Université de Montréal

À la chasse aux métaux traces dans un Nord canadien en évolution rapide : approches limnologiques, écologiques et collaboratives

Hunting for trace metals in a rapidly changing North: limnological, ecological, and collaborative approaches

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État des contributions

Les principaux résultats des chapitres 1 à 4 sont présentés sous forme d'articles publiés dans des revues scientifiques, ou sous forme de manuscrits soumis ou prêts à être soumis pour publication. En tant qu'auteure principale, mes contributions sont essentielles, majeures et déterminantes aux articles. Les chapitres sont rédigés avec mes deux superviseurs de thèse ainsi qu'avec d'autres chercheurs collaborateurs. Mes superviseurs ont contribué aux plans de recherche, à l'interprétation des données, à la révision des articles, aux ressources de laboratoire et au soutien financier. Les annexes 1 à 3 sont aussi présentées sous forme d'articles publiés ou prêts à être soumis et elles se rapportent aux travaux connexes de cette thèse.

Chapitres

Chapitre 1: Concentrations élevées de MeHg au sein des petits étangs de l'est de l'Arctique canadien

Article publié : MacMillan, G. A., Girard, C., Chételat, J., Laurion, I., & Amyot, M. (2015). **High methylmercury in Arctic and Subarctic ponds is related to nutrient levels in the warming eastern Canadian Arctic**. *Environmental Science & Technology,* 49(13), 7743-7753. DOI: 10.1021/acs.est.5b00763

Plan de recherche : Amyot, Laurion.
Collecte de données : MacMillan, Girard, Laurion
Analyses au laboratoire : MacMillan, Girard, Laurion
Analyses statistiques : MacMillan, Girard, Chételat
Tableaux et figures : MacMillan, Girard
Rédaction : MacMillan, Amyot
Révision : Tous les auteurs

Chapitre 2: Effets de la stœchiométrie nutritive sur la bioaccumulation de mercure dans le zooplancton d'eau douce de l'Arctique

Article en préparation : MacMillan, G. A., Chételat, J., Richardson, M. C., & Amyot, M. (2018). **Influence of nutrient stoichiometry on mercury bioaccumulation in Arctic freshwater zooplankton**. À soumettre à *Limnology & Oceanography*.

Plan de recherche : MacMillan, Chételat, Richardson, Amyot
Collecte de données et analyses : MacMillan, Richardson, Chételat
Tableaux et figures : MacMillan
Rédaction : MacMillan
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Chapitre 3: Bioaccumulation de terres rares dans les écosystèmes marins, terrestres, et d'eau douce dans l'est de l'Arctique canadien

Article publié : MacMillan, G. A., Chételat, J., Heath, J. P., Mickpegak, R., & Amyot, M. (2017). **Rare earth elements in freshwater, marine, and terrestrial ecosystems in the eastern Canadian Arctic**. *Environmental Science: Processes & Impacts,* 19(10), 1336-1345. DOI: 10.1039/C7EM00082K

Plan de recherche : MacMillan, Chételat, Heath, Raymond, Amyot
Collecte de données : Chételat, Heath, Raymond
Analyses en laboratoire et statistiques : MacMillan
Tableaux et figures : MacMillan
Rédaction : MacMillan
Révision : MacMillan, Chételat, Amyot

Chapitre 4: Facteurs environnementaux influençant la bioaccumulation de terres rares dans le zooplancton d'eau douce

Article publié : MacMillan, G. A., Clayden, M. G., Chételat, J., Richardson, M. C., Perron, T., M. C., & Amyot, M. (2018). **Environmental drivers of rare earth elements bioaccumulation in freshwater zooplankton**. *Environmental Science & Technology,* Article publié en ligne le 26 décembre 2018. DOI: 10.1021/acs.est.8b05547

Plan de recherche : MacMillan, Perron, Richardson, Chételat, Amyot
Collecte de données : MacMillan, Perron, Chételat, Richardson
Analyses en laboratoire : MacMillan
Analyses statistiques : MacMillan, Clayden
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Annexes

Annexe 1: Destin et transfert trophique des terres rares dans les réseaux trophiques aquatiques des lacs tempérés

Article publié : Amyot, M., Clayden, M. G., MacMillan, G. A., Perron, T., & Arscott-Gauvin, A. (2017). **Fate and trophic transfer of rare earth elements in temperate lake food webs**. *Environmental Science & Technology*, 51(11), 6009-6017. DOI: 10.1021/acs.est.7b00739

Plan de recherche : Amyot, Perron
Collecte de données : Perron, Arscott-Gauvin, MacMillan
Analyses en laboratoire et statistiques : Perron, Clayden, MacMillan
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Annexe 2 : IMALIRIJIIT: un programme de suivi environnemental communautaire dans le bassin versant de la rivière George, Nunavik

Article publié : Gérin-Lajoie, J., Herrmann, T.M., MacMillan, G.A., Hébert-Houle, É., Monfette, M., Rowell, J.A., Anaviapik Soucie, T., Snowball, H., Townley, E., Lévesque, E. and Amyot, M., (2018). IMALIRIJIIT: a community-based environmental monitoring program in the George River watershed, Nunavik, Canada. Écoscience, pp.1-19.

Plan de recherche : Gérin-Lajoie, Herrmann, Hébert-Houle, Townley. Snowball
Collecte de données : MacMillan, Monfette, Rowell, Gérin-Lajoie, Hébert-Houle, Anaviapik Soucie
Analyses en laboratoire : MacMillan, Rowell, Amyot
Analyses des données : MacMillan, Amyot, Monfette, Franssen, Dedieu
Tableaux et figures : Gérin-Lajoie, Monfette, Dedieu
Rédaction : Gérin-Lajoie, Herrmann, MacMillan
Révision : MacMillan, Amyot, Franssen, Dedieu, Lévesque
Collaborateurs sur le terrain: Snowball, Townley

Annexe 3: Former les chercheurs en début de carrière à la recherche en contexte autochtone : le potentiel des ateliers par les pairs

Article soumis : MacMillan, G.A.*, Falardeau, M.*, Girard C., Dufour-Beauséjour, S., Lacombe-Bergeron, J., Menzies, A., Henri, D. (2018). **Highlighting the potential of peer-led workshops in training early career researchers for conducting research with Indigenous communities.** Soumis le 7 novembre 2018 à *Facets.*

** Co-premières auteures*

Plan : MacMillan, Falardeau, Girard
Collecte de données et analyses : MacMillan, Falardeau, Girard, Dufour-Beauséjour, Lacombe-Bergeron, Menzies
Tableaux et figures : MacMillan, Dufour-Beauséjour
Rédaction : Tous les auteurs
Révision : Tous les auteurs

Annexe 4: Autres contributions

Annexe 5: Bande dessinée « Une moule dans la mine »

BD réalisée par Martin PM (www.martinpm.info) et Gwyneth MacMillan, gagnante du concours « *L'illustre recherche* » édition 2017-2018 avec la Fédération des associations étudiantes du campus de l'Université de Montréal (FAÉCUM)

Résumé

Actuellement, l'Arctique canadien subit de grands changements, tant climatiques que socio-environnementaux, auxquels s'ajoute une pression croissante d'y exploiter les ressources naturelles. Les écosystèmes arctiques étant d'importants indicateurs des changements globaux futurs, il s'avère essentiel de mieux comprendre l'impact de ces changements sur la santé humaine et celle des écosystèmes. Pourtant, notre compréhension des cycles biogéochimiques des contaminants présente des lacunes importantes, notamment pour le cycle des métaux traces, qui subit d'importants déséquilibres en réponse aux changements climatiques. Dans la présente thèse, j'ai cherché à mieux comprendre les tendances écologiques à grande échelle des métaux traces dans les écosystèmes du Grand Nord canadien.

Dans un premier temps, j'ai étudié les effets potentiels d'un climat en changement sur le cycle du mercure dans les lacs et les étangs nordiques. Cette étude pluriannuelle à grande échelle cherchait à déterminer si les mares thermokarstiques à forte activité microbienne pourraient être une source de méthylmercure dans l'est de l'Arctique canadien. Nos résultats démontrent que les mares de fonte de petite taille, omniprésentes dans le Grand Nord, pourraient devenir des sources de méthylmercure pour les écosystèmes aquatiques voisins, en réponse aux changements climatiques. Dans un second temps, cette thèse a examiné l'effet de la productivité aquatique sur la bioaccumulation de méthylmercure dans les organismes aquatiques à la base des réseaux trophiques. J'ai échantillonné des écosystèmes suivant une gamme décroissante de productivité afin d'étudier les implications des changements de productivité sur la bioaccumulation de mercure. Nos résultats suggèrent que dans ces lacs nordiques peu productifs, les indicateurs de la productivité, tels que la biomasse algale et la stoechiométrie des nutriments, ne sont pas les facteurs contrôlant l'accumulation de mercure à la base des réseaux aquatiques.

Les troisième et quatrième chapitres de cette thèse se sont concentrées sur le comportement et le destin des éléments de terres rares dans les écosystèmes nordiques. Peu d'études écotoxicologiques ont été menées sur ces métaux et notre objectif principal était d'établir la base de référence avant la prolifération de projets d'exploitation minière aux latitudes nordiques. Nos résultats démontrent que les terres rares suivent des patrons de bioaccumulation spécifiques aux taxons et aux tissus, et que ces contaminants ne sont pas bioamplifiés dans les réseaux trophiques naturels. J'ai également

identifié les facteurs environnementaux clés qui influencent la bioaccumulation de terres rares dans le zooplancton d'eau douce, incluant le pH, le carbone organique dissous, et la concentration de terres rares sous forme d'ion libre. Nos études soulignent la pertinence du zooplancton dans le suivi biologique de ces contaminants dans les écosystèmes d'eau douce.

Dans un dernier temps, cette thèse met en lumière l'importance de mener de la recherche collaborative avec les communautés autochtones en Arctique, en examinant le succès d'un programme de suivi environnemental communautaire au Nunavik. J'ai contribué à ce projet de surveillance environnementale et à la création d'activités éducatives participatives visant l'intégration du savoir autochtone dans la recherche en écologie. J'ai également examiné comment la mise en place d'ateliers pour chercheurs en début de carrière pouvait jouer un rôle de plateforme-clé pour la réflexion sur les avantages et les défis de la recherche collaborative avec les communautés autochtones. En somme, la présente thèse a grandement amélioré notre compréhension de l'effet des changements socio-environnementaux sur la biodisponibilité et les dynamiques trophiques de mercure et des éléments de terres rares dans les écosystèmes de l'est de l'Arctique canadien. Mieux comprendre les répercussions des changements futurs sur le devenir des métaux traces dans l'environnement est crucial à l'évaluation de l'impact de ces changements sur le Nord et sur les communautés qui y vivent.

Mots-clés : environnement, mercure, méthylmercure, éléments de terres rares, métaux, arctiques, subarctiques, eau douce, réseaux trophiques, bioaccumulation, zooplancton, lacs, étangs, suivi environnemental communautaire, recherche collaborative

Abstract

Climate change will have wide-ranging effects on Arctic ecosystems and communities. Accelerated warming combined with significant pressure to exploit natural resources has led to Arctic ecosystems vulnerable to both climatic and socio-environmental change. As the Arctic is an important indicator of future global changes, it is important to study the impact of these changes on human and ecosystem health. A key knowledge gap in our understanding is how rapid changes in the North will affect the transport and biogeochemical cycling of key contaminants, including trace metals. In this thesis, I used a large-scale ecological approach to study the environmental fate, bioaccumulation, and trophic transfer of trace metals in Canada's northern ecosystems.

