Université de Montréal

Rare earth element bioaccumulation and anomalies in organisms of northeastern Nunavik (Quebec, Canada)

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Ce mémoire intitulé

La bioaccumulation et des anomalies des éléments terres rares dans les organismes du nord-est du Nunavik (Québec, Canada)

Présenté par

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A été évalué par un jury composé des personnes suivantes

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Résumé

Comme la demande mondiale des éléments de terres rares (ETR) ne cesse d'augmenter, de nouveaux projets d'exploration ont été lancés dans de nombreux pays, incluant au Canada. Le présent projet découle d'un programme communautaire environnemental issu d'une collaboration entre des chercheurs et la communauté inuite de Kangiqsualujjuaq suite à la proposition d’un projet minier d'ETR au Nunavik. Pour répondre aux études limitées sur la distribution des ETR dans les environnements non pertubés, cette étude rapporte les niveaux actuellement observés des sédiments, des lichens et de multiples espèces animales provenant d'écosystèmes terrestres, d’eau douce et du milieu marin du subarctique de l’est du Canada. Les résultats suggèrent que toutes les matrices ont la capacité d'accumuler les ETR, bien qu'une dilution trophique soit notée. De plus, l’analyse des tissus d’espèces alimentaires traditionnelles a démontré que le foie des vertébrés avait des concentrations d'ETR plus élevées que le muscle et le gras, tandis que les tissus osseux et rénaux présentaient généralement des concentrations intermédiaires. En outre, les tendances observées pendant l'analyse des anomalies du cérium sensibles aux transformations d’oxydoréduction ont suggéré que ces anomalies peuvent servir de biomarqueur dans l’exposition aux ETR et leur transformation biologique. Dans l'ensemble, cette étude présente une bioaccumulation et un fractionnement d’ETR spécifiques aux espèces et aux tissus, ce qui justifie des recherches plus approfondies afin de comprendre les facteurs de contrôle du comportement d’ETR au sein des espèces animales. Ces résultats peuvent également servir à établir des lignes directrices nationales d’ETR, et servir de référence dans les futures études de biosurveillance.

Mots-clés : éléments terres rares, lanthanides, bioaccumulation, biodistribution, organes, subarctique, anomalies de cérium

Abstract

A gradual increase in the release of rare earth elements (REE) to the environment has been reported, as well as a continuous rise in their global demand. New REE exploration projects have been initiated in multiple countries, including within Canada where REE deposits are frequently located in northern regions. This project stems from a community-based environmental program between researchers and the Inuit community of Kangiqsualujjuaq in the context of a prospective REE mine in Nunavik. To address the limited review of REE distribution in natural environments, the present study reports the current REE values for sediments, lichens, and multiple animal species from terrestrial, freshwater and marine ecosystems of the eastern Canadian subarctic. Results suggest that all matrices have the capacity to accumulate REE, though a biodilution across taxonomic groups is noted. Also, a study of animal tissue samples from country food species demonstrated that liver tissues have significantly higher concentrations of REE than the muscle and blubber, with bone and kidney tissues typically presenting intermediate concentrations. Further, the analysis of redox-sensitive cerium anomalies supported the presence of tissue-specific mechanisms that suggest these anomalies may serve as a biomarker in REE exposure and biological transformation. Overall, this study presents a species- and tissue- specific bioaccumulation and fractionation of REE that warrants further investigation to better understand the controlling factors of REE processing within animal species. The results may additionally serve in the establishment of national REE guidelines for environmental health and human consumption, and act as a reference in future biomonitoring studies.

Keywords: rare earth elements (REE), lanthanides, bioaccumulation, biodistribution, organs, subarctic, cerium anomalies

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List of Acronyms and Abbreviations

ADFG	Alaska Department of Fish and Game
Ag	silver
AMDE	atmospheric mercury depletion events
ANOVA	analysis of variance
Br.	Breast, of animal muscle
BMF	biomagnification factor
Ca	calcium
CBEM	community-based environmental monitoring
Cd	cadmium
Ce	cerium
Ce/Ce*	cerium anomaly
CeO_2	cerium oxide
CESD	Commissioner of the Environment and Sustainable Development
Chl-a	chlorophyll-a
cm	centimeter
CO_3^{2-}	carbonate ion
COSEWIC	Committee on the Status of Endangered Wildlife in Canada
Cr	chromium
CVRB	*Comité de valorisation de la rivière Beauport*
Dfc	climate type
DIC	dissolved inorganic carbon

DL	detection limit(s)
DOC	dissolved organic carbon
dw	dry weight
EC_{50}	effective concentration at 50% of the maximum response
ECCC	Environment and Climate Change Canada
EPA	Environmental Protection Agency
ETR	*éléments des terres rares*
Fe	iron
g	gram
GI	gastrointestinal
GRB	George River Basin (study area)
HCl	hydrochloric acid
Hg	mercury
H_2O_2	hydrogen peroxide
HNO_3	nitric acid
HREE	heavy rare earth elements
H_2SO_4	sulfuric acid
ICP-MS/MS	inductively coupled plasma mass spectrometry
IUPAC	International Union of Pure and Applied Chemistry
K	potassium
kg	kilogram
km	kilometer
km^2	square kilometer

KRB	Koroc River Basin (study area)
KRG	Kativik Regional Government
L	litre
La_N/Yb_N	ratio of normalized concentrations of lanthanum to ytterbium
LOI	loss on ignition
LREE	light rare earth elements
LREE/HREE	ratio of concentrations of light to heavy rare earth elements
m	metres
m^3	cubic metres
MΩcm	megaohm centimeters
MDDEFP	*Ministère du Développement durable, de l'Environnement, de la Faune et des Parcs*
MDL	method detection limit
MeHg	methylmercury
mg	milligram
mL	millilitre
mm	millimeter
Mn	manganese
MREE	middle rare earth elements
MRI	magnetic resonance imaging
n	sample size
NASC	North American shale composite
ND; nd	not detected
ng	nanogram

nmol	nanomole
NOAA	National Oceanic and Atmospheric Administration
NR Can.	Natural Resources Canada
PAAS	post-Archean Australian shale
Pb	lead
PFS	prefeasibility study
PSI	pound per square inch
Pt	platinum
R^2	R-squared; coefficient of determination
Ra	radium
REE	rare earth elements
REE_N	normalized rare earth elements (to a reference value)
REO	rare earth oxide
s	second, as in unit of time
Sc	scandium
SD	standard deviation
SH	thiol
SI	supporting information, or supplementary information
SO_4^{2-}	sulfate ion
SPC	specific conductance
Temp	temperature (°C)
Th	thorium
Th.	Thigh, of animal muscle

THg	total mercury
Ti	titanium
TN	total nitrogen
TP	total phosphorus
U	uranium
ug	microgram
um	micrometer
uS	microsiemen
USGS	United States Geological Survey
WDDEC	Wildlife Division Department of Environment & Conservation
ww	wet weight
Y	yttrium
Zn	zinc
α	significance level
∂C^{13}	stable carbon-13 isotope
ΣREE	sum of REE concentrations; total REE concentration
% MeHg	percent methylmercury out of total mercury concentration
$\pm$	addition or subtraction; plus or minus

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Chapter 1 – Introduction

1.1 Project Context

The REE are naturally present at background levels, however their increased exploitation and use in various applications have raised questions regarding their release to the environment. Discussions of REE mining projects can cause concerns within communities residing in proximity to the proposed mining sites due to uncertainties relating to the potential outcomes of these activities on the surrounding regions. The prospective REE mining project of the Strange Lake deposit, located in Nunavik within the Canadian subarctic, raised concerns within the Inuit community of Kangiqsualujjuaq upon its proposal (Gérin-Lajoie et al., 2018). This led to collaborations between the community and researchers through the development of a community-based environmental monitoring (CBEM) program from which the current project originates. Driven by community concerns, this thesis will contribute to the currently limited understanding of REE bioaccumulation and behaviour in largely undisturbed ecosystems, with a focus on biotic species important to northern populations and in biomonitoring studies.

1.2 Literature Review

The following literature review addresses the main topics considered within the present study and serves as an introduction to each. First, the use of community-based environmental monitoring in the context of a collaboration with Indigenous communities is addressed, including the development of a project with the Inuit community of Kangiqsualujjuaq. Second, REE mining is explored both from a global point of view, such as the supply of REE and availability concerns, and from a more regional scale through the study of the Strange Lake deposit. Next, relevant background information on the geochemical properties of REE is provided, followed by current knowledge of REE distribution, speciation, and bioaccumulation in various environments, alongside identified knowledge gaps. The study of REE accumulation is further supplemented using biomonitoring species common to atmospheric and aquatic monitoring. Finally, while the REE are often considered to be a relatively similarly behaved group of metals, the anomalies of redox-sensitive REE are introduced, with a focus on the recent findings of cerium (Ce) anomalies in biota.

1.2.1 Community-based Environmental Monitoring

Environmental monitoring involves the analysis of environmental quality and its change over time that can focus on diverse matrices, such as vegetative and animal species, air, snow, ice, or surface waters, among others (CESD, 2011; Gov. of Canada, 2020). Data acquired through these initiatives is used in various domains, such as for the tracking and modeling of contaminants, in risk assessments, and to act as a reference in the determination of different strategies and policies (CESD, 2011; Gov. of Canada, 2018). In northern scientific research, increasing interest is being placed on the study of environmental change (Brunet et al., 2014), which these subarctic and arctic systems are particularly susceptible to (Ford et al., 2021). Local communities in these regions experience added pressures due to resource exploitation and food insecurity (The Communities of Ivujivik et al., 2012; Egeland et al., 2013; Stern & Gaden, 2015). Implementation of community-based environmental monitoring (CBEM) puts a focus on the involvement of the communities directly impacted by such environmental changes. CBEM aims to include Indigenous

Peoples in multiple levels of these monitoring programs, such as in program formation, sample collection and/or the interpretation of results, alongside researchers and other involved institutions (Herrmann et al., 2014; e.g., Gérin-Lajoie et al., 2018; Reed et al., 2020).

Though representation of community involvement is currently limited in studies (Brunet et al., 2014), various advantages of CBEM have been suggested. First, there is the incorporation of local and traditional knowledge, which can strengthen field observations and offer different perspectives in result interpretation (Herrmann et al., 2014; Outridge et al., 2015; Reed et al., 2020). Second, community participation in these often-remote regions can facilitate a year-round data collection (Gérin-Lajoie et al., 2018), while also potentially lowering field work costs (Fry, 2011). Further, these collaborations may improve awareness and community engagement in environmental monitoring (Danielsen et al., 2013; Herrmann et al., 2014). In fact, previous studies have demonstrated the implementation of successful CBEM programs in the Arctic, such as a collaboration with Inuit from the community of Pangnirtung (Nunavut, Canada) during a long-term whale study that was effective in terms of addressing research objectives (e.g., efficient data collection, long term sampling) and for local growth (e.g., employment opportunities, technical skill development) (Young et al., 2022). However, there have also been potential concerns relating to the methods in which CBEM programs are implemented (Reed et al., 2020). Additionally, uncertainties regarding CBEM project sustainability and inconsistencies in sampling methods have been stated (Fry, 2011; Herrmann et al., 2014). Altogether, CBEM programs aim to take a collaborative approach to scientific research and support the exchange of data between parties (Gov. of Canada, 2018), that overall may improve research conducted in these northern regions.

1.2.1.1 The IMALIRIJIIT Project

A CBEM program focused on northeastern Nunavik (eastern Canada) was put in place in 2016 and consists of a long-term collaboration with the Inuit community of Kangiqsualujjuaq. This program, named IMALIRIJIIT, which translates to “Those who study water”, came about when residents responded to a message from researchers, bringing forth their desire to conduct independent research to address their concerns over the proposed Strange Lake REE mining project within the George River basin (GRB) (Gérin-Lajoie et al., 2018). The community members were heavily implicated in the development of project objectives (detailed in Section 1.3), which centered around the potential outcomes of mining activities within the region, and possible effects on environmental health that may impact their traditional activities of hunting, fishing, and gathering (Gérin-Lajoie et al., 2018; Dubois et al., 2019), and transportation/land access (Boisjoly et al., 2015). Throughout the project, local hunters and experts have also been essential in the collection of animals samples. To facilitate this process, ensure a consistency in methodology, and acquire pertinent collection details, sampling protocols and kits were provided in both English and Inuktitut, and financial compensation was also given (Gérin-Lajoie et al., 2018). Land Camps were also founded in the context of this collaboration, which further strengthened the relationships of those involved (Dubois et al., 2019). The camps included activities that centered on teaching both youth and adult participants about field methods and involving them in data collection, encouraging interest in performing land-based science and supporting the exchange of traditional knowledge (Gérin-Lajoie et al., 2018; Dubois et al., 2019). To further the sharing of information, annual scientific reports prepared by researchers were presented to community members, which included the results from analysis of field samples. Sections of the 2021 IMALIRIJIIT Scientific Report that are relevant to this Thesis are provided in Annex B.

1.2.2 REE Mining Overview

The proposed REE mining project in the George River Basin, Nunavik, (Figure 1) is one example out of the 18 or so advanced REE projects currently in discussion in Canada. Of these, one is actively in production since 2021 (i.e., Nechalacho Project, Northwest Territories; Vital Metals, 2020), 12 are in various stages of active study, and the remainder are on hold at various stages of study (NR Can., 2022). REE resource exploitation in Canada will contribute to the supply of these materials, for which there has been a continuous increase in the global demand for over the past decade, and growth projections show that no break in this trend should be expected (Alonso et al., 2012). The importance of a reliable availability of REE is demonstrated by their wide variety of uses, such as in magnets, as catalysts (e.g., petroleum industry, automobiles), for polishing, in the medical and agrochemical industries, and more (Balaram, 2019; Abdelnour et al., 2019; NR Can., 2022). The REE are also considered 'technologically critical elements' due to their applications in electronics and other technologies, and are especially known for their key role in 'clean' energy products, such as in hybrid or electric vehicles, wind turbines, energy-efficient lighting, among various others (Alonso et al., 2012; Balaram, 2019). For the past few decades, China has dominated the supply and processing industries, such that from 2010 to 2021 the Chinese supplies have accounted for between 56% and ~98% of the global rare earth oxide[1] (REO) production (annual averages calculated from the USGS Mineral Commodities Summaries). Further, China is also thought to host at least 80% of the world's reserves of heavy REE (HREE; defined in Section 1.2.3), which are in high demand (Huang et al., 2015). To a lesser extent, other countries, including the United States, Myanmar and Australia, have also had some production of REE (USGS, 2020). However, this domination of the market by China can make the REE supply vulnerable, as there have been reports of exportation tariffs and restrictions, and sudden changes in costs of these products (Jacoby & Jiang, 2010; Alonso et al., 2012; Humphries, 2013; Haque et al., 2014). Other factors contributing to supply concerns relate to the difficulties in efficiently, cost-effectively, and sustainably extracting and separating the REE due to their unique and similar chemical properties (Alonso et al., 2012; Huang et al., 2015), further discussed in Section 1.2.3.1.

Due to supply and demand pressures, it is of interest to other countries that contain REE deposits to begin exploration as well. In fact, an increase in world production is forecasted for the coming decades (Wang et al., 2020). Estimates for how much of the world's REE deposits the Canadian reserves of advanced projects (14 million tonnes REO, NR Can., 2022) account for tend to vary between sources, as exact amounts are difficult to determine due to the variability of host minerals and richness in which the REE are found within these deposits (Chakhmouradian, 2014). For example, some sources have stated Canadian deposits account for up to about 1-10% of global reserves, depending on calculations (USGS, 2022), while others estimate this amount is closer to

[1] Rare earth oxides (REO) are frequently discussed in the context of REE deposits and production as the rare earths strongly associate with oxygen and form these compounds (EPA, 2012).

30% (Chakhmouradian, 2014). Of particular interest is the presence of minerals containing the highly sought after HREE within certain Canadian deposits (Williams-Jones et al., 2012; Humphries, 2013). Important to note is that the REE deposits in Canada are often located in the more northern regions of the country, in proximity to Indigenous communities.

Some considerations in REE mining are the radioactive elements uranium (U) and thorium (Th) that are often incorporated into minerals associated with REE deposits; where this is the case, attention must be paid to their management (EPA, 2012; Haque et al., 2014). These radioactive metals, in addition to the REE and heavy metals (e.g., Pb, Zn, Cd), may be found in trace amounts in the waste rocks or tailings (Migaszewski & Galuszka, 2015). The methods for REE processing depend on various factors such as deposit type, host minerals, and available technologies; though in general the use of strong acids (e.g., hydrochloric acid [HCl], sulfuric acid [H_2SO_4]) is common, as is the consumption of large amounts of water, energy, and other reactive chemicals (e.g., strong bases, chlorides, oxides) (Haque et al., 2014; Huang et al., 2015). These activities bring about various concerns including the release of heavy metals, REE, and radioactive materials through dust particles to the atmosphere; to nearby surface waters through surface runoff of exposed rocks; and leaching of these metals in addition to strong chemicals into soils and groundwaters (EPA, 2012; Weng et al., 2013; Haque et al., 2014; Huang et al., 2015; Migaszewski & Galuszka, 2015; Yin et al., 2021). Environmental assessments of regions prior to mining production, in addition to monitoring post-opening, is therefore important in assuring the health of ecosystems are maintained. To note, mining companies involved in Canadian projects have been cited in assuring efforts are being taken to put environmentally sustainable processes in place, with plans for the majority of post-mining processing to occur off-site at designated plants (Avalon, 2021; Torngat Metals, 2021), as is the plan for the Strange Lake REE project in Nunavik.

1.2.2.1 Strange Lake REE Deposit

Plans for the Strange Lake REE mine puts its location within the GRB (Boisjoly et al., 2015), with Kangiqsualujjuaq located approximately 280 km to the northwest (Figure 1). Even though individual Indigenous villages are located at a distance from the proposed mine site, the Inuit, Naskapi and Innu territories extend throughout the basin, and therefore impacts on these Indigenous lands are possible. The area is also in a vegetation and permafrost transition zone (Figure 1), with climate change subjecting the region to permafrost thaw and affecting the landscape, such as through the formation of thermokarst lakes (Allard et al., 2012).

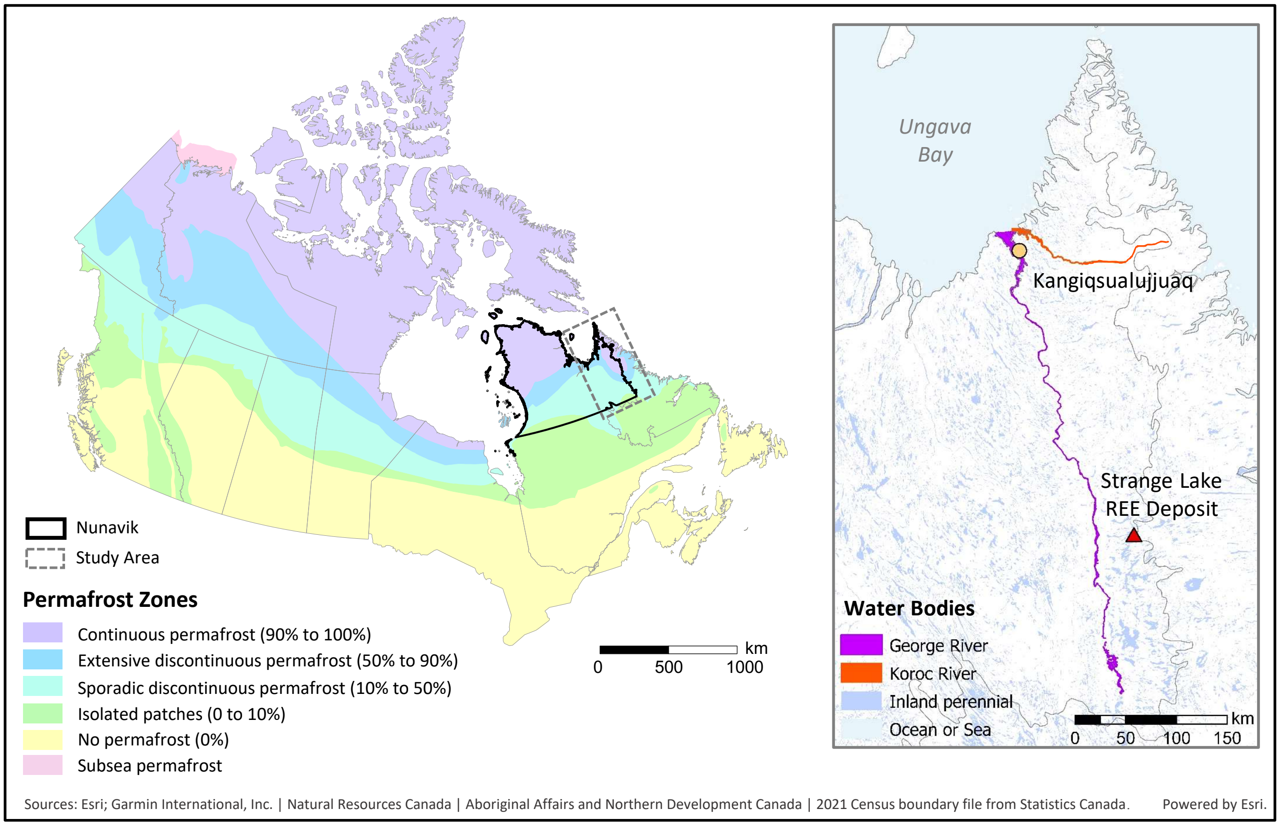

Figure 1. – Map of permafrost zones across Canada. The village of Kangiqsualujjuaq and the proposed Strange Lake REE mine location are depicted in the panel zoomed in on the study area. Created in ArcGIS software by Esri.

Originally presented by Quest Rare Minerals Ltd., the Strange Lake project has since been taken over by Torngat Metals Ltd. who state they are currently in piloting and engineering phases of operation (Torngat Metals, 2021). In the initial prefeasibility study, for which an updated version was not available, the construction of an open pit mine and its facilities were planned to be in close proximity to Lake Brisson (Boisjoly et al., 2015). Within the report, authors state that a majority (~80%) of the mine area falls within the drainage basin of Lake Brisson, which reportedly has a level of connection to the George River about 100 km downstream. This operation has an expected lifespan of 30 years for extraction of REE from the B-Zone deposit, which contains REE in high-grade peralkaline granitic pegmatites and aplites (Gysi & Williams-Jones, 2013; Boisjoly et al., 2015). The minerals of interest are primarily allanite-(Ce), gadolinite-(Y) and kainosite-(Y), which are concentrated in REE, especially HREE, due to remineralization of the granitic pluton during hydrothermal processing (Williams-Jones et al., 2012; Gysi & Williams-Jones, 2013). The grade of the ore being processed will likely depend on the age of the operation, with higher concentrated ores in the beginning stages and lesser concentrated ores in the final stages, varying on average from 1.2 weight % REO down to 0.9 weight % REO, respectively (Boisjoly et al., 2015).

1.2.3 Rare Earth Elements

Particular attention is given to the REE due to community concerns related to the proposed Strange Lake REE project, in addition to the knowledge gaps regarding the natural distribution, behaviour and bioaccumulation of REE in northern ecosystems, particularly within animal species and their tissues. To address these topics, a general understanding of REE is necessary, including their chemical properties, important interactions and controlling factors on their behaviour, and their main species in the environment.

The REE are composed of the lanthanides (or, lanthanoids), which are as follows, in order of increasing atomic number: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu), in addition to the element yttrium (Y) as it shares many chemical properties with this group and therefore they are often associated together in nature (IUPAC, 2005; EPA, 2012). In some discussions, scandium (Sc) is also considered as part of the REE, though the present study excludes it. The REE are frequently referred to as either part of the light REE (LREE) or the heavy REE (HREE) and can be divided into these two categories based on their relative atomic masses and electron configurations, with LREE being elements from La to Gd, and the HREE going from Tb to Lu and including Y (Van Gosen et al., 2017). However, the defining point between the two groups is not always consistent between studies (Haque et al., 2014) and at times the REE are considered as three groups with the addition of the middle REE (MREE) (McLennan, 2018), which again varies in its constituents depending on the study.

All individual REE are naturally occurring in the environment except for Pm, which is a radioactive, instable element (Haque et al., 2014; Migaszewski & Galuszka, 2015). Compared to other elements, the REE are found in lower quantities within the Earth's crust relative to the major elements (e.g., oxygen, silicon, aluminum) and metals such as iron (Fe), titanium (Ti) and chromium (Cr), but exist in greater quantities than others like silver (Ag), mercury (Hg), and platinum (Pt) (CRC Handbook, 2012 as presented by Labbé & Lefebvre, 2016). The use of the word 'rare' in their name therefore does not reflect their abundance, but rather considers the difficulty in extracting them due to the complex processes required, and the infrequency in which they are concentrated in ores (EPA, 2012; Gonzalez et al., 2014; Migaszewski & Galuszka, 2015; Balaram, 2019).

1.2.3.1 Chemical Properties of REE

The relatively similar geochemical behaviour of the REE is due to the many properties that they share, contributing to the common way in which we refer to them as a group. In general, the REE are quite insoluble, however their solubility increases with decreased pH (i.e., more acidic), lower water conductivity (e.g., freshwater), and increased temperatures (Sholkovitz, 1995; Gonzalez et al., 2014). There are however slight deviations in properties from one element to the next in the periodic table. First, while all REE have a stable trivalent charge (i.e., REE^{3+}), certain REE also have a second stable valency state (i.e., Ce^{4+} and Eu^{2+}) (Manini, 2017) that will be discussed in greater detail in Section 1.2.4. Second, the REE follow a unique trend titled the "lanthanide contraction".

This effect refers to a decreasing ionic radius with an increasing atomic number, meaning that the heaviest REE (i.e., Lu) will have the smallest radius and vice versa (Nozaki, 2001; Cotton, 2006; McLennan, 2018). In addition, this contributes to the tendency of the REE to display differences in their relative behaviour within the environment (Nozaki, 2001; EPA, 2012; Migaszewski & Galuszka, 2015), especially notable between LREE and HREE (Arienzo et al., 2022; e.g., Cantrell & Byrne, 1987; Sholkovitz, 1995; Sneller et al., 2000). Their electron configuration is what causes this group of elements to display distinct properties such as strong magnetic abilities (EPA, 2012; Van Gosen et al., 2017), high reactivity, and the ability to act as good reducing agents (Manini, 2017; Gwenzi et al., 2018), explaining their widespread applications (summarized in Section 1.2.2). Further, the REE act as Class A metals, which are hard acids that preferentially form ionic bonds with hard bases like hydroxide, sulphate, and carbonates (Pearson, 1963; Mason, 2013; EPA, 2017). Overall, there is some predictability in the behaviours of REE due to these highlighted properties, however their response to various environmental conditions must be further explored to better understand their distribution, speciation, and availability within ecosystems.

1.2.3.2 Global REE Cycling

There is a general knowledge of the global distribution of REE, which is understood in the literature to different degrees depending on the environment or matrix of study, and is also often very dependent on the specific or unique characteristics of each local environment. The main pathways by which the REE are transported and modified that have been identified are presented in Figure 2. This includes information relevant to the terrestrial, atmospheric, freshwater, and marine environments. The purpose of this diagram is to offer a summary of the global REE cycling and is not an exhaustive presentation of the species or movements of REE.

Figure 2 was completed with information from the selection of sources already referenced throughout the current literature review, with particular interest in diagrams presented by: El-Ramady (2010); EPA (2012); Migaszewski & Galuszka (2015); Khan et al. (2017); Deng et al. (2017); Gwenzi et al. (2018); Balaram (2019); Piarulli et al. (2021). Information was also obtained from the following references, not cited elsewhere: German et al. (1990); Sholkovitz (1992); Dia et al. (2000); Aubert et al. (2001, 2006); Dubinin (2004); Censi et al. (2010); Suzuki et al. (2011); Zhu et al. (2016); and Radomskaya et al. (2018).

