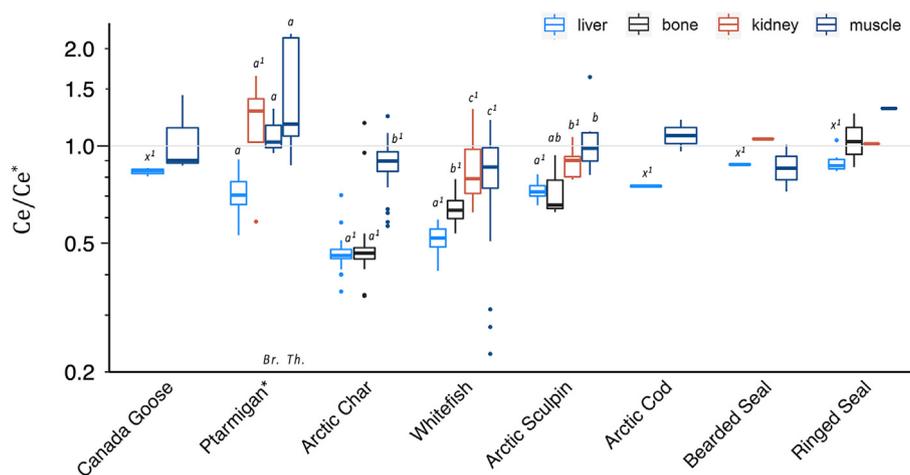


Fig. 4. Ce anomalies (\log_{10} -scaled) in the animal liver, bone, kidney, and muscle tissues. Seal* taxonomic group comprised of both seal species. Letters (i.e., a, b, c) represent significantly different means within each animal group. Superscript of '1' denotes a mean Ce/Ce^* value that was significantly different from 1.0; superscript placed on 'x' where no ANOVA was reported. (For interpretation of the references to color the reader is referred to the web version of this article).

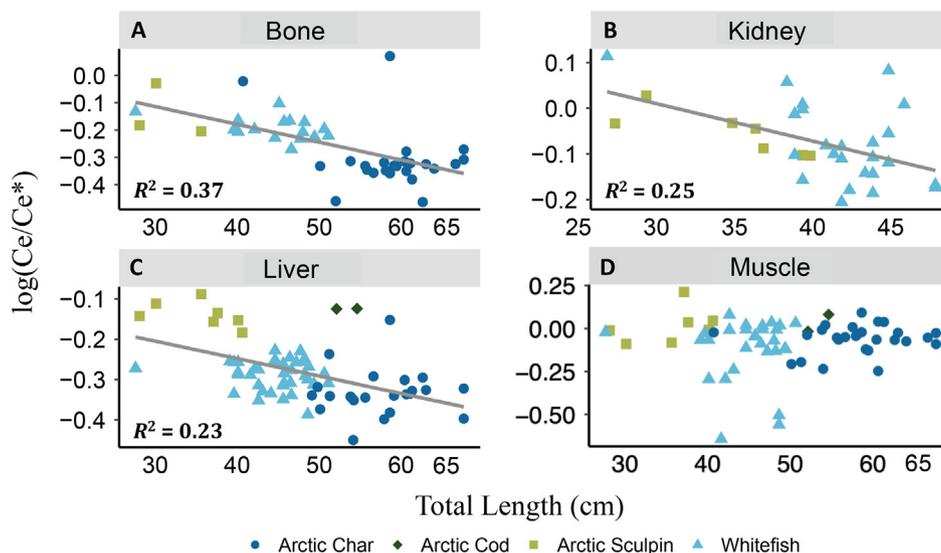


Fig. 5. Ce anomalies (\log_{10} -transformed) within tissues of all four fish species studied, explained by fish total length (cm). R^2 values and regression lines are shown where the linear model was significant ($p < 0.01$). (For interpretation of the references to color the reader is referred to the web version of this article).