In the first chapter of this thesis, I studied the potential impacts of a changing climate on mercury cycling within Arctic lakes and ponds. This large-scale, multi-year study investigated whether microbially-active permafrost thaw ponds were potential sources of mercury in the eastern Canadian Arctic. Our results showed that thaw ponds are small but abundant sources of methylmercury, with potentially significant downstream effects linked to permafrost thaw. The second chapter of this thesis examined the effects of aquatic productivity on the uptake of methylmercury in biota at the base of freshwater food webs. I sampled a gradient in ecosystem productivity to study the implications of climate-induced changes in productivity on mercury bioaccumulation. Our results suggested that indicators of productivity, such as algal biomass and nutrient stoichiometry, are not the main drivers of methylmercury accumulation within unproductive Arctic lakes.

The third and fourth chapters of this thesis focused on the behaviour and environmental fate of rare earth elements in Arctic ecosystems. Few ecotoxicological studies exist for rare earth elements and our goal was to establish baseline data before the proliferation of rare earth mining projects at northern latitudes. Our results found that rare earth element bioaccumulation patterns appear to be species- and tissue-specific and they do not biomagnify in natural food webs. I also identified key environmental drivers of bioaccumulation in zooplankton, including, pH, dissolved organic carbon and the rare earth element free-ion concentrations. These studies highlight the utility of zooplankton as a biomonitor for rare earth elements in freshwater ecosystems.

Lastly, my thesis highlights the importance of collaborative research with Indigenous communities by examining a successful community-based environmental monitoring program in Nunavik. I participated in a collaborative and land-based environmental monitoring and science education program with the aim of integrating Indigenous knowledge into ecological research. I also examined the role of peer-led workshops as an effective platform for early-career researchers to reflect on the benefits and challenges of conducting community-collaborative research in Indigenous communities. Overall, my thesis greatly improves our understanding of how rapid socio-environmental change may affect the bioavailability and trophic transfer of mercury and rare earth elements in the eastern Canadian Arctic. Understanding the impact of future changes on the environmental fate of metals is crucial to ensuring the health of Arctic ecosystems and communities.

Keywords: environment, mercury, methylmercury, rare earth elements, metals, arctic, subarctic, freshwater, food webs, bioaccumulation, zooplankton, lakes, ponds, community-based monitoring, community-collaborative research

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AMAP: Arctic Monitoring and Assessment Programme

AMDE : événement de déplétion atmosphérique de Hg | atmospheric mercury depletion event

ANOVA : analysis of variance

BLM : biotic ligand model

C : carbone | carbon

Cond. : conductivity

DO : dissolved oxygen

DOC: dissolved organic carbon

DOM : dissolved organic matter

Chla : chlorophyll *a*

FIAM: free ion activity model

Hg : mercure | mercury

LOI : loss on ignition

MeHg: methylmercury

OM: organic matter

PCA: principal component analysis

PHREEQC : PH REdox EQuilibrium

RNA : ribonucleic acid

DNA : deoxyribonucleic acid

REE : rare earth element

REEs : rare earth elements

SD : standard deviation

Temp : temperature

THg : total mercury

TP : total phosphorus

TN : total nitrogen

WHAM : Windermere Humic Aqueous Model

Zmax : maximum depth

For my grandmother, Eluned MacMillan

(grand)mother, poet & activist

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AVANT-PROPOS

La science est en perpétuel changement. En effet, afin de pallier les défis complexes émergeant de la société moderne, il importe d'élaborer de nouveaux concepts et des applications novatrices. Ces défis, qui incluent les changements climatiques, la pollution, la perte de biodiversité ainsi que la méfiance croissante envers la science, nous poussent à réinventer cette dernière afin de pouvoir répondre aux besoins de la société et de la planète de manière plus efficace. Bien que la science représente un outil extrêmement puissant permettant de résoudre les problèmes les plus complexes, certains concepts vont au-delà du savoir scientifique. En effet, les données actuelles ouvrent la voie à des mécanismes, des tendances et des relations existant dans la nature, mais elles ne peuvent enseigner à l'Homme la valeur intrinsèque du monde qui l'entoure. La science prenant actuellement une tangente multidisciplinaire dans l'optique d'intégrer des connaissances provenant d'autres disciplines et d'autres écoles de pensée, les scientifiques s'allient progressivement avec les industries, les différents paliers gouvernementaux et les communautés. Les acteurs du milieu universitaire prennent ainsi de plus en plus conscience de l'importance de reconnaître et d'honorer le savoir écologique et traditionnel des peuples autochtones. Bien que l'avenir environnemental demeure précaire et incertain, il convient d'espérer que ce savoir scientifique en pleine évolution permettra, du moins en partie, de faire face aux défis découlant de l'Anthropocène. Peut-être arriverons-nous alors à reconstruire les ponts qui unissaient autrefois l'Homme et la nature.

INTRODUCTION

Introduction à l'écotoxicologie

écotoxicologie / ekɔ tɔksikɔlɔʒi/ *origine écologie et toxicologie, première utilisation 1977*

L'écotoxicologie est une discipline collaborative alliant le savoir de la biologie, de la chimie, de l'écologie, de la géographie et de la toxicologie de manière à étudier le devenir des contaminants dans la biosphère et leurs effets sur le vivant. La santé humaine et écologique étant étroitement liées (Newman, 2014), les connaissances en écotoxicologie sont essentielles au rétablissement du bien-être global altéré par la société moderne. Les contaminants peuvent être définis de manière générale comme des substances qui se retrouvent dans l'environnement, du moins en partie, par des activités humaines (Edwards, 2001). La présente thèse porte sur l'étude du mercure (Hg) et des éléments de terres rares (REEs), tous deux des métaux traces. Bien que naturellement présents dans l'environnement, la quantité de métaux trace dans l'air, le sol et l'eau a augmenté dû à une multitude d'activités humaines. Les contaminants peuvent avoir plusieurs sources, qu'elles soient ponctuelles ou diffuses. Les sources ponctuelles sont associées à une origine identifiable de laquelle sont rejetés les contaminants, soit des rejets d'usines, des navires ou des cheminées industrielles (EPA, 2018). Les sources diffuses résultent quant à elles des précipitations, du dépôt atmosphérique et du ruissellement (EPA, 2018). Contrairement à la représentation de la pollution dans les médias qui met souvent l'accent sur les sources ponctuelles, les sources diffuses de contaminants peuvent être considérées comme étant la cause principale de la détérioration de la qualité de l'eau dans les écosystèmes aquatiques. En effet, les précipitations et la fonte des glaces ruissellent à l'échelle du paysage, emportant les contaminants pour les déposer dans les lacs, les milieux humides, les rivières et les océans. Ainsi, les écosystèmes aquatiques représentent des zones clés pour le transport, la transformation et le transfert trophique de plusieurs contaminants. L'eau étant un solvant efficace pour une grande variété de molécules, ces écosystèmes sont également particulièrement sensibles à la pollution chimique. Pour toutes ces raisons, les champs de connaissances liés à l'écotoxicologie et à la limnologie, soit l'étude des écosystèmes aquatiques des eaux intérieures, sont étroitement associés.

Les contaminants et les écosystèmes d'eau douce en Arctique

Arctique /aʁktik/ origine grecque arktikós ou ours, première utilisation 1540, se réfère à la constellation polaire ou le pays du Grand Ours

Bien que souvent considéré comme un environnement intact et vierge, l'Arctique est graduellement devenu un puits pour les contaminants provenant des quatre coins du globe. À la suite de la découverte des niveaux élevés de contamination des prédateurs supérieurs tels que les ours polaires, les phoques, les baleines et même les habitants de l'Arctique (AMAP, 2016, AMAP, 2011), l'étude des contaminants dans cette région est désormais critique et prioritaire. En effet, la présence de contaminants en Arctique soulève des préoccupations importantes pour la santé humaine et celle des écosystèmes. Plusieurs contaminants tirent leur origine des régions industrialisées de la planète pour s'accumuler en Arctique via le transport atmosphérique sur de longues distances, les courants océaniques, les rivières et les espèces migratrices (Fig. 1). Par exemple, le processus de distillation planétaire engendre une relocalisation des contaminants organiques volatils et persistants tels que les pesticides des régions plus chaudes du globe vers les pôles (Simonich and Hites, 1995). Le mercure, métal trace toxique, peut également être transporté vers l'Arctique par l'atmosphère depuis ses sources d'émission se trouvant en latitudes tempérées. Bien que le transport des contaminants sur de longues distances à partir des régions industrialisées représente une source majeure de pollution en Arctique, certains contaminants émergents tirent également leur source au sein même de ces régions. Ces sources locales incluent la génération de déchets municipaux, les produits de consommation, ainsi que l'accroissement du développement économique à travers l'Arctique (AMAP, 2016). L'exploitation minière et l'exploration gazière augmentent également le risque d'exposition à des contaminants émergents, tels que les retardateurs de flamme, les hydrocarbures et les REEs, qui sont des métaux traces.

Le mercure est naturellement omniprésent dans l'environnement, mais à une faible abondance géochimique (Krauskopf, 1979). Depuis l'ère industrielle, les activités humaines ont augmenté l'abondance et la disponibilité biologique de cet élément de façon préoccupante. Ces activités sont principalement la combustion des combustibles fossiles et des déchets municipaux, l'exploitation minière, et l'inondation de territoire avec le développement hydro-électrique (Wiener et al., 2003, Nriagu and Pacyna, 1988). Les évènements de dépôt atmosphérique de masse (*atmospheric mercury depletion events*, *AMDE*) et les dépôts humides du mercure oxydé via les

précipitations ont longtemps été considérés comme les principales sources de mercure en milieu arctique (Steffen et al., 2007, Wiener et al., 2003, Muir et al., 1999). Toutefois, il a récemment été rapporté que le dépôt atmosphérique de mercure élémentaire gazeux représenterait la principale source de ce métal dans la toundra arctique ainsi que dans d'autres écosystèmes éloignés (Obrist et al., 2017). Ainsi, bien que ces contaminants aient été bannis ou encore jamais exploités dans ces régions éloignées, ils se retrouvent en Arctique par des processus globaux.