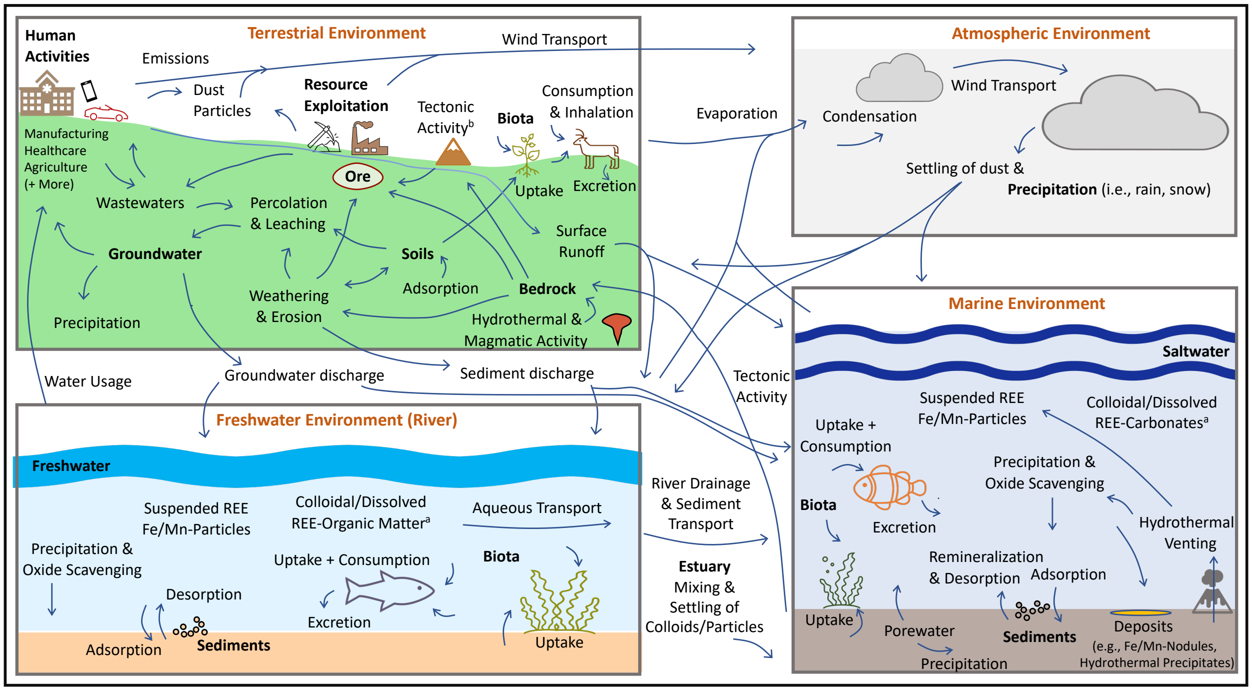

Figure 2. – Diagram summarizing the main pathways in REE global movement, with a focus on environments referenced in the present study. Not to scale. [a] Speciation of REE is given in phases where a major species is generally accepted in the literature. [b] Tectonic activity includes movement such as orogenesis, rifting, volcanic activity, and other plate-movement induced processes.

1.2.3.3 REE Distribution Within Natural Ecosystems

The REE have been studied to a greater degree within domains such as geology (Gonzalez et al., 2014) and industry (Migaszewski & Galuszka, 2015), however the interest for studying REE within ecosystems, especially in terms of biotic species, has begun receiving more attention and concern in recent years (Li et al., 2013; Piarulli et al., 2021). This interest stems from the rise in extraction and uses of REE, which has led to their increased release into the environment without an extensive knowledge of what the effects of this could be (Riondato et al., 2001; Adeel et al., 2019). In fact, some studies have referred to the REE as contaminants of emerging concern (Migaszewski & Galuszka, 2015; Gwenzi et al., 2018; Wang et al., 2019), further supporting the need for a more comprehensive understanding of their natural distribution, bioaccumulation, and the determining factors in their behaviour and availability to wildlife and humans (Arienzo et al., 2022).

The REE are typically found in low concentrations in natural environments, with their concentrations and bioavailability being dependent on the matrix in question. The soil and sediment matrices are those which contain the highest amounts of REE (Adeel et al., 2019; Benabdelkader et al., 2019), with total concentrations often on the order of approximately 100 to 1000 nmol/g dw in undisturbed locations (Sneller et al., 2000; Gonzalez et al., 2014; e.g., Romero-Freire et al., 2019). The REE content in soils and sediments is influenced by the region's geology, geochemical conditions, and weathering processes, among other factors (Goldstein & Jacobsen, 1988; El-Ramady, 2010; Ramos et al., 2016; Adeel et al., 2019). This favorable association of REE to solid particles is especially true for the LREE (Arienzo et al., 2022), and is attributed to multiple factors. First, the REE are reported to have a strong adsorption to sediments, such as clay particles for LREE (Ramos et al., 2016; Benabdelkader et al., 2019), or scavenging by particulate matter and Mn- or Fe-(oxyhydr)oxides (De Carlo et al., 1998; Bau, 1999; Ingri et al., 2000; Piarulli et al., 2021). Also, the low solubility of REE in aqueous solutions makes them relatively resistant to dissolution from their host rocks (Garcia et al., 2007), and favors their precipitation from solution or their complexation with ligands (Arienzo et al., 2022). Organic ligands are especially important in freshwaters, where REE complexes to organic matter (Matsunaga et al., 2015), or more specifically, with dissolved organic carbon (DOC) (Johannesson et al., 2004; Vázquez-Ortega et al., 2015). The REE have a particularly high affinity for the humic acid component of DOC, which is thought to dominate the dissolved and/or colloidal species of REE in freshwaters, except at very acidic pH (Dupré et al., 1999; Tang & Johannesson, 2003; Pourret et al., 2007; Mason, 2013; Marsac et al., 2013; Matsunaga et al., 2015). As for inorganic ligands, they tend to dominate REE complexation in saltwater environments, where the dissolved fraction is primarily present as carbonate species (i.e., complexed to CO_3^{2-}), which is especially stable for the HREE (Millero, 1992; Sholkovitz, 1995, Gonzalez et al., 2014). In fact, at alkaline pH, any natural waters are expected to have the majority of dissolved REE in carbonate complexes; while acidic waters would be expected to have the dissolved REE present primarily in the free ion form and in sulfate complexes (i.e., SO_4^{2-}) (Wood, 1990; Pourret et al., 2007; El-Ramady et al., 2010). The differences in water physiochemistry and available ligands between rivers and the oceans in which they discharge has a significant effect on REE speciation. This leads to a favorable precipitation of REE within estuaries, primarily for the LREE, with coagulation of the colloidal fraction (Lawrence & Kamber, 2006; Pourret & Tuduri, 2017).

The REE have shown the potential to get accumulated across a range of environments and taxonomic groups, such as in bacteria (e.g., Técher et al., 2020), plants (e.g., Chu et al., 2014), and animals (e.g., Tu et al., 1994). In terrestrial environments, plants can absorb REE in the soil by their roots and from the atmosphere by their leaves (Liang et al., 2014), while organisms are exposed to REE through consumption and inhalation (Redling, 2006, El-Ramady et al., 2010). In aquatic environments, consumers are thought to accumulate REE through their diet (Gonzalez et al., 2014) and absorption through gills (Cardon et al., 2019) and skin (Tu et al., 1994), and plants via roots and their leaves (Redling, 2006; Fu et al., 2014; Xu et al., 2019). Recent studies regarding undisturbed food webs support a biodilution of REE, such that greater concentrations are found at lower trophic levels and decreasing concentrations at higher trophic levels (Amyot et al., 2017; MacMillan et al., 2017). For example, Arctic above-ground plant specimen had average total REE concentrations two orders of magnitude (~100-fold) higher those of caribou muscles, being 1.12 nmol/g, and 0.027 nmol/g, respectively (MacMillan et al., 2017). A similar relationship was also seen in Italy’s Ligurian Sea, with seaweed (12 mg/kg) having mean REE concentrations two orders of magnitude greater than marine fish muscles (0.21 mg/kg) (Squadrone et al., 2019).

For studies on natural concentrations of REE in the environment, a greater focus has been placed on REE bioaccumulation in plant species than in animal species. Further, when comparing across different habitat types, the literature regarding animals primarily involves aquatic species rather than terrestrial animal species, with a predominance for invertebrates and fish (SI of Squadrone et al., 2019). Overall, literature on REE in animals often involves laboratory exposure and toxicity studies with model organisms; or field studies of various matrices in areas that are subject to anthropogenic activity (e.g., REE-rich fertilizers, mining activities, wastewaters) (Migaszewski & Galuszka, 2015; Gwenzi et al., 2018). To keep in mind, it has also been suggested that the REE resulting from certain anthropogenic activities may in fact be in more bioavailable forms than the naturally distributed REE in the environment (Redling, 2006). This further highlights the need for REE bioaccumulation studies in undisturbed regions in order to better understand their natural distribution and background concentrations, previously identified as a knowledge gap (Migaszewski & Galuszka, 2015), while incorporating species from different ecosystems, climates, and tissue types. This, along with an in-depth study of the internal distribution and fractionation of REE upon absorption, would help in assessing the REE's potential exposure to other species and to humans, and may assist in the development of reliable environmental and health guidelines that will become increasingly necessary as the REE are further released to the environment.

1.2.3.4 REE Accumulation Within Biotic Species

In the study of REE bioaccumulation it is also important to consider the partitioning of these elements between the various tissues of an organism, as well as their subcellular distribution. Various plant species have demonstrated a bioaccumulation of REE across their parts, with greater concentrations often reported in the roots than the shoots and leaves (Li et al., 2001; Wang & Liu, 2017). In REE-exposure studies concentrating on the subcellular distribution across plant tissues, REE concentrations were higher in cell walls, followed by the organelles, with the lowest amounts in soluble fractions (Wang & Liu, 2017; Fu et al., 2014; Zhang et al., 2015). Further studies with aquatic plants reported that the main biomacromolecules to which Y associated with were polysaccharides in *Potamogeton crispus* (Xu et al., 2019), or pectin and cellulose in

Nymphoides peltata (Fu et al., 2014). Where multiple animal tissues have been studied from field samples, greater concentrations of REE were reported for the livers (Korda et al., 1977; MacMillan et al., 2019) and kidneys (Squadrone et al., 2020) relative to the muscles or flesh. One example that involves laboratory experiments on carp (*Cyprinus carpio*) under REE-dosed treatments (i.e., Y, La, or Gd) led to an accumulation of these metals across all tested tissues, in decreasing order from internal organs, gills, skeleton, to muscles (Tu et al., 1994). Another consideration is the fraction of accumulated REE that would in fact be bioavailable to the organism itself, as well as to prey. Cardon et al. (2019) performed laboratory experiments looking at the subcellular fractions of Y in model organisms and found varied amounts (0-75%) of Y within presumably metal-detoxified fractions, with this distribution being highly dependent on the species. It was further suggested that the association of Y to subcellular granules may contribute to detoxification of this metal (Cardon et al., 2019). The formation of granules is a process more commonly seen within invertebrates, such as mussels, and these granules contain certain metals as insoluble species that are thought to be metabolically unavailable (Lobel et al., 1991).

1.2.3.5 REE in Animal Health

As REE have recently been considered as contaminants of emerging concern due to their release in the environment from anthropogenic activities, discussions related to their ecotoxicity (Pagano et al., 2015) and potential exposure to food webs have recently increased. It is accepted that to some extent the REE seem to have a hormetic effect on biota, meaning that positive effects are seen at low concentration and negative effects occur at higher concentrations (Pagano et al., 2015; Agathokleous et al., 2018; Técher et al., 2020). In laboratory exposure experiments, toxic effects have been reported at a range of concentrations, though they are typically multiple orders of magnitude greater than those found in natural environments (Malhotra et al., 2020). Some of the effects reported for these studies include developmental and morphological abnormalities (*Danio rerio*, Cui et al., 2012; *Paracentrotus lividus and Arbacia lixula*, Oral et al., 2017*; P. lividus*, Martino et al., 2017; *Escherichia coli*, Técher et al., 2020), a decreased survival (*D. rerio*, Cui et al., 2012), changes in enzymatic functions and suspected cytogenetic issues in various model organisms (reviewed by Pagano et al., 2015), and induction of oxidative stress and tissue damage (e.g., liver, lungs) in REE-dosed rats and mice (reviewed by Pagano et al., 2015b). Due to the similar ionic radii of the REE with the calcium ion (Ca^{2+}), one pathway of accumulation could be through the substitution for calcium ions, such as in bones (Chen et al., 2001; Ramos et al., 2016); and then they could be forming stable REE-containing compounds (Zaichick et al., 2011). Other suggested fates for REE within animals include the association of REE to proteins and the formation of insoluble complexes (Das et al., 1988; Gonzalez et al., 2014); and their accumulation within the nucleus and mitochondria (Huang et al., 2011).

Bioaccumulation of REE in humans has been reported for populations residing in proximity to mining activities (Li et al., 2014), such as in hair, blood, (Zhang et al., 2000; Li et al., 2013), liver (Chen et al., 2001) and bone (Chen & Zhu, 2008; Li et al., 2013); though multiple sources of contamination in these regions is possible, leading to a cumulative exposure. In any case, the main route of REE exposure for humans is reportedly the diet (Li et al., 2013), inhalation of REE containing particles (Liang et al., 2014; Pagano et al., 2015) and various medical procedures (i.e., MRI; Zaichick et al., 2011). Higher concentrations of REE have been reported for waters, soils, air particles, and certain plants in mining areas compared to non-mining areas (Liang et al., 2014). For example, a study by Li et al. (2013) reported REE concentrations significantly greater for vegetable crops from mining regions compared to control sites, however these sites were only separated by a 5 km distance. Overall, the REE do not seem to pose a problem at their naturally low levels, though the effects of REE on animals and environmental health at higher concentrations and under chronic conditions are not fully understood, acting as an area of potential concern (Li et al., 2013; Pagano et al., 2015).

1.2.4 REE Anomalies

While in general the REE tend to behave similarly due to their above-mentioned shared properties, the fractionation of certain REE can lead to the formation of distinct patterns in REE distribution plots (e.g., Fig. 3). The identification of such anomalous behaviour is frequently used to characterize and trace geochemical processes (Skylarova et al., 2017). There is a natural difference in the concentrations of elements in the environment that follows a pattern called the "Oddo-Harkins Effect" (Fig. 3A), in which individual elements with an odd atomic number (e.g., $_{57}$La) have lower concentrations than those with an even atomic number (e.g., $_{58}$Ce) (Cicconi et al., 2021). This creates what is commonly referred to as a 'saw-tooth pattern' in a plot of element versus natural abundance in the Earth's crust. The concentrations of REE are then typically normalized to reference materials in order to create a smooth pattern and better visualize any deviations of individual REE from the expected trend (Lawrence & Kamber, 2006; Tostevin, 2021). To perform this normalization, the concentrations of individual REE are divided by their respective REE concentrations within the reference material. Various reference materials are available in the literature, such as chondritic values, the Post-Archean Australian Shale (PAAS, e.g., Pourmand et al., 2012), and the North American Shale Composite (NASC, e.g., Gromet et al., 1984; Taylor & McLennan, 1985).

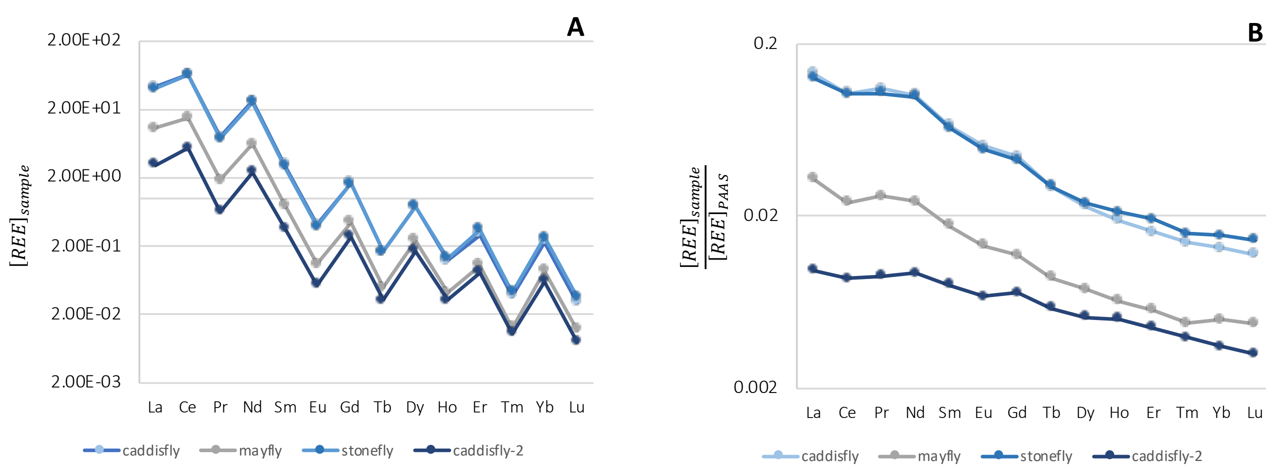

Figure 3. – (A) REE concentrations (nmol/g) and (B) PAAS-normalized REE concentrations in the George River benthic invertebrate samples (log-scaled y-axis). Pm is excluded.

Deviations of individual REE from their expected trend can be visualized on a log-scaled plot of normalized REE values (Fig. 3B). An enrichment in LREE relative to the reference material would be suggested by a downward slope (e.g., Fig. 3B), while an enrichment of HREE would be represented by an upwards slope. The normalized distribution may also demonstrate peaks or dips in the pattern, known as anomalies. For example, a small negative Ce anomaly can be observed in Figure 3B for the benthic invertebrates of the GRB, most visible here in the mayfly pattern. Anomalies can be quantified by use of an equation that compares the normalized concentration of the element of interest to the normalized concentrations of neighbouring elements in the periodic table (i.e., often one to two atomic numbers below and above) (Tostevin, 2021). Further, a positive anomaly is represented by a peak, or a value above 1, while a negative anomaly is represented by a dip, or a value below 1. There are various equations available in the literature for each anomaly calculation (e.g., Akagi & Masuda, 1998; Slack et al., 2004; Lawrence & Kamber, 2006; Tostevin, 2021).

When it comes to REE fractionation, two elements are more likely to behave anomalously than the others: Ce and Eu. This is because both Ce and Eu are redox sensitive due to having stability in two valence states: Ce^{3+} and Ce^{4+}; Eu^{2+} and Eu^{3+} (Manini, 2017). Their valency depends primarily on the redox state of their environment, such that they will lose an electron when they are in oxidizing conditions and gain an electron under reducing conditions (Fig. 4). For example, negative Ce anomalies are commonly found in oxic aquatic environments, such as in surface waters, as these oxygen-rich waters favor Ce in the 4+ state, which is insoluble and will tend to precipitate out of solution (Sholkovitz, 1995; Alibo & Nozaki, 1999; Tostevin, 2021). Ce oxidation on the surface of Fe-Mn (oxyhydr)oxide colloids leads to the formation of negative anomalies that are especially present in seawaters (Sholkovitz et al., 1994; Bau, 1999; Tostevin et al., 2016). Additionally, negative Ce anomalies in ocean waters may be enhanced by the species of Ce within rain and surface river waters, with Ce transported as insoluble particles such as CeO_2 (Akagi & Masuda, 1998). In any case, positive Ce anomalies may therefore be found in the particles themselves (Sholkovitz et al., 1994).

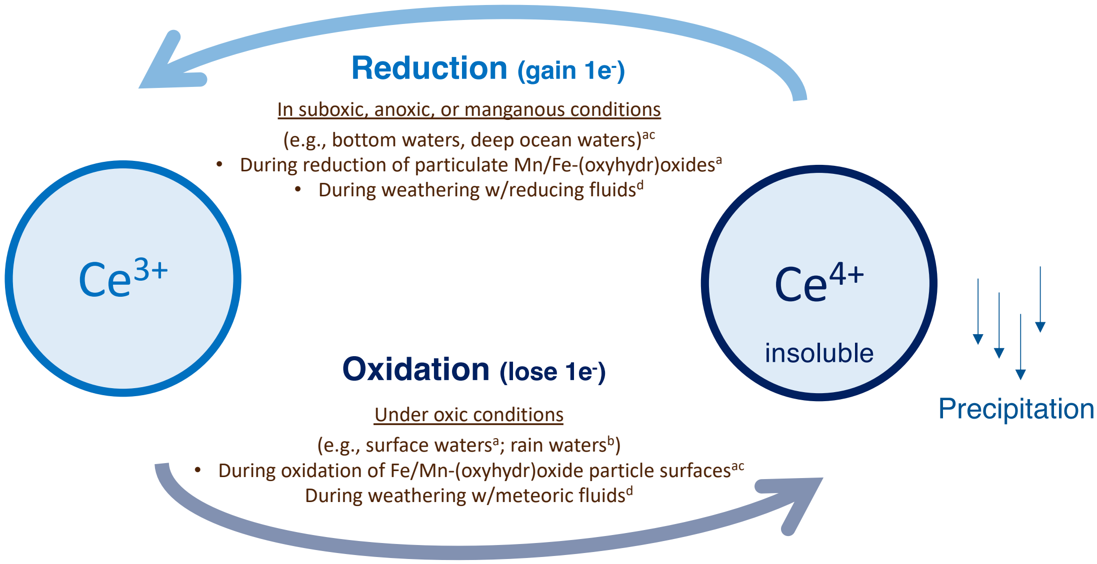

Figure 4. – Simplified graphic of Ce redox cycling with relevant examples of processes involved. [a] Adebayo et al., 2020; [b] Akagi & Masuda, 1998; [c] Wu et al., 2019; [d] Möller, 2002.

1.2.4.1 Cerium Anomalies in Ecosystems

Recent studies have reported a variety of Ce anomalies (Ce/Ce*) across biota that have yet to be fully explained and therefore require further investigation. For example, one study regarding coastal lagoon species from China found variable Ce anomalies between different species of fish (Ce/Ce* averages: 0.75 - 0.95), molluscs (0.73 - 0.94), and crustaceans (0.46 - 1.21), which authors hypothesized may in part be explained by redox state changes upon deposition or enrichment (Wang et al., 2019). Another study found a significant relationship between Ce anomalies in brook trout and stable carbon isotopes (∂C^{13}), that was thought to be caused by differences in productivity between sampling lakes (MacMillan et al., 2017). Some positive Ce anomalies were reported for species of marine fish (Ce/Ce* averages: 1.58-4.30), shellfish (1.62-2.91) and crustaceans (1.81-2.13), thought to reflect a unique mineralization process for the animals relative to sedimentation (Li et al., 2016). Findings of variable Ce anomalies between shells and soft tissues of bivalves led to the hypothesis that the anomalies provide information regarding the source of REE and potential segregation of accumulated Ce (Akagi & Edanami, 2017). In a few other cases Ce anomalies were presented for aquatic species, but no discussion on their potential causes were available (e.g., Yang et al., 2016), or they were solely attributed to the depletion of Ce within seawater (e.g., Figueiredo et al., 2021). Altogether, due to the redox control on Ce and therefore its unique geochemistry relative to the other REE, further investigation into Ce anomalies within biota may provide knowledge on REE mode of actions, cellular mechanisms and conditions, or even REE bioavailability.

1.2.5 Biomonitoring Species

When discussing REE distribution or exposure to organisms and humans, there are certain species which better assist in monitoring the quality of different environments. First, there are a few terms that are important to define: (1) Biomonitors (quantitative), are species that can accumulate a metal (or other) of interest and upon analysis, the measured concentrations are said to be reflective of their exposure in the environment over time; (2) Bioindicators (qualitative), are species or groups of species that provide information about environmental health based on their presence/absence or other qualitative properties (Holt & Miller, 2010; Van der Wat & Forbes, 2015). Measuring metals in biomonitors in the George River Basin will provide insight into environmental health over time, such as for comparison of pre- and post-mining levels.

In aquatic systems, macro-invertebrates are a long-standing, common biomonitoring tool (e.g., Cairns & Pratt, 1993; Bonada et al., 2006), as they accumulate contaminants that reflect the levels in their surroundings (Holt & Miller, 2010), and they have the ability to accumulate them to a high degree, demonstrating a good level of tolerance (Moisan, 2017). Invertebrates are also the prey of many higher-level animals, therefore acting as entry points for contaminants to the food web (Pickhardt et al., 2006; Sizmur et al., 2019). Their contaminant levels increase before the effects are necessarily seen in consumable fish, and so studying these organisms may act as a warning for consumer and human health (Sizmur et al., 2019). The use of benthic invertebrates like stoneflies, mayflies and caddisflies as biomonitors is common in freshwater literature (e.g., Matsuo et al., 2021; Mason et al., 2000), and their presence has been reported in a study of streams and rivers from the Ungava Bay region of Nunavik (Moisan, 2017). As REE are poorly soluble in natural, circumneutral pH waters and are strongly particle reactive (Tang & Johannesson., 2003; Ng et al., 2011), a large portion of the REE present in northern freshwaters may adsorb to the surface of sediment or other particles in the water column and deposit. Therefore, benthic macro-invertebrates could track the presence of contaminants both in the water column and from sediments (Hare et al., 2001). They are further reliable for reflecting the conditions of a particular location due to their limited movements (Parmar et al., 2016). It has also been stated that the sampling of benthic invertebrates does not seem to have significant negative consequences on their source ecosystem (Moisan, 2017).

In terms of studying atmospheric changes, it is common to use moss and lichen species as biomonitors of metal contamination (Leonardo et al., 2011; Van der Wat & Forbes, 2015); there has even been an increase over time in their application within such studies (Abas, 2021). These species are ideal for the purpose of atmospheric monitoring because they acquire their nutrients from the air, as they do not have roots, (Rusu et al., 2006) and therefore can reflect atmospheric concentrations of the contaminant (Van der Wat & Forbes, 2015). They are exposed to air-borne particles containing contaminants, which can deposit on their external structures and accumulate in their tissues (Naeth et Wilkinson, 2008; Van der Wat & Forbes, 2015; Abas, 2021). Other factors that contribute to the biomonitoring property of lichens include their large surface area, high accumulation potential, and their long residence time (Van der Wat & Forbes, 2015). Atmospheric biomonitoring is of interest in the George River Basin due to the concern that potential dust from the mining site could lead to contamination of biota by REE, and radioactive and trace metals. For example, Hasselbach et al. (2005) showed that heavy metal concentrations in moss (*Hylocomium Splendens)* reflected an accumulation from a nearby point source of Pb, Zn and Cd, and these concentrations decreased with distance up to tens of kilometers away. Similarly, an investigation into the use of lichens in detecting the extent of atmospheric pollution from tin plant emissions demonstrated that the selected species (*Canoparmelia texana*) accumulated radionuclides in concentrations up to 25-times the background levels within 2 km from the source, with the highest concentrations at downwind sites (Leonardo et al., 2011). The current study had the opportunity to monitor lichens prior to the introduction of a mining disturbance, and during a time of significant climate change, including warming temperatures, permafrost degradation, and changing vegetation (Box et al., 2019).

1.3 Objectives

The onset of REE exploration projects in northern regions, including within Canada, brings with it a level of concern for communities that rely on the health of nearby resources. Additionally, the increase in extraction and use of REE in a wide variety of applications has led to the release of these emerging contaminants from their deposits into the environment. These factors contribute to the need for a greater knowledge of REE distribution and a comprehensive understanding of the behaviour of these metals in order to better predict their fate in the environment, including their bioaccumulation and toxicity in aquatic and terrestrial biota, and whether they may become increasingly bioavailable to humans. The objectives presented herein were developed in the context of the CBEM project with the Inuit community of Kangiqsualujjuaq in subarctic Eastern Canada. The overall goal was to respond to concerns regarding REE exploration within the GRB and contribute to the enrichment of scientific knowledge regarding REE in natural, northern environments.

1.3.1 Objective 1

The first objective was to establish a reliable database of REE concentrations in the GRB prior to the commencement of production at the proposed Strange Lake REE mine. This study offers the unique opportunity to acquire background concentrations of metals in a relatively undisturbed area that will be subject to influences from both climate change and resource exploitation events, addressing the previously identified knowledge gap stating the need for REE baseline concentrations in Canada (Yin et al., 2021). This objective aimed to include field samples from multiple matrices in order to gain a comprehensive assessment of the current levels of REE in the region. Where feasible, sampling also aimed to acquire specimen from across a wide range of the GRB, including around Strange Lake and with a focus on regions near to the community that resides in the basin. In support of future environmental monitoring projects in northern climates, a goal within the context of this objective was to collect background data for atmospheric and aquatic biomonitoring species, being lichens and benthic invertebrates, respectively.

1.3.1.1 Hypothesis 1

The REE are expected to be present in low concentrations within the GRB, respective of the sample matrices, that are comparable to other studies which focus on ecosystems without sources of contamination. This is supported by the knowledge that the study area is in a relatively undisturbed region, with only the northern community of Kangiqsualujjuaq as a source of significant human activity. To note, comparable studies are limited, especially in terms of those with biotic samples from subarctic or arctic environments.

1.3.2 Objective 2

The second objective was to complete an in-depth study of REE accumulation patterns in a widespread subarctic region. This investigation was performed by the collection and analysis of various specimens from the field. Current knowledge gaps exist regarding the distribution of REE in the environment from uncontaminated regions, in particular for northern systems. This study allowed for a comprehensive assessment of REE bioaccumulation at presumably low environmental levels by examining various species from multiple ecosystems of the same region. With a focus on the GRB, the Koroc River Basin (KRB), and nearby regions of the Ungava Bay (Figure 1), REE distribution was addressed in adjacent terrestrial, freshwater, and coastal marine ecosystems. It also offers the first source of information for certain species not yet reported in REE literature (e.g., biofilm, Arctic sculpin, bearded seals); and supplements existing literature for species previously studied, but where data is missing for select tissues (e.g., seal blubber, ptarmigan digestive tract contents; kidneys for multiple species). The study further helps address the knowledge gap regarding REE accumulation in an uncontaminated environmental exposure by providing the first known data for REE concentrations in bones of wild animals. This is of interest due to the similar ionic radius of Ca^{2+} and REE^{3+}, potentially facilitating REE uptake through the same channels (Chen et al., 2001).