MacMillan et al. (2019) and Amyot et al. (2017) reported values of around 2–270 nmol/g dw for Σ REE in zooplankton and benthic invertebrates of various species from freshwater bodies within arctic to temperate Quebec, respectively, which is comparable to the pooled benthic invertebrates from the current study. REE concentrations in GRB benthos and common mussels were at least 100-times greater than those presented in fish muscles of freshwater and saltwater species, respectively. This is consistent with the literature where comparisons were available between low-level groups and vertebrate consumers of the same environment (MacMillan et al., 2017; Wang et al., 2019; Squadroni et al., 2019; Pastorino et al., 2020), altogether supporting a biodilution of REE. However, common mussel reported herein are an order of magnitude greater than those presented in clam species from coastal China (Wang et al., 2019) or soft parts of bivalves from the Mediterranean Sea (Squadroni et al., 2019) and Tokyo Bay (Akagi and Edanami, 2017). While the cause of this elevation in GRB mussels is unknown, it is proposedly linked to inter-species variability, or, as it is located within subarctic marine conditions, perhaps linked to temperature or REE bioavailability influences. Further, concentrations of REE appeared consistently greater in the consumed portion of molluscs (i.e., soft tissues) than in the shells; with significant inter-site variability reported in the literature (Weltje et al., 2002). To note, invertebrates were not depurated in the current study to represent the levels consumers are exposed to in the food web. As depuration has reportedly shown an influence on REE content by a factor of 1.75 in chironomids (Amyot et al., 2017), or 1.62 (La) and 1.71 (Ce) in amphipods (Labrie, 2022), the REE concentrations presented herein likely represent upper values for invertebrates.

REE concentrations within individual fish organs are not widely reported, with data often limited to muscle or whole-body values. In similar environments, river whitefish muscle from the Canadian Arctic, fish dorsal muscle of various species from Southern Quebec, and fish muscles from the Southern Baltic Sea demonstrated average REE concentrations within the same range as fish muscles from the current study (MacMillan et al., 2017; Amyot et al., 2017; Reindl et al., 2021), while their other organs were not presented. Whole-body whitefish (Lake and mountain) and sculpin (unknown species) analyses of Washington State were comparable to concentrations of organs from the present study; however, their muscle concentrations were undetected (Mayfield and Fairbrother, 2015). Bioaccumulation up to approximately 10-times greater in liver than flesh or muscle was reported for Minnesota sculpin (Korda et al., 1977) and Arctic vertebrates (MacMillan et al., 2017), respectively. A similar relationship between kidney and dorsal muscle tissues was seen in the Indo-Pacific

lionfish, with REE concentrations 3-times higher in the kidney samples; however, no significant difference between liver and muscle was seen (Squadroni et al., 2020). Laboratory studies have also supported a varied bioaccumulation among tissues, with higher concentrations reported for internal organs (e.g., liver) than for muscle (Cardon et al., 2020), skeleton, and gills (Tu et al., 1994). As the liver and kidneys are known sites of detoxification, higher levels of REE therein could be indicative of sequestration processes at play, in which case it is possible that while REE were more strongly bioaccumulated in these organs, they may be stored to some extent in detoxified granules (Lobel et al., 1991; Cardon et al., 2019). Additionally, the association of these metals to certain proteins, such as metallothioneins that bind metals and affect biodistribution, may be contributing to this preferential accumulation in the liver and kidneys (Squadroni et al., 2020; Hanana et al., 2021; Sabolić et al., 2010).

Some studies have reported greater REE concentrations in benthic fish species than those of pelagic species (Guo et al., 2003; Yang et al., 2016), and in freshwater fish species compared to marine species (Yang et al., 2016). Neither trend was consistent across all tissues or species within the present study. However, marine fish species at higher trophic levels demonstrated a lower mean REE, with the predatory Arctic cod concentrations up to 9-fold lower than the more benthic Arctic sculpin. Additionally, freshwater fish livers displayed mean REE concentrations up to 20-fold the marine fish livers, which could suggest a potential decrease in REE bioavailability in saltwater (Herrmann et al., 2016). In general, precipitation of REE is expected in estuarine environments due to changes in water conditions (e.g., salinity, pH, temperature, available ligands) affecting solubility and flocculation of REE particles during the mixing of waters (Pouret and Tuduri, 2017; Gonzalez et al., 2014). Therefore, a change in total REE concentration in the water column, as well as their speciation, could affect both the bioavailability and uptake of REE between freshwater and marine environments.

The present study contributed the first reports of REE concentrations for certain species and/or tissues important to northern ecosystems. This study additionally reported the first BMF values for REE in ptarmigan organs. A potential magnification in REE concentration from crop contents to liver tissues was unique in that REE biodilution has been otherwise presented. This further suggests the liver is important to consider in monitoring of wildlife exposure and brings forth the recommendation that consumption guidelines be considerate of inter-tissue accumulation trends.