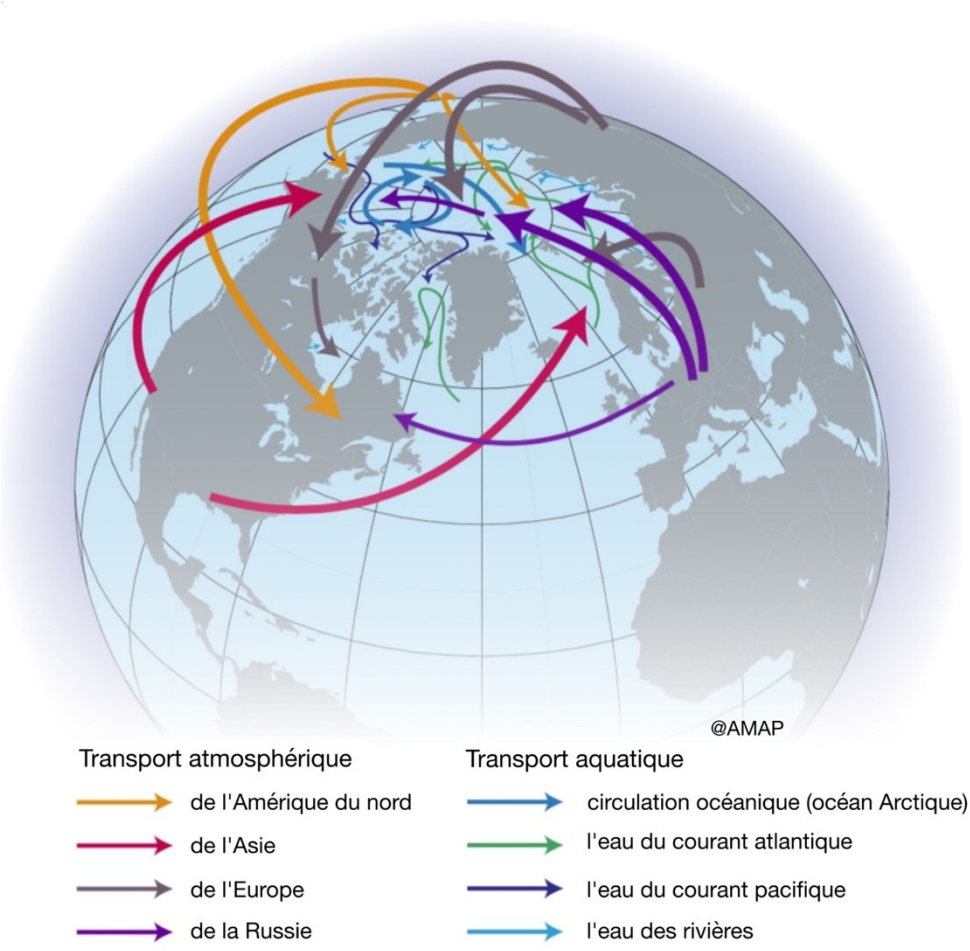

FIGURE 1. Les contaminants provenant des sources majeures situées aux latitudes moyennes de l'hémisphère nord sont principalement transportés en Arctique par les vents dominants et les courants océaniques. Figure adaptée de AMAP (2011).

L'étude des contaminants et leurs effets en Arctique sont d'une importance cruciale dans le contexte des changements climatiques, puisque cette région subit des changements environnementaux beaucoup plus rapides que les régions tempérées. En effet, l'Arctique se réchauffe de deux à trois fois plus que la moyenne planétaire (IPCC, 2018, Serreze and Francis, 2006, Polyakov et al., 2002). Les changements climatiques causeront également de vastes

modifications en Arctique, engendrant des conséquences pour tout le reste de la planète (Hassol, 2004). Dans les écosystèmes d'eau douce, les effets potentiels d'un climat en changement incluent une altération des paramètres physiques, chimiques et biologiques, modifiant directement le cycle des contaminants (Macdonald et al., 2005). Par exemple, les modèles climatiques prédisent une réduction importante (> 95%) du pergélisol de surface d'ici 2100, selon les scénarios d'émissions basses et élevées de gaz à effet de serre (Lawrence and Slater, 2005). Le dégel du pergélisol ainsi que l'augmentation de l'écoulement des eaux auront pour effet de favoriser le transport des contaminants accumulés dans les sols et les tourbières vers les systèmes aquatiques (Vonk et al., 2015, Rautio et al., 2011, Rydberg et al., 2010). Une étude récente estime que ~5% du mercure du pergélisol des régions circumpolaires (~88 Gg) risque d'être remobilisé dans les réseaux fluviaux par les processus d'érosion thermokarstique (St. Pierre et al., 2018). Le relargage de nutriments et de matière organique associé à cette fonte pourrait également augmenter la productivité de ces écosystèmes. Les lacs arctiques sont généralement caractérisés par un faible niveau de nutriments et de biomasse algale et ils sont donc considérés comme étant peu productifs ou oligotrophes.

Les conséquences liées aux changements climatiques auront notamment pour effet d'augmenter la productivité de ces lacs. Ces modifications des paramètres biologiques engendreront une altération des transformations microbiennes et du transfert trophique des contaminants dans les écosystèmes d'eau douce arctiques. Une augmentation de la productivité aura également une incidence sur la composition et la distribution des espèces. De plus, la migration progressive des espèces vers le Nord en réponse au réchauffement climatique aura sans contredit un impact sur le transfert des contaminants, puisque certaines de ces espèces représentent des vecteurs plus importants que d'autres (Chételat and Amyot, 2009, Sweetman et al., 2008, Patalas, 1990). Ainsi, bien que le dégel du pergélisol cause initialement une augmentation du transport des contaminants métalliques vers les systèmes aquatiques, la biodisponibilité des métaux dans ces écosystèmes dépendra ultimement d'un grand nombre de changements intrinsèques, chimiques et biologiques (Vonk et al., 2015). L'accélération du réchauffement climatique et la pression croissante d'exploiter les ressources naturelles en Arctique pourraient nuire aux écosystèmes. Il est donc d'une importance cruciale d'étudier les effets des changements climatiques et du développement économique sur les différentes composantes environnementales en Arctique, dans l'optique de maintenir l'équilibre des écosystèmes et de favoriser la santé humaine.

Dynamique des contaminants et le rôle clé de zooplancton dans les réseaux trophiques aquatiques

zooplancton /zo(o) plæŋktən/ origine grecque plankton, première utilisation en 1897, se réfère aux animaux qui « errent » ou qui sont « à la dérive »

L'accumulation des métaux dans les organismes vivants dépend des caractéristiques intrinsèques de ces contaminants, de l'environnement et de la nature de ces organismes (Newman, 2014). La biodisponibilité d'un métal peut être définie comme sa propension à s'accumuler dans les organismes vivants. Cette biodisponibilité dépend de la capacité du métal à être solubilisé et relargué des différents compartiments environnementaux tels que les sols, les sédiments et les particules (Caussy et al., 2003). La compréhension du partitionnement des métaux entre la colonne d'eau, les particules et les sédiments est donc essentielle afin de faire la distinction entre les fractions biodisponibles et inertes des métaux dans les écosystèmes aquatiques. La biodisponibilité des métaux dans ces écosystèmes dépend de leur spéciation, soit leur forme chimique, qui est quant à elle influencée par un grand nombre de facteurs environnementaux. Les facteurs les plus importants sont le pH, la présence d'autres cations (H^+, Ca^{2+}), la compétition avec d'autres métaux et la complexation potentielle avec des ligands organiques et inorganiques. Certains modèles sont utilisés dans l'optique de prédire la biodisponibilité des métaux dans les écosystèmes aquatiques. Ces modèles, spécifiques à un site donné présentant des paramètres chimiques particuliers, incluent notamment le modèle de l'ion libre (FIAM) et, plus récemment, le modèle du ligand biotique (BLM). Ces deux modèles d'équilibre chimique sont basés sur les mêmes cadres conceptuels, mais diffèrent au niveau de leurs paramètres fondamentaux. En effet, le FIAM utilise l'activité de l'ion libre en solution, alors que le BLM dépend de l'adsorption du métal sur les sites sensibles des surfaces biologiques (Hassler et al., 2004).

Selon ces modèles, la bioaccumulation de certains métaux peut être prédite par leur forme ionique libre (M^{Z+}) (Campbell, 1995). Par contre, ces ions libres ne représentent qu'une infime fraction des concentrations totales des métaux dans les eaux naturelles et il est souvent ardu de détecter de faibles niveaux de ces ions avec les méthodes analytiques actuelles. Ainsi, des logiciels informatiques générant des modèles de spéciation basés sur des constantes d'équilibre métallique en tenant compte d'un grand nombre de ligands organiques et inorganiques (MINEQL+, PHREEQC, WHAM) sont généralement utilisés afin d'estimer les concentrations d'ions libres.

Les modèles générés par ces logiciels sont cependant basés en grande partie sur des hypothèses, limitant leur application à certains métaux et aux systèmes environnementaux complexes. De plus, le rôle des ions compétitifs n'est pas toujours expliqué de manière efficace. En effet, la température et l'exposition des organismes via l'alimentation ne sont pas tenues en compte par ces modèles (Slaveykova and Wilkinson, 2005, Hassler et al., 2004). De plus, la validité de ces derniers pour les métaux trivalents, tels que les REEs, demeure ambiguë. Certaines études ont validé ces modèles pour les REEs (Vukov et al., 2016, El-Akl et al., 2015, Weltje et al., 2004), alors que d'autres démontrent que les éléments trivalents constituent des exceptions à ces modèles (Tan et al., 2017, Zhao and Wilkinson, 2015). Ainsi, les modèles WHAM semblent surestimer la complexation des REEs, bien que l'ampleur varie d'une minime (Leguay et al., 2016) à une forte surestimation (Rowell et al., 2018), dépendamment de l'étude.

La bioaccumulation et la bioamplification sont deux processus biologiques clés dans la dynamique trophique des contaminants (Fig. 2). La bioaccumulation peut être définie comme l'accumulation nette de contaminants dans les organismes vivants par l'eau, l'air, les sols et sédiments, et l'alimentation, couplée avec les pertes potentielles par excrétion, élimination et/ou biotransformation (Newman, 2014). Cette bioaccumulation a donc lieu lorsque la prise en charge des contaminants par les organismes se produit à des taux plus élevés que leur élimination, comme c'est le cas pour le méthylmercure, une forme organique du mercure. La bioamplification, quant à elle, se produit lorsque les substances chimiques sont transférées et augmentent successivement à chacun des niveaux trophiques supérieurs. Une fois à l'intérieur de l'organisme, les contaminants peuvent être redistribués entre les différents compartiments internes ou transformés en vue de leur détoxification ou excrétion. Les modèles mathématiques décrivant la bioaccumulation prédisent généralement une augmentation graduelle des niveaux de contaminants jusqu'à l'atteinte d'une concentration à l'équilibre dans l'organisme, se traduisant par une prise en charge et une élimination équivalentes. Or, les concentrations de méthylmercure dans certains poissons augmentent avec la taille et l'âge de ces derniers. Le taux de bioaccumulation peut donc varier avec le niveau de contamination des proies, les coûts métaboliques des activités, et les taux de croissance des poissons (Trudel and Rasmussen, 2006).