First, this objective aims to address REE bioaccumulation within the different ecosystems studied by analyzing specimen across a range of trophic levels. This goal includes the determination of whether the bioaccumulation of REE in aquatic species is dependent on ecological zones, such as by the comparison of benthic and pelagic species; and whether it is influenced by habitat type, performed through the analysis of both saltwater and freshwater species. Additionally, a particular focus was placed on the study of animal species important to northern communities, as no consumption guidelines are currently in place for the REE, demonstrating the need for a greater understanding of the fate and current levels of REE within animal tissues. Secondly, the goal of determining the intra-species bioaccumulation patterns was studied by testing various animal tissue subsamples of interest, such as muscle, liver, kidney, bone, and blubber, where available. The CBEM program was essential in meeting this objective as it supported the collection of animal specimens by local hunters and fishermen and allowed for field sites to be concentrated in areas frequently accessed by the community.

1.3.2.1 Hypothesis 2

The REE are expected to display a biodilution across each ecosystem, meaning decreasing concentrations with increasing trophic level, as reported recently for Arctic (MacMillan et al., 2017) and temperate food webs (Amyot et al., 2017). In a related hypothesis, the REE may be present in higher concentrations in benthic species, due to the favored association of REE with the solid phase (Gonzalez et al., 2014). This relationship has previously been noted in a couple of studies on fish species from China (Guo et al., 2003; Yang et al., 2006) and freshwater fish from Washington (Mayfield & Fairbrother, 2015). Further, the freshwater fish may display greater bioaccumulation of REE compared to the marine fish species. This would be supported by the expectedly higher concentrations of REE in freshwater than saltwater, as a large portion of dissolved and colloidal REE from rivers is removed in estuaries due to the changes in water physicochemical conditions (Pourret & Tuduri, 2017). This trend between species from different aquatic habitats has been observed in a study focused on fish species from the Tokyo Bay region, which proposed REE dilution in the marine system as one potential explanation (Yang et al., 2006).

Additionally, a greater bioaccumulation of REE within internal organs relative to muscle tissues is expected for all animal species studied herein. In particular, a greater accumulation of REE is hypothesized for the liver tissues, which have demonstrated elevated concentrations relative to muscles in various Arctic species (MacMillan et al., 2017), two fish species in Washington (Korda et al., 1977), and in feed-supplemented bulls (Schwabe et al., 2012). This is further supported by the knowledge that the liver, along with the kidneys, are often considered organs that act in metal detoxification within animals (Squadrone et al., 2020) and may therefore play an important role in the processing of REE within the body. Further, the bone is also expected to be a tissue that can accumulate a high concentration of REE because of the reported substitution of Ca^{2+} by REE^{3+} due to their similar ionic radii (Zhu et al., 2005; Gonzalez et al., 2014).

1.3.3 Objective 3

A subset of REE studies report not only the concentrations of REE, but also the fractionation between light and heavy REE, and to a lesser extent, their anomalies. Currently there exists unexplained variability in these values across studies, and a limited understanding has been demonstrated regarding the cause of such fractionation. Due to the large scale of the present study, it aims to provide some of the first accounts of patterns in REE fractionation, and hopes to put forth possible explanatory factors. The third objective was therefore to investigate the relative behaviour of certain individual REE, or REE groups, to uncover potential influencing factors on inter- and intra-species bioaccumulation trends. This was first addressed by evaluating the relative concentrations of LREE and HREE groups, such as with the analysis of LREE/HREE ratios. Second, a focus was placed on the redox sensitive elements, specifically through calculation of Ce anomalies. By comparing the ratios and anomalies in vertebrate tissues to those in sediments and low trophic level taxonomic groups (e.g., lichen, biofilm, benthic invertebrates), a deviation from values for the latter would likely be suggestive of ecological or biochemical influences on vertebrate REE uptake and transformation. Overall, the following hypotheses were prepared in consideration of factors that may influence REE bioaccumulation, such as the slight differences in electrochemical properties between REE (i.e., ionic radii, oxidation states, electron configuration; see Section 1.2.3.1), an organism's environment and ecology, and on the specific mechanisms of the vertebrates' studied tissues. To note, due to the novelty of this research topic, there are limited field studies that discuss REE ratios and anomalies from which to form the basis of the following hypotheses. The data acquired will therefore present first accounts of Ce anomalies in a variety of northern species and offers insight into REE fractionation through the study of Ce anomalies in multiple tissues of animal species.

1.3.3.1 Hypothesis 3

It is hypothesized that a difference in LREE/HREE values and Ce anomalies would be seen between species, especially those from different ecosystems due to the changes in environmental conditions, REE speciation and availability within each. In general, the LREE/HREE ratio was expected to be significantly greater than 1 across all taxonomic groups due to the naturally higher concentrations of the LREE in the environment (Van Gosen et al., 2017). This is also supported by studies that have demonstrated LREE/HREE values upwards of approximately 3.0 for plant and/or animal species (Wang et al., 2019; Squadrone et al., 2019). To keep in mind however is the variability between values from the several relevant studies (e.g., compared to Yang et al., 2016; Li et al., 2016), which limits the predictability of ratios for the present research. Additionally, in regard to the Ce anomalies, this expectation is supported first by the findings that Ce anomalies in brook trout seemed to depend on habitat conditions (MacMillan et al., 2017). Further, negative Ce anomalies are expected primarily for aquatic organisms as Ce is more sensitive to oxidation and subsequent precipitation from the water column than its neighbouring REE. In support of this, negative Ce anomalies have been reported by a few authors investigating aquatic specimen (Wang et al., 2019; Figueiredo et al., 2021). Overall, certain studies (e.g., Agnan et al., 2014; Li et al., 2016) presented Ce anomalies or trends not consistent with the present hypothesis. It should therefore be stated that variability in values presented in a small number of field studies limits the predictability of results for Ce anomalies in biota.

Finally, fractionation of REE is also predicted to differ between the studied tissues of each animal species. For example, greater LREE/HREE ratios (>1) have been reported for fish kidney compared to the liver and muscle (<1), which suggested a higher affinity of the LREE for kidney tissues (Squadrone et al., 2020). Intra-species anomalies have not been reported in the REE literature for different vertebrate tissues. However, the hypothesis is based on the knowledge that some unique processing of REE within an organism relative to the environment's sedimentation has been suggested (Li et al., 2016). Additionally, a field study investigating various bivalve species reported Ce anomalies in the soft tissues, without significant Ce anomalies in the secreted shells (Akagi & Edanami, 2017), demonstrating a difference in anomalies between body compartments.

1.3.4 Supplemental Objectives

An additional objective came from the collaboration between researchers and the community of Kangiqsualujjuaq, which was to determine the levels and speciation of mercury (Hg) present in the studied matrices. Mercury is a trace metal of particular concern in arctic and subarctic environments due to long-range transport and subsequent year-round atmospheric deposition of elemental Hg (Hg^0), with some addition by other processes such as the seasonal atmospheric mercury depletion events (AMDE) of inorganic mercury (Hg^{2+}) (Obrist et al., 2017; Douglas & Blum, 2019). The mercury then undergoes methylation to produce methylmercury (MeHg), a toxic and biomagnifying form of mercury (Douglas et al., 2012; Kirk et al., 2014). The goal was to determine the bioaccumulation of mercury within animal tissues acquired through the CBEM program in relation to national health guidelines. More specifically, to analyze the concentrations of total mercury (THg) and MeHg within muscles, bones, livers, kidneys, and blubber of country food (traditional food) species. As caribou is also consumed by northern populations, the intention was to acquire tissues from *Rangifer tarandus* to supplement the terrestrial ecosystem, however none were available at the time of specimen collection. Finally, a comprehensive analysis of river and tributary surface waters was also completed in order to study the potential geochemical influences on REE behaviour. The relevant information and preliminary results pertaining to this objective are presented in the Scientific Report, provided in Annex B.

Chapter 2 – Article

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

2.1 Author contributions

The following statement regarding author contributions is in reference to the article presented in this chapter (as of Section 2.2), as well as the scientific report provided in Annex B.

The co-authors contributed to a greater measure in the project conceptualization, the field work and other data collection, and contributed to revision and editing. The lead author was responsible for the conceptualization and analysis of certain sections of the research, with a significant contribution to the data interpretation. The lead author's contributions also focused on data treatment, preparation of graphics, statistical analysis, writing of original drafts, corrections, and revisions. The co-authors led laboratory analyses of 2016 to 2018 samples, while the lead author participated in laboratory analyses of samples as of 2019, which were limited due to cancellation of field expeditions related to COVID travel restrictions in Nunavik.

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

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2.2 Abstract

Recent increases in the demand for rare earth elements (REE) and supply concerns 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. This study provides background REE values and investigates REE anomalies across terrestrial, freshwater, and marine ecosystems in an area where REE mining is planned. Results suggest a biodilution of REE, with the highest mean ΣREE concentrations reported in sediments (10^2 nmol/g) and low trophic level organisms (i.e., lichens, biofilm, invertebrates; 10^1 - 10^2 nmol/g), and the lowest mean concentrations in consumers (i.e., ptarmigans, fish, and seal; 10^{-2} - 10^1 nmol/g). The analysis of animal tissues of importance to northern villages demonstrates a species-specific bioaccumulation of REE, with mean concentrations frequently greatest in liver (up to 40-times) and bones (up to 10-times) compared to muscle and blubber, with the kidneys usually presenting intermediate concentrations. Further, a tissue-specific fractionation was presented, with significant LREE enrichment in consumer livers (LREE/HREE: 10^1 - 10^2) and the most pronounced negative Ce anomalies (<0.80) in liver and bones of fish species. These fractionation patterns, along with novel relationships presented between fish size (length, mass) and Ce anomalies suggest a potential metabolic, ecological, and/or environmental influences on REE bioaccumulation and distribution within biota. Background concentration data presented herein will be 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.

Key words: lanthanides, bioaccumulation, biodistribution, organs, anomalies, subarctic, community-based monitoring, cerium redox, REE

Key Messages:

- Trophic dilution of REE is displayed across three subarctic northern ecosystems with established baseline REE concentrations prior to mining development
- Bioaccumulation of REE in country food species was typically greatest in liver, followed by bone and often kidney tissues, relative to muscle and blubber tissues
- Ce anomalies of biotic species and animal tissues suggest a metabolic, physiological, and ecological influence on REE behaviour and transformation

2.3 Introduction

The rare earth elements (REE) are technologically critical elements with applications in permanent magnets, as catalysts, in polishing, in the medical field, and various other industries, especially for 'clean' technologies and electronics (Ng et al., 2011; Humphries, 2013; NR Can., 2022). This group of 17 metals includes the lanthanides (La to Lu), yttrium and scandium (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 (estimated total of ~250,000 tonnes REO), Canada also hosts multiple (~20) REE deposits that altogether may contribute approximately 14 million tonnes of REO to the market (NR Can., 2022; USGS, 2022). In Canada, mining activity has commenced at one of these locations, with the others in various stages of study (NR Can., 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 and are often in proximity to Indigenous communities (Yin et al., 2021). These areas are under 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 experienced at these latitudes 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). Collaboration between community members and researchers led to the development of a community-based environmental monitoring (CBEM) program. 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).

There is limited data 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 et Pratt, 1993; Bonada et al., 2006) and lichens (Leonardo et al., 2011; Abas, 2021) as they can reflect levels of metals in the aquatic environment and atmosphere, respectively (Holt & Miller, 2010) and are the prey of many consumers, acting as entry points to food webs (Naeth & Wilkinsen, 2008). Additionally important is the study of country food 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 natural 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) 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 & Edanami, 2017). Investigating the fractionation of REE may provide additional insight on REE behaviour in the environment and throughout ecosystems.

Studies on the accumulation of REE 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, animal liver (MacMillan et al., 2017) and kidneys (Squadrone et al., 2020) have shown a greater accumulation of REE than muscles, with 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, and uptake mechanisms of the various tissues (Wells & 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 like atomic masses, ionic radii, electron configuration, and trivalent charges (Gonzalez et al., 2014; Van Gosen et al., 2017), deviations from this trend exist. For instance, the redox chemistry of certain REE can affect their fate: cerium (Ce) can be oxidized to the 4+ state, which is less soluble than its 3+ state, and Eu can be reduced to the 2+ state (Manini, 2017). Normalized REE patterns, by comparison to standard concentrations, highlight enrichments or depletions (i.e., anomalies) of elements in relation to their neighbours in the periodic table (Lawrence & Kamber, 2006; Piper & Bau, 2013; Tostevin, 2021). 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 & Edanami, 2017), and whole fish (Wang et al., 2019). Typically, anomalies in waters and sediments have been thought to reflect the matrices' source, weathering, and other processes, and could be used to track changes in geochemistry (Akagi & Masuda, 1998; Lawrence & Kamber, 2006; Benabdelkader et al., 2019; Tostevin, 2021) or anthropogenic inputs (Bau & 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 behavior 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 (QC, Canada), 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 country food species; and (3) the fractionation of REE within biota through exploratory analyses of Ce anomalies and their possible control variables.

2.4 Methods

2.4.1 Study Sites

Field locations were in Nunavik, Quebec, Canada (Annex A Figure A.1) with a focus on sites utilized by the local community for hunting and fishing. The field area is within the subarctic regions of the George River Basin (GRB) and Koroc River Basin (KRB), which discharge into the Ungava Bay and cover drainage areas of 41700 km^2 (Laycock, 2020) and 4050 km^2 (Bunn et al., 1989), respectively. Within the Southeastern Churchill Province of the Canadian Shield (Énergie et Ressources Naturelles Québec), the area is in a transition zone with boreal forests to treed shrublands and primarily discontinuous permafrost in the GRB; and tundra and more continuous permafrost to the northeast into the KRB (NR Can., 2009; Allard et al., 2012; Brackley, 2019). 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. The Strange Lake forecasted REE mine site is located on the eastern side of Lake Brisson, within the George River Basin (Boisjoly et al., 2015).

2.4.2. Sampling Methods

Field sampling took place in collaboration with the community of Kangiqsualujjuaq during the summer seasons (June – August) of 2017 to 2019 except for ptarmigans and hare which were collected in March of 2018. Field equipment and sampling containers were acid-washed (glassware: 45% HNO_3, 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.

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 mainstem and one in a small tributary (approximate length <10 km) of the George River. Triplicates were taken using a hand-corer with a 5 cm diameter tubing and stored in double-wrapped plastic bags. Samples were collected from two different depths at each site: 0-5 cm and 5-10 cm. Riverbanks often had steep slopes and were comprised of rocky material, leading to a limited access of sediment deposition zones.

Biofilm samples (n=9) 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 um) was used to collect individuals after brushing rocks located 0.5 m upstream of the net (MDDEFP, 2013) 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 (CVRB & MDDEP, 2005). The individual invertebrates 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).

The above-ground plant segments were cut from lichen 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., caribou) and can act as a biomonitor for the atmosphere (Naeth and Wilkinson, 2008; Abas, 2021). No pre-analysis rinsing of lichen (n=62) was done as to obtain concentrations representative of those to which wildlife would be exposed (MacMillan et al., 2017).

The fish (Arctic char, *Salvelinus alpinus*; whitefish, *Coregonus clupeaformis*; Arctic sculpin, *Myoxocephalus scorpioides*; Arctic cod, *Boreogadus saida*), seal (bearded seal, *Erignathus* *barbatus*; ringed seal, *Pusa hispida*), ptarmigan (presumed to be rock ptarmigan, *Lagopus muta* and willow ptarmigan, *Lagopus lagopus*), and Arctic hare (*Lepus arcticus*) specimens were collected through the CBEM program, where participation and knowledge of local Inuit hunters 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 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. All fish were within the size range of 26 cm to 66 cm, with an average ($\pm$ standard deviation) of 47 $\pm$ 9.1 cm in total length. The fish masses fell within the range of 304 g to 2860 g. Seals had total lengths of 39 cm to 171 cm, with varied blubber thicknesses of 1.0 to 5.5 cm (measured in the field). Sizes of ptarmigans ranged from 500 g to 592 g, where measured. The arctic hare had a mass of 3610 g.

Arctic char is considered a freshwater species due to their sampling location, though they can migrate (Curry et al., 2014). They feed on zooplankton, aquatic invertebrates, copepods, and depending on their size, smaller fish including their own species (Svenning et al., 2007; ADFG, nd), often in pelagic areas (Coad & Reist, 2004). Whitefish reside in pelagic to benthic zones of freshwaters where they feed on insects, mussels, and zooplankton (NOAA, 2009; Sandlund et al., 2010). Arctic sculpins are benthic marine fish that primarily consume crustaceans (e.g., amphipods) and other invertebrates from shallow zones (Coad & Reist, 2004; Thorsteinson & Love, 2016). Arctic cod live in pelagic to benthic marine areas (Fortier et al., 2015) and feed on other fish, including sculpins, and zooplankton (Cui et al., 2012; Buckley and Whitehouse, 2017). Ringed seals and bearded seals are marine mammals that feed on invertebrates and fish (NOAA, 2022), such as the Arctic sculpin (KRG, 2005) and Arctic cod (Fortier et al., 2015) included here. Willow ptarmigans primarily feed on various parts of the Arctic willow shrub (e.g., leaves, twigs, buds), and berries (ADFG, nd). Rock ptarmigans consume parts of the draft birch (e.g., buds, catkins) and Arctic willows, in addition to berries, spiders and insects (Cornell University, 2019; AFDG, nd). Arctic hares commonly feed on lichens and various plants (e.g., forbs, grasses, mosses), including the berries, buds, leaves, twigs, and roots (Hearn, 2012).

Sample Group		n	Consumed or Not
Seal*	*Muscle*	7	Yes
	Liver	7	Yes
	Blubber	4	Historically*
	Bone	3	Boiled in stew
Whitefish	*Muscle*	40	Yes
	Liver	39	No
	Kidney	24	No
	Bone	17	Boiled in fish chowder
Sculpin	*Muscle*	7	Yes
	Liver	7	No
	Kidney	7	No
	Bone	3	-
Arctic Char	*Muscle*	26	Yes
	Liver	16	No
	Bone	24	Boiled in fish chowder
Arctic Cod	*Muscle*	2	Yes
	Liver	2	-
Ptarmigan*	*Th. Muscle*	18	Yes
	Br. Muscle	10	Yes
	Liver	18	Yes
	Kidney	11	Yes
	Crop†	11	No
	Gizzard†	12	No
Arctic Hare	*Th. Muscle*	1	Yes
	Liver	1	Yes
	Kidney	1	Yes

Table 1. – Sample size (n) and details about the consumption of each species and tissue type by the Inuit community of Kangiqsualujjuaq. (-) Indicates an unknown field. (*) Historically blubber was consumed in a traditional dish; present habits are unknown. (†) Sample comprised solely of the contents of the crop or gizzard. The seal* and ptarmigan* groups each include the two species analysed in this study. Th. and Br. muscle refers to thigh and breast muscle, respectively. Consumption data provided by José Gérin-Lajoie, research professional.

2.4.3 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 identifying and removing their organs. Subsamples of interest were muscle, liver, kidney, and opercula from fish; muscle, liver, blubber, and jawbone from seal; and crop contents, gizzard contents, muscle, liver, and kidney from ptarmigans. 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 web. The material itself was largely undigested and consisted of berries, branches, twigs, and fibrous material.

Animal tissues as well as the lichen and benthic invertebrate (no depuration) samples were lyophilised for at least 24 hours; sediment and biofilm samples were lyophilised for at least 72 hours as they contained a significant amount of water. Samples were then 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. Between 10 and 15 mg of sample material was digested (similar to Khadra et al., 2019; Charette et al., 2020) in pre-washed (HNO_3 45%, HCl 5%) Teflon vials by equal volumes (0.25 mL) of HCl and HNO_3 (trace metal grade) in a pressure cooker (50X-120V, All American) at 15-20 PSI for 3 hours. Once cooled, 0.25 mL of hydrogen peroxide (30% H_2O_2, OPTIMA grade) was added to each sample and left to react overnight. Finally, samples were transferred to trace-metal free vials and diluted with ultra-pure water (Milli-Q) for analysis.

A total of 16 REE [lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu); excluding promethium (Pm); including yttrium (Y) and scandium (Sc)], were analyzed by inductively coupled plasma mass spectrometry (ICP-MS/MS, 8900 Triple Quadrupole, Agilent Technologies) at the Université de Montréal. The following certified reference materials were used to test for analysis accuracy: BCR-668 (Mussel Tissue), BCR-670 (Aquatic Plant), and SLRS-6 (River Water; National Research Council Canada). The recovery for reference materials (Table A.1) varied between analyses but was on average 94 $\pm$ 16 % for LREE and 88 $\pm$ 14 % for HREE. Blanks and standards were treated identically to the samples and were run approximately every 10 samples to assure accuracy was maintained. Iridium (Ir), germanium (Ge), rhodium (Rh) and rhenium (Re) 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 they were greater than the DL. Element DL (Table A.2) ranged on average from 0.0004 to 0.003 ug/L across all analyses.

The detection frequencies of REE (>DL) were dependent on the matrix (Table A.3), with 100% detectability across all individual REE for the sediment, biofilm, and benthic invertebrate ("benthos") samples; 100% detectability of LREE and 50-100% detectability of HREE for lichens; and varied detectability across the REE for fish (18 – 98%), ptarmigans (0 – 87%), and seals (0 – 95%). Metal concentrations in digestion blanks were subtracted from sample concentrations where detected. The total REE concentration (ΣREE) was calculated as the sum of individual REE, where concentrations were detected, as all individual REE were analyzed in the samples and demonstrate a strong correlation (Table A.4; R^2 = 0.77 to 1.00). The sum includes Y as it also demonstrates a strong positive linear relationship to the other REE with Pearson's correlation coefficients of R^2 = 0.88 to 0.99, but it excludes Sc due to analytical interferences.

2.4.4 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, and values were $\log_{10}$-transformed to improve normality where required. Levene's test was done 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 ($\neq 1$). 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. In select figures, both species of seal were organized into one group due to the low sample size for bearded seal. Linear model analyses were performed using the 'lm' function. The R-squared value and regression line were reported where the model was significant (α = 0.01). Further investigation into the validity of each model was conducted through an evaluation of residuals and coefficient significance values.

2.4.5 Data Analysis

REE concentrations are given in nanomoles per gram of dry weight (nmol/g dw) and often presented as the mean value $\pm$ SD. The LREE included La – Gd and HREE were considered Yb – Lu with Y (Voncken, 2016; Van Gosen et al., 2017). Biomagnification factors (BMF) for ptarmigans were calculated according to equation (1) 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 & Masuda, 1998; Slack et al., 2004; Lawrence & Kamber, 2006; Tostevin, 2021) and results were compared. All calculation results were similar, with average anomaly values within 10% of each other across all samples and therefore equation (2) as mentioned in Slack et al. (2004) was selected based on its slightly stronger linear correlations (R^2) during statistical analyses. Anomaly values <1 signify the sample has a negative Ce anomaly, while values >1 signify a positive Ce anomaly is present. The Eu and Gd anomalies were also investigated, however the Ce anomalies allowed for a more complete database and is therefore focused on within this study. Two whitefish muscle samples were removed from anomaly analyses due to their low REE concentrations causing oversensitivity and therefore inaccuracies in ratio calculations.

$$BMF_{ptarmigan} = \frac{[REE]_{tissue}}{[REE]_{crop\ contents}} \tag{1}$$

$$\frac{Ce}{Ce^*} = \frac{Ce_N}{La_N^{0.667} \cdot Nd_N^{0.333}} \tag{2}$$

2.5 Results

2.5.1 Bioaccumulation of REE in Ecosystems

A large variation in REE concentrations is seen among the biota and sediments studied (Fig. 5; Table 3). The average individual REE concentrations decrease in % of ΣREE (Annex A Table A.5) 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 (Table A.3).

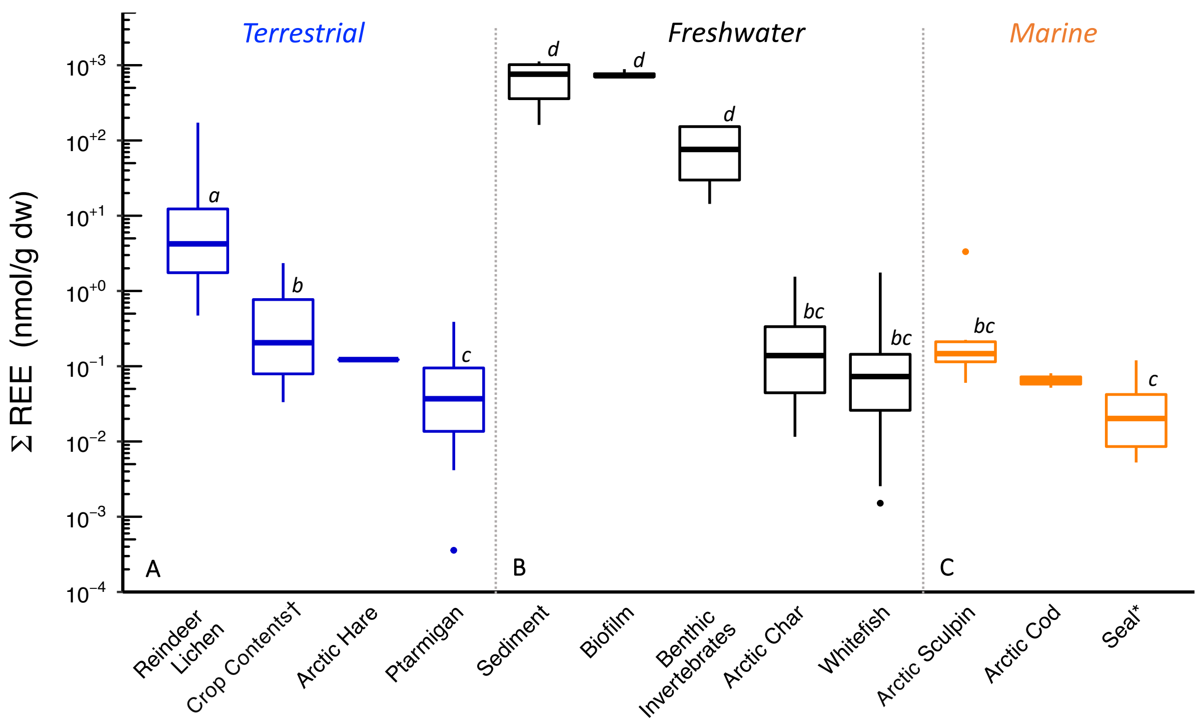

Figure 5. – Concentrations of total REE by taxonomic group (log_{10}-scaled axis) organized by ecosystem. Muscle tissue concentrations presented for the animal samples. Different letters represent significantly different means across all taxonomic groups where n > 2. *Seal group comprised of bearded and ringed seals. 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.

Sample Group		ΣREE *nmol/g*	Ce/Ce*	LREE/HREE	BMF
Lichen		17.07 (35.05)	1.01 (0.11)	6.8 (2.0)	
Biofilm		750.1 (94.89)	0.95 (0.03)	6.4 (0.9)	
Benthic Invertebrates		90.01 (74.32)	0.86 (0.04)	12.9 (5.1)	
Sediment		713.4 (337.1)	0.93 (0.06)	7.3 (1.9)	
Arctic Hare	*Liver*	19.76 (NA)	0.75 (NA)	440.6 (NA)	
	Muscle Th.	0.12 (NA)	NA	NA	
	Kidney	0.49 (NA)	0.80 (NA)	13.1 (NA)	
Ptarmigan*	*Crop†*	0.56 (0.73)	0.72 (0.17)	16.3 (8.8)	
	Gizzard†	18.02 (28.81)	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)	4.2 (2.7)	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*	12.90 (9.10)	0.47 (0.07)	27.8 (18.7)	
	Muscle	0.27 (0.37)	0.90 (0.14)	7.0 (4.1)	
	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)	
Seals*	*Liver*	1.10 (1.20)	0.87 (0.03)	28.0 (17.7)	
	Blubber	0.01 (0.02)	1.13 (NA)	NA	
	Muscle	0.04 (0.04)	1.01 (0.41)	2.3 (2.1)	
	Bone	0.12 (0.14)	1.05 (0.20)	4.1 (1.3)	

Table 2. – Mean values with (standard deviations) for total REE concentration ($\Sigma\mathrm{REE}, \mathrm{nmol/g}$), Ce anomaly (Ce/Ce*), the ratio of light to heavy REE (LREE/HREE), and biomagnification factor (BMF). (*) Denotes where two species are combined in a single sample group. NA where no data is available. Muscle Th. and Br. refer to thigh and breast muscle, respectively.