4.2. LREE enrichment

LREE enrichment can be attributed in part to the more frequent detection of LREE (Table S3) because there is slightly better recovery of LREE (Table S1) and naturally higher concentrations of LREE in the environment, as seen in the GRB sediments (LREE/HREE of 7.3 ± 1.9). An enrichment of LREE, with LREE/HREE values >1 , across sediment and biota of this study (Table 2) was consistent with various values reported in the literature for biota, which were often in the range of 3 to 50 (Li et al., 2016; Yang et al., 2016; Wang et al., 2019; Figueiredo et al., 2021); or more generally, simplified as LREE $>$ HREE across studies (reviewed by Piarulli et al., 2021). Interestingly, the present study suggested a further partitioning of REE compared to sediments upon bioaccumulation in biotic specimens, with similar ratios among sediments and low-level organisms (i.e., lichens, biofilm, and algae). LREE enrichment was seen to a greater degree in vertebrate livers (e.g., LREE/HREE whitefish liver: 28.5 ± 15.7), whereas a weaker LREE enrichment was seen in bones and muscles (e.g., LREE/HREE whitefish bone 4.9 ± 1.8); suggesting a potential for tissue-dependent partitioning of individual REE in the vertebrate species. While it is accepted that lanthanides deposit in bones (reviewed by Vidaud et al., 2012), the present LREE/HREE trend may be related to the stronger accumulation of HREE, which has been reported for a study on REE-administered rats (Durbin, 1962). Some exceptions to the LREE enrichment trend were reported in the literature, such as for fruits (LREE/HREE = 0.14) of the Piedmont Region of Italy (Squadrone et al., 2019), and for the livers and kidneys of predatory marine lionfish (*Pterois volitans/miles*; LREE/HREE <1) from Cuba (Squadrone et al., 2020), though no comparison to sediments were presented within those studies. The LREE/HREE patterns presented herein may be indicative of an accumulation and subsequent biodistribution of REE that is more sensitive to one group of elements (e.g., the LREE); or an elimination process that is potentially more efficient for one group of REE (e.g., the HREE), relative to the other. The relative abundances of REE are important to consider when discussing toxicity, as studies have shown lower EC₅₀ values (i.e., more toxic) for HREE over LREE (Cui et al., 2012; Techer et al., 2020). Overall, additional variability in LREE/HREE fractionation could be introduced by factors such as differences in studied species and their environmental exposures (Reindl et al., 2021); differences in cellular pH levels across organs; or differences in REE ionic radii and solubility affecting bioaccumulation potential (Wells and Wells, 2012; Gonzalez et al., 2014).

4.3. Cerium anomalies in biota

Relative to the other REE, Ce is more easily subject to changes in redox state due to its electron configuration and the insolubility of tetravalent Ce (Dahle and Arai, 2015), contributing to its frequent anomalous behaviour in this context. Ce anomalies within biota have been seldom discussed in the literature to date, and where present, no consensus is made on the factors controlling their variability across species and locations. While it has been suggested that Ce anomalies are reflective of the local sediment or soil profile (Castorina and Masi, 2015; Squadrone et al., 2019), the present study only noted a Ce/Ce* value near 1.0 in sediments, whereas anomalies were reported to varying degrees in animals across ecosystems. The Ce/Ce* values therefore do not consistently reflect the sediments but rather they suggest a further fractionation is occurring during REE uptake and biodistribution. The results presented herein (Fig. 3) displaying varied Ce anomalies were consistent with the assorted values reported in the literature across ecosystems and species: Yang et al. (2016) presented negative Ce anomalies ranging from 0.48 to 0.74 across ten fish species; Squadrone et al. (2019) found only slightly negative Ce anomalies in fruits and honey but not in other vegetation or animal specimens; Wang et al. (2019) reported negative Ce anomalies in fish and molluscs, and variable Ce/Ce* values in crustacean; and positive Ce anomalies were shown for Li et al. (2016) fish, shellfish and crustacean species. Additionally, negative Ce anomalies are expected in oxic aqueous environments, such as in surface waters, due to

the decreased solubility of oxidized cerium (Ce⁴⁺) compared to Ce³⁺ (Tostevin, 2021). In seawater, Ce is known to be in low availability, likely linked to interactions with oxyhydroxide particles (Adebayo et al., 2020), further enhancing this feature (Figueiredo et al., 2021; Tostevin, 2021). Surprisingly then, fractionation was found to be less pronounced in Nunavik marine animals than freshwater ones, once again indicating that while Ce/Ce* values may in part reflect an individual's environment (i.e., sediment or water) (e.g., MacMillan et al., 2017), they also depend on physiological processing of REE.