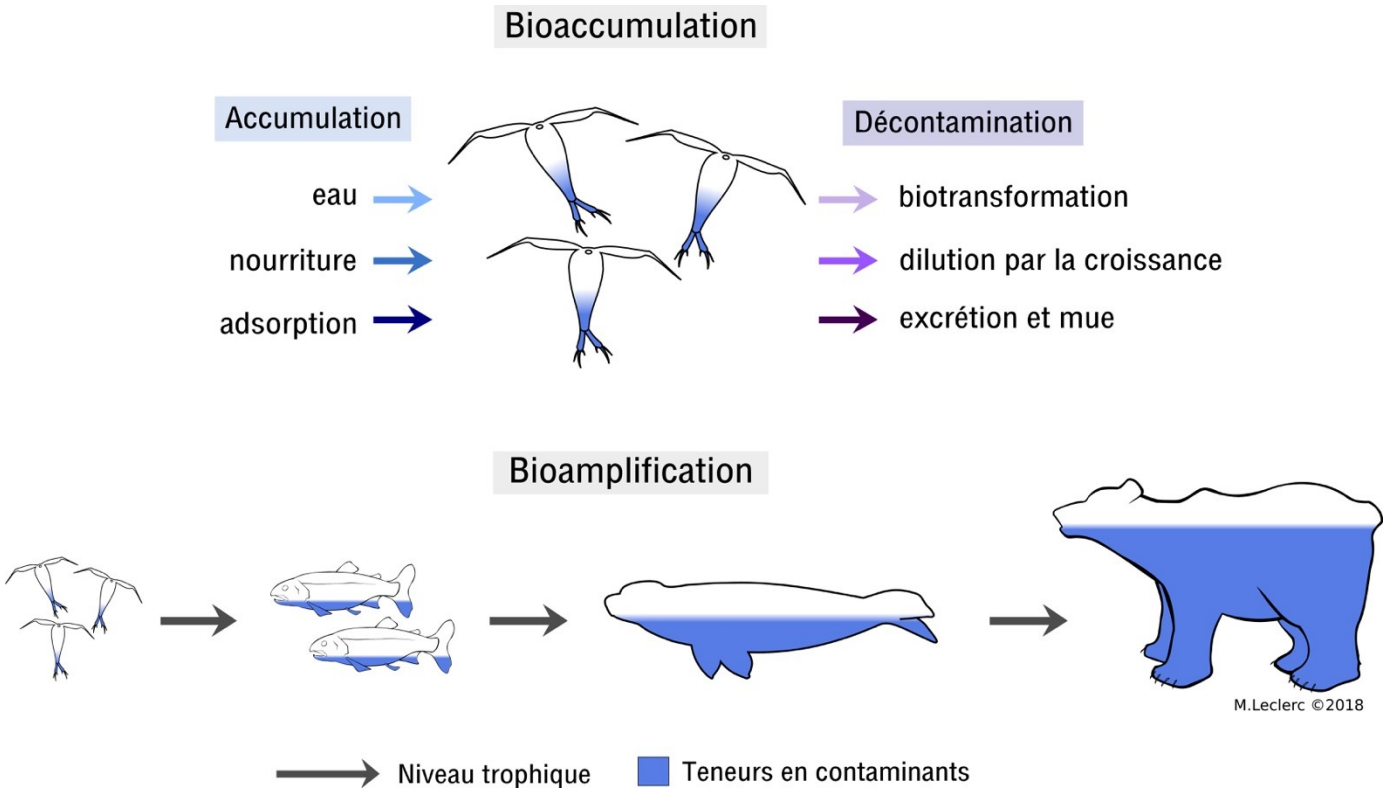

FIGURE 2. Schéma illustrant les processus simplifiés de bioaccumulation et de bioamplification. Figure adaptée de Maxime Leclerc © 2018.

Les contaminants organiques persistants, tels que les pesticides, sont considérés comme étant non essentiels pour les organismes, c'est-à-dire qu'ils n'ont aucune fonction biologique. Ces contaminants se bioaccumulent et se bioamplifient aisément dans les réseaux trophiques. Les contaminants inorganiques, quant à eux, peuvent se bioaccumuler dans les organismes, mais ne se bioamplifient généralement pas, à l'exception notable du méthylmercure. En effet, ce dernier est bioaccumulé et bioamplifié de manière très importante dans les réseaux trophiques (Douglas et al., 2012). Certains métaux traces sont quant à eux essentiels aux fonctions biologiques et peuvent donc être aisément régulés et/ou excrétés par la synthèse de petites protéines, telles que la métallothionéine, qui se lient aux métaux et les séquestrent, réduisant leur potentiel de toxicité. Les mécanismes associés à l'homéostasie métallique induisent notamment le potentiel de toxicité (Knapen et al., 2007).

Peu d'études se sont penchées sur les processus de bioaccumulation et la bioamplification à la base des réseaux trophiques dans les lacs arctiques, probablement en raison de la difficulté

associée à l'échantillonnage d'organismes de petite taille pour l'analyse de métaux traces. Cependant, une meilleure compréhension des processus de bioaccumulation à ces niveaux de base est nécessaire afin d'élucider la dynamique des contaminants. En effet, les organismes aquatiques de petite taille se trouvant à la base des réseaux trophiques sont souvent le point d'entrée pour les métaux traces. La plus grande augmentation associée à la bioaccumulation du méthylmercure est observée entre l'eau et les algues, avec des niveaux 10 à 100 000 fois plus élevés dans le seston (Watras et al., 1998). Le seston est l'ensemble des organismes vivants et des particules inertes flottant passivement dans l'eau, tels que le phytoplancton de petite taille et les détritus organiques. Ces organismes sont généralement peu étudiés en écotoxicologie, en raison du niveau de difficulté associé à l'échantillonnage pour l'analyse de métaux traces, qui requiert un investissement important de temps et des méthodes de travail intensives.

Le zooplancton inclut l'ensemble des invertébrés compris dans la colonne d'eau qui flottent, dérivent ou qui présentent de faibles capacités natatoires. Ce sont donc des organismes qui suivent le courant (Thorp et al., 2009). Le zooplancton lacustre occupe deux habitats différents, soit la zone pélagique (eau libre), ainsi que la zone littorale près du rivage. Le zooplancton pélagique comprend le microzooplancton (protozoaires, rotifères) et le macrozooplancton (cladocères, copépodes, larves de diptères). Ces organismes sont parfois herbivores, se nourrissant principalement d'algues, ou parfois détritivores, consommant des bactéries retrouvées sur la matière organique benthique ou en suspension (Desvilettes et al., 1997). Il importe de comprendre le type d'alimentation du zooplancton, puisqu'un apport algal ou bactérien contribue grandement à prédire l'accumulation des contaminants (Kainz and Mazumder, 2005). Le zooplancton est également une source majeure d'alimentation pour les poissons et les invertébrés de grande taille, comme les larves de *Chaoborus*. Bien que le seston et le zooplancton réfèrent normalement à des groupes taxonomiques différents, ces derniers seront distingués uniquement par leur taille dans la présente thèse en raison de la difficulté de les séparer taxonomiquement sur le terrain. Nous présumons en effet que la majorité de la biomasse présente dans chacune de ces deux classes de taille est représentative des différents niveaux trophiques (Dobberfuhl and Elser, 2000).

Le zooplancton crustacé, qui comprend notamment des cladocères et des copépodes, occupe une place importante dans les réseaux trophiques en raison de son implication dans le transfert d'énergie et de matière, incluant les contaminants, vers les niveaux supérieurs. Les métaux traces s'accumulent généralement dans le zooplancton via les surfaces respiratoires et par

l'alimentation. Ces individus ont subséquemment la capacité d'excréter les métaux ou de les accumuler dans des fractions physiologiquement inertes de l'organisme, telles que la carapace, ou même dans des structures dites « de détoxification » de la cellule (Gray, 2002). Chez les invertébrés aquatiques, cette répartition subcellulaire se produit à la suite de l'assimilation des métaux, au cours du processus de bioaccumulation. Lorsque les métaux se retrouvent principalement dans les fractions solubles de la cellule, telles que le cytosol, ils sont aisément transférés vers les prédateurs. Au contraire, les métaux qui sont associés aux parois cellulaires ainsi qu'à l'exosquelette ne sont pas solubilisés par les prédateurs (Wallace et al., 2003). Le fractionnement subcellulaire a donc une influence considérable sur la toxicité des métaux et leur transfert trophique vers les niveaux supérieurs. Ainsi, l'étude du fractionnement subcellulaire des métaux permet de dresser un portrait global des mécanismes de toxicité et de la bioaccumulation, contrairement aux mesures de concentrations dans les individus entiers. Il a été prouvé que l'alimentation représente la source majeure de méthylmercure pour le zooplancton, en comparaison avec l'exposition par l'eau (Kainz and Mazumder, 2005, Tsui and Wang, 2004). La voie d'exposition principale des autres métaux traces dépend fortement du métal et de l'espèce à l'étude (Hare et al., 2003, Yu and Wang, 2002). Il semble également que l'absorption directe des métaux par les invertébrés aquatiques soit proportionnelle à la concentration de métaux dissous dans l'eau (Fisher et al., 2000, Reinfelder et al., 1998).

Le cycle du mercure dans le Nord

mercure /mɛʀkyʀ/ origine latin mercurius, première utilisation 14 siècles, se réfère au dieu messager romain et à la planète

Le mercure est un polluant planétaire sur lequel plusieurs études écotoxicologiques se sont penchées depuis le début des années 1950 en raison de sa forte toxicité et de son potentiel de bioaccumulation et de bioamplification dans les réseaux trophiques. Contrairement à la majorité des métaux, le mercure s'accumule en grande quantité dans les prédateurs supérieurs, dont les ours polaires et les humains. Ce contaminant soulève donc des préoccupations importantes pour la santé humaine et celle des écosystèmes en Arctique. L'adoption récente d'un traité juridiquement contraignant par 128 pays dans le but de réduire les émissions de mercure dans l'environnement, soit la Convention de Minamata sur le mercure, démontre que le mercure demeure un contaminant mondial hautement prioritaire (UNEP, 2013). Bien que les niveaux retrouvés dans la croûte

terrestre soient relativement bas en comparaison à d'autres éléments chimiques, le mercure est naturellement omniprésent dans l'environnement (Krauskopf, 1979). L'industrialisation a cependant grandement contribué à l'accroissement du mercure dans l'environnement. Ainsi, le potentiel de biodisponibilité de cet élément toxique a augmenté de façon critique en raison de plusieurs activités anthropiques, telles que les combustibles fossiles, l'incinération d'ordures municipales, l'exploitation minière et la création de réservoirs hydroélectriques (Wiener et al., 2003, Nriagu and Pacyna, 1988). Bien que le cycle du mercure soit largement étudié depuis des dizaines d'années, il importe de mener des recherches plus approfondies sur son occurrence dans les écosystèmes arctiques, qui subissent actuellement des transformations environnementales rapides et accrues (Kidd et al., 2012, AMAP, 2011).

Le mercure se distingue des autres métaux par le fait qu'il possède la capacité de passer aisément entre les phases gazeuse, liquide et solide à des températures relativement basses. Il existe trois formes différentes de mercure qui sont naturellement présentes dans les systèmes aquatiques d'eau douce: le mercure inorganique sous forme du mercure élémentaire, Hg(0), ou du mercure oxydé, Hg(II), et le mercure organique, notamment le méthylmercure (MeHg). La forme réduite, Hg(0), est stable, peu soluble et hautement volatile. Le Hg(0) peut donc être transporté sur de longues distances dans l'atmosphère avant d'être déposé dans l'environnement arctique. La forme oxydée, Hg(II), est soluble et réactive, formant des liens stables avec d'autres composés, principalement avec les groupements soufrés. Le méthylmercure (MeHg) est également soluble et constitue la forme la plus toxique du mercure. Le MeHg est bioaccumulé à de hautes concentrations dans les organismes vivants (Douglas et al., 2012). Les lacs et les mares représentent des sites clés pour la transformation du mercure inorganique Hg(II) en MeHg. Ce processus, appelé méthylation, est régulé par diverses communautés de microorganismes retrouvées principalement dans les sédiments lacustres (Wiener et al., 2003). Ces mécanismes sont nécessaires à la compréhension du cycle du mercure dans le Nord, puisqu'on retrouve un nombre important d'écosystèmes d'eau douce de petite taille dans les régions circumpolaires (Pienitz et al., 2008). Les substances toxiques présentant un potentiel de bioaccumulation, telles que le MeHg, peuvent également se bioamplifier dans les niveaux trophiques supérieurs. Le MeHg étant une neurotoxine puissante, une exposition à ce dernier peut avoir des effets sur les systèmes nerveux, reproducteur et immunitaire des vertébrés, incluant les poissons, les oiseaux et les humains (Scheuhammer et al., 2015, Clarkson, 1997). Ces conséquences sont particulièrement critiques

pour les communautés autochtones du Nord, puisque ces dernières dépendent en grande partie de la consommation de poisson ou de mammifères marins comme moyen de subsistance (Wheatley and Wheatley, 2000).