Within the terrestrial ecosystem (Fig. 5A), REE concentrations are significantly different between taxonomic groups. The highest concentrations of REE are seen in the lowest taxonomic groups, namely the reindeer lichens at 17.07 ± 35.05 nmol/g and the ptarmigan crop contents at 0.56 ± 0.73 nmol/g. Concentrations decrease into the higher taxonomic groups, with ptarmigan thigh muscles having mean concentrations of 0.08 ± 0.11 nmol/g. This reflects an approximate 10-fold decrease in REE concentration between the ptarmigan muscles and their diet (i.e., crop contents). REE concentrations for each taxonomic group are also provided in mg/kg in Table A.6.

The same pattern of decreasing REE concentrations with increasing trophic level is seen within the freshwater ecosystem (Fig. 5B). Though not all taxonomic groups show significantly different means, concentrations decrease as follows: sediment ≈ biofilm ≈ benthic invertebrates > Arctic char ≈ whitefish. As expected, the highest levels of REE are seen in the sediments with concentrations of 714 ± 337 nmol/g. Freshwater fish muscles have mean REE concentrations on the order of 10^{-1} nmol/g, which are around 100-times less than those for the riverine invertebrates. The marine species studied (Fig. 5C) do not have significantly different REE concentrations, however, the seal muscle group still demonstrates an average concentration up to 10 times lower than the saltwater fish species. Across all aquatic ecosystems, the fish species demonstrate similar levels of REE in their muscles.

2.5.2 Bioaccumulation of REE in Animal Tissues

Animal tissues demonstrate greater REE accumulation in the liver than the muscles (Fig. 6), up to about 40-times greater (exc., hare: 100-times). Bones have a REE accumulation that typically fall in the middle of the range for tissues, with REE values up to 10-times their respective muscle concentrations. Kidney REE concentrations are more variable among species, however the aquatic animals (Fig. 6B, E) have REE values 6- to 10-times greater than their respective muscle concentrations. Ptarmigan digestive tract contents (Fig. 6A) include the gizzard contents with REE values (18.02 ± 28.81 nmol/g) being 10-times greater than their liver tissues. Overall, the typical distribution of REE in the studied species is as follows (where analyzed): liver ≳ kidney ≳ bone ≳ muscle ≈ blubber.

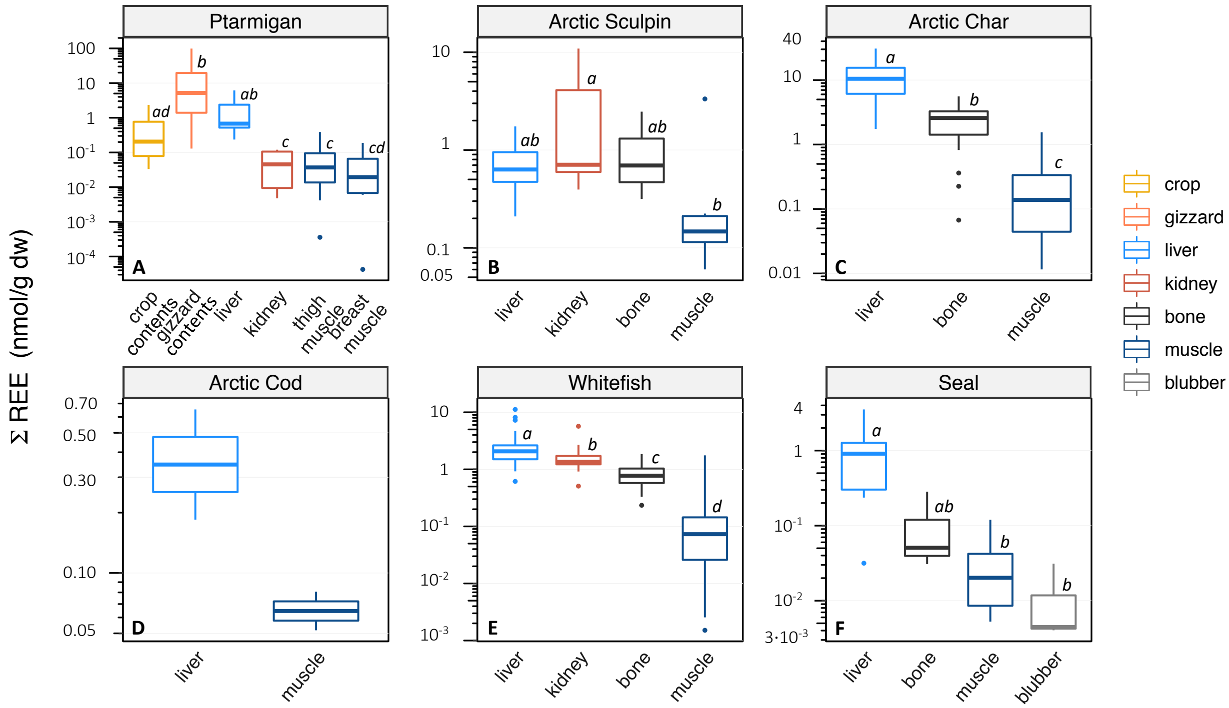

Figure 6. – Concentrations of total REE in various animal tissues (log_{10}-scaled axis). Seal group comprised of bearded and ringed seals. Different letters represent significantly different means within each animal group. Hare samples not shown as n = 1 for each tissue type.

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 are highly variable, even within a single tissue type, the thigh and breast muscle BMF reflect 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 is also supported by the kidney BMF, with an average below 1. However, the ptarmigan liver tissues do not follow the same pattern: instead, 72 % of individuals show a magnification of REE with an average BMF of 10.55 ± 11.98.

2.5.3 LREE Enrichment in Biota

Calculation of LREE/HREE ratios (Table 2) demonstrate the presence of a LREE enrichment across all taxonomic groups with averages ranging from 2.3 to 68 (exc., hare: 440). While the LREE were bioaccumulated to a greater extent than HREE in all tissues, this is especially true for the animal livers which displayed average LREE/HREE values up to 30-fold greater than those for other tissues.

2.5.4. Cerium Anomalies in Ecosystems

Ce anomalies for each taxonomic group (Fig. 7; Table 2) are significantly different from 1.0 by the two-sided t-test, except for the lichens with a mean Ce/Ce^* value of 1.0 ± 0.11. Ce anomalies vary from 0.23 to 2.2 across all biota and sediment (Table A.6). The lower taxonomic groups and sediments display Ce/Ce^* values near to 1.0, or representative of geogenic background concentrations, and higher-level taxonomic groups tend to have significant negative anomalies ($Ce/Ce^* \lesssim 0.8$), suggesting a possible transformation of Ce. For example, the freshwater environment offers the opportunity to view anomalies across multiple taxonomic levels (Fig. 7B). Biofilms have Ce/Ce^* values of 0.95 ± 0.03 that, while significantly different from 1.0, aren't necessarily low enough to be considered negative anomalies. The benthic invertebrates demonstrate negative anomalies of 0.86 ± 0.04, followed by the whitefish and Arctic char with stronger negative anomalies (liver) of 0.52 ± 0.04 and 0.47 ± 0.07, respectively. On the contrary, no significant difference is noted in the anomaly between ptarmigan crop contents and the liver (Fig. 7A), instead, this transformation is only visible in comparison of Ce/Ce* values between the crop and other analysed body compartments (Table 2; Fig. 8).

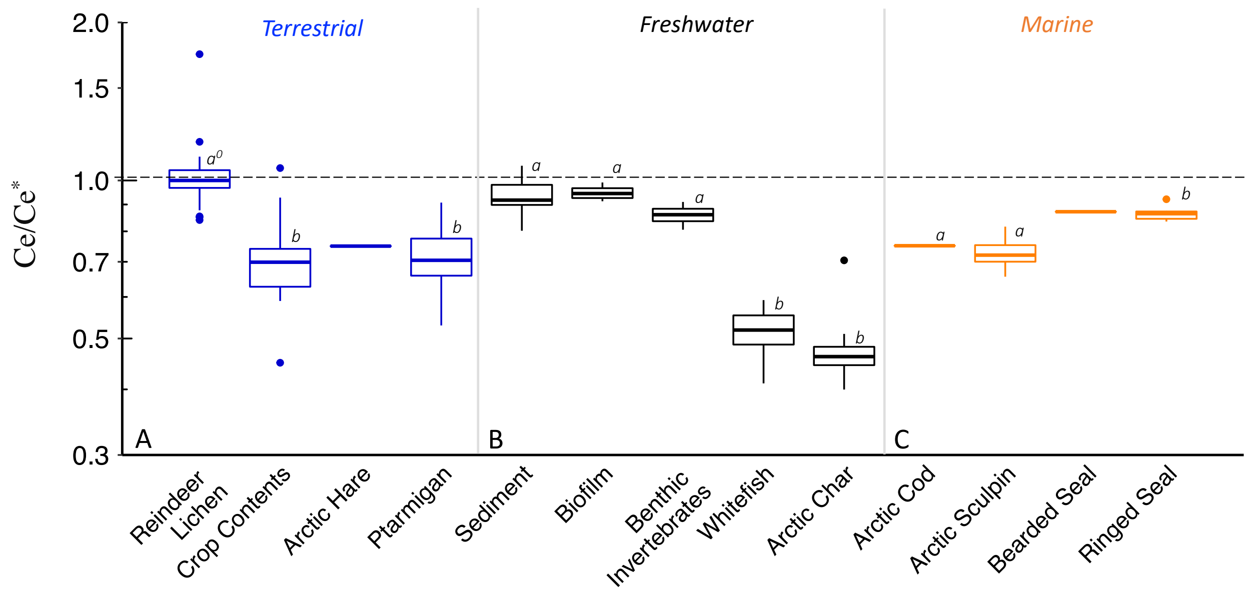

Figure 7. – Ce anomalies by taxonomic group across ecosystems (log_{10}-scaled). Significantly different means within each ecosystem denoted by different letters. A group mean that is not significantly different from 1.0 is denoted by superscript "0". Anomaly values from the liver tissues were used for the animal groups.

2.5.5 Cerium Anomalies in Animal Tissues

Significant differences in Ce anomaly between animal tissues within a species were also detected (Fig. 8). For ptarmigans, fish and seal species, there is a general trend of near 1.0 Ce/Ce* values in muscle, and a significant negative Ce anomaly in the livers with mean values that range from 0.47 in Arctic char to 0.87 in seals. While bone and kidney tissues do not consistently differ significantly from the other tissues, they tend to have anomaly values that fall in the 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 total length (Fig. 9) or fish mass (Annex Fig. A.2). The total length had a significant relationship to the log-transformed Ce anomaly values in bone with an R^2 of 0.37 (Fig. 9A), in kidneys with an R^2 of 0.25 (Fig. 9B) and in liver with an R^2 of 0.22 (Fig. 9C). The total mass (log-transformed) also had a significant relationship to Ce anomalies in the bones with an R^2 of 0.34 (Fig. A.2A), in kidneys with an R^2 of

0.14 (Fig. A.2B), and in liver with an R^2 of 0.17 (Fig. A.2C). No significant relationships were made for Ce/Ce* values of muscle tissues in fish, keeping in mind that detection of REE in muscle tissues was analytically challenging due to low REE concentrations. These relationships therefore demonstrate a stronger and more negative Ce anomaly for fish species that tend to be larger in size, which in general follow the trend: Arctic char > Arctic cod > whitefish > Arctic sculpin.

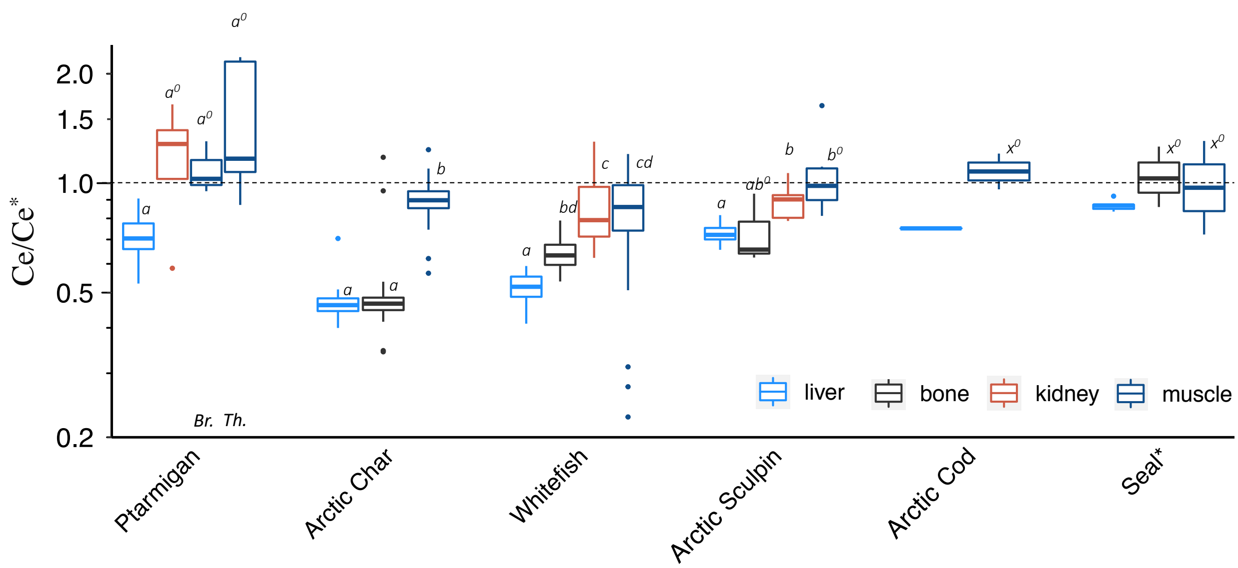

Figure 8. – Ce anomalies (log_{10}-scaled) in the animal liver, bone, kidney, and muscle tissues. Seal* taxonomic group comprised of both seal species. Letters (i.e., a, b, c) represent significantly different means within each animal group. Superscript of ‘0’ denotes a mean Ce/Ce* value that is not significantly different from 1.0 (i.e., no anomaly); superscript placed on ‘x’ where no ANOVA is reported.

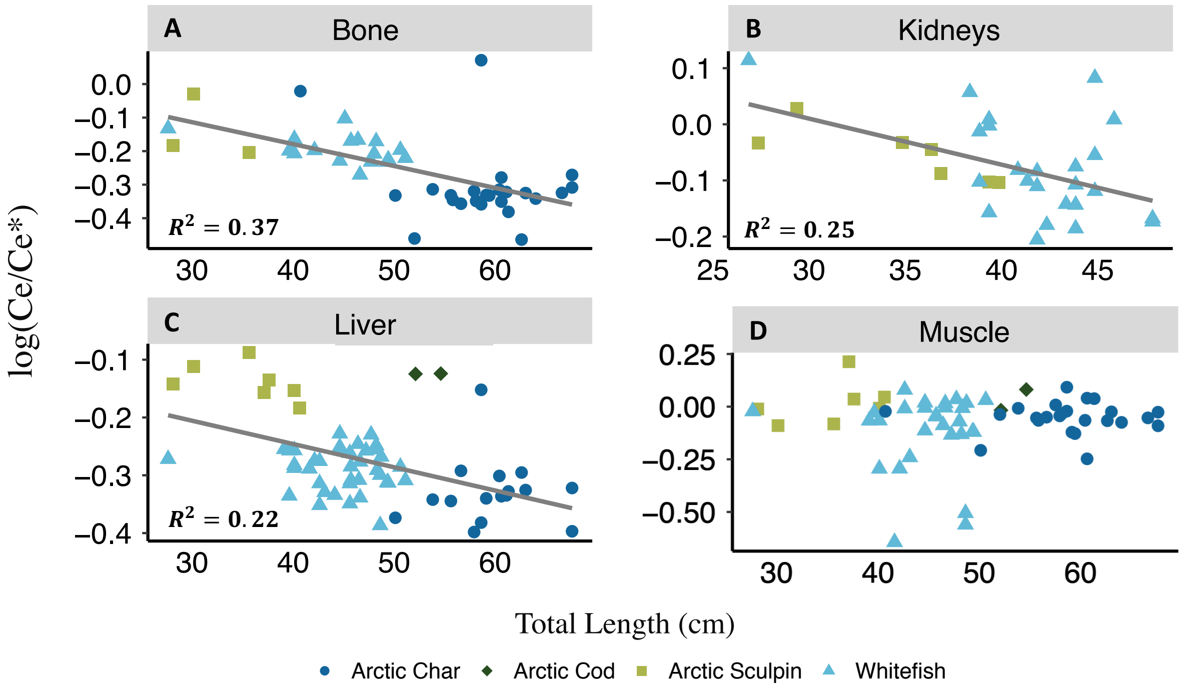

Figure 9. – Ce anomalies ($\log_{10}$-transformed) within tissues of all four fish species studied, explained by fish total length (cm). R^2 values and regression lines are shown where the linear model is significant ($p < 0.01$).

2.6 Discussion

2.6.1 Distribution of REE In Ecosystems and Animal Tissues

The mean REE concentrations presented for sediments, vegetative species, and animal tissues (Table 2) in the study region provide background values for use in future studies. For further insight into these current levels prior to any significant disturbance, the concentration ranges and geometric means are also provided in Table A.6. Certain taxonomic groups display 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. Second, in the case of the vertebrate muscles, this can likely be explained in part by the very low REE concentrations present (often near the DL), causing the total REE concentrations to be very sensitive to small differences. Overall, higher concentrations of REE were presented in vegetation and other low trophic level taxonomic groups, with a decrease into the higher trophic levels, such as in predatory animals. This trend is referred to as trophic dilution, or biominification, and has been displayed in available literature regarding REE concentrations across trophic levels (MacMillan et al., 2017; Amyot et al., 2017; Squadrone et al., 2019).

The REE concentrations of George River lichens is comparable to fruticose lichens and moss from the Eastern Canadian Arctic (MacMillan et al., 2017), which displayed ΣREE concentrations of 41.5 ± 81.4 nmol/g (dw, geometric mean ± SD). Sediments of the GRB have a range of values from 160.99 to 1122.1 nmol/g (Table A.6), 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 ΣREE concentrations of 71 – 185 ug/g (Romero-Freire et al., 2019) (present study: 22 – 155 ug/g). As for the biofilm samples, their 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.

MacMillan et al. (2019) and Amyot et al. (2017) reported values of around 2 – 270 nmol/g dw for ΣREE 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. The GRB concentrations of REE in riverine invertebrates were reported as 100-times greater than freshwater fish muscle average concentrations. 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; Squadrone et al., 2019; Pastorino et al., 2020), altogether supporting a biodilution of REE. To consider is that the 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 the benthic invertebrates.

REE concentrations within individual fish organs is scarcely 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 George River fish muscles (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 & 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 is 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 (Squadrone 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 are more strongly bioaccumulated in these organs, they may be stored to some extent in detoxified granules (Lobel et al., 1991; Cardon et al., 2019).

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 is consistent across all tissues or species within the present study. However, marine fish species at higher trophic levels did demonstrate a lower mean REE, with the predatory Arctic cod concentrations up to 8-fold lower than the more benthic Arctic sculpin. Additionally, freshwater fish livers displayed mean REE concentrations up to 30-fold the marine fish livers, which could suggest a potential decrease in REE bioavailability in saltwater (Herrmann et al., 2016). The present study contributes the first reports of REE concentrations for certain species and/or tissues important to northern ecosystems.

This study presents the first BMF values for REE in ptarmigan organs. A potential magnification in REE concentration from crop contents to liver tissues is 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.

2.6.2 LREE Enrichment

While LREE enrichment can be attributed in part to the greater recovery of LREE, there are also frequently naturally higher concentrations of LREE in the environment, as is the case for 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) is 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 suggests a further partitioning of REE compared to sediments upon bioaccumulation in biotic specimens. Stronger LREE enrichment is seen for animal livers (e.g., LREE/HREE whitefish liver: 28.5 $\pm$ 15.7), whereas a weaker LREE enrichment is seen in animal bones and muscles (e.g., LREE/HREE whitefish bone 4.9 $\pm$ 1.8); suggesting a potential for tissue-dependent partitioning of individual REE in the vertebrate species. Some exceptions to the LREE enrichment trend are 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 volitas/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 EC_{50} values (i.e., more toxic) for HREE over LREE (Cui et al., 2012; Técher et al., 2020;). Overall, additional variability in LREE/HREE fractionation could be introduced by factors such as different 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 & Wells, 2012; Gonzalez et al., 2014).

2.6.3 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 & Arai, 2015), contributing to its frequent anomalous behavior 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 & Masi, 2015; Squadrone et al., 2019), the present study only noted a near unit Ce/Ce* value 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. 7) displaying varied Ce anomalies are 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. Further, Ce is known to be in low availability in seawater (Figueiredo et al., 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 presents novel intra-species Ce/Ce* distributions for four tissue types among terrestrial, freshwater, and marine animals (Fig. 8), that demonstrate 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 & Sohal, 2004). Further, an explanation for why certain tissues for the fish species consistently demonstrate strong Ce/Ce* relationships to fish size (Fig. 9) while others are 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 ($\lesssim 10$ 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.

Further investigation into these relationships (Fig. 9) suggests 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 demonstrate 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 suggest 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 Ce^{3+}/Ce^{4+} and Ce/Ce* ratios among subcellular fractions, cellular conditions of different cell types, and REE sequestration processes.

2.7 Conclusion

The study presents 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 offer the first reports of REE bioaccumulation for certain species and/or tissues. Sampling performed in collaboration with a remote 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 a trophic dilution, or lack of biomagnification, in natural, northern environments, with concentrations up to 10^4 times greater in lower trophic level groups (e.g., biofilm) relative to muscles of predatory animals. Notable is 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 highlights 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 suggest 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 findings suggest 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.

Chapter 3 – Discussion and Conclusions

The project objectives were met through the collaboration with the community of Kangiqsualujjuaq, and the data acquired will help to respond to concerns about possible REE exploration in the George River Basin, Nunavik. The objectives were addressed through the sampling of the following matrices: terrestrial lichens, Arctic hare, willow and rock ptarmigans; freshwater sediments, biofilm, benthic invertebrates, Arctic char and river whitefish; and marine Arctic cod, Arctic sculpin, bearded seal and ringed seal. As caribou is also consumed by northern populations, the goal was to acquire tissues from *Rangifer tarandus* to supplement the terrestrial ecosystem, however none were available at the time of specimen collection. Finally, a comprehensive analysis of river and tributary surface waters was also completed and are preliminarily presented within the IMALIRIJIIT Scientific Report in Annex B.

3.1 Discussion

3.1.1 Natural REE Levels

The first objective of determining the current levels, or background concentrations, of individual and total REE in the study areas was attained through ICP-MS/MS analyses of the above-mentioned samples that represented a range of trophic levels and ecosystems in the study area. The background values (Table 2; Table A.6) can serve as a reference tool in future studies, which upon comparison would allow for determination of any changes introduced, such as due to resource exploitation and/or climate change effects. Additionally, there are no national guidelines currently in place for the REE, including within Canada, in terms of environmental health or human consumption. A comprehensive database of the levels of REE in undisturbed environments can therefore help in the formation of guidelines that are realistic and reflective of actual natural concentrations. In summary, the highest total REE concentrations were in the abiotic environment, being the GRB sediment, and in the biofilm, which was presumed to be related to their natural incorporation of sediments. The approximate range of their concentrations were 160 to 1100 nmol/g and 670 to 890 nmol/g, respectively (greater details are provided in Table A.6). Both of these matrices had average concentrations an order of magnitude greater than the REE contents of reindeer lichens, whose reported mean concentration was 17 nmol/g (0.47 to 170 nmol/g), and the benthic invertebrates, with a mean concentration of 90 nmol/g (14 to 160 nmol/g). The vertebrate animal tissues consistently demonstrated lower REE concentrations, with values that were both species and tissue-specific. Animal liver samples frequently presented the highest accumulation of REE across studied tissues, with average concentrations of 0.42 nmol/g in Arctic cod to 13 nmol/g in Arctic char. Liver tissues typically displayed REE concentrations up to 40-times their respective muscle tissues. Both kidneys and bones demonstrated an ability to accumulate REE, and usually presented concentrations that fell between liver and muscle values, though the order of importance in REE accumulation was species-specific. Muscle tissues presented low background concentrations among animal tissues, frequently with individual REE concentrations below the detection limits. Where detected, the average total REE concentrations in vertebrate muscles ranged from 0.04 nmol/g in seals to 0.60 nmol/g in Arctic sculpin. Finally, seal blubber also showed a low mean REE concentration (0.01 nmol/g). Overall, the majority of concentration data was consistent with the literature for other environments deemed to be relatively undisturbed, where comparisons were possible. For some species studied, and in particular for various organs, especially the bone, kidneys, and digestive tract contents, this study presents the first REE values from field studies. Altogether, the findings help address the knowledge gap of the natural distribution and bioaccumulation of REE, in particular for species that are important to northern ecosystems and serve as resources to Indigenous populations. Finally, the reliability of presented background concentrations is strengthened by the fact that collection of most samples occurred over the course of more than one year, which implies that the values presented will account for some natural inter-annual variation in REE. A level of consistency was otherwise maintained in terms of the collection methods, approximate sampling locations, or the season in which samples were collected.

3.1.2 Strengths and Challenges with the CBEM Program

The use of CBEM programs in the context of northern studies presented itself with certain strengths and weaknesses. Noted benefits to this method of sample collection in the context of the current project include: first, the incorporation of traditional knowledge, especially in relation to the selection of the samples of interest to collect based on those used by northern populations; and in terms of the collection methods, as hunters and fishers would frequent sites that they were knowledgeable about and utilized for gathering their own resources. Therefore, the samples focused on throughout the project are representative of the diets of northern communities and so relevant discussions can be made regarding the REE content of local food species. Operating in a community-based manner also allows for the sampling of species that may otherwise not necessarily be feasible or resource-responsible to sample as researchers, such as the seal species. In this way, the majority of the animal can be consumed by the community, with only subsamples of each tissue of interest removed for science purposes. Finally, with the necessary resources provided (i.e., sampling kits, sampling protocols, financial compensation), animal tissue collection was completed in an efficient manner, with less travel and time constraints, and was more cost-effective.

Some challenges that were met, or rather aspects that were less easily controlled through the collaborative approach, include the selection of samples. For example, there was not always a control on the sample size for select species, seen through the low number of Arctic cod ($n = 2$) and bearded seal ($n = 1$) relative to other species, as samples were provided based on availability. Also, some of the samples were collected throughout the duration of the land camps as an activity to encourage participation and interest in sciences with community members. As a level of quality must still be maintained during sample collection, certain situations may have proved to be less time efficient, more constrained in location, and put a limit on the number of samples (e.g., benthic macroinvertebrates) that were collected for analyses purposes. Finally, there was less control on the field information that got recorded upon sample collection. For example, the identification of samples down to the species level was at times missing (e.g., for ptarmigans). In other cases, there were sample locations that were written in a more qualitative manner (e.g., across river from town) rather than quantitatively using a GPS location. For the purpose of this study, the latter did not pose a problem as this information was sufficient, however this point could be worth revisiting in future collections. Researchers also encountered difficulties with COVID travel restrictions throughout the project, not related to the CBEM project. In fact, the COVID restrictions experienced over the past couple years further highlight the importance of having good, long-term relationships among collaborators, as this may assist in the uninterrupted continuation of projects during any future periods of unprecedented events that may disrupt travelling to the field, or similar.

3.1.3 Bioaccumulation of REE in Natural Systems

The second objective of studying bioaccumulation across ecosystems and tissues was met by the same analysis of REE concentrations as for the above-mentioned samples, in this case with a focus on interspecies relationships. As expected, a biodilution in REE concentrations along food webs was found, which is primarily displayed in the terrestrial and freshwater ecosystems. The biodilution of REE can be seen with concentrations orders of magnitude greater for sediment and low trophic level organisms than for higher level organisms, such as consumer muscle tissues. In the marine ecosystem, this biodilution trend could be strengthened by the addition of new taxonomic groups at lower trophic levels, such as with primary producers and invertebrates. Recent sampling acquired macroalgae (*Alaria* sp.) and common mussels (*Mytilus edulis*) from various sites along the southeastern coastal regions of the Ungava Bay, in Nunavik. These new samples will supplement the database and address the taxonomic levels in the coastal marine ecosystem that are currently absent. The intention is for these new analyses to be incorporated into the article (see Chapter 2) prior to publication. Following the observed bioaccumulation trends presented herein, the hypothesis moving forward is that the macroalgae will display the highest REE concentrations among tested marine taxa, followed by the common mussels, with potential concentrations up to 1000- and 100-times greater, respectively, than those reported for the muscles of the marine fish and seal species (see Chapter 2).

Another hypothesis presented was that REE bioaccumulation would be stronger in benthic and freshwater fish species, compared to pelagic and marine fish, respectively (Yang et al., 2016; Wang et al., 2019). Results showed there was no distinguishable trend in terms of REE bioaccumulation between pelagic or benthic species, likely due to the habitats of the selected species which had some crossover in ecological zones or a difference in ecosystem, limiting the ability to make clear comparisons. The relationship between freshwater and marine species was in part consistent with the hypothesis, as fish livers demonstrated REE values approximately 10-fold greater in freshwater than marine fish species. However, this pattern was not consistent across tissues, as muscle concentrations across the four fish species were not significantly different. Continued research including a greater selection of species is therefore suggested prior to making a concluding remark addressing this hypothesis.