This study presented novel intra-species Ce/Ce* distributions for four tissue types among terrestrial, freshwater, and marine animals (Fig. 4), that demonstrated a consistently greater fractionation of REE in liver and to a lesser extent also in bone, relative to kidneys and the near-unit muscle values. As Ce is sensitive to changes in redox, we put forth the hypothesis that the anomalies may be reflecting changes in redox state between tissues and cells within an individual. This hypothesis is in line with findings from a study in which varying redox states were reported across mice tissues, such as between liver, kidneys, and skeletal muscles (Rebrin and Sohal, 2004). Further, an explanation for why certain tissues for the fish species consistently demonstrated strong Ce/Ce* relationships to fish size (Fig. 5) while others were less significant, could be due to varying residence times for REE within different tissues. In a study on human REE accumulation it was reported that REE have long residence time within bone tissue, reflecting exposure over many years (≤ 10 years) (Zaichick et al., 2011), whereas the liver of rats exposed to select REE displayed shorter residence times on the order of weeks to months (reviewed by Bengtsson, 2021). The relative residence times presented within these studies would be consistent with the interpretation of our present results. In bones, the lanthanides can likely form stable complexes with calcium phosphate minerals, as well as certain glycoproteins (reviewed by Vidaud et al., 2012; Williams and Peacocke, 1967).

Further investigation into these relationships (Fig. 5) suggested that the main explanatory fact may be differences in fish species rather than a spread of Ce fractionation over fish length within any single species. This is due to the insignificant linear models attained from testing of the same relationships within an individual species ($p > 0.01$). Altogether the Ce anomaly trends demonstrated the most significant fractionation for the larger pelagic Arctic char, while the smaller benthic marine Arctic sculpin displayed slightly weaker negative anomalies, suggesting a potential influence of fish ecology and habitat on REE fractionation. Indeed, the influence of animal metabolism on REE accumulation in wildlife (Squadrone et al., 2019) and the species-specific subcellular partitioning of Y in aquatic model organisms (Cardon et al., 2019) have been reported. Altogether, Ce/Ce* results suggested there may be potential for Ce anomalies to be used as biomarkers for REE exposure and/or biological transformation in future studies, with further investigation required to confirm the presence and main drivers of biological fractionation in animal tissues, such as through laboratory exposure experiments with a focus on Ce³⁺/Ce⁴⁺ and Ce/Ce* ratios among subcellular fractions, cellular conditions of different cell types, and REE sequestration processes.

5. Conclusion

The study presented current values for REE within undisturbed ecosystems of subarctic Canada, prior to the forecasted opening of a REE mine in the study area, that can hereinafter be used as a reference in environmental monitoring. Total REE concentrations across matrices studied were representative of natural environments and offered the first reports of REE bioaccumulation for certain species and/or tissues. Sampling performed in collaboration with a local community demonstrated the ability of CBEM programs to provide quality data and proved to be both efficient and essential in the collection of traditional food species representative of the diet of northern populations of Nunavik. Investigation of terrestrial, freshwater, and marine ecosystems displayed REE trends consistent with a trophic dilution, or lack of biomagnification, in undisturbed northern environments, with concentrations up to 10⁴ times greater in lower trophic level groups

(e.g., biofilm) relative to muscles of predatory animals. Notable was the species- and tissue-specific bioaccumulation of REE, with a greater bioaccumulation of REE in liver by up to approximately 40-times compared to muscles, and both bone and kidney tissues often showing intermediate accumulation across species. This database highlighted the importance of considering animal organ tissues in addition to muscle meat in the development of health directives for both wildlife safety and consumption of animal products, and can serve in their determinations as no national guidelines currently exist for REE in biota. Additionally, Ce/Ce* values were reported with significant variation among taxonomic groups and demonstrated a further fractionation upon bioaccumulation within biota, represented in particular by inter-tissues differences in the magnitude of Ce anomalies, which were more pronounced for liver across all species. Altogether these results suggested a potential interest for considering liver cells in laboratory studies of REE toxicity as they have consistently demonstrated the highest degrees of REE bioaccumulation and fractionation. Further investigation is needed to confirm this fractionation; however, the present finding suggested potential use of Ce/Ce* values as a biomarker in REE studies that may reflect the redox potential of their matrix, element-specific uptake or subcellular sequestration processes, or other biological mechanisms. Future research addressing these hypotheses may assist in determining the availability and toxicity of REE to the environment and human health.

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CRediT authorship contribution statement

Holly Marginson: Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Data curation, Writing – original draft, Writing – review & editing. **Gwyneth A. MacMillan:** Conceptualization, Methodology, Investigation, Data curation, Writing – review & editing. **Éliane Grant:** Investigation, Writing – review & editing. **José Gérin-Lajoie:** Conceptualization, Investigation, Funding acquisition, Writing – review & editing. **Marc Amyot:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Funding acquisition.

Data availability

Data will be made available on request.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2023.163024>.

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