L'un des domaines clés de la recherche actuelle vise à localiser la méthylation du Hg (II), soit la production de MeHg, dans les écosystèmes aquatiques de l'Arctique, en comparaison aux écosystèmes des latitudes plus tempérées. En effet, il est établi qu'à ces latitudes tempérées, la production de MeHg a lieu principalement dans les sédiments anaérobiques et dans l'hypolimnion des lacs et des mares, ou encore dans les zones humides (Lehnherr, 2014). Des études préalables dans l'extrême Arctique ont également démontré que les mares d'eau douce de petite taille sont très favorables à la méthylation microbienne du Hg(II) (Lehnherr et al., 2012a, Lehnherr et al., 2012b, St. Louis et al., 2005). Bien que ces mares soient assez répandues dans les régions nordiques, elles sont peu accessibles et ne contiennent typiquement pas de poisson et, par conséquent, elles sont peu étudiées. De plus, le dégel du pergélisol peut entraîner une augmentation du transport du mercure accumulé dans les sols et les tourbières vers les systèmes aquatiques, ces derniers étant souvent des mares thermokarstiques, ou mares de fonte (Stern et al., 2012, Macdonald et al., 2005). Ces mares sont d'une importance cruciale dans le domaine de la recherche, puisque le pergélisol stocke davantage de mercure que tous les autres types de sols, la végétation, les océans et l'atmosphère combinés (Schuster et al., 2018). L'augmentation de la connectivité hydrologique résultant du dégel du pergélisol peut également accroître le transport du MeHg des mares de fonte vers les lacs et les rivières avoisinantes, causant potentiellement des conséquences écologiques à grande échelle.

Un autre domaine d'importance de la recherche actuelle vise à comprendre les effets des changements climatiques sur le cycle du mercure en Arctique, puisque les conséquences qui y sont associés seront fort probablement complexes et présenteront une dimension géographique variable (Stern et al., 2012). Comme discuté précédemment, les changements climatiques sont susceptibles de causer des effets physiques, dont le dégel du pergélisol, qui risquent de modifier les flux de Hg en Arctique. Les modifications chimiques et biologiques causées par les changements climatiques ont également le potentiel d'altérer le cycle du Hg dans les réseaux trophiques aquatiques. Par ailleurs, le réchauffement climatique peut engendrer une augmentation des apports de matière organique et de nutriments dans les lacs arctiques et les mares thermokarstiques, favorisant la productivité aquatique (Chételat and Amyot, 2009, Pickhardt et al., 2005). Une étude récente a

démontré qu'une augmentation de la production aquatique semble mener à une réduction de la bioaccumulation du MeHg dans les réseaux trophiques, puisque les lacs arctiques oligotrophes sont davantage sensibles à la contamination au MeHg (Chételat et al., 2018).

Un accroissement de la productivité aquatique pourrait altérer le cycle du Hg en modifiant les taux d'assimilation de MeHg et la biodilution dans les organismes. Ce principe de biodilution stipule que la bioaccumulation du MeHg serait plus importante dans les organismes provenant de lacs peu productifs, en comparaison avec les systèmes davantage productifs (Pickhardt et al., 2002). En effet, une étude a mesuré des taux de Hg deux à six fois plus élevés dans du zooplancton et du poisson récoltés dans un lac oligotrophe, comparativement aux organismes d'un lac eutrophe voisin (Kidd et al., 2012, Kidd et al., 1999). La biodilution peut être causée par la croissance algale (*algal bloom dilution*), selon laquelle une plus grande biomasse ou un taux de croissance élevé durant la prolifération d'algues entraîne des niveaux de Hg plus faibles à la base des réseaux trophiques (Pickhardt et al., 2002, Pickhardt et al., 2005). La biodilution peut aussi être causée par une augmentation de la densité de zooplancton (*zooplankton growth dilution*) (Chen and Folt, 2005), ou par croissance somatique *(somatic growth dilution*) où les organismes consommateurs présentent de faibles niveaux de bioaccumulation de MeHg dus à leur croissance rapide (Karimi et al., 2010, Karimi et al., 2007, Hill and Larsen, 2005). Il n'existe aucune étude sur l'effet d'une augmentation de la productivité aquatique dans les lacs nordiques sur le potentiel de biodilution du Hg dans un contexte de réchauffement climatique. En raison de la faible productivité déjà prévalente dans les écosystèmes arctiques, il est possible que l'ampleur des changements prévus soit insuffisante pour engendrer la biodilution.

Le cycle des éléments de terres rares

lanthanide /lan(t)-thə-ˌnīd/ origine grecque lanthanein, première utilisation 1926, se réfère aux éléments qui sont "caché" ou peu connus

Contrairement au Hg, les éléments de terres rares (REEs) ne sont que récemment devenus un sujet d'intérêt des études écotoxicologiques. Les REEs sont un groupe de contaminants émergents présentant des propriétés chimiques similaires et qui comprennent 15 métaux lanthanides trivalents, en plus du scandium (Sc) et de l'yttrium (Y) (Fig. 3). Le groupe des lanthanides est considéré comme étant chimiquement uniforme, puisqu'il comprend des éléments similaires quant à leur numéro atomique (Z=51-71), leur valence (+3) et leur rayon atomique, qui

diffère du numéro atomique. N'étant pas particulièrement rare, l'exploitation des REEs augmente de façon critique en raison de leur utilisation dans les industries de haute technologie, notamment dans les domaines des appareils électroniques, de la médecine, des énergies renouvelables et de l'agriculture (Gonzalez et al., 2014, Barry and Meehan, 2000). Ainsi, bien que les activités agricoles et industrielles récentes aient engendré une augmentation significative de REEs dans l'environnement, l'état des connaissances sur leur devenir dans l'environnement et leurs effets sur les écosystèmes naturels est limité.

Puisqu'ils sont peu solubles et immobiles dans les sols, les REEs ont souvent été considérés comme présentant un faible risque pour l'environnement et la santé humaine (Šmuc et al., 2012, Hedrick, 1995). Des effets positifs potentiels ont également été attribués au REEs en Europe et en Asie, notamment liés à leur ajout à des niveaux traces aux engrais et à la nourriture d'élevage (Pang et al., 2002). Bien que la majorité des engrais phosphatés contienne naturellement des REEs, ces derniers sont rarement ajoutés aux engrais et à la nourriture d'élevage au Canada. Par ailleurs, plusieurs études récentes menées en laboratoire ont démontré que les REEs présentent un potentiel de bioaccumulation ainsi qu'un potentiel de toxicité chez plusieurs espèces, notamment chez les microorganismes, les plantes, les invertébrés, les poissons et les humains (Tai et al., 2010, Cui et al., 2012, Borgmann et al., 2005, Barry and Meehan, 2000). Les REEs sont donc susceptibles de suivre une courbe dose-réponse hormétique pour un grand nombre d'espèces, exprimée par des effets positifs à faibles doses et des effets toxiques à doses élevées. Des recherches exhaustives sont cependant nécessaires afin de mieux estimer les seuils de toxicité et les effets à long terme d'une exposition aux REEs (Pagano et al., 2015). Des données écotoxicologiques sont donc cruciales à la création de recommandations environnementales pour ces contaminants (Gonzalez et al., 2014).

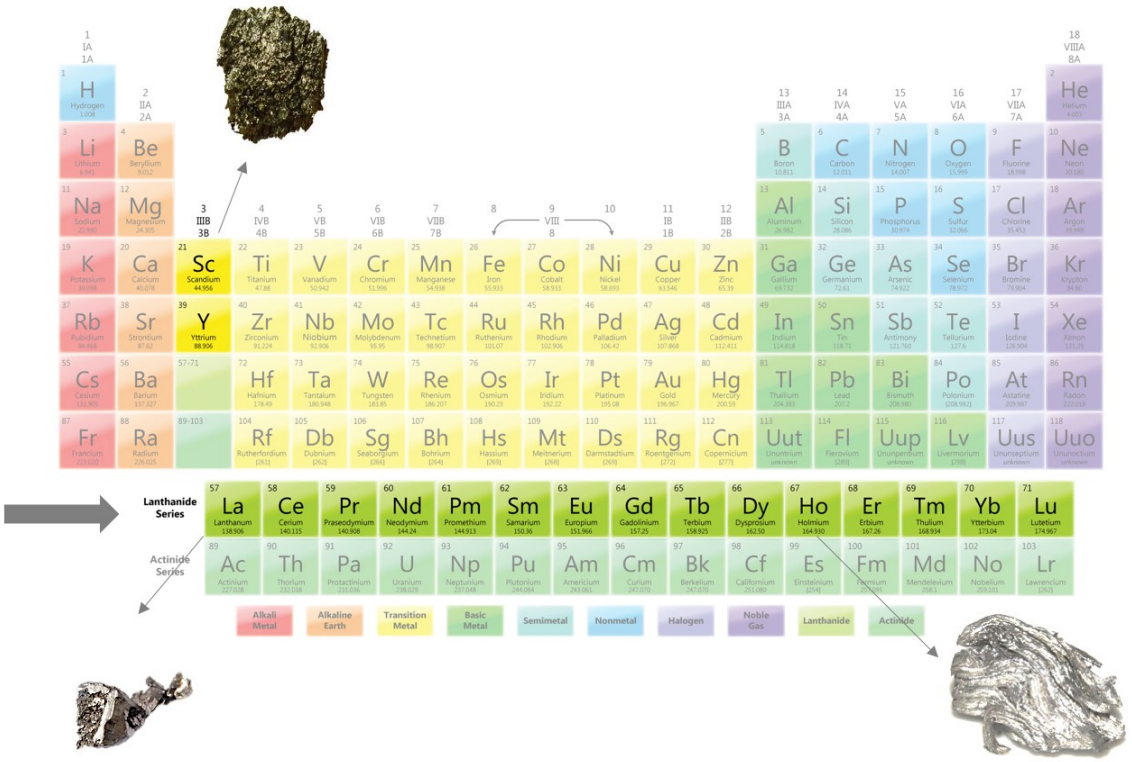

FIGURE 3. Schéma illustrant les éléments de terres rares (REEs) dans le tableau périodique. Ces derniers incluent la série de métaux lanthanides (La-Lu), le scandium (Sc) et l'yttrium (Y). Les REEs Sc, La et Ho sont imagés sur la figure.