Further, the intra-species REE relationships demonstrated a stronger bioaccumulation in the liver, bone and/or kidney tissues across all species compared to the muscle and/or blubber. This was especially consistent for the liver, with concentrations up to approximately 40-times greater than in muscle tissues. In general, the liver and kidneys are more commonly known sites of high metal accumulation, linked to their role in metal detoxification (Lortholarie et al., 2021). However, it was also presented by Cardon et al. (2019) that in fish liver cells (*O. mykiss*) less than 15% of accumulated Y was located in subcellular fractions considered to be detoxified. Instead, Y was primarily found in the hepatic mitochondrial membranes, potentially linked to the presence of Ca^{2+} channels. The liver then, presenting as a major site of REE accumulation in the current study, may in fact contain a significant portion of accumulated REE in mental-sensitive fractions, as reported by Cardon et al. (2019). In a study on REE accumulation in humans, it was discussed that a transformation of REE^{3+} to REE-hydroxide and REE-phosphate in human blood could favor their uptake by the liver and bones, supporting a capacity for long-term REE storage (Zaichick et al., 2011). The presence of ligands favorable to REE complexation could be a factor controlling the distribution of REE in vertebrate liver and bone, with variability depending on each species' unique metabolic activities. If true, then the dominant ligands present may have a greater affinity for LREE over HREE, especially those in the liver, as the present study reported high LREE enrichment trends in this organ relative to other studied tissues (Table 2). Since the REE are considered Class A metals, their ideal ligands would presumably be oxygen-rich (e.g., OH^-, CO_3^{2-}) (Mason, 2013). In any case, further experiments investigating the subcellular fractionation of all REE across different cell types is required to better interpret the speciation, stability and bioavailability of REE in animal tissues.

Other studies have also reported a strong bioaccumulation of REE in additional tissues not presented herein, such as the gills and spleen of aquatic species (Tu et al., 1994; Lortholarie et al., 2021). The gills are thought to be important not only during respiration, but also for the cycling of calcium; and the discussion regarding spleen concentrations considered its function in fish immunology (Lortholarie et al., 2021). Based on these reports, it may be suggested that the spleen and lungs of terrestrial animals are likely also important to consider in discussions of REE bioaccumulation. In fact, human lung tissue is often the site of disease for people exposed to REE occupationally (Pagano et al., 2015b). Overall, the difference in REE bioaccumulation between tissues suggests the presence of tissue-specific processes for the cellular uptake, detoxification or storage capacities (e.g., in relation to available ligands), and/or partitioning of these metals within animals. An area which merits further research is the intracellular distribution of the REE, to determine the fractions in which they preferentially accumulate, their speciation and their bioavailability in biotic matrices, alongside the cellular mechanisms responsible. Many questions regarding these topics remain, such as whether there are element-wise pathways or processes that favor one group of REE over another (e.g., HREE versus LREE; redox-sensitive REE versus trivalently-stable REE). Further discussion is provided in Section 3.1.5.

In addition, bioaccumulation trends are not only important for understanding the behavior and uptake of REE in biota, but may also be useful for creating environmental and health guidelines. When considering human consumption, one must consider that some communities, particularly in northern environments, tend to consume tissues other than just the muscles for these species. For example, as displayed in Table 1, the community of Kangiqsualujjuaq eats seal muscle and liver, use the bones in soups, and historically the blubber was used in a traditional dish. On the one hand, it may be reassuring to note that the most consumed tissue across animal species, the muscle, has the lowest bioaccumulation. For this sample group, the concentrations of individual REE were frequently below the detection limits, especially for the HREE. Therefore, the vertebrate muscle tissues are not likely to be a source of concern in REE exposure through the diet.

3.1.4 Biomonitoring Challenges and Future Directions

Select species were of interest for biomonitoring in the George River Basin, notably the lichens and the benthic macroinvertebrates, the latter of which was comprised of caddisflies, mayflies, and stoneflies. There were some challenges identified, notably for biomonitoring of the freshwater aquatic system using these invertebrate species. Field researchers did not obtain a large amount of samples for these invertebrates. While some limitations were addressed above, the mainstem of the river presented the challenge of accessibility for this type of sampling due to the often-steep river banks, rocky shores, and strong current. The benthic macroinvertebrate sampling requires sedimentation zones to use material such as a grab sampler for specimen collection, which were limited due to the rocky riverbed. This influenced sampling sites, which were instead focused within tributaries. In any case, future sampling would aim to acquire a greater sample size with a variety of invertebrate species in order to better address their use in biomonitoring of this system.

An area of interest for future biomonitoring studies in the GRB relates to the collection of reindeer lichen, and investigation of the relationship between soil substrate and the lichen plant matter. This would help in determining if lichens are truly influenced by the atmosphere in the GRB, as hypothesized, or if proven untrue, would allow for the determination of the fraction that is controlled by substrate. In either case, the data can serve as a baseline moving forward to better address changes related to the settling of atmospheric particles. This can be further accomplished by normalizing the lichen REE concentrations to the REE concentrations within their own substrate, which will further identify any atmospheric-related fractionation of REE patterns and potentially uncover future anthropogenic dust deposition within the basin.

In terms of future biomonitoring of animal species, or the assessment of REE exposure in the basin, the results of the present study suggest that if an assessment of REE in a region was desired, liver or bone might be a better indicator of an animal's contamination than the commonly assessed muscle. However, other studies have also suggested the possibility of biomonitoring of animal species with a non-invasive, conservative approach. To accomplish this, some of the propositions have included the use of feathers, as reported for Humboldt penguins (Squadrone et al., 2019) and Sandwich terns (Picone et al., 2022), and fur or feces from Arctic and Antarctic seal species (Reindl et al., 2021). Of additional interest in the GRB may be the use of caribou antlers, as they have previously been reported as good bioindicators of lead (Kierdorf & Kierdorf, 2005), which could perhaps suggest their potential use for monitoring of metals of interest in the current study. While these matrices would not be consumed by human populations, if deemed to be reliable biomonitors, then they may be useful in reflecting REE exposure during long-term monitoring. In any case, baseline values would need to be acquired moving forward for any new potential matrices of interest.

When discussing the presence of REE in the environment in terms of mining activities and REE deposit exploitation, it is also important to consider other related potential contaminants. Most notable is the co-occurrence of these elements with uranium (U) and thorium (Th) commonly seen in REE deposits (Haque et al., 2014; Khan et al., 2017), as briefly mentioned in Section 1.2.2. This is true for the Strange Lake REE deposit, where REE-hosted rocks display enrichment of these radioactive elements (Kerr & Rafuse, 2012). In some ores, concentrations of U and Th are present in significant quantities and can be economically mined in addition to the REE. In any case, these elements will be present in dust particles and in wastes from mine sites, and could release radioactive gas during decay (EPA, 2012). As radioactivity can pose a health threat, special protocols and management is required (Khan et al., 2017). Future reports should therefore include the background concentrations and bioaccumulation of U and Th, where detectable, in the surface waters, sediments, and biotic species.

3.1.5 Ce Anomalies: Further Investigations

The third objective regarding the fractionation of REE was met through evaluation of the Ce anomalies of each taxonomic group, which were found to be species- and tissue-specific. In particular, the livers and bones consistently demonstrated a greater fractionation of Ce with more significantly negative anomalies compared to the kidneys and muscles that often demonstrated near unit Ce/Ce* values (i.e., no anomaly). It is a new concept in the literature to study anomalies present in animal species, and it is at least one of the first times that the Ce anomaly is presented for different types of biological tissues from field studies. Therefore, the current discussion is limited to various hypotheses and possible explanations for these findings.

The discussions in Chapter 2 mentioned a hypothesis for these tissue-dependent anomaly values that centered on the difference in redox states between tissues, which would affect the valency of Ce and consequently its speciation and processing. A second hypothesis put forth the suspected differences in residence times for REE depending on tissue type, with a longer residence time expected for tissues with more negative Ce anomalies, representing a greater degree of fractionation. Another hypothesis introduced in Section 2.6.1 that merits further exploration is the possibility that REE are stored in cellular granules. It is therefore put forth that Ce anomalies may be created during the cellular mechanisms involved in this sequestration process. In general, cellular granules are thought to constitute a metal-detoxified fraction of cells (Rainbow, 2002; Bustamante & Miramand, 2005), and this has been hypothesized to occur during REE biodistribution (Zhu et al., 2005; Cardon et al., 2019). Lobel et al. (1991) proposed that the high variability displayed in concentrations of insoluble metals compared to soluble metals within mussels could be due to the storage of the former metals in insoluble granules. Seeing as though oxidized Ce tends to precipitate out of solution as insoluble compounds, granules that are rich in Ce might be consistent with these findings. In a laboratory exposure experiment, the accumulation of Y in rainbow trout liver cells was hypothesized to be related to metal storage within calcium carbonate-type granules, though the greatest point of accumulation was in metal-sensitive fractions (Cardon et al., 2019). The same authors also noted that the distribution of Y between cellular fractions was highly dependent on the species, as both *Daphnia magna* and *Chironomus riparius* showed greater REE detoxification with higher percentages of Y within metal-detoxified fractions (approximately 75% and 25%, respectively). This species variability is further reflected in a subcellular distribution study on field-collected *Hyalella azteca*, which reported the greatest fraction of Ce and La was in the metal-detoxified exoskeleton and granules containing 75% and 66% of their total concentrations, respectively (Labrie, 2022). It was hypothesized that the REE within these amphipods were stored within calcium or iron-type granules (Mason & Jenkins, 1995; Labrie, 2022). Further, authors describing the storage of La have suggested the types of granules present may be of the phosphate-type in bacteria cytoplasm (Roszczenko-Jasińska et al., 2020) and common mussel lysosomes (Chassard-Bouchard & Hallegot, 1984; reviewed by Herrmann et al., 2016). Altogether, these findings might suggest that if Ce anomalies were markers of REE storage within cellular granules, that the taxonomic groups expected to have a lot of granules, being the invertebrates (Deb & Fukushima, 1999), would also likely demonstrate the greatest fractionation of Ce with significant anomalies. This is consistent with the negative Ce anomalies reported by Akagi & Edanami (2017) in bivalve soft tissues. However, the present findings for George River benthic macroinvertebrates (i.e., insect species) do not follow this hypothesis as they demonstrate only a weak Ce anomaly of approximately 0.85. This may be related to the specimens not being depurated, which has previously been shown to affect REE accumulation (Amyot et al., 2017; Labrie, 2022). Future studies should therefore aim to include depurated samples to determine if this step alters the magnitude of anomaly presented by macroinvertebrates. Overall, this research question merits further investigation, such as through the separation and extraction of subcellular fractions followed by REE analysis. It would also be of interest to determine the Ce^{3+} to Ce^{4+} ratios in each compartment to better understand the mechanisms influencing this redox-sensitive REE.

A second finding that was introduced in Section 2.6.3 is the relationship of Ce anomalies between species from different ecosystems. There appears to be a certain level of environmental influence displayed by the aquatic animals, where marine species tend to present less-negative anomalies compared to freshwater species. The only comparable results found in the literature were limited to Ce anomalies from the livers of marine ringed seal and lake brook trout, which were in agreement with the present findings as the seal species demonstrated anomaly values nearer to 1 and the trout species displayed more negative anomalies (MacMillan et al., 2017). No significant difference in average Ce anomalies between fish muscle tissues from freshwater and marine environments were found in the other study that presented this data (Yang et al., 2016). Again, the animal tissues from the present study still all display similar intra-species trends in Ce anomalies, but this variation seen between ecosystems may be demonstrating a control of REE bioavailability and/or speciation that is dependent on the aquatic environmental conditions. Finally, while in general it is accepted that Ce is oxidized in surface waters, negative Ce anomalies may be even more pronounced in seawaters (Tostevin et al., 2016). Together these ideas therefore support the importance of both environmental conditions and biological transformation in the study of REE.

3.2 Concluding Remarks

This project aimed to address the concerns raised by the northern community of Kangiqsualujjuaq in the context of a proposed REE mining project within the George River Basin, as well as contribute to the currently limited database on the natural environmental distribution and behaviour of the REE. This was accomplished through the study of multiple terrestrial, freshwater, and marine species, with a particular focus on the tissues of animals consumed by northern communities. Emphasis was placed on the biodistribution and bioaccumulation of REE, as well as the anomalies of Ce, a redox-sensitive REE. These results aimed to further the understanding of the behaviour of REE in undisturbed subarctic ecosystems and the discussions put forth various hypotheses to explain the observed trends. Overall, certain areas of interest for our future studies were proposed. The findings suggest a particular interest may lie in the study of REE fractionation within different subcellular compartments, and in the investigation of the potential use of Ce anomalies as biomarkers for the biological processing of REE.

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Annex A – Supplementary Information

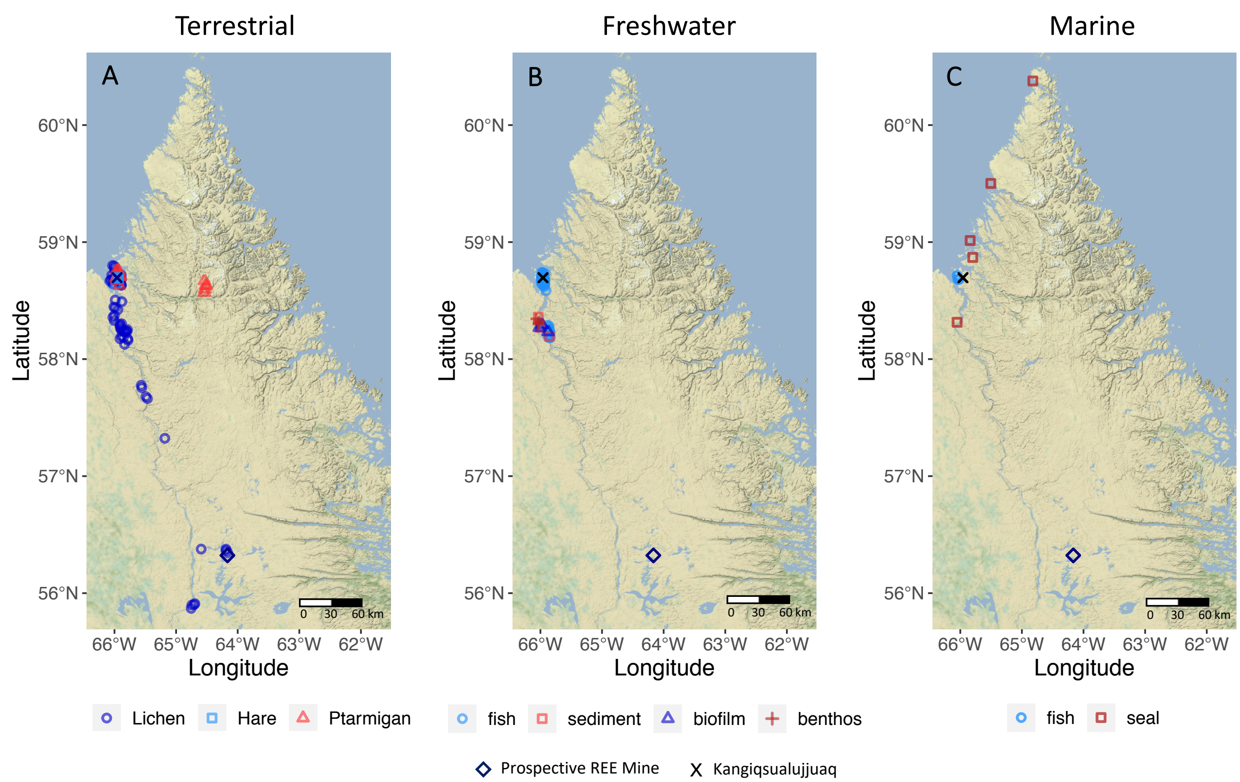

Figure A.1 – Location of samples in the George River Basin and Koroc River Basin of the Ungava Bay region of Nunavik, Quebec, Canada from 2017-2019 organized by sample ecosystem and symbolized by broad taxonomic group. The prospective REE mine site of Strange Lake and the Inuit community of Kangiqsualujjuaq are also depicted.

Reference	n	Y	La	Ce	Pr	Nd	Sm	Eu-151	Eu-153	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
BCR-670	17	84 ± 11	84 ± 12	86 ± 12	91 ± 22	90 ± 11	93 ± 10	84 ± 11	93 ± 10	93 ± 30	81 ± 7	87 ± 8	85 ± 5	87 ± 10	87 ± 7	87 ± 10	66 ± 6
BCR-668	13	76 ± 4	96 ± 6	95 ± 7	98 ± 8	96 ± 4	95 ± 6	98 ± 6	99 ± 8	93 ± 35	92 ± 8	89 ± 7	89 ± 12	86 ± 6	89 ± 9	104 ± 12	95 ± 23
SLRS-6	4	NA	111 ± 4	110 ± 3	118 ± 2	113 ± 3	115 ± 3	NA	NA	118 ± 6	110 ± 9	108 ± 8	111 ± 7	113 ± 4	109 ± 5	107 ± 8	101 ± 16

Table A.1 – Element-wise average ± SD of percent recovery (%) across all analyses runs of certified reference materials.

Element	Detection Limit
Y	0.0011
La	0.0019
Ce	0.0030
Pr	0.0006
Nd	0.0009
Sm	0.0007
Eu	0.0005
Gd	0.0009
Tb	0.0005
Dy	0.0006
Ho	0.0004
Er	0.0006
Tm	0.0004
Yb	0.0004
Lu	0.0004
units:	ug/L, mean

Table A.2 – The detection limits for each element averaged across all ICP-MS/MS analyses.

Group	Y	La	Ce	Pr	Nd	Sm	Eu-151*	Eu-153*	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
sediment	100	100	100	100	100	100	100	NA	100	100	100	100	100	100	100	100
biofilm	100	100	100	100	100	100	100	NA	100	100	100	100	100	100	100	100
benthos	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
lichen	100	100	100	100	100	100	55	95	100	71	100	79	98	55	100	50
fish	94	97	96	96	98	82	58	64	71	46	75	47	63	18	56	21
ptarmigan	54	87	86	63	65	0	41	50	28	0	18	10	12	5	12	4
seal	62	90	95	57	57	29	19	10	29	0	10	0	10	0	0	0

Table A.3. – The frequency of detection (where sample >DL) in percentage (%) for individual REE, according to sample group. NA where element was not analyzed. *Eu-153 was used in calculation of ΣREE where available, otherwise Eu-151 was considered.

	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE
Y	1.00	0.88	0.91	0.92	0.92	0.95	0.89	0.96	0.99	0.97	0.98	0.95	0.99	0.94	0.98	0.93
La		1.00	0.98	0.98	0.98	0.95	0.77	0.90	0.92	0.89	0.90	0.85	0.95	0.82	0.94	0.98
Ce			1.00	0.99	0.99	0.98	0.82	0.94	0.95	0.93	0.94	0.89	0.97	0.88	0.95	0.99
Pr				1.00	1.00	0.98	0.84	0.95	0.95	0.93	0.94	0.90	0.97	0.88	0.95	0.99
Nd					1.00	0.98	0.83	0.95	0.96	0.94	0.95	0.91	0.97	0.89	0.96	0.99
Sm						1.00	0.93	0.97	0.98	0.98	0.97	0.97	0.99	0.92	0.98	0.97
Eu							1.00	0.97	0.99	0.96	0.99	0.97	0.99	0.95	0.99	0.82
Gd								1.00	0.99	0.98	0.98	0.98	0.99	0.95	0.99	0.95
Tb									1.00	1.00	1.00	1.00	1.00	0.97	0.99	0.96
Dy										1.00	1.00	0.99	1.00	0.96	0.99	0.94
Ho											1.00	1.00	1.00	0.97	1.00	0.94
Er												1.00	1.00	0.97	1.00	0.90
Tm													1.00	1.00	1.00	0.97
Yb														1.00	0.99	0.88
Lu															1.00	0.96
ΣREE																1.00

Table A.4 – Pearson's correlation coefficients ('corrplot' in R) for relationships between individual REE, performed on log-normalized data across all samples where concentrations were detected (>DL).

Element	Mean % REE
La	27.9
Ce	37.5
Pr	4.3
Nd	14.9
Sm	2.8
Eu	2.7
Gd	1.9
Y	14.3
Yb	0.4
Tb	0.2
Dy	1.2
Ho	0.2
Er	1.3
Tm	0.1
Lu	0.1

Table A.5 – The mean % of total REE concentrations for each individual REE. Calculated across all samples where concentrations were detected (>DL). The dashed line separates the LREE (upper) and HREE (lower).

Sample Group		[REE] nmol/g Range	[REE] nmol/g Mean (SD)	[REE] nmol/g Geometric Mean (SD)	[REE] mg/kg Range	[REE] mg/kg Mean (SD)	[LREE] nmol/g Range	[LREE] nmol/g Mean (SD)
Lichen		0.47 - 172.40	17.07 (35.05)	5.30 (4.29)	0.06 - 23.62	2.33 (4.80)	0.39 - 153.97	15.03 (31.18)
Biofilm		665.63 - 885.61	750.14 (94.89)	745.87 (1.13)	90.51 - 121.79	102.64 (13.45)	559.06 - 781.23	648.52 (94.22)
Benthic Invertebrates		14.36 - 155.74	90.01 (74.32)	59.96 (3.18)	1.95 - 21.65	12.48 (10.34)	12.34 - 147.43	84.44 (70.74)
Sediment		160.99 - 1122.09	713.45 (337.10)	616.68 (1.83)	22.11 - 154.81	98.02 (46.76)	142.51 - 1010.60	630.10 (310.87)
Arctic Hare	*Liver*	/	19.76 (NA)		/	2.77 (NA)	/	19.72 (NA)
	Muscle Th.	/	0.12 (NA)		/	0.02 (NA)	/	0.12 (NA)
	Kidney	/	0.49 (NA)		/	0.07 (NA)	/	0.45 (NA)
Ptarmigan	*Crop**	0.03 - 2.35	0.56 (0.73)	0.24 (4.18)	0.005 - 0.32	0.08 (0.10)	0.03 - 2.26	0.54 (0.71)
	Gizzard	0.13 - 98.92	18.02 (28.81)	4.97 (6.87)	0.02 - 13.74	2.35 (3.95)	0.10 - 94.41	14.21 (26.91)
	Liver	0.24 - 6.16	1.80 (2.10)	1.00 (2.94)	0.03 - 0.86	0.25 (0.29)	0.24 - 6.14	1.74 (2.02)
	Muscle Th.	0.0004 - 0.39	0.08 (0.11)	0.03 (6.24)	0.00005 - 0.05	0.010 (0.01)	0.0004 - 0.35	0.07 (0.10)
	Muscle Br.	0.00004 - 0.19	0.05 (0.06)	0.01 (11.68)	0.00001 - 0.03	0.006 (0.009)	0.0000 - 0.19	0.05 (0.06)
	Kidney	0.0048 - 0.12	0.06 (0.05)	0.03 (3.77)	0.0007 - 0.02	0.008 (0.007)	0.005 - 0.11	0.05 (0.04)
Whitefish	*Liver*	0.61 - 11.21	2.58 (2.07)	2.12 (1.80)	0.08 - 1.57	0.36 (0.29)	0.57 - 11.01	2.48 (2.05)
	Muscle	0.002 - 1.76	0.16 (0.29)	0.06 (4.67)	0.0002 - 0.24	0.02 (0.04)	0.0007 - 1.60	0.13 (0.26)
	Bone	0.23 - 1.85	0.83 (0.41)	0.74 (1.69)	0.03 - 0.25	0.11 (0.06)	0.20 - 1.51	0.68 (0.35)
	Kidney	0.51 - 5.69	1.65 (1.00)	1.47 (1.58)	0.07 - 0.78	0.23 (0.14)	0.45 - 5.09	1.48 (0.90)
Arctic Char	*Liver*	1.74 - 30.81	12.90 (9.10)	9.82 (2.30)	0.24 - 4.29	1.78 (1.27)	1.54 - 30.12	12.24 (9.04)
	Muscle	0.01 - 1.55	0.27 (0.37)	0.12 (3.74)	0.002 - 0.15	0.04 (0.04)	0.01 - 0.82	0.20 (0.23)
	Bone	0.07 - 5.58	2.59 (1.56)	1.85 (2.92)	0.009 - 0.74	0.34 (0.20)	0.06 - 4.35	1.91 (1.16)
Arctic Cod	*Liver*	0.18 - 0.65	0.42 (0.33)	0.35 (2.45)	0.03 - 0.09	0.06 (0.05)	0.17 - 0.64	0.40 (0.33)
	Muscle	0.05 - 0.08	0.07 (0.02)	0.06 (1.37)	0.007 - 0.01	0.009 (0.002)	0.05 - 0.06	0.05 (0.00)
Arctic Sculpin	*Liver*	0.21 - 1.74	0.80 (0.55)	0.65 (2.04)	0.03 - 0.24	0.11 (0.08)	0.18 - 1.63	0.71 (0.51)
	Muscle	0.06 - 3.33	0.60 (1.21)	0.21 (3.66)	0.008 - 0.46	0.08 (0.17)	0.05 - 3.22	0.57 (1.17)
	Bone	0.32 - 2.47	1.16 (1.15)	0.82 (2.82)	0.04 - 0.33	0.15 (0.16)	0.19 - 2.08	0.91 (1.02)
	Kidney	0.39 - 10.90	3.54 (4.72)	1.51 (4.01)	0.05 - 1.45	0.47 (0.63)	0.36 - 8.08	2.77 (3.54)
Seals	*Liver*	0.03 - 3.53	1.10 (1.20)	0.55 (4.67)	0.003 - 0.49	0.15 (0.17)	0.010 - 3.46	1.07 (1.18)
	Blubber	0.0040 - 0.03	0.01 (0.02)	0.008 (3.16)	0.0006 - 0.00	0.002 (0.00)	0.004 - 0.03	0.01 (0.02)
	Muscle	0.005 - 0.12	0.04 (0.04)	0.02 (3.22)	0.0007 - 0.02	0.005 (0.006)	0.005 - 0.07	0.03 (0.03)
	Bone	0.03 - 0.28	0.12 (0.14)	0.08 (3.21)	0.004 - 0.04	0.02 (0.02)	0.02 - 0.24	0.10 (0.12)

Sample Group		[HREE] nmol/g Range	[HREE] nmol/g Mean (SD)	[LREE]/[HREE] Mean (SD)	Ce/Ce* Range	Ce/Ce* Mean (SD)	La_N/Yb_N Mean (SD)
Lichen		0.09 - 25.00	2.03 (4.33)	6.80 (2.04)	0.84 - 1.74	1.01 (0.11)	2.67 (1.33)
Biofilm		93.69 - 106.57	101.62 (5.63)	6.39 (0.93)	0.91 - 0.99	0.95 (0.03)	1.82 (0.32)
Benthic Invertebrates		2.02 - 8.99	5.57 (3.59)	12.92 (5.14)	0.81 - 0.91	0.86 (0.04)	6.92 (3.17)
Sediment		18.48 - 118.05	83.34 (30.07)	7.33 (1.85)	0.80 - 1.07	0.93 (0.06)	2.26 (0.59)
Arctic Hare	*Liver*	/	0.04 (NA)	440.61 (NA)	/	0.75 (NA)	/
	Muscle Th.	/		/	/		/
	Kidney	/	0.03 (NA)	13.09 (NA)	/	0.80 (NA)	/
Ptarmigan	*Crop**	0.01 - 0.08	0.03 (0.02)	16.30 (8.79)	0.45 - 1.06	0.72 (0.17)	/
	Gizzard	0.02 - 23.36	3.81 (7.14)	8.71 (7.11)	0.49 - 2.15	1.02 (0.43)	8.11 (5.59)
	Liver	0.01 - 0.51	0.10 (0.16)	67.56 (96.66)	0.53 - 0.91	0.72 (0.10)	11.18 (NA)
	Muscle Th.	0.01 - 0.08	0.03 (0.02)	5.59 (4.97)	0.87 - 2.22	1.50 (0.64)	/
	Muscle Br.	/	0.01 (NA)	5.69 (NA)	0.95 - 1.30	1.09 (0.19)	/
	Kidney	0.01 - 0.03	0.02 (0.007)	4.19 (2.70)	0.58 - 1.65	1.20 (0.45)	/
Whitefish	*Liver*	0.04 - 0.29	0.10 (0.07)	28.53 (15.72)	0.41 - 0.59	0.52 (0.04)	238.87 (625.76)
	Muscle	0.001 - 0.16	0.03 (0.03)	4.20 (3.33)	0.23 - 1.20	0.82 (0.25)	2.97 (3.37)
	Bone	0.04 - 0.34	0.16 (0.08)	4.86 (1.83)	0.54 - 0.79	0.64 (0.06)	3.19 (1.03)
	Kidney	0.05 - 0.60	0.16 (0.11)	9.32 (1.76)	0.62 - 1.30	0.85 (0.18)	5.57 (1.09)
Arctic Char	*Liver*	0.04 - 3.41	0.66 (0.77)	27.79 (18.71)	0.40 - 0.70	0.47 (0.07)	55.58 (48.10)
	Muscle	0.007 - 1.26	0.12 (0.30)	7.02 (4.11)	0.57 - 1.24	0.90 (0.14)	0.74 (NA)
	Bone	0.01 - 1.47	0.68 (0.42)	3.12 (0.89)	0.34 - 1.18	0.51 (0.18)	7.29 (3.07)
Arctic Cod	*Liver*	0.01 - 0.02	0.01 (0.003)	26.06 (17.57)	0.75 - 0.75	0.75 (0.00)	/
	Muscle	/	0.02 (NA)	2.48 (NA)	0.96 - 1.21	1.08 (0.17)	/
Arctic Sculpin	*Liver*	0.03 - 0.18	0.08 (0.05)	9.18 (4.83)	0.66 - 0.82	0.73 (0.05)	24.50 (30.48)
	Muscle	0.01 - 0.11	0.03 (0.03)	9.37 (9.29)	0.81 - 1.63	1.06 (0.28)	36.37 (43.70)
	Bone	0.12 - 0.39	0.25 (0.13)	2.92 (2.12)	0.62 - 0.94	0.74 (0.17)	2.83 (1.46)
	Kidney	0.03 - 2.82	0.78 (1.19)	6.78 (3.00)	0.79 - 1.07	0.89 (0.10)	1.64 (1.14)
Seals	*Liver*	0.01 - 0.07	0.03 (0.02)	28.03 (17.72)	0.84 - 0.92	0.87 (0.03)	/
	Blubber	/		/	/	1.13 NA	/
	Muscle	0.005 - 0.05	0.02 (0.02)	2.35 (2.12)	0.72 - 1.31	1.01 (0.41)	/
	Bone	0.008 - 0.04	0.02 (0.02)	4.12 (1.26)	0.86 - 1.26	1.05 (0.20)	/

Table A.6 – Detailed information for REE concentrations, ratios and anomalies organized by sample group with the units listed, where applicable. Outliers (n=2) have been removed from the database. Standard deviation (SD) values not available (NA) where <2 samples had concentrations above detection limit.

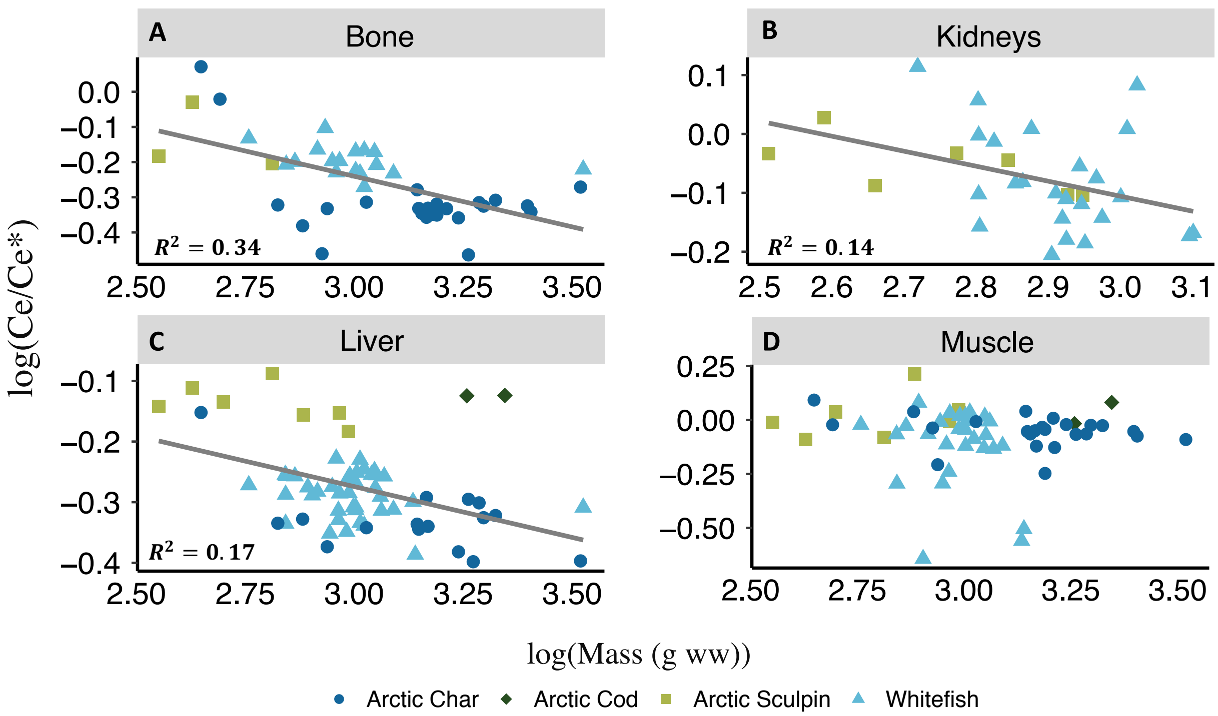

Figure A.2 – Ce anomalies (log-transformed) in (A) bone, (B) kidneys, (C) liver, and (D) muscle tissues of all four fish species studied, explained by animal mass (log-transformed, g ww). R^2 values and regression lines are shown where the linear model is significant (p < 0.01).

Annex B – Scientific Report

IMALIRIJJIT: A Community-based environmental monitoring of the George River Basin, Nunavik, Quebec

Editied by José-Gérin-Lajoie.

Summer 2021.

Included herein:

Chapter 1. Origin of the Project

Chapter 3. Water Quality and Contaminants

Other chapters are found within the original report.

B.1 Origin of the Project

Authors: Holly Marginson [(1)], Gwyneth MacMillan [(2)(3)], Marc Amyot [(1)(3)] and José Gérin-Lajoie [(3)(4)]

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A multi-year study of the George River commenced in 2016 through the Imalirijiit Project, which aimed at forming a collaborative partnership with the Kangiqsualujjuaq community. Kangiqsualujjuaq is located in Nunavik, near where the mouth of George River meets the Ungava Bay. Science and Culture Land Camps were put in place during each field season beginning in the summer of 2016 to help the youth community gain knowledge about research methods, encourage interest in performing land-based science and support the exchange of traditional knowledge with Elders (Gérin-Lajoie et al., 2017; Dubois et al., 2019). The Imalirijiit Project focused on the bilateral exchange of information and joint learning that allowed for researchers to acquire knowledge about a northern fluvial system prior to novel disturbances, and for community members to become better familiarized with data collection and measurements of various parameters in the George River and other nearby rivers (Gérin-Lajoie et al., 2017; Herrmann, 2018; Dubois et al., 2019).

The initial collaboration between research groups and the Inuit community came after a rare earth element mining project was proposed by Quest in the Strange Lake B-zone deposit. The forecasted mining site (56°19'22" N and 64°09'58" W) is located on the eastern side of Lake Brisson and approximately 30 km east of George River (Boisjoly et al., 2015). The originally proposed plan included the construction of the open mine pit, an access road, storage areas for ores and for wastes, tailing management facilities, a treatment plant, and landfill sites (Boisjoly et al., 2015). The project has since been taken over by the Torngat Metals company, who are currently in their prefeasibility study (PFS) phase, with construction planned for 2022 and production forecasted to commence in 2024 (Torngat Metals, 2019). No new site plan is publicly available at this time. As a majority (80%) of the mine area is within the drainage basin of Lake Brisson (Boisjoly et al., 2015), it is an environmental concern that metals from rocks exposed at the surface will reach the George River through atmospheric deposition, surface runoff or leaching. The community of Kangiqsualujjuaq was interested in having their own research carried out, and therefore the information collected aimed at addressing the concerns of the northern communities and contributing to a better understanding of the current situation within George River water, aquatic biota and lichens.

George River is located in Nunavik, Quebec and flows northward from Lac Jannière to Ungava Bay, extending approximately 560 km. It is fed by many tributaries across a drainage area of 41,700 km^2 and has an average discharge of 940 m^3/s (Maccallum, 2014; Laycock, 2015). The George River Basin acts as an important reservoir of resources to Inuit, Innu and Naskapi communities and their traditional activities, such as hunting, fishing and gathering (Brisson, 2005; Pearce et al., 2015; Gérin-Lajoie et al., 2017). It is also home to a variety of northern wildlife species, including the George River caribou herd which migrates through the basin each fall (WDDEC, 2010).

The George River Basin is in a vegetation transition zone, with boreal forest towards the southwest, dominated by coniferous trees at a medium density; and arctic tundra in the northeast, containing primarily lichens and shrubs; then more barren soil and rock towards the Torngat mountains (NR Can., 2009). The treeline runs through the basin, approximately parallel to the George River (Brackley, 2019). The basin is also within a permafrost transition zone, as George River and its surrounding area has discontinuous but widespread permafrost, with more sporadic discontinuous permafrost moving into the southern section and more continuous permafrost towards the northeast in the Torngat mountains (Allard et al., 2012; Brackley, 2019).

The George River Basin is found in the Southeastern Churchill Province of the Canadian Shield, with very old bedrock, primarily Archean (>2.5 billion years ago) and Proterozoic (542 million to 2.5 billion years ago) and includes plutonic and metaplutonic rocks. Evidence of Paleoproterozoic intrusions of various compositions (K-rich, mafic) and volcanic activity have been observed in the area, alongside outcrops showing partial melting. Deformation patterns are also associated with the major shear zones that run N-S, in proximity and parallel to the southern half of the George River (Énergie et Ressources Naturelles Québec; Wardle, 2002). The Strange Lake mining operation aims to extract the rare earth elements from the veins of high-grade peralkaline granitic pegmatite (Gysi & Williams-Jones, 2012, 2013; Boisjoly et al., 2015).

In terms of the Köppen-Geiger climate index, the study area is classified as type *Dfc*, which by definition are continental, snowy and humid zones with short cold summers; and similar precipitation amounts in both seasons (Kottek et al., 2006; Beck et al., 2018). This is reflected in the annual temperature and precipitation trends collected over the past year in Kangiqsualujjuaq by Environmental and Climate Change Canada (ECCC). In 2019-20, the months with an average temperature below zero were November to May, and only August and July saw an average temperature above 10^{o}C. Historical precipitation data was only available for the nearby weather station in Kuujjuaq, provided by ECCC (accessed via Weather Stats). For the past five years (2016-2020), the average yearly rainfall was 260 mm and the average yearly snowfall was 210 cm.

B.2 Water Quality and Contaminants

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B.2.1 Context and Objectives

The water quality and background levels of trace elements, rare earth elements (REE) and mercury within the George River were not well known prior to the commencement of this research project. The first scientific objective was to evaluate the baseline values for selected parameters by sampling George River water over the past five field seasons (2016-2020). These baseline values are expected to reflect the natural levels of the measured parameters prior to any disturbance and are often low relative to estimated toxicity thresholds. As climate change and the opening of the Strange Lake mine may lead to variations in the George River Basin, this collected data will act as a reference in determining if perturbations are introduced. Long-term temporal and spatial observations will be made possible by continued monitoring of the river at various points along its length.

A second objective involved assessing the water quality of the George River, which was accomplished by evaluating water samples, and supplemented by the identification and analysis of invertebrates, biofilm and sediments in order to compile an overall assessment of the ecological state of the area. Each year, Science and Culture Land Camp attendees participated in collecting and sorting through macro-invertebrates while referencing a guide to aid in classification; they learnt how these different benthic species can provide information about long-term water quality. In 2019, terrestrial insects were also gathered in the field and included in this identification activity. The Science Camps shared scientific knowledge with attendees as they were shown how water quality data is taken and they learnt how to use both manual testing kits and YSI probes. This data will also help determine the drivers of change in the George River Basin in relation to changing basin hydrogeomorphology, for example, by locating and sampling sediment from deposition zones in the river. This study will contribute to a better understanding of the behaviour of metals, especially the rare earth elements, in a northern fluvial environment and how their transport relates to carbon fluxes within the basin.

Additionally, a community-based monitoring of biota was carried out on key food species, namely fish (*iqaluk*), seal (*natsiq*) and ptarmigan (*aqiggik*), to assess baseline levels of trace elements, REE, and mercury. The hunters' skills were essential for collecting biological samples and camp participants assisted with the cleaning and dissecting process for fish samples. The sampling intended to collect caribou (*tuktu*) samples, but no caribou hunting occurred near the community during the collection period. Finally, lichens (*tingaujait*) were sampled at a variety of locations within the George River Basin, with interest in areas near human activity. Lichens are sensitive to changes in air quality as they acquire their nutrients, and consequently contaminants, from the air. The goal in sampling lichens throughout the basin was to determine a baseline value for metals in lichen, and to track any spatial or temporal atmospheric changes. During the 2018 and 2019 land camps, the youth participated in collecting lichen samples. Overall, contributions from Science Camp participants, youth, Elders and guides were important in meeting the objectives of this project in collaboration with the researchers. (Gérin- Lajoie et al., 2017; Gérin-Lajoie et al., 2018; Dubois et al., 2019; Dubois et al., 2020).

B.2.2 Methods

B.2.2.1 Water Samples

From 2016 to 2019 there were a total of 19 water sampling stations within the George River Basin and one within the Koroc River (Figure B.1). While some stations were resampled in various years, others were only sampled in a single year. An extensive length of the river was studied, with samples taken at points from the confluence with De Pas River in the south, to the estuary at the mouth of the river where it meets the Ungava Bay. During these years, sampling took place across a period of 4 to 11 days in late June to end of July, weather permitting. Parks Nunavik helped with data collection in areas requiring helicopter transportation, in particular those in the Koroc River. The field season of 2020 was postponed until August due to the COVID-19 travel restrictions set in place. Fortunately, Parks Nunavik generously offered to collect water samples for the team. Ten stations were sampled from August 17th to 19th: five of these stations were within the George River and the remaining half were located within the Koroc River. The 2020 surface water data is currently being analyzed in Amyot's Lab at the University of Montreal.

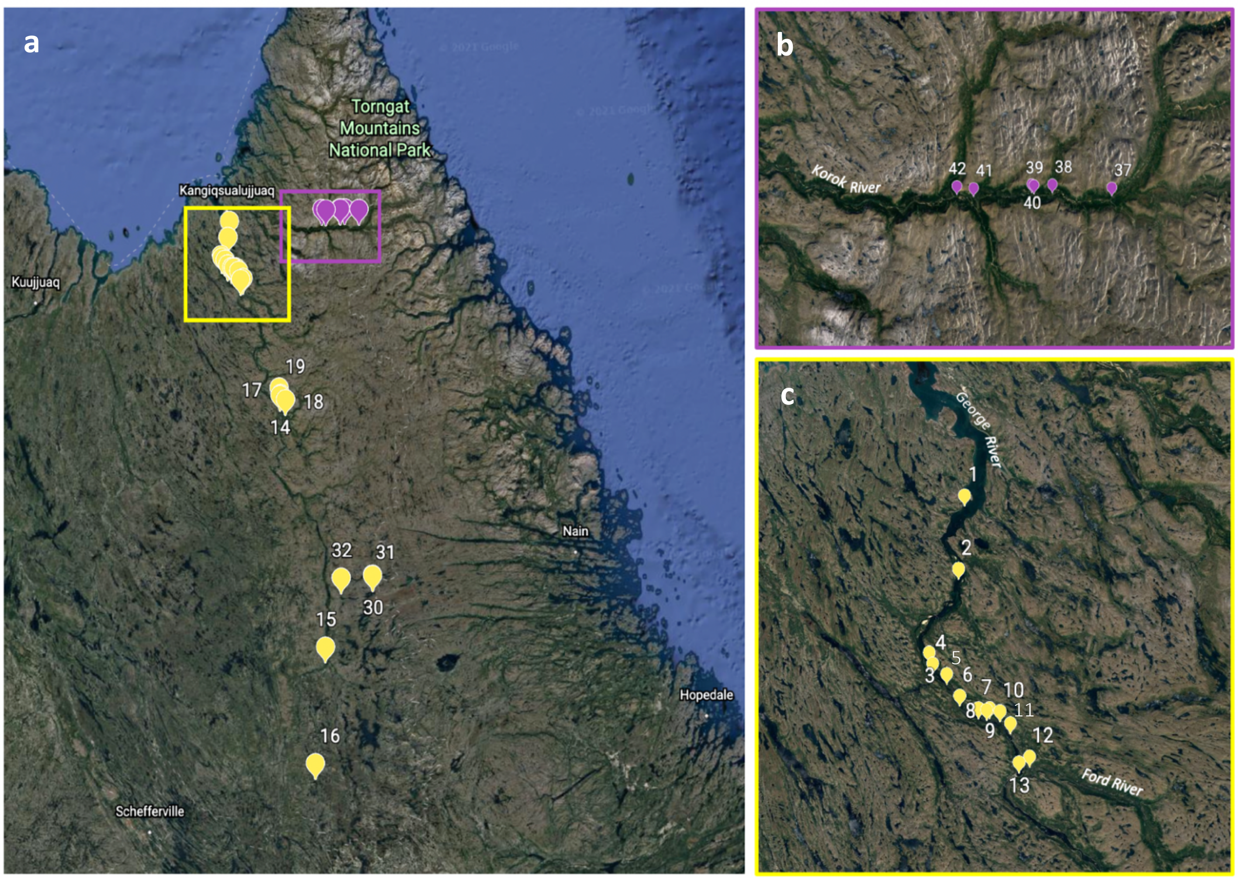

Figure B.1 – Left **(a)** Map of all stations from 2016-2020. George River Basin stations marked in yellow; Koroc River stations marked in purple. The boxes outline the areas that are in zoom view in 'b' and 'c'. Upper right **(b)**: Zoomed in view of Koroc River stations 37 to 42. Bottom right **(c)**: Zoomed in view of George River stations 1 to 13, located near the mouth of the river. The confluence with Ford River is visible at the bottom of the map. *Prepared using Google Earth.*

Water surface samples were collected from the shore or directly from the boat where applicable, from an arm's length depth of approximately 30 cm using the clean-hands, dirty-hands protocol (St-Louis et al., 1994). On-site water filtration was performed prior to transferring the water into sample bottles, for samples that required this step. Once prepared, sample bottles were stored in coolers within double plastic bags. All field blanks were prepared using ultra-pure (Milli-Q) water and treated in the same manner as their respective samples, including filtration and preservation by acid, if applicable, as well as transportation and storage methods.

Each year the surface water physicochemistry was tested using a handheld electronic YSI Probe (*Pro Plus*). This instrument provides *in situ* readings of the following parameters: water temperature, water pressure, dissolved oxygen, conductivity, and pH. Water samples were analyzed for major ions, nutrients, dissolved organic and inorganic carbon (DOC/DIC), mercury, trace metals and rare earth elements, and in 2016 and 2017 for chlorophyll-a. In 2016 and 2017 physicochemical analysis were performed by Environment and Climate Change Canada (ECCC) at the Burlington National Lab for Environmental Testing. In the following years, surface water anions were tested by the INRS Centre Eau Terre Environnement by ionic chromatography, and the TP (Astoria 2), TN (Lachat Quickchem 8500) and DOC (OI Instrument Aurora) were analyzed in Amyot's Lab at the University of Montreal. Trace metals were analyzed in Kevin Wilkinson's lab in 2016 (ICP-MS), then in the following years at Amyot's Lab (University of Montreal) along with the rare earth elements (ICP-MS/MS) and mercury analyses (Tekran 2700, DMA80). There was a total of 25 metals and 16 rare earth elements (excludes Pm) analyzed from 2016 to 2019.

B.2.2.2 Sediment Samples

Sediment samples were taken in 2017 at a distance of 3 m from the shore of the river, or small tributaries of the river, where the water depth was between 0.3 and 0.5 m. Triplicates were taken at three stations using a hand-corer with a 5 cm diameter tubing. Samples were collected from two different depths at each site: 0-5 cm and 5-10 cm, and often contained a majority of rock and sand material. The sediments were freeze-dried for at least 72 hours before analysis, digested, centrifuged and then analyzed at Amyot's Lab at the University of Montreal for trace metals, rare earth elements and mercury. It should be noted that having only 3 sediment sites is considered a small sample size.

B.2.2.3 Biota Samples

A total of 39 lichen samples were collected across a large field area in 2017 and 2018, including areas near the town of Kangiqsualujjuaq, along George River, and at Lake Brisson. The above-ground segments of the lichens were sampled, placed in bags and frozen until laboratory work. Reindeer lichens were subsampled in the lab by selecting for this dominant species of genus *Cladonia* (*Tingaujait*)*,* then freeze-dried for 24 hours. Samples were crushed first by hand, then transferred to vials using an anti-static apparatus and further homogenized using a glass rod until powdered. Lichen samples were digested, centrifuged and then analyzed for trace metals, rare earth elements and mercury.

In 2017, biofilm samples were collected at three sites in triplicate by brushing multiple (3) rocks for each replicate. Samples were freeze-dried prior to analysis for at least 72 hours. Biofilm samples were then digested, centrifuged due to formation of a deposit in the vial, and analyzed for trace metals, rare earth elements and mercury.

Benthic invertebrates were collected in 2017 within a northern tributary site of the George River. The individuals were sorted by taxonomic group and four samples were obtained: 1 for stoneflies, 1 for mayflies, and 2 caddisfly groups. All invertebrate samples were freeze-dried, homogenized, digested, and finally analyzed for trace metals, rare earth elements and methylmercury (MeHg).

A total of 76 fish (Arctic char/*iqalupik*, whitefish/*kasivilik*, sculpin/*kanayuk* and cod/*uugaq*) and 7 seal (bearded seal/*udjuk* and ringed seal/*natsiq*) samples were collected in 2017 and 2018.

Hunters were provided with sampling kits and protocols, as well as forms to identify and provide details of each sample. Financial compensation was given for the samples collected. The fish and seal sub-samples were prepared by removing and separating their organs/tissues into different bags. Dissections were performed using acid-washed tools. The samples of interest were muscle, liver, kidney and bone from fish; and muscle, liver, blubber (fat) and bone from seal. Fish bones included the opercula, which were taken from the head of the fish, and 2-4 vertebrates located at the dorsal fin level. However, the vertebras always had a small amount of material remaining on them after cleaning, which affected the analysis and were therefore not included in the results. Bones were removed from the back of the jaw for the seal samples. Animal tissues were homogenized, except for bones, which were simply crushed using a hammer on the exterior of the sample bag to avoid contamination. The samples were then digested and analysed for metals, rare earth elements and mercury. Finally, there are a total of 20 ptarmigan/*aqiggik* samples from 2018, and 23 lichen/*tingaujait* samples from 2019 that are currently being analyzed in Amyot's Lab.

B.2.3 Results and Discussion

B.2.3.1 Water

B.2.3.1.1 Physicochemistry

The surface water physicochemical variables are of interest in a river study as they reflect the water quality, which can be considered a measure of the health of the water body. Each parameter plays a role in the distribution of nutrients and trace metals in the environment, affecting what form they are found in and consequently, their availability to biological life. The water quality also provides an idea of the general state of the river at the time of sampling and can be traced across multiple years in order to assess changes occurring. These values can reflect the health of producers and consumers, as well as certain anthropogenic influences acting on the water body.

The **pH level** is measured on a scale of 0 to 14, with a 10-fold difference between each value. A pH level of 7 means the water is considered neutral, with equal concentrations of H^+ and OH^- ions. Values lower than 7 are considered acidic, meaning there is a greater $[H^+]$ present, while values higher than 7 are referred to as alkaline, having a larger $[OH^-]$. This value is important as it affects different aspects of river health, such as the bioavailability of nutrients and metals, toxicity effects, and the success of aquatic species. The George River and its tributaries, as well as the Koroc River, have similar average pH values of 7.0 to 7.2 (Table B.1). These pH levels are consistent with the literature, which suggests that typical pH values of northern subarctic to arctic rivers fall within an approximate range of 4.7 to 8.1 (Niemi, 2010; Pokrovsky et al., 2015). There is some inter-site variation within the George River, seen by values ranging between 6.2 and 7.8, though all values hover around a neutral pH. A slight elevation in pH is observed at Lake Brisson and within the estuary at the mouth of the river, suggesting this water is more alkaline.

Temperature is a parameter that can vary greatly between sites, time of day and sampling day due to fluctuations in atmospheric temperature, amount of sunlight reaching the water and water depth. Aquatic animal life often benefits from lower water temperatures, which is expected of these northern rivers. On average, George River and its tributaries were found to have temperatures averaging around 10-12 °C in the summer sampling months (Table B.1). In comparison, Lake Brisson and Koroc River waters were both colder at an average of 4 °C. As a note, Lake Brisson was almost entirely frozen at the time of sampling.

Chlorophyll-a is the pigment that gives plants, algae and cyanobacteria their green colour and plays a role in oxygen photosynthesis by allowing sunlight energy to be transformed into usable energy. The concentration of chlorophyll-a in the surface water can act as an estimate of the amount of primary productivity in the river (Tundisi, & Tundisi, 2012), as it is related to the amount of phytoplankton and micro-algae present (Gérin-Lajoie et al., 2017). The greater the chlorophyll-a concentration, the more primary productivity is present in the river, which is related to plant growth. Many of the samples were found to have concentrations below the detection limit (<0.1 ug/L), and in the George River and its measured tributaries values never exceeded 0.7 ug/L (Table B.1). These concentrations are on the same orders of magnitude as other northern freshwater bodies studied (Filazzola et al., 2020) and demonstrate a low productivity in the George River Basin.

Certain molecules, such as salts, dissociate when present in water. This leads to the presence of ions, which can be either negatively charged anions or positively charged cations. Charged particles in an aqueous solution have the ability to conduct electricity – this is measured by the **specific conductance (SPC)**. Presence of ions such as bicarbonate can aid in the maintenance of pH level as they have the ability to buffer the water. High concentrations of ions are associated with sedimentary (carbonate) bedrocks, which are susceptible to the release of ions from minerals by dissolution. Pollution and climate change may contribute to increased conductivity in water systems. The George River had an average SPC of 13 uS/cm, with slightly higher values seen in the northern tributaries and the Koroc River at 26 and 30 uS/cm, respectively (Table B.1). These values represent low conductance in the watersheds (EPA, 2012b). This is more noticeable in comparison to the SPC found in the estuary, 5206 uS/cm, due to the mixing of the river with the saltwater of the Ungava Bay.

Dissolved organic carbon (DOC) is a parameter of interest in the study of water quality for its application to ecotoxicology. DOC is the fraction of organic carbon that can pass through a filter with fine pores; in this study a 0.45 μm pore size cellulose acetate filter was used (*Nalge Nunc International)*. DOC originates from the decomposition of dead plants and animals, either within the river or from surface runoff transporting material from nearby terrestrial environments. The dissolved organic carbon can complex certain metals, which can affect metal transport and bioavailability, and decrease metal toxicity to organisms living in the water (Baken et al., 2011; Mostofa et al., 2013). It can also be metabolized by aquatic microbes (Dodds & Whiles 2010). Freshwater sources may be considered organic-rich when the DOC level surpasses approximately 7 mg/L (Pourrett et al., 2007) or 5 mg/L (Marsac et al., 2010). DOC concentrations were low in the

George River at an average of 2.5 mg/L, which is also seen in the Koroc River at 1.9 mg/L (Table B.1). The water source with the greatest amount of DOC was the northern tributaries, which was expected due to their darker brown colour relative to the clearer water of the main river. Overall, the DOC concentrations presented in this report are at the lower end of values characteristic of northern freshwater bodies (Chételat et al., 2015; Filazzola et al., 2020). For example, Chételat et al. (2015) compiled a list of Canadian Arctic rivers and streams with DOC concentrations, where available, that presents DOC values ranging from 0.9 – 20.5 mg/L. Further, Filazzola et al. (2020) produced a dataset of lake characteristics found in the literature that when filtered for subarctic and arctic (latitude > 55°N) gave an average DOC of 5.59 mg/L (range 0.6 – 33.6 mg/L).

Total nitrogen (TN) and **total phosphorus (TP)** are nutrients in the river that can limit production at low concentrations, or favor growth at higher concentrations, as plants require them for growth and reproduction. Excess levels can cause problems with overgrowth of algae/*kuannik*, which would lead to a decreased concentration of dissolved oxygen available for animals, including fish, and may lead to a reduction of their populations. The average TN across field samples was on the order of 0.1 mg/L, and the average TP concentration was on the order of 0.01 mg/L (Table B.1). These low values indicate that the George River Basin and nearby Koroc River are not likely being affected by anthropogenic sources and contain a naturally low level of nutrients, which is often the case for undisturbed northern rivers (Niemi, 2010; Filazzola et al., 2020). The rivers are therefore considered oligotrophic in nature, with low nutrient levels and plant growth.

Overall, the George River has oligotrophic, relatively neutral waters with low productivity and conductivity.