Peu d'études écotoxicologiques ont été menées sur les REEs, particulièrement les études conduites sur le terrain, touchant à la bioaccumulation et à la dynamique des REEs dans les réseaux trophiques. Un domaine émergent de la recherche vise donc à évaluer les niveaux de référence et le comportement des REEs dans les écosystèmes naturels. La demande croissante associée à ces éléments a mené au développement de l'exploitation des REEs aux quatre coins de la planète, dont le Nord du Canada (EPA, 2012, Paulick and Machacek, 2017). Bien qu'actuellement il n'y ait aucune production ou raffinage de REEs au Canada, plus de 200 projets d'explorations sont en développement. Plusieurs projets touchent le Nord canadien, incluant 5 projets au Nord du Québec et 2 dans les Territoires du Nord-Ouest (GC, 2014). L'exploitation minière et la transformation subséquente des minerais de REEs peuvent causer des impacts environnementaux majeurs, en raison de la production de pollution atmosphérique, de rejets d'eaux usées acides et de résidus radioactifs (EPA, 2012). Cependant, un enrichissement significatif en REEs dans l'eau, le sol et la végétation près de sites miniers en Chine a récemment soulevé des préoccupations importantes

liées aux effets directs de ces éléments (Li et al., 2010, Wang et al., 2010, Zhang et al., 2010, Liang et al., 2005). Par exemple, il a été démontré que des rivières situées près de mines de REEs dans la région du fleuve Jaune en Chine contiennent des concentrations en REEs dissous 200 fois plus élevées que les rivières non touchées par ces exploitations (Liang et al., 2014). Malgré l'enrichissement potentiel en REEs aux latitudes élevées en lien aux projets d'exploitation minière, l'état des connaissances sur les concentrations de références, la bioaccumulation et le transfert trophique de ces contaminants est limité au Canada.

Dans les écosystèmes d'eau douce, les voies de transports des REEs des sols vers l'eau, puis vers les réseaux trophiques aquatiques, demeurent peu explorées par rapport aux autres métaux traces (Weltje et al., 2002, Mayfield and Fairbrother, 2015, Twiss and Campbell, 1998). Les sources naturelles potentielles de REEs pour ces écosystèmes, et conséquemment de tous les autres métaux traces, incluent les roches locales, les sols et les sédiments aquatiques, en plus des eaux souterraines et des particules atmosphériques. Étant peu solubles dans les environnements naturels, ces éléments sont retrouvés à des concentrations très faibles, ou traces ($<0.01\ \mu gL^{-1}$), dans la majorité des systèmes aquatiques non contaminés (Gonzalez et al., 2014). Puisqu'ils sont lithophiles et forment des complexes stables avec les ligands organiques et inorganiques (notamment les ions carbonate et phosphate), la majorité des REEs se lie fortement aux sédiments ou aux particules en suspension dans la colonne d'eau. Bien que peu concentrés dans les eaux de surface, ces éléments présentent un potentiel de bioaccumulation dans les organismes aquatiques. Ainsi, le zooplancton d'eau douce semble représenter un bon indicateur de la contamination en REEs.

En effet, comme pour les autres métaux, la biodisponibilité de ces éléments est fortement influencée par plusieurs facteurs, dont le pH, la compétition avec les autres métaux ainsi que la complexation avec des ligands. Certaines études ont démontré que le modèle de l'ion libre (FIAM) peut être appliqué aux REEs (Vukov et al., 2016, El-Akl et al., 2015, Weltje et al., 2004), alors que d'autres stipulent que les éléments trivalents constituent plutôt des exceptions à ce modèle (Tan et al., 2017, Zhao and Wilkinson, 2015). Les REEs semblent s'accumuler dans les organismes à la suite de certaines réactions avec d'autres molécules, via un transport membranaire et/ou par liaison à des récepteurs spécifiques (Parisi et al., 2017). Des recherches plus approfondies sont nécessaires à la récolte de données écotoxicologiques fondamentales sur le partitionnement des REEs, leur bioaccumulation et leur transfert trophique dans l'environnement. Cependant, l'étude

des effets environnementaux des contaminants en Arctique ne représente pas seulement une priorité pour les chercheurs du Sud, mais également une préoccupation majeure pour les peuples autochtones de l'Arctique circumpolaire. La santé, le mode de vie, les valeurs et les traditions de ces communautés sont grandement ébranlés par les contaminants environnementaux. Conséquemment, les habitants du Nord prennent de plus en plus d'actions afin de reprendre le contrôle sur leur santé et celle de leur territoire (Pearce et al., 2015, Watt-Cloutier, 2003).

Approches collaboratives avec les communautés

communauté /kɔmynote/ origine latin communitas, première utilisation 14^{e} siècle, se réfère à un ensemble unifié d'individus

Depuis des dizaines d'années, les peuples autochtones, tels que les Inuit, revendiquent une plus grande implication dans la prise de décisions liées aux priorités en recherche, à l'élaboration de méthodes de travail éthiques, ainsi qu'à l'archivage, l'interprétation et la diffusion des données (ITK, 2018, INQ, 2017). Une prise de conscience de l'importance, en recherche, des approches collaboratives avec les communautés autochtones a pris une certaine ampleur au sein de plusieurs institutions académiques (Johnson et al., 2015, Adams et al., 2014). De plus, dans le contexte des changements climatiques rapides, les chercheurs sont de plus en plus appelés à mener des travaux de recherche adaptatifs, qui tiennent compte des priorités de gestion locales (Lindenmayer and Likens, 2009). La recherche communautaire est une démarche méthodologique qui soutient les efforts visant à s'associer avec les communautés autochtones, et qui est de plus en plus employée par les chercheurs en milieu académique au Canada (Castleden et al., 2012). Cependant, les approches communautaires demeurent sous-représentées au sein des scientifiques en sciences naturelles conduisant des travaux de recherche dans les communautés du Nord (Johnson et al., 2015, Adams et al., 2014, Brunet et al., 2014). Dans le cadre de travaux sur le terrain menés en Arctique, il peut parfois devenir évident que :

> […] les chercheurs de certaines disciplines, notamment dans le domaine des sciences naturelles, ne sont pas habitués à traiter avec des êtres humains et ne savent pas comment réagir face aux Autochtones qui leur disent qu'ils ont été créés pour être les gardiens de la Terre-Mère et qu'à ce titre c'est à eux qu'il incombe de définir comment les recherches sur le territoire, sur les animaux ou les plantes doivent être définies (INQ, 2017, Martin, 2013).

Dans la présente thèse, j'utiliserai le terme recherche collaborative avec les communautés (*community-collaborative research*), comme un terme général qui englobe différentes approches

de la recherche visant l'implication des communautés locales et des individus dans le but de partager ou de cogénérer des connaissances afin de mieux résoudre des problèmes complexes (Tondu et al., 2014). La recherche collaborative avec les communautés a été démontrée comme comportant plusieurs avantages bilatéraux, incluant la création de liens entre le savoir scientifique et autochtone, l'instauration d'une relation de confiance entre les chercheurs et les communautés, l'implication des membres des communautés dans les processus de recherche, ainsi que la possibilité pour les chercheurs d'obtenir des échantillons à longueur d'année (Dickinson et al., 2010, Danielsen et al., 2005). L'intégration du savoir autochtone (*indigenous knowledge,* ou IK), ou savoir écologique traditionnel (*traditional ecological knowledge*, ou TEK), dans la recherche en écologie contribue grandement à l'envergure des retombées qui en découlent (Pearce et al., 2009). Il existe cependant d'importants défis découlant de l'intégration d'un modèle de recherche communautaire dans le Nord. Pour les chercheurs, ces défis incluent notamment des limites au niveau du financement et du temps, ainsi qu'un manque de formation officielle axée sur l'importance de l'engagement interculturel. La méfiance à l'égard de la recherche et des chercheurs peut également être présente dans certaines communautés autochtones, compliquant la création de nouvelles collaborations. Afin de mener des travaux de recherche en collaboration avec les communautés, les chercheurs doivent souvent naviguer entre des définitions, des approches et des attentes divergentes envers la recherche qui découlent des différences entre les systèmes de connaissances et les visions du monde des chercheurs et des membres des communautés autochtones (Johnson et al., 2015, Adams et al., 2014).

Structure de la thèse et contributions

L'objectif général de mes recherches doctorales vise à approfondir nos connaissances sur les effets des changements climatiques et socio-environnementaux sur les contaminants dans le Nord. Via l'étude du devenir dans l'environnement et de la bioaccumulation des métaux traces dans le Nord en évolution rapide, je fournirai des informations cruciales sur le cycle des métaux traces. La présente thèse met l'accent sur la biogéochimie du mercure et des éléments de terres rares au sein des écosystèmes arctiques, ainsi que leur dynamique dans les réseaux trophiques. Les écosystèmes arctiques sont d'importants indicateurs des changements globaux futurs, puisque les régions nordiques se réchauffent plus rapidement que les régions tempérées. Par ailleurs, ces informations fourniront des outils nécessaires à l'évaluation de l'impact de ces changements dans le Nord et sur les communautés qui y vivent. Idéalement, les conclusions de la présente thèse pourraient contribuer à l'élaboration de politiques et favoriseraient également la collaboration mutuellement bénéfique et l'échange de connaissances entre les scientifiques et les communautés autochtones.

La structure de ma thèse suivra le modèle de la « thèse par articles », comportant quatre articles scientifiques publiés ou publiables sur les aspects spécifiques du devenir dans l'environnement et de la bioaccumulation des métaux traces dans le Nord. Tous les chapitres étant rédigés sous la forme de manuscrits indépendants, il est possible que certaines redondances existent au sein des différentes introductions, ainsi que dans la description des méthodes d'échantillonnage et analytiques. Une brève revue de la littérature pertinente a été présentée dans le chapitre d'introduction générale. Les objectifs spécifiques et les retombées associées aux différents travaux de mon projet de doctorat seront quant à eux discutés dans la présente section. J'ai employé une méthode empirique basée sur l'utilisation de données quantitatives provenant d'études écotoxicologiques dans le but d'évaluer le comportement des métaux traces sur le terrain. J'ai également utilisé des données quantitatives et qualitatives afin d'étudier les avantages et les défis de la recherche collaborative avec les communautés autochtones dans le domaine des sciences naturelles. Les chapitres 1 et 2 se concentrent sur la dynamique du mercure et les chapitres 3 et 4 visent l'étude de la bioaccumulation et du transfert trophique des REEs. Cette thèse comporte 5 annexes, incluant 1 article dont je suis la co-première auteure et 2 manuscrits co-rédigés. Ces articles sont pertinents dans le cadre des travaux de la présente thèse et soulignent mon implication

liée à la recherche collaborative avec les communautés. La contribution détaillée de chacun des auteurs est décrite au début du présent document (ii-iv).

Dans un premier temps, j'ai étudié les effets potentiels d'un climat en changement sur le cycle du mercure dans les lacs et les étangs nordiques. Nous examinons le mercure au sein des lacs et étangs, car la méthylation et bioaccumulation de mercure ont principalement lieu dans les milieux aquatiques grâce à l'activité de certains microorganismes (Wiener et al., 2003). Les étangs nordiques sont également des écosystèmes simplifiés et relativement peu perturbés, pouvant servir de sites de référence pour les eaux polluées à plus faible latitude. Le nombre élevé de ces étangs sur une petite superficie et leur grande variabilité physicochimique en font de véritables laboratoires en milieu naturel. Les liens existant entre les grands changements globaux et le cycle du mercure sont relativement bien explorés. Cependant, il demeure difficile de prédire les changements futurs en raison de la complexité et l'antagonisme de facteurs influençant le cycle du mercure (Krabbenhoft and Sunderland, 2013). Les chapitres 1 et 2 visent à mieux comprendre les effets d'un climat en changement sur le cycle du mercure en examinant les mécanismes potentiels associés à l'influence ces changements sur le transport, la transformation et le transfert de mercure au sein des écosystèmes d'eau douce.

Le chapitre 1 examine la question suivante : Les mares thermokarstiques sont-elles une source potentielle de méthylmercure toxique dans l'est de l'Arctique canadien? Bien que les mares thermokarstiques, ou mares de fonte, soient omniprésentes dans l'est de l'Arctique canadien, on en sait peu sur leur potentiel de constituer des sources de MeHg pour les eaux douces. Ces travaux, qui se sont échelonnés sur plusieurs années, ont permis d'étudier les mares de fontes d'une région au pergélisol discontinu dans la taïga subarctique (Kuujjuarapik-Whapmagoostui, Québec) ainsi que d'une région au pergélisol continu dans la toundra arctique (île Bylot, Nunavut). Les objectifs principaux du chapitre 1 étaient de (1) caractériser les niveaux de MeHg dans différents types de mares de fonte et les comparer au niveau des plans d'eau avoisinants, et de (2) déterminer l'importance des variables environnementales, incluant les nutriments et le carbone organique, dans ces différences de concentrations entre les mares. Les résultats clés de cette étude démontrent que les concentrations de MeHg dans les mares thermokarstiques sont bien supérieures aux niveaux mesurés dans la majorité des écosystèmes d'eau douce de l'Arctique canadien. En raison de la connectivité hydrologique croissante résultant des changements climatiques, ces observations infèrent que les mares de fonte sont potentiellement des sources de MeHg pour les écosystèmes

aquatiques arctiques voisins. Les concentrations élevées de MeHg mesurées dans l'eau de ces mares étaient également fortement corrélées aux variables associées aux apports élevés de matière organique (DOC, a320, Fe), aux nutriments (TP, TN), et à l'activité microbienne (CO_2 et CH_4 dissous). Ces observations sont d'une importance cruciale, puisqu'elles suggèrent qu'il existe une forte relation entre la production de MeHg dans ces mares et l'érosion de la matière organique résultant du dégel du pergélisol.

Le chapitre 2 s'appuie sur les résultats du chapitre 1 soulignant la forte relation entre le dégel du pergélisol, l'érosion de la matière organique, et la remobilisation du mercure dans les cours d'eau de l'Arctique. L'apport de nutriments et de matière organique par le dégel du pergélisol risque également de stimuler la productivité aquatique dans les écosystèmes d'eau douce, qui à son tour aura des conséquences importantes sur la stœchiométrie des nutriments et le transfert trophique du MeHg. Le chapitre 2 se penche sur la question suivante : Une augmentation de la productivité aquatique dans les lacs arctiques engendrera-t-elle une diminution des concentrations de MeHg aux niveaux trophiques inférieurs? Les objectifs principaux de cette étude étaient (1) de déterminer la valeur nutritionnelle du seston et du zooplancton des eaux douces arctiques et (2) d'évaluer l'occurrence de biodilution causée par les algues ou par la croissance du zooplancton dans les lacs arctiques. Nous avons émis l'hypothèse qu'une augmentation de la productivité aquatique dans les lacs arctiques engendrerait une augmentation de biomasse algale, ou une croissance zooplanctonique plus rapide, réduisant ainsi les concentrations de MeHg dans le zooplancton. Afin d'évaluer cette hypothèse, nous avons échantillonné des écosystèmes suivant une gamme décroissante de productivité sur 20 degrés de latitude du Subarctique jusqu'en Arctique dans l'est du Canada. Au total, 47 lacs et mares ont été échantillonnés près de Kuujjuarapik-Whapmagoostui (Québec), d'Iqaluit (Nunavut), et de Resolute Bay (Nunavut). Aucune corrélation significative n'a été constatée entre les concentrations de MeHg dans le seston et les indices de productivité aquatique (concentrations d'azote, de phosphore et de chlorophylle-a dans l'eau). Nous n'avons pas non plus observé de corrélation négative entre la valeur nutritionnelle du seston et la concentration de MeHg dans le zooplancton. Nos résultats suggèrent que l'exposition au mercure serait le facteur dominant qui contrôle l'accumulation de mercure à la base des réseaux aquatiques, et que la biodilution n'est pas un facteur important pour l'accumulation de MeHg dans le seston et dans le zooplancton des régions subarctiques et arctiques.

Bien que le mercure soit un polluant global important et la cible d'un grand intérêt écotoxicologique, les changements climatiques et socio-environnementaux auront des effets importants sur les cycles d'autres métaux traces dans le Nord. Contrairement au mercure, les éléments de terres rares (REEs) sont un groupe de contaminants émergents qui ne sont que récemment devenus un sujet d'intérêt des études écotoxicologiques. En raison de l'augmentation de leur émission dans l'environnement, les communautés scientifiques et du Nord sont de plus en plus inquiètes face aux impacts d'un enrichissement en REEs dans les écosystèmes naturels. Peu d'études menées sur le terrain se sont penchées sur le comportement des REEs dans l'environnement et donc la deuxième partie de cette thèse s'est concentrée sur leur bioaccumulation et de leur dynamique dans les réseaux trophiques les écosystèmes nordiques.

Dans le chapitre 3, l'objectif principal était d'établir les conditions de référence des REEs avant la prolifération de projets d'exploitation minière aux latitudes nordiques. Le chapitre 3 se penche sur les questions suivantes : Est-il possible de détecter les REEs dans l'eau douce, les plantes marines et terrestres ainsi que dans les animaux? Les REEs sont-ils bioaccumulables et bioamplifiables dans les réseaux trophiques nordiques? Les réponses à ces questions constituent des informations écotoxicologiques de référence, puisque les écosystèmes nordiques sont potentiellement susceptibles à un enrichissement en REEs résultant de projets d'exploration minière. Les objectifs principaux de ce chapitre étaient d'évaluer (1) la bioaccumulation des REEs spécifique aux espèces et aux tissus dans certains taxons d'importance et (2) le transfert trophique des REEs au sein des écosystèmes nordiques en utilisant des mesures de ratios d'isotopes stables de carbone et d'azote (∂15N, ∂13C) de la structure des réseaux trophiques. Nous avons mesuré les concentrations de REEs ainsi que ces ratios dans les organismes provenant d'écosystèmes marins, d'eau douce et terrestres. La récolte de la faune et l'échantillonnage des tissus ont été partiellement réalisés par les chasseurs locaux dans le cadre d'un projet de suivi à vocation communautaire. Nos résultats démontrent que les concentrations de REEs les plus élevées ont été mesurées aux niveaux trophiques inférieurs, principalement dans la végétation et les invertébrés aquatiques. Les herbivores terrestres, les phoques annelés, et les poissons présentaient de faibles niveaux de REEs totaux dans leurs tissus. Cependant, cette accumulation était d'un ordre de grandeur supérieur dans les tissus du foie. Cette étude indique que les patrons de bioaccumulation des REEs sont spécifiques aux taxons et aux tissus, et que ces contaminants présentent un faible potentiel de bioamplification. Les conclusions du chapitre 3 sont appuyées par l'article en Annexe 1, qui

examine le devenir dans l'environnement et le transfert trophique des REEs dans des lacs tempérés. Le chapitre 3 et l'annexe 1 fournissent des données novatrices sur le comportement des REEs qui peuvent être appliquées à l'évaluation de l'impact environnemental d'un enrichissement en REEs dans les écosystèmes d'eau douce.

Le chapitre suivant examine de plus près la bioaccumulation de terres rares dans le zooplancton d'eau douce afin de l'utiliser comme indicateur clé de la bioaccumulation dans les lacs naturels. Des comparaisons entre les lacs en régions tempérées et arctiques s'avèrent plutôt rares, mais ces études sont importantes, car ils nous informent sur les facteurs clés influençant la bioaccumulation des contaminants à travers un paysage géographique hétérogène. Le chapitre 4 se penche sur un gradient d'écosystèmes d'eau douce et tente de répondre à la question suivante : Quels sont les facteurs environnementaux expliquant les niveaux de REEs dans les écosystèmes d'eau douce de différents types de lacs suivant un gradient géographique des régions tempérées vers les régions arctiques? Les principaux objectifs étaient de (1) déterminer les concentrations de REEs dans l'eau, les sédiments et le zooplancton dans les écosystèmes d'eau douce, (2) étudier l'influence de la spéciation des REEs et des concentrations d'ions libres sur leur bioaccumulation dans le zooplancton et (3) d'évaluer l'influence des caractéristiques du bassin versant et des facteurs environnementaux intrinsèques des lacs sur la bioaccumulation des REEs dans le zooplancton. Dans le cadre de cette étude, des échantillons de zooplancton non triés ont été récoltés dans 39 lacs provenant de 5 régions géographiques présentant des conditions environnementales variées. Nous avons observé une plus grande variation au niveau des concentrations aqueuses de REE (ordre de 200) qu'au niveau des concentrations dans les sédiments (ordre de 10). Cette étude a également démontré que les concentrations totales de REEs dans l'eau prédisent de façon hautement significative les concentrations dans le zooplancton. Les concentrations de REEs dans le zooplancton sont également fortement corrélées aux concentrations d'ions libres (REE^{3+}) dans la colonne d'eau. Les résultats soulignent la pertinence du zooplancton dans le suivi biologique de ces contaminants dans les écosystèmes d'eau douce. Ce chapitre fournit l'une des bases de données les plus détaillées sur la répartition naturelle des éléments de terres rares dans les lacs et les mares situés sur une vaste région géographique présentant une géologie ainsi que des conditions environnementales diverses.

Dans le contexte des changements climatiques rapides, les chercheurs sont de plus en plus appelés à mener des travaux de recherche collaborative, qui tiennent compte des priorités de

gestion locales. Plusieurs communautés du Nord sont inquiètes face à l'impact des changements climatiques et de l'exploitation minière sur la santé humaine et des écosystèmes. Au cours de mes études doctorales, j'ai également contribué à ce projet de surveillance environnementale et à la création d'activités éducatives participatives (*outreach*) visant l'intégration du savoir autochtone dans la recherche en écologie. Dans un dernier temps, cette thèse met en lumière l'importance de mener de la recherche collaborative visant à accroître les interactions positives entre les chercheurs et les membres des communautés autochtones. Les annexes 2 et 3 de la présente thèse contribuent aux débats actuels portant sur les avantages et les défis de la recherche collaborative avec les communautés autochtones dans le domaine de l'écologie.

L'annexe 2 porte sur la description d'un programme de suivi environnemental communautaire qui a été initié par la collaboration entre la communauté de Kangiqsualujjuaq et les chercheurs universitaires, en prévision du début des opérations de l'exploitation d'une mine de REEs dans le bassin versant de la rivière George. J'ai contribué à ce projet en aidant à créer des activités éducatives participatives, en menant des projets d'apprentissage sur le terrain ainsi qu'en offrant des formations sur la collecte de données de concentrations de contaminants dans la rivière George. Les résultats de ce projet démontrent qu'il existe plusieurs défis et avantages à la recherche collaborative avec les communautés du Nord. Certains de ces défis peuvent cependant être surmontés grâce à la création de liens de confiance, à l'établissement d'objectifs et de priorités clairs, à l'intégration du savoir local ainsi qu'en mettant l'accent sur les activités de partage des connaissances et l'éducation.