Water Source	pH		Temp		Chl-a	SPC		DOC		TN		TP		∑ REE	
	Mean	Range	Mean	Range	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	SD
	0 - 14 Scale		*°C*		*ug/L*	*uS/cm*		*mg/L*		*mg/L*		*mg/L*		*nmol/L*	
George River	7.1	6.2 – 7.8	12	4 – 18	<0.1 – 0.7	13	7 – 16	2.5	1.5 - 4.7	0.118	0.096 - 0.175	0.007	0.002 - 0.034	5.55	1.79
Northern Tributaries	7.2	6.8 – 7.6	10	7 – 16	<0.1 – 0.5	26	15 – 35	5.6	3.3 - 10.5	0.135	0.123 - 0.146	0.005	0.004 - 0.006	29.51	11.81
Ford River (T)	7	6.9 – 7.2	10	3 – 14	NA	13	11 – 14	1.1	0.7- 1.9	0.075	0.063 - 0.095	0.004	0.003 - 0.006	3.63	1.28
Lake Brisson	7.5	7.0 – 9.6	4	2 – 6	NA	NA	NA	2.1	1.9 - 2.9	NA	NA	NA	NA	4.64	1.50
Estuary	7.6	NA	13	NA	0.4 – 0.7	5206	4920 – 5492	NA	NA	0.120	0.111 - 0.128	0.005	NA	2.34	NA
Korok River	7.2	NA	4	NA	NA	30	NA	1.9	1.8 - 2.0	NA	NA	NA	NA	5.62	3.33

Table B.1 – The table displays mean values and the range or standard deviation of the following variables measured in surface waters: temperature (Temp); chlorophyll a (Chl-a); specific conductance (SPC); dissolved organic carbon (DOC); total nitrogen (TN); total phosphorus (TP); sum of rare earth elements (ΣREE; as described in the following section). A (T) in water source indicates the river is a tributary of the George River. Northern tributaries include two creeks that flow into the George River.

B.2.3.1.2 Rare Earth Elements

The rare earth elements (REE) are a group of metals present in the earth's crust and are named for their low concentration densities in rocks, but not for their low concentrations as a whole in the earth's crust (Ng et al., 2011). The name comes from the fact that they were not as available for commercial use as other metals, as they required extensive processing by difficult and complex steps in order to extract them from their host minerals (EPA, 2012). The REE are of interest to mining companies for their use in processing, such as of glass, ceramics, and petroleum refining and in products such as catalytic converters, magnets, electronics, and fertilizers (Ng et al., 2011). The REE are composed of the lanthanides divided into two groups: the light rare earth elements (LREE) and the heavy rare earth elements (HREE). The LREE consist of elements 57 to 64: cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), and gadolinium (Gd); the HREE are elements 65 – 71: terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). Two additional elements, Yttrium (Y) and scandium (Sc), are also classified with the rare earths, heavy and light respectively, as they share many chemical properties with this group and are therefore often associated with them (EPA, 2012).

It is known that the REE are predictable in their behaviour relative to each other, as they react in like ways within a specific environment in response to the area's water physicochemistry and hydrogeomorphology (EPA, 2012). This is due to their similar molecular weights, molecular sizes and oxidation states. For example, REE are known to be more soluble at lower pH values and lower water conductivity (Humphris, 1984; Gonzalez et al., 2014). Though present naturally from the weathering of rocks, the toxic effects of rare earths at higher concentrations on animal and environmental health are not fully understood. Current samples contribute to the development of baseline REE concentrations in the George River Basin, an interest to the community as development of a Rare Earth Mine at Strange Lake, near Lake Brisson, brings with it concerns about environmental changes and potential impacts. Continued study of REE controls and their environmental pathways will allow for a better prediction of the potential outcomes of mining and climate change in this northern setting.

The total concentration of rare earth elements (ΣREE) was calculated by summing the elements that had a 60% or greater percent recovery for the sample group and low analytical blanks (<15%) (Figure B.2). Measurements that were below detection limit, determined in each analysis by method detection limit (MDL), were marked as ND (not detected) and were therefore not considered in the calculation.

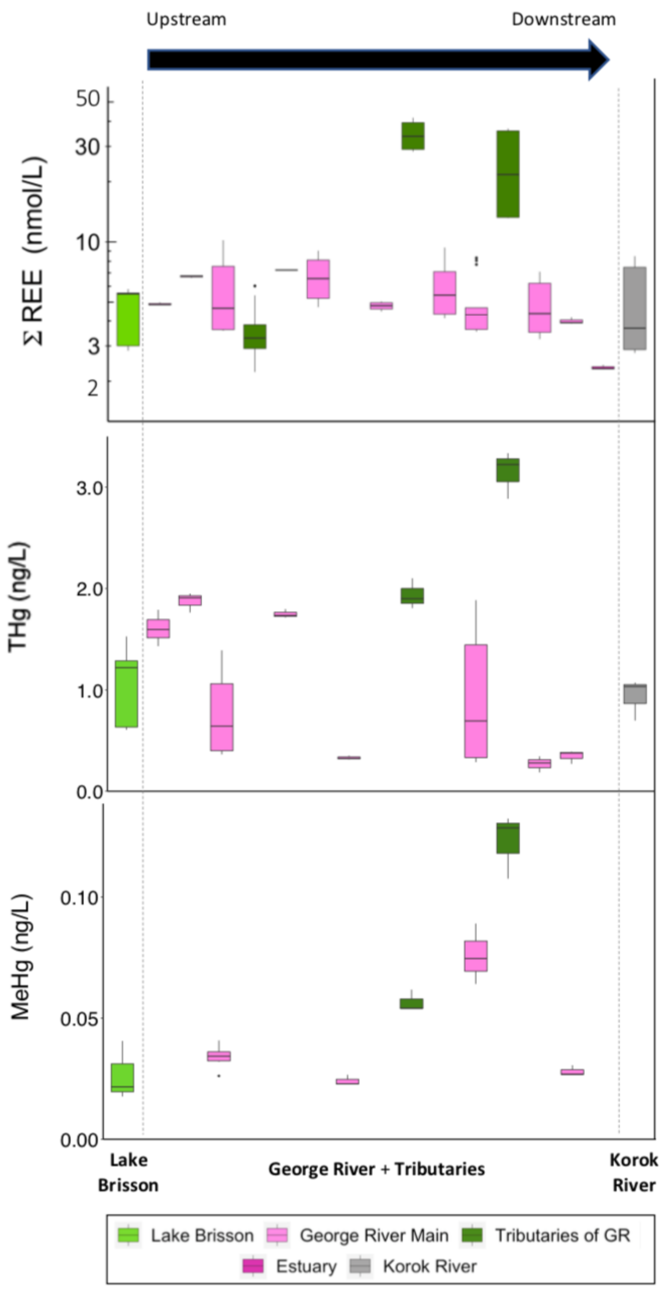

Figure B.2 – The REE, total mercury (THg) and methylmercury (MeHg) concentrations of surface waters of Lake Brisson, George River and its tributaries, and Koroc River to demonstrate the relative concentrations between stations – data from 2016 to 2019 included. Elements included were Y, La, Ce, Pr, Nd, Sm, Gd, Dy, and Er.

The concentration of REE within the mainstem of the George River ranged from 3.2 nmol/L to 10.2 nmol/L with an average of 5.5 ± 1.8 nmol/L. The REE concentration of the surface waters was quite constant along the length of the river studied (Fig. B.2). The tributaries showed unique rare earth concentrations compared to the mainstem, seen especially in the higher concentrations for the northern tributaries with an average value of 29.5 ± 11.8 nmol/L – almost six times larger. However, the inflow of water from these tributaries did not appear to have any observable effect on the concentration of REE within the George River, which remained constant until it met the Ungava Bay. The REE near the mine site at Lake Brisson showed relatively low concentrations as well, with a range of 2.8 – 5.8 nmol/L. As a comparison, the range in the Koroc River is 2.8 – 8.5 nmol/L. These values are representative of uncontaminated freshwater surface waters, as summarized by MacMillan et al. (2019), where REE values were found between 0.1 – 20.8 nmol/L in 39 lakes of Eastern Canada.

Two stations were sampled in each year from 2016 to 2019 and were looked at in greater detail in order to assess if there were any noticeable interannual changes in REE concentrations (Fig. B.3). One of the stations was located within the mainstem of the George River and the other was within one of its tributaries with a relatively low concentration of REE, the Ford River. The Ford River was classified separately than the northern tributaries as it is larger in output, and has a more transparent and greener colour.

There was a 2- to 3-fold difference between REE across the four sample years, as well as an almost 3-fold difference in total rainfall calculated from January to July for each field year from data collected by ECCC in the nearby town of Kuujjuaq, located approximately 160 km southwest of Kangiqsualujjuaq (Weather Stats, n.d.). Figure B.3 suggests there is a similar trend in the two water sources between years. However, as there is not a direct correlation between all rainfall and REE data, the information here encourages further study of the relationship between hydrology and REE distribution in the river system. One hypothesis is that there may be a dilution effect from increased rainfall contributing to the rare earth element concentrations.

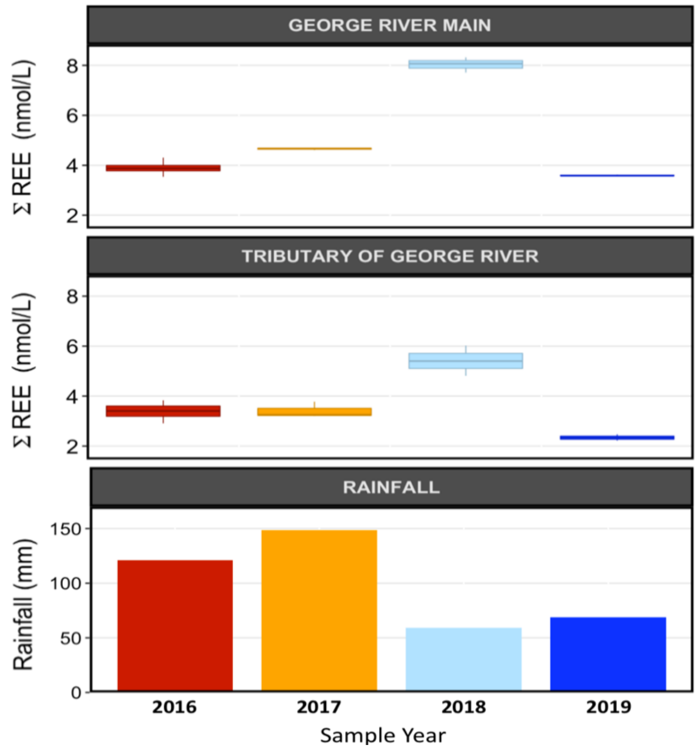

Figure B.3 – The comparison of REE concentrations between a George River station and a tributary station across four sampling years, in relation to rainfall levels.

Dissolved organic matter complexes with REE are important components of REE speciation (Pourret et al., 2007; Matsunaga et al., 2015). DOC, a measure of the carbon content in organic matter, has been shown in previous studies to positively correlate with dissolved REE concentrations in freshwater systems (Johannesson et al., 2004; Vázquez-Ortega et al., 2015). The relationship between DOC and REE has been further studied within the George River Basin and Koroc River freshwater samples presented in the current study (Fig. B.4). All samples were considered in the determination of this relationship, which was found to represent a significant positive linear correlation ($p<0.001$; $R^2 = 0.47$). This suggests that as the DOC concentration increases in the surface water of a river system, there will be greater concentration of dissolved REE. This is supported by the favorable association between REE and oxygen-rich groups within the dissolved organic matter. Another study hypothesized that this association between REE and DOC may decrease the bioavailability of these metal elements for aquatic invertebrates

(MacMillan et al., 2019), which would decrease their presence in the food chain and therefore could potentially aid in decreasing any toxic effects.

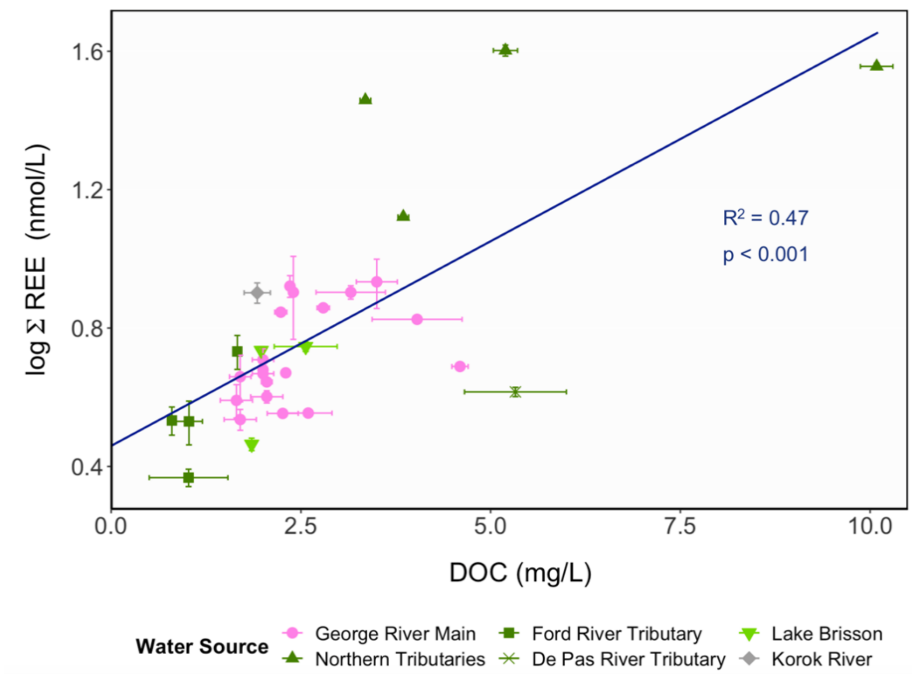

Figure B.4 – The relationship between DOC (mg/L) and total rare earth element concentration (log-transformed; nmol/L) in the northern freshwater surface water of George River, its tributaries, Lake Brisson and the Koroc River. The REE values were logged for a better visualization of the points.

B.2.3.1.3 Mercury

Mercury is naturally present in the environment from sources such as weathering of minerals containing traces of mercury, and volcanic activity. In addition, increases are also seen from human activity, such as by combustion of mercury in fossil fuels and use of products containing mercury (Lavoie et al., 2013; EPA, 2020). Atmospheric mercury can deposit on land or on the surface of water. In aquatic systems, bacteria living in the water can methylate the inorganic mercury, which produces the more toxic form called methylmercury (MeHg). This form of mercury can get absorbed into tissues, muscle, and organs of fish, humans and other animals, and tends to display biomagnification along the food chain (AMAP, 2011; Depew et al., 2013), meaning there is an increase in MeHg expected at higher trophic levels. The bioavailability of MeHg in an aquatic environment is dependent on physicochemical variables, among others (Depew et al., 2013).

The total mercury (THg) and MeHg concentrations of surface water samples are reported in Figure B.2, for stations where mercury sampling was carried out. The range of THg in surface water samples was found to be 0.19 to 3.34 ng/L with a mean of 1.12 ng/L. These concentrations were lower for MeHg, at 0.02 – 0.13 ng/L with a mean of 0.05 ng/L. The THg and MeHg measurements in the George River Basin and nearby water sources were on the same orders of magnitude as data presented in the literature for Canadian Arctic and subarctic freshwater sources, such as lakes and rivers (Chételat et al., 2015; Warnock, 2015).

B.2.3.2 Sediments

B.2.3.2.1 Rare Earth Elements

REE are highly associated with sediments due to their poor solubility in water, especially when aqueous conditions are not acidic. They tend to be preferentially found in complexes with organic matter and inorganic molecules, rather than in the dissolved form (Ng et al., 2011). Therefore, a large portion of the REE present will adsorb to the surface of sediment particles in the water column and deposit. These sediments could potentially serve as a way of monitoring the transport and deposition of REE and other metals of interest.

The sediment samples from the three different stations demonstrated a range of values from 160 nmol/g to 1120 nmol/g (Fig. B.5). The REE concentrations seen in the George River samples were similar to values found in the literature for remote, undisturbed locations. For example, in the previously mentioned study by MacMillan et al. (2019), they found a REE range of 300 – 3000 nmol/g for surface sediments among 39 sampled Eastern Canada lakes. Additionally, a study by Marmolejo-Rodríguez et al. (2017) of 13 sites within the Marabasco River in Mexico recorded REE concentrations of 318 to 872 nmol/g. Further, Amyot et al. (2017) reported an average REE concentration of 1150 ± 500 nmol/g from 10 sediment samples within temperature lakes of Southern Quebec. Variations in sediment concentrations were observed among locations, which could indicate a future application of sediment analysis in tracking REE behaviour. Organic matter measurements by loss on ignition (LOI) method will be taken for George River sediments with the hypothesis that it will contribute to the explanation of REE distribution in the basin (Ramos et al., 2016; Amyot et al., 2017).

B.2.3.2.2 Mercury

A large intra-site variability in MeHg content was seen in two sites with concentrations that ranged by a factor of approximately 3 (Fig. B.5). Overall, total mercury in the sediments was between 1.0 and 27 ng/g with an average of 9.9 ng/g. The concentration of MeHg in the sediments was found to be within 0.01 – 0.6 ng/g with a mean value of 0.2 ng/g. The amount of MeHg relative to THg within the sediments represented a percentage of 0.5 - 5.0 % MeHg. The mean sediment MeHg concentration in this study was an order of magnitude lower than the average seen in a study of surface sediments from various northern American freshwater bodies, which was given as 3.83 ng/g (Kamman et al., 2005). In comparison to the same study, the George River mean sediment THg concentration was found to be two orders of magnitude lower than their average of 190 ng/g. It was noted in the Kamman (2005) study that rivers had the lowest concentrations relative to the lakes and reservoirs sampled. However, the George River sediments THg and MeHg concentrations were on the same orders of magnitude as sites without disturbances in other freshwater studies (Mosher et al., 2012; Ferriz et al., 2020).

Figure B.5 demonstrates the REE and MeHg concentrations and the % MeHg relative to the depth of the sediment sample. Often sediment depth correlates with time since sediment deposition, though in this case the top 10 cm of sediments in a river system are being examined, which are unstable due to the flow of water. The presence of metals may also be correlated to organic matter in the sediments (Ferriz et al., 2020) and will therefore be analyzed in the George River samples through a loss on ignition analysis, as mentioned in B.2.3.2.1.

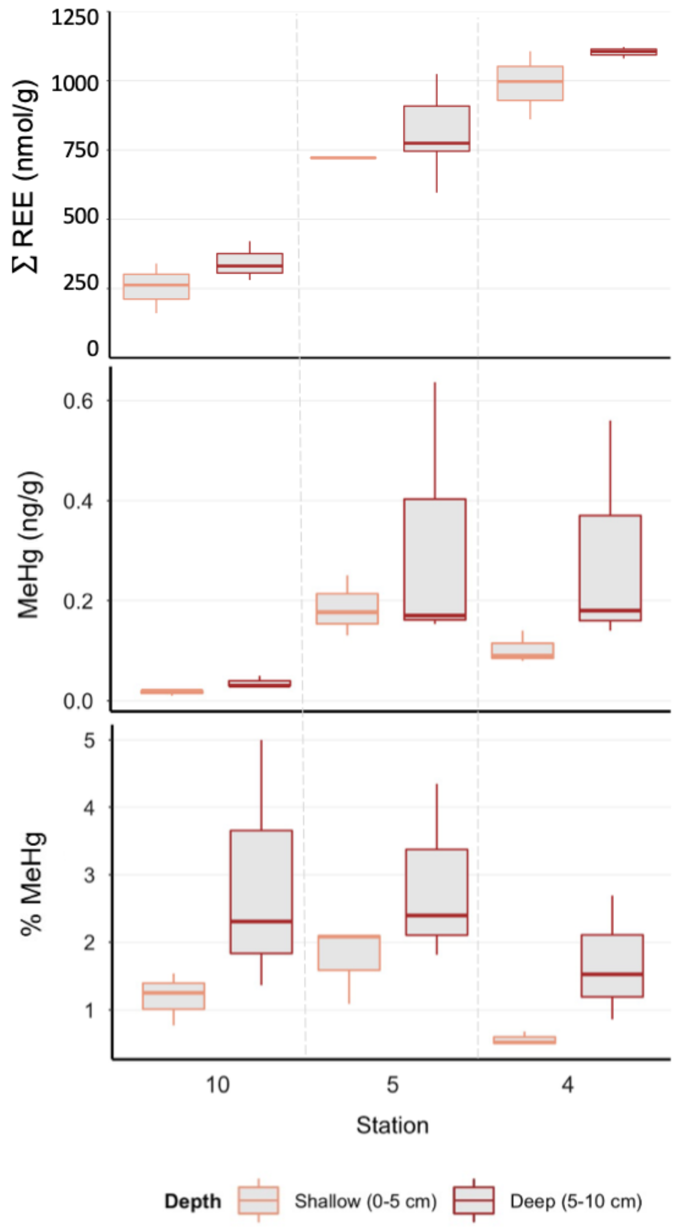

Figure B.5 – Total rare earth element concentrations (nmol/g), methylmercury content (ug/g) and % MeHg in sediment samples taken at three sites along the George River. The two colors of boxplots represent samples from different depths: 0-5 cm (left side of each section) and 5-10 cm. Sample size (n) of 3 per box.

B.2.3.3 Biota

B.2.3.3.1 Rare Earth Elements

There was a large variation in total REE concentrations among the biota samples studied (Fig. B.6). This was reflected in an inter-group variation across 7 orders of magnitude, and some intra-group variations that span up to 3 orders of magnitude. The trend in terms of the medians of the sample groups went in decreasing order from: biofilm > benthos > lichen > fish > seals. The differences among taxonomic groups could be associated with the speciation of REE in the range of environments studied, and therefore influencing the bioavailability of REE to each group. Additionally, for both invertebrate and vertebrate animals, differences can be attributed to their unique behaviours and physiological characteristics (Malhotra et al., 2020).

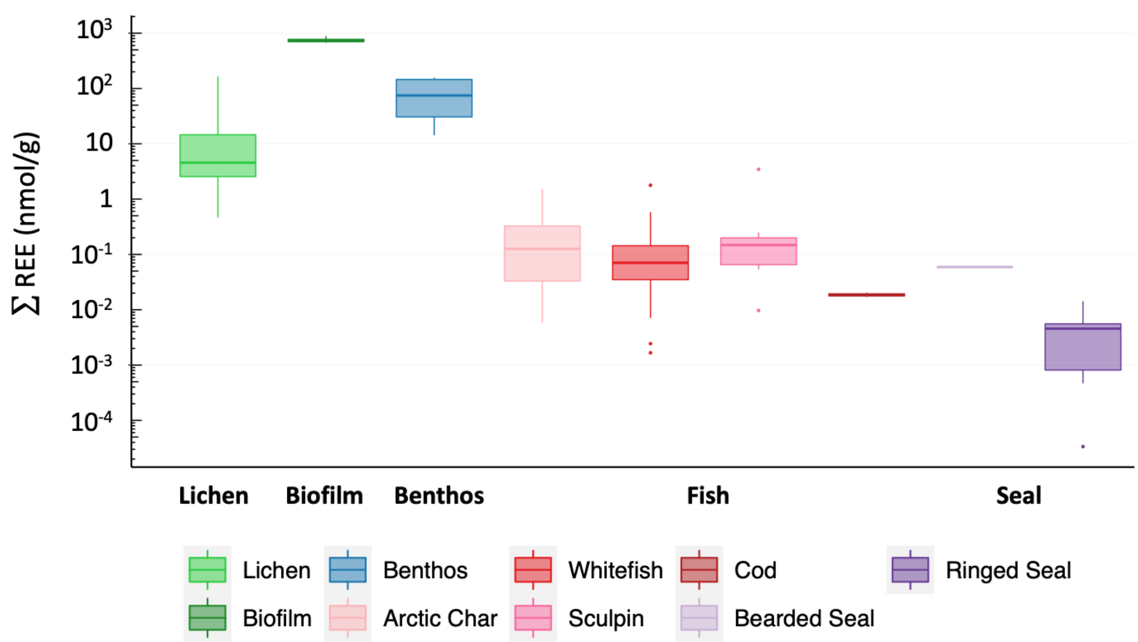

Figure B.6 – The total rare earth element concentration of biota samples (nmol/g dw). The fish and seal muscle data were used to make this figure. Sample number (n): lichen (n=39), biofilm (n=4), benthos (n=4), arctic char (n=26), whitefish (n=41), sculpin (n=7), cod (n=2), bearded seal (n=1), and ringed seal (n=6).

The high concentration of REE among biofilm samples may be due to the presence of sediment particles that can be naturally associated with this matrix. Additionally, a trophic dilution (or biominification) is expected for REE concentration with an increase in trophic level (Amyot et al., 2017), meaning that levels of REE tend to decrease towards higher trophic levels. This trend can at most be seen in Figure B.6 by the tendency for vertebrate animals (fish, seal) to have lower concentrations of REE than invertebrates (benthos) and producers (lichen). The differences in fish habitat among all four species does not allow for inference of their relationship from this type of figure alone.

The concentration of REE in lichen samples varied between 0.5 nmol/g and 170 nmol/g, with an average (± 1 SD) of 22 ± 40 nmol/g (Fig. B.6). In comparison to concentrations seen in a study performed in the Eastern Canadian Arctic (MacMillan et al., 2017) the range of REE from the George River samples fell within the same orders of magnitude. In their study, lichen and moss were found to have total REE concentrations on the scale of $1–10^2$ nmol/g. Lichens are of interest because they accumulate REE from the deposition of atmospheric sources, such as dust particles containing traces of rare earth elements. In the George River study, only 4 compiled benthos samples were available for analysis, therefore concentrations here of 14 – 160 nmol/g may not necessarily be representative of the environment as a whole in the George River Basin. However, their concentrations were comparable to values found in the literature. For example, MacMillan et al. (2017) reported values on the order of $1–10^2$ nmol/g for total REE in benthic invertebrates. Additionally, freshwater microbenthic invertebrates from a northeast Italy lake study by Pastorino et al. (2020) had values that fell within the same range as the George River Basin samples. The authors suggested that benthic invertebrates accumulate more rare earths than higher level organisms, such as the fish and seal studied herein. Fish and seal samples will be taken a greater look at in the following section by analyzing different organs and tissues (see section B.2.3.3.2), however the REE concentrations of these vertebrate consumers are commonly orders of magnitude less than their producers, as seen in MacMillan et al. (2017). Guo et al. (2003) noted no obvious biomagnification from benthic seaweeds, molluscs and crustaceans to the seawater fish muscle.

B.2.3.3.2 Rare Earth Element Distribution in Animal Organs

The mean REE concentrations for all fish organs varied across four orders of magnitude (10^{-2} to 10^{1} nmol/g) for the four species: arctic char, sculpin, whitefish and cod (Fig. B.7). On average (± 1 SD), the highest concentration of rare earth elements was found in the arctic char liver (13 ± 9.3 nmol/g) and the lowest sum was in the cod muscle (10^{-2} ± 10^{-3} nmol/g). As these four species do not live in the same kinds or depths of water, the differences in rare earth level among them may be a reflection of their exposure to REE in the water. Stable carbon and nitrogen isotopes analysis of these samples would serve to better determine the trophic relationship of the fish and may contribute to an understanding of their relative REE levels.

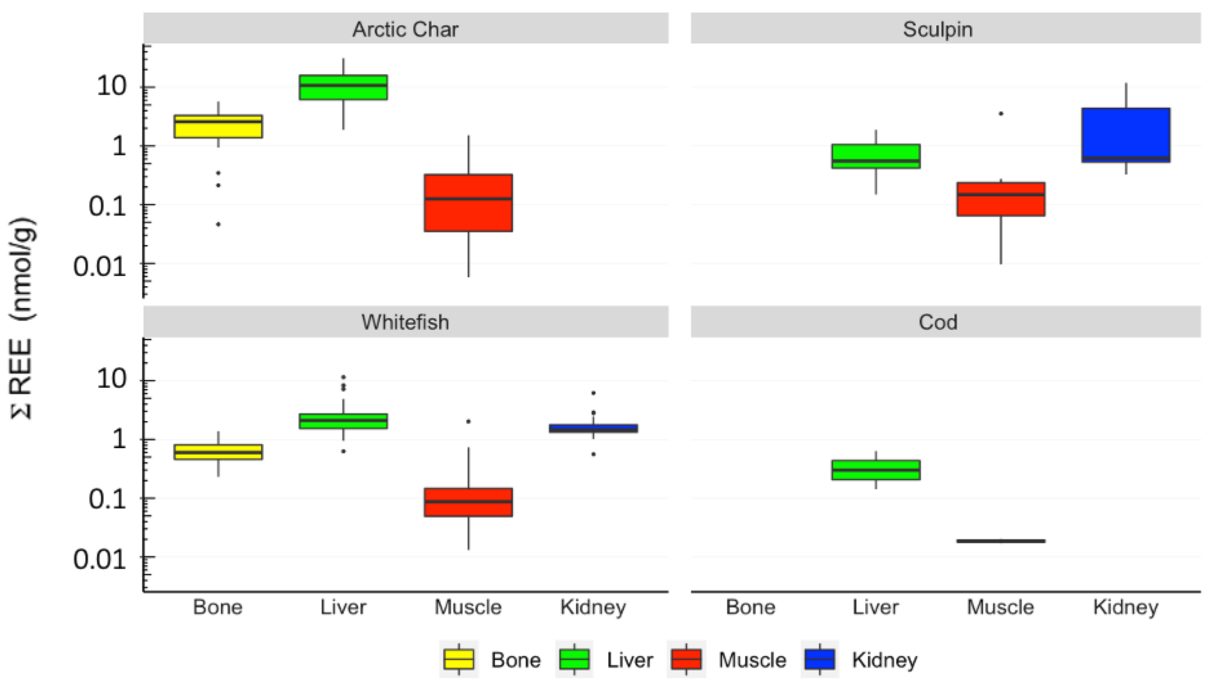

Figure B.7 – The total rare earth elements concentrations of four organs in different species of fish studied, with n as sum of all organ samples: arctic char (n = 68), sculpin (n = 21), whitefish (n = 114) and cod (n = 4).