L'annexe 3 examine le rôle de la création d'ateliers étudiants dans la promotion de la recherche en collaboration avec les communautés pour les chercheurs en début de carrière (*early career researchers,* ECRs). L'annexe 3 traite d'un défi majeur découlant de la recherche collaborative avec les communautés en répondant à la question suivante : Des ateliers menés par des étudiants peuvent-ils aider de manière efficace les chercheurs en début de carrière à travailler *avec* ou *auprès de* communautés autochtones? Les résultats de cet article mettent en perspective le fait que les ateliers organisés par les pairs sont efficaces dans l'optique de partager des points de vue et de sensibiliser les participants aux cultures, à l'histoire et aux langues autochtones, ainsi que d'offrir une plateforme d'échanges et de réflexion sur ces questions. Cependant, bien que ces ateliers soient extrêmement importants, ils sont insuffisants en eux-mêmes pour instaurer un changement des méthodes de recherche en sciences naturelles afin d'y intégrer des approches

collaboratives avec les communautés. Enfin, les annexes 4 et 5 mettent en lumière mon travail d'éducation et ma contribution aux activités de partage des connaissances au cours de mes études doctorales, dont le but premier était de favoriser les interactions positives entre les chercheurs et les communautés autochtones dans le Nord.

En somme, la présente thèse a grandement amélioré notre compréhension de l'effet des changements socio-environnementaux sur la biodisponibilité et les dynamiques trophiques de mercure et des éléments de terres rares dans les écosystèmes de l'est de l'Arctique canadien. Mieux comprendre les répercussions des changements futurs sur le devenir des métaux traces dans l'environnement est crucial à l'évaluation de l'impact de ces changements sur le Nord et sur les communautés qui y vivent.

Bonne lecture!

CHAPITRE 1: Concentrations élevées de MeHg au sein des petits étangs de l'est de l'Arctique canadien

High Methylmercury in Arctic and Subarctic Ponds is Related to Nutrient Levels in the Warming Eastern Canadian Arctic

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Abstract

Permafrost thaw ponds are ubiquitous in the eastern Canadian Arctic, yet little information exists on their potential as sources of methylmercury (MeHg) to freshwaters. They are microbially-active and conducive to methylation of inorganic mercury, and are also affected by Arctic warming. This multi-year study investigates thaw ponds in a discontinuous permafrost region in the Subarctic taiga (Kuujjuarapik-Whapmagoostui, QC) and a continuous permafrost region in the Arctic tundra (Bylot Island, NU). MeHg concentrations in thaw ponds were well above levels measured in most freshwater ecosystems in the Canadian Arctic (> 0.1 ng L^{-1}). On Bylot, ice-wedge trough ponds showed significantly higher MeHg (0.3 - 2.2 ng L^{-1}) than polygonal ponds (0.1 - 0.3 ng L^{-1}) or lakes (< 0.1 ng L^{-1}). High MeHg were measured in the bottom waters of Subarctic thaw ponds near Kuujjuarapik (0.1 - 3.1 ngL^{-1}). High water MeHg concentrations in thaw ponds were strongly correlated with variables associated with high inputs of organic matter (DOC, a_{320}, Fe), nutrients (TP, TN), and microbial activity (dissolved CO_2 and CH_4). Thawing permafrost due to Arctic warming will continue to release nutrients and organic carbon into these systems and increase ponding in some regions, likely stimulating higher water concentrations of MeHg. Greater hydrological connectivity from permafrost thawing may potentially increase transport of MeHg from thaw ponds to neighbouring aquatic ecosystems.

Introduction

The Minamata Convention on Mercury, a global legally-binding treaty designed to reduce the emission of mercury to the environment, has recently been adopted by 198 countries (UNEP, 2013). Nearly a half-century after the discovery of Minamata disease, mercury (Hg) remains a high-priority global contaminant, especially in the form of methylmercury (MeHg), which bioaccumulates and biomagnifies to high levels in aquatic food webs. Exposure to MeHg can affect the nervous, reproductive, and immune systems of vertebrates, including fish, birds, and humans (Donaldson et al., 2010). Arctic ecosystems are especially vulnerable to Hg pollution due to atmospheric deposition and higher rates of biomagnification in the cold and unproductive food webs of the Arctic (Lavoie et al., 2013, AMAP, 2011, Steffen et al., 2007).

Mercury reaches the Arctic through long-range atmospheric transport in the form of elemental mercury, or Hg(0), where it is deposited into the environment after oxidation into Hg(II) (Ariya et al., 2004). Once deposited, inorganic Hg(II) can be microbially methylated *in situ* to the toxic and biomagnifying form, organic MeHg. A key area of current Arctic research is to establish where Hg(II) methylation occurs in Arctic systems (Barkay and Poulain, 2007). For inland fresh waters, MeHg is produced in anaerobic sediments and hypolimnia of lakes and ponds or in wetlands (Lehnherr et al., 2012a). Spring snowmelt may also be an important source of MeHg to freshwater ecosystems (Oiffer and Siciliano, 2009, Loseto et al., 2004).

In the High Arctic, small ponds have been identified as important sites of microbial Hg(II) methylation (Lehnherr et al., 2012a, St. Louis et al., 2005). However, only a few studies have examined the mercury cycle in permafrost thaw lakes and ponds. Although often overlooked, these systems are now considered the most abundant type of aquatic ecosystem at circumpolar Arctic and Subarctic latitudes (Pienitz et al., 2008). They are formed in depressions created by permafrost thawing and may persist from days to hundreds of years, depending on local geomorphology and hydrology (Boike et al., 2012). Most are small and shallow systems receiving nutrients and organic matter from thawing permafrost and are often colonized by biofilms (Breton et al., 2009).

One recent study in the western Canadian Arctic found that lakes affected by the development of retrogressive thaw slumps had lower Hg levels in surface sediments when compared to

reference lakes (Deison et al., 2012). In this case, slumping of permafrost soils resulted in high inorganic sedimentation rates and the dilution of Hg in the sediments. However, a study of a peat palsa mire in Norway showed that long-term changes in climate can cause the release of Hg into lake surface waters through increased permafrost thaw depth and thermokarst erosion (Rydberg et al., 2010). Warm and microbially-active thaw ponds receiving inputs from adjacent slumping permafrost soils may in fact be sources of MeHg in the Arctic environment.

Unlike other types of shallow ponds, thaw ponds often show stable thermal stratification in summer with hypoxic to anoxic hypolimnia, some keeping unfrozen bottom waters during the winter months potentially allowing for ongoing microbial activity (Rautio et al., 2011). In stratified thaw ponds having anoxic bottom waters or sediments, reducing conditions promote microbial Hg(II) methylation. Although many ponds are physically isolated in permafrost landscapes, shifts in the hydrological regime may allow for MeHg to reach surrounding lakes, rivers and marine coastal waters (Jolivel and Allard, 2013, Rydberg et al., 2010, Fortier et al., 2007, Yoshikawa and Hinzman, 2003, Allard, 1996).

Climate warming and rising permafrost temperatures are increasing the impacts of thermokarst processes on Arctic aquatic ecosystems (Kokelj and Jorgenson, 2013, Schuur et al., 2008). Thawing permafrost may also affect the mercury cycle by modifying hydrological regimes and the transport of mercury from soils and peatlands to nearby aquatic ecosystems (AMAP, 2011, Klaminder et al., 2008, Macdonald et al., 2005). The release of nutrients and organic carbon and the accelerated microbial transformations of contaminants associated with these changes will also likely affect the accumulation or *in situ* production of MeHg in thermokarst aquatic systems (Stern et al., 2012, Faithfull et al., 2011, Roehm et al., 2009, Guo et al., 2007).

The main objectives of this study were to assess Arctic and Subarctic thaw ponds as a potential source of MeHg by 1) characterizing MeHg levels encountered in different types of thaw ponds and comparing them to other nearby water bodies, and 2) determining the importance of environmental variables, including nutrients and organic carbon, in explaining among-site differences in MeHg levels in thaw ponds. Two geographic areas were investigated in the eastern Canadian Arctic, one located on a discontinuous permafrost landscape in the Subarctic taiga near Kuujjuarapik-Whapmagoostui, Nunavik (Northern Quebec), and the other in an area of continuous permafrost in the High Arctic tundra on Bylot Island, Nunavut.

Materials and Methods

Study sites. Sampling was conducted in the Qarlikturvik Valley on Bylot Island in Nunavut (73°09'23"N, 79°58'19"W) and in the area surrounding the Kuujjuarapik-Whapmagoostui community in Nunavik (55°16'30"N, 77°45'30"W) (Fig. S1). Sites on Bylot Island were sampled in July and August 2008, 2009, 2010 and 2011, whereas sites near Kuujjuarapik-Whapmagoostui were sampled in July and August 2006, 2009, 2012 and 2013. Bylot Island thaw ponds can be classified into two types: 1) polygonal ponds created by the rise of peat polygon ridges and 2) trough ponds that form over melted ice wedges between the polygon mounds. Trough ponds, elsewhere called runnel ponds (Negandhi et al., 2013), are elongated aquatic systems featuring peat erosion and higher turbidity than polygonal ponds, therefore classified as thermokarstic (Laurion et al., 2010). Both types of ponds examined were no more than a few meters in diameter and generally less than 1.5 m in depth. Seven larger aquatic systems on Bylot Island were categorized as "lakes" for this study, given their much larger surface area and depth. Subarctic sample sites included thermokarst and taiga/rock basin ponds sampled near Kuujjuarapik-Whapmagoostui. Here, thermokarst thaw ponds develop in depressions left after the ice has melted below mineral or besides organic permafrost mounds (Bhiry et al., 2011, Breton et al., 2009). They are 10 to 30 m in diameter and have a maximum depth of 3.5 m (Laurion et al., 2010). Taiga/rock basin ponds (pooled into one group) are formed on granite or carbonate-derived bedrock respectively and are 10-20 m in diameter with a maximum depth of 1 m. For more information on the formation of study sites see SI.

Physico-chemical sampling. Study lakes and ponds were sampled for water chemistry, including dissolved organic carbon (DOC), total nitrogen (TN), total phosphorus (TP), chlorophyll *a* (Chla), anions, cations, major metals, carbon dioxide (CO_2), methane (CH_4) and aqueous total Hg and MeHg concentrations. Additionally, the physico-chemical properties of the water column, including temperature, pH, conductivity, and dissolved oxygen, were measured at the water surface using a YSI 600QS meter (YSI Incorporated). Vertical profiles were also conducted in 3 Subarctic thermokarst ponds. For details on methods, see SI.

Aqueous total mercury (THg) and MeHg concentrations. Water samples were collected for Hg at the surface and 30 cm above the bottom sediments, either from shore or from a raft. Samples were collected using the clean hands, dirty hands sampling protocol for trace metals

(St. Louis et al., 1994). Both unfiltered and filtered water samples were taken at each site to determine the proportion of dissolved and particle-bound total mercury (THg or Hg(II) + MeHg) and methylmercury (MeHg). Water samples for total THg and MeHg analyses were pumped through acid-washed Teflon tubing with a peristaltic pump, after the apparatus was flushed with site water for 5 minutes. Samples were stored in acid-cleaned amber glass bottles. Water samples for dissolved Hg and MeHg concentrations were filtered (pore size 0.45 μm) using a peristaltic pump, acid-cleaned Teflon tubing and a GWV High Capacity In-Line Groundwater Sampling Capsule (Pall Corporation) or filtered with pre-ashed glass-fibre filters (0.7 um pore size, Whatman GF-F) on a clean Teflon filtration tower (HCl 10%). All Hg samples were preserved with ultrapure hydrochloric acid to 0.4% final concentration