The relative distribution of REE among organs was consistent among fish species, though not all species had samples for each of the four organs tested (Fig. B.7). The same relative order of REE concentrations in the organs sampled was seen with the seal samples (Fig. B.8). The sequence of these concentrations (where analyzed) were approximately as follows: liver and kidney > bone > muscle > fat (blubber). A favored association of REE with liver over muscle is also seen in the literature for various Arctic vertebrates (MacMillan et al., 2017) and rainbow trout (Cardon et al., 2020). For example with the whitefish samples, both average REE concentrations for liver (2.7 ± 2.1 nmol/g) and kidney (1.8 ± 1.1 nmol/g) tissues were an order of magnitude greater than those for bone (0.7 ± 0.4 nmol/g) and muscle (0.2 ± 0.3 nmol/g). In the seal samples, the mean of the liver REE concentration (1.1 ± 1.2 nmol/g) was 10 times greater than the mean concentrations of the bone (0.1 ± 0.1 nmol/g), 100 times greater than muscle (10^{-2} nmol/g) and 1000 times greater than the blubber (10^{-3} nmol/g), or 2 and 3 orders of magnitude greater respectively in muscle and blubber.

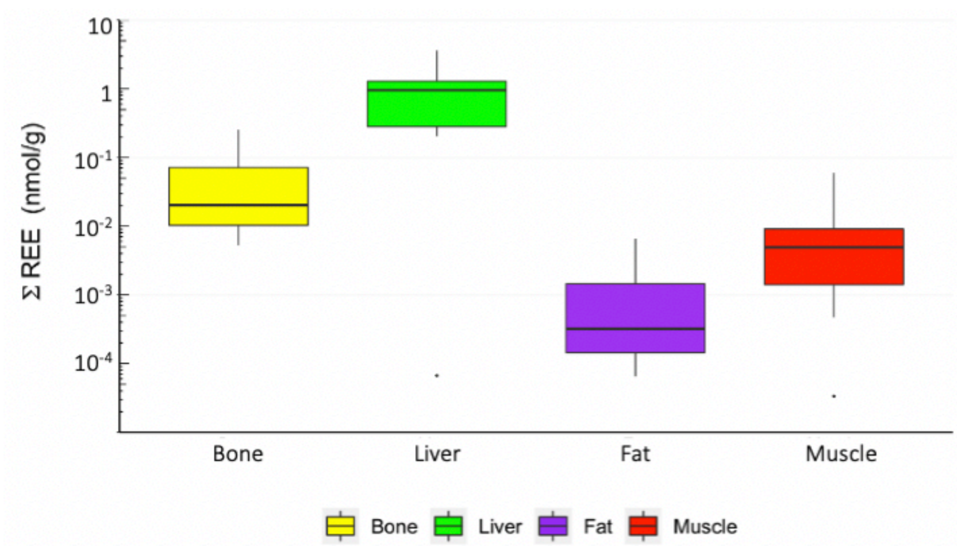

Figure B.8 – Total rare earth elements concentrations of seal samples: bone, liver, fat (blubber), and muscle. The two species of seal were compiled into the same plot area due to the small number of samples for the bearded seal (n = 3) equating to each organ tested having only one measured value; (ringed seal n = 18).

The 10- to 100-fold increase from muscle to liver tissue in fish and seal samples is consistent with the REE distribution between these two organs seen in the MacMillan et al. (2017) study. Though limited information is available for REE distribution of aquatic vertebrates, this study did also observe a higher concentration in liver than in muscle for their study of arctic vertebrates, including fish, seals and others. They noted concentrations that ranged from 4 to 200 times greater. In a study of the Indo-Pacific lionfish, the concentrations of REE were 3 times higher in the kidney compared to muscle tissues, yet no significant difference between liver and muscle was seen (Squadrone et al., 2020). The toxicity and modes of action of the rare earth elements is not clearly understood, however they are known to form complexes with certain proteins in animals and can substitute for calcium in bones (Chen et al., 2001; Ramos et al., 2016; Khadra et al., 2019).

George River fish REE concentrations were on the same order of magnitude as those found in lake brook trout of the eastern Canadian Arctic by MacMillan et al. (2017), which were approximately 0.1 nmol/g for muscle and 1 nmol/g for liver samples. Additionally, George River seal liver samples had REE concentrations similar to the ringed seal values seen in the MacMillan et al. (2017) study.

B.2.3.3.3 Mercury

The relationship between biota group and MeHg concentrations is presented in Figure B.9. There was a concentration variation of approximately 1000-fold (or 3 orders of magnitude) across all groups studied, excluding outliers. Lichen, biofilm and benthic invertebrates had the lowest MeHg concentrations of the biota studied in the George River Basin with group mean concentrations up to only 10^{-3} ug/g. Further, this represented only a small percentage of the total mercury in these samples with % MeHg under 15%. These biotic groups are not sources of human food, however as producers and lower-level consumers they can act as entry points for MeHg into the food web. Additionally, MeHg tends to demonstrate biomagnification. This characteristic can be seen in George River samples by the relative concentrations of MeHg between lower trophic level groups (lichen, biofilm, benthos) and higher-level groups (fish and seal), the latter of which had mean MeHg concentrations on the order of up to 0.1 ug/g.

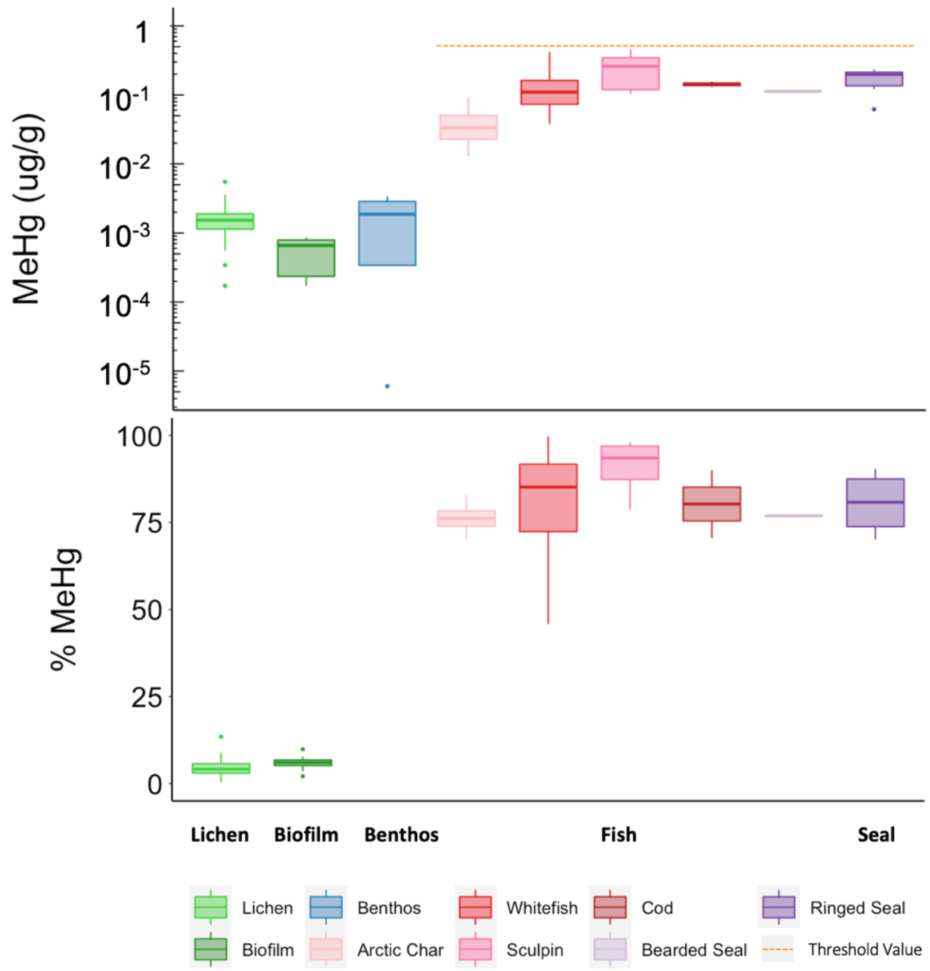

Figure B.9 – Methylmercury (MeHg; ug/g) concentrations and % MeHg of biota samples. The fish and seal muscle data were used to make this figure. Lichen (n=39), biofilm (n=9) and benthos (n=4) are in dry weight; arctic char (n=26), sculpin (n=7), whitefish (n=41), cod (n=2), bearded seal (n=1), and ringed seal (n=6) are in wet weights. The dotted orange line at a MeHg value of 0.5 ug/g represents the Health Canada Guideline for mercury in fish (w.w.).

It is important to note that all fish and seal muscle samples fell under the guideline value for MeHg in food sources, which is set at 0.5 ug/g (ww) by Health Canada (2004). This limit was introduced as a guideline in the 1970's with the goal of minimizing human exposure to mercury through consumption of fish. MeHg represented a larger proportion of total Hg (% MeHg) in vertebrate animals compared to other groups studied in the George River Basin (Fig. B.9). For example, the majority of all muscle samples for the different fish and seal species had average values above 75% MeHg. The distribution of methylmercury in the organs of these two biota groups will be discussed in further detail in section B.2.3.3.4. The explanation for why larger proportions of MeHg over total Hg were present in fish and seal relative to the lower-level groups could be the observation that other forms of mercury do not accumulate up the food chain, whereas MeHg does (Chételat et al., 2014). This efficient transfer of MeHg from prey to predator is called biomagnification.

B.2.3.3.4 Mercury Distribution in Animal Organs

Studying the distribution of MeHg within different organs and tissues of food species is important in trying to understand and predict human exposure to this form of mercury. The fish MeHg concentrations had a range among all samples of 10^{-2} ug/g to 0.46 ug/g (Fig. B.10). The distribution in MeHg concentrations between the different organs was not easily discernible for Arctic char and whitefish, however there was a 2- to 3-fold higher concentration of MeHg found in sculpin/*kanayuk* and cod/*uugaq* muscle relative to the liver and kidney, where available. For each species of fish, the approximate order of average % MeHg was as follows: muscle > liver > kidney (where analyzed), though there was a greater difference between muscle and liver % MeHg than for kidney and liver data (Fig. B.11). For example, the mean percentage of methylmercury values for the whitefish samples were 84% for muscle tissue, 59% for liver tissue and 56% for kidney tissue.

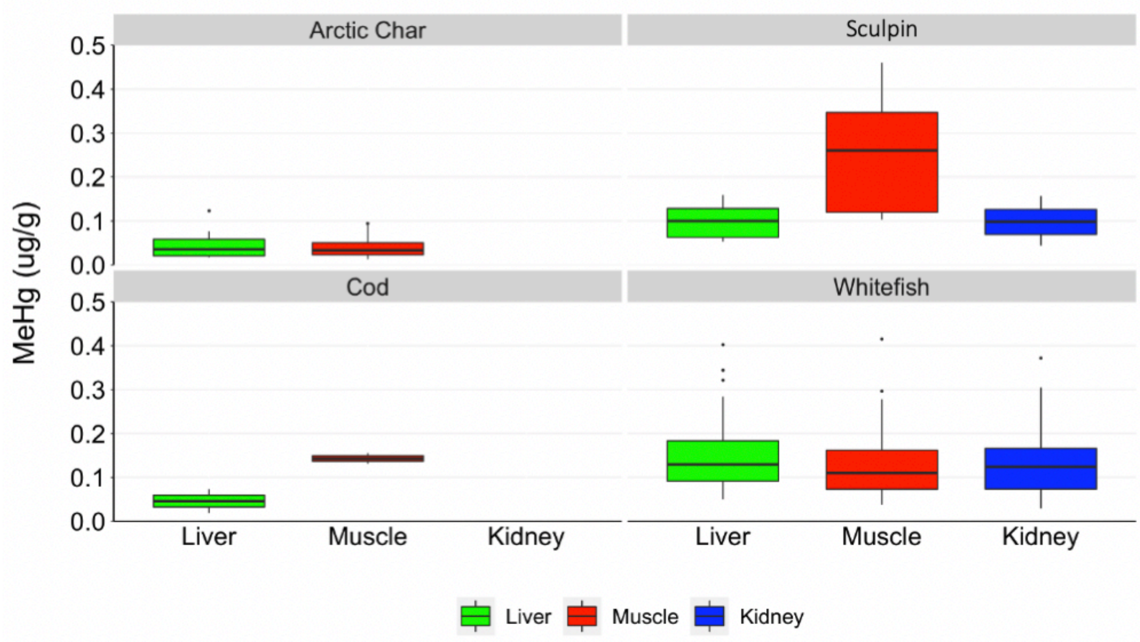

Figure B.10 – Methylmercury (MeHg) (ug/g ww) concentrations in liver, muscle and kidney samples for different species of fish from the George River Basin.

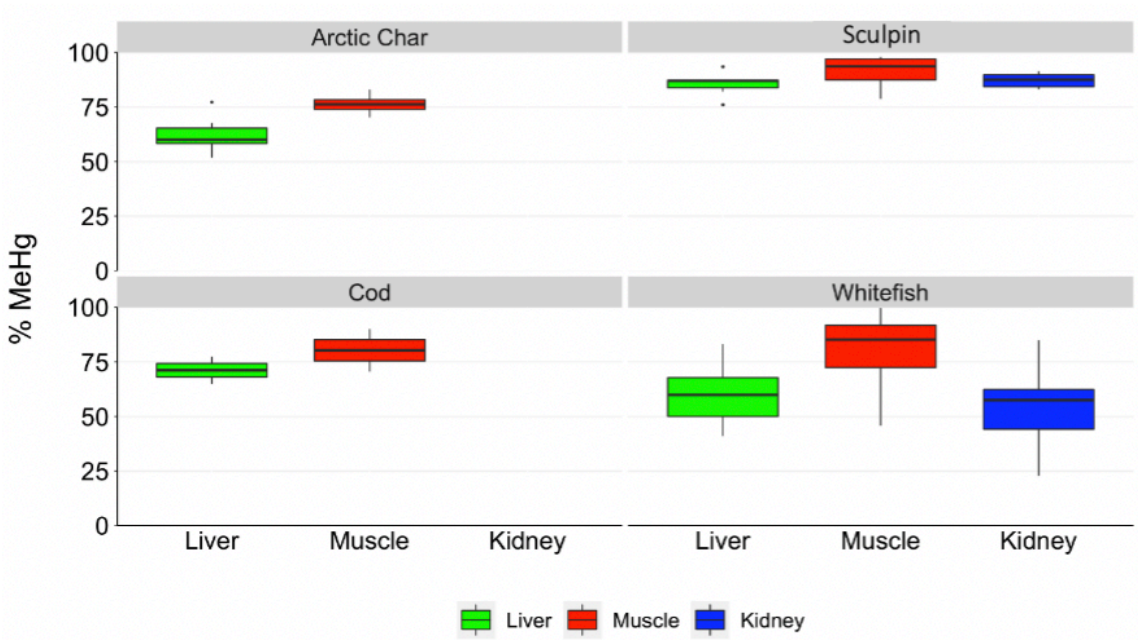

Figure B.11 – Percentage of methylmercury (% MeHg) of liver, muscle and kidney samples for different species of fish from the George River Basin.

A study of mercury distribution in yellow perch from a fluvial lake in Quebec (Khadra et al., 2019) found a similar relationship for the relative concentrations of mercury among different tissues. The muscle MeHg concentrations of the yellow perch were four times greater than the liver concentrations. The study proposed that the sulfhydryl groups present in muscle protein may account for the higher concentrations in this organ in fish. Harley et al. (2015) also found greater accumulation of MeHg in muscle (approximately 0.27 ug/g) than in liver (0.06 ± 0.04 ug/g), kidney (0.05 ± 0.03 ug/g) or heart tissue (0.04 ± 0.03 ug/g) of Bering Sea sculpin. The higher % MeHg seen in George River fish muscle was also consistent with the findings of these two studies (Harley et al., 2015; Khadra et al., 2019).

The accumulation of MeHg in seal organs is shown in Figure B.12 and demonstrates a range of values across three orders of magnitude. The average concentration for each type in decreasing order was found to be: liver (0.3 ± 0.1 ug/g) > muscle (0.2 ± 0.1 ug/g) > fat (10^{-4} ug/g). However, the % MeHg did not follow the same trend as the concentrations of MeHg for the seal groups. Instead their averages were as follows: muscle (80 ± 8 %) > liver (17 ± 14 %) > fat (2.5 ± 1.3 %). As previously stated, the MeHg concentrations of seal tissue sampled in the George River Basin were under the Health Canada guideline limit of 0.5 ug/g.

The higher % MeHg in seal muscle relative to liver in the current study is consistent with findings in the literature for ringed seal/*natsiq* and bearded seal/*udjuk* (Wagemann et al., 1998; Dehn et al., 2005; Ewald et al., 2019). For example, Ewald et al., (2019) performed a study on youth ringed seals (age < 1 yrs) from Labrador and found a similar % MeHg relationship, with muscle % MeHg (82 +/- 13%) being approximately 3-fold greater than the liver (24 +/-19 %). This is also the case for a study by Dehn et al., (2005) on ringed and bearded seals from the Arctic that showed % MeHg in ringed seal muscle (82 +/- 25 %) as approximately 7-fold greater than for the liver (12 +/- 12 %). The low % of MeHg in seal liver has been attributed to an efficient demethylation process involving the formation of mercuric selenide, an inert form of mercury (Wagemann et al., 1998).

Whereas the majority of seal samples within the above-mentioned studies (Dehn et al., 2005; Ewald et al, 2019) had average (± 1 SD) MeHg concentrations on the same order of magnitude as the George River Basin seals, the bearded seal muscle (Dehn et al., 2005) had concentrations on average one order of magnitude lower than the present study. In comparison, Wagemann et al. (1998) reported average values approximately 2 times greater than the MeHg concentrations in this study.

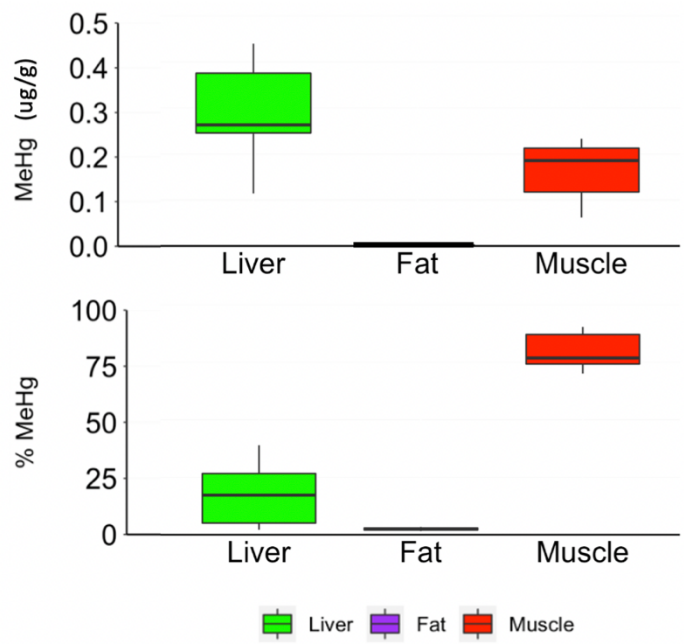

Figure B.12 – Methylmercury (MeHg) concentrations (top) in ug/g ww and % MeHg (bottom) in seal liver, blubber and muscle samples. Both species of seal were kept within one group due to a limited number of samples.

The low concentration and % MeHg in seal fat are consistent with studies involving MeHg analysis of arctic animal blubber (Wagemann et al., 1998; Gmelch et al., 2017). This behaviour is due to the high affinity of MeHg for compounds containing thiol groups (SH), such as the amino acid cysteine (Harris et al., 2003; Aschner & Syversen, 2005). However, blubber is composed largely of lipids and some protein, primarily collagen, which rarely contains a cysteine molecule (Lockyer et al., 2011; Micalizio, 2013).

B.2.3.4 Lichen

The lichen/*tingaujait* samples covered an extensive area of the George River Basin and are being explored as a method of tracking atmospheric contaminants. It is visible in Figure B.13 that certain locations had increased concentrations of selected metals, such as in the NW corner of the plot where the town and airport of Kangiqsualujjuaq are located. An area of future study will be to look at lichen metal analysis alongside the wind trend data in Nunavik.

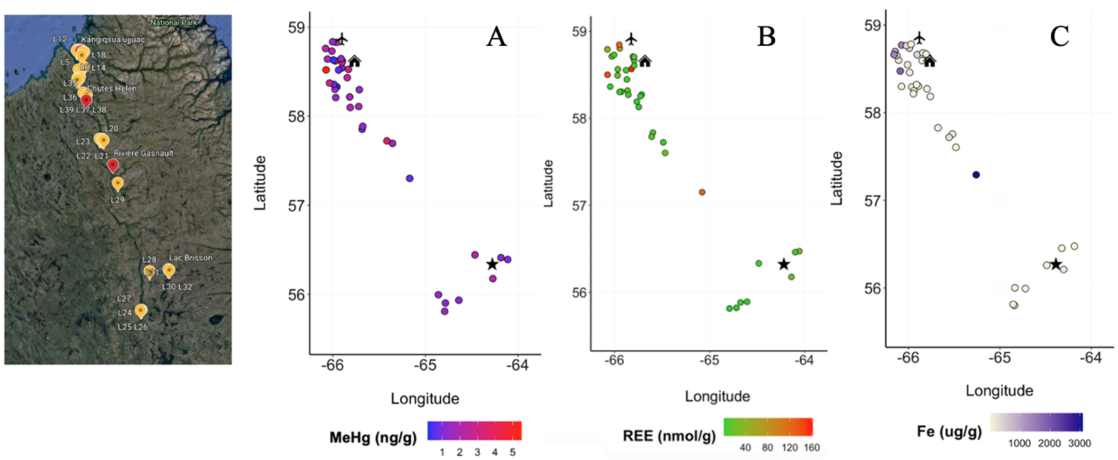

Figure B.13 – Google map image (left) highlighting the lichen samples analyzed in 2017 and 2018 with a yellow pin. The highest red pin highlights the town of Kangiqsualujjuaq; the middle red pin marks Helen Falls; the lowest red pin shows the confluence with Gasnault River. Longitude vs. latitude plots (right) displaying metal concentrations by use of a color scale: (**A**) MeHg (ng/g), (**B**) Total REE (nmol/g), and (**C**) Fe (ug/g). Points were jittered in plot A-C for better visualization. The house icon represents the location of Kangiqsualujjuaq, the airplane represents an airport, and the star is where the Strange Lake Mine is forecasted to be.

B.2.4 Conclusion and Perspectives

A first objective of this study was to evaluate the water quality of the George River Basin over five field seasons (2016-2020), which was accomplished by analyzing water samples from the mainstem of the river, its tributaries, and Lake Brisson. The George River Basin freshwater sources were found to have cold and relatively neutral waters with low nutrients, low productivity (plant growth) and low conductivity. The findings suggest that the George River is not likely affected by any major anthropogenic sources and naturally contains low levels of nutrients (TN, TP) and contaminants. Additionally, dissolved organic carbon (DOC) content was investigated as it is an important influencer of the behaviour, transport, availability and toxicity of trace elements in aqueous environments. The George River and Koroc River surface waters had DOC concentrations on the lower end of values previously measured within circumpolar Arctic freshwaters. There was little variation in DOC concentrations within the mainstem of the George River, though levels were a bit lower in the Ford River and Lake Brisson, and approximately four-fold higher in the northern tributaries.

A main scientific objective was to measure baseline values for selected trace elements, including mercury and REE, in the river over the 5-year study (2016-2019 presented within this report). The baseline values were expected to reflect the natural levels of these parameters prior to disturbances and allow for comparisons to be made in future studies, contributing to the detection of any changes in the area. Baseline values of REE in George River surface waters were low (10^1 nmol/L) and representative of undisturbed arctic freshwaters. Higher concentrations were measured in the northern tributaries compared to the George River mainstem, and slightly lower concentrations were measured in Lake Brisson and the Ford River tributary. Though guidelines for the mode of action and toxicity of REE have not been established in Canada, the REE levels within the George River Basin were likely orders of magnitude lower (est. $10^1 - 10^3$ times) than estimates of toxic concentrations from laboratory experiments (Cardon et al., 2019). Lastly, DOC, which is a known transporter of metals in riverscapes, was a good predictor of REE concentrations in all freshwater samples within this study, including the tributaries of George River, Lake Brisson, and the Koroc River.

Mercury is another trace element of interest within the current study, with a particular interest in its more toxic and bioaccumulating form, MeHg. The total mercury (THg) and MeHg levels of the George River Basin and nearby water sources were typical of Canadian Arctic and subarctic freshwaters. Further, the surface water concentrations for THg and MeHg were low relative to estimated toxicity guidelines, with averages respectively 10 to 100 times less than these values (Canadian Council of Ministers of the Environment, 2003). Finally, it is important to note that trace metals, such as REE, THg, and MeHg, are naturally occurring in the environment and the concentrations reported are likely representative of baseline (or natural) levels in surface waters.

The sediment samples collected from three sites within the George River Basin were analysed for their REE and trace metals. Firstly, the REE concentrations within the George River sediments were similar to those typical of areas without disturbances. As for the MeHg of the sediments, there was some significant intra-site variability for two stations. Overall, the sediment mercury content was at the lower end, and even an order of magnitude below, THg and MeHg concentrations from other studies looking at sediments from undisturbed, freshwater systems. A future area of interest is to use the loss on ignition (LOI) method for determining organic matter content within the George River sediments. The goal of completing this analysis is to better understand the metal distribution within the basin, as organic matter is known to complex with metals.

A community-driven assessment of fish and seal from within the George River Basin was completed in order to evaluate the locals' food quality, and baseline values were determined for a variety of biota within the basin. As seen in previous studies, REE concentrations decreased with increasing trophic level: biota at the base of the food web, such as lichens, biofilm and benthic invertebrates, were found to have higher concentrations of REE relative to the vertebrates (fish, seal). The REE concentrations in the biota samples were comparable to values found in the literature for other undisturbed, Arctic or subarctic ecosystems. Additionally, there was a similar relative distribution of average REE level among the different organs (where analyzed) for all four fish species and the seal group: liver and kidney > bone > muscle > fat (blubber). A favored association of REE with liver and kidney over muscle was consistent with the literature. The concentrations of REE found within the biota in the George River Basin are well below levels shown to elicit adverse effects (Cardon et al., 2019), though no national guidelines are available at this time for REE in food species.

Furthermore, vertebrate animals had higher MeHg and % MeHg values than lower trophic level groups, namely invertebrates and vegetation. All MeHg concentrations were below the Health Canada recommended threshold of 0.5 ug/g w.w. for food sources, with concentrations in food specimens ranging from 10^{-2} ug/g to 0.46 ug/g across fish samples and 10^{-4} ug/g to 0.3 ug/g within the seal samples. There were some interspecies differences for both MeHg concentrations as well as the organ sample % MeHg. However, the trend in relative % MeHg between organs (where available) was similar across all vertebrates: muscle > liver > kidney > fat (blubber). The interspecies REE and mercury variation seen among fish warrants further investigation, as it may reflect environmental, physiological or behavioural differences.

A baseline was established for lichen trace metals, REE and MeHg in the George River Basin. Lichen is thought to be an excellent atmospheric biomonitor in that it is sensitive to air quality changes and naturally incorporates contaminants. Therefore, concentration gradients across the basin will be further studied in order to better understand if lichen can provide information on temporal changes in the basin or the presence of any local influences such as the airport, housing, and/or waste site.

Altogether, the data collected and presented within this report provides baseline values for the water quality, as well as for trace metals and REE of sediment and various biota groups within the George River Basin. This information can serve as a reference point in future studies, where it will assist in determining if any changes have occurred, such as by climate change or with the forecasted opening of the Strange Lake mine.

B.2.5 Report Ackowledgements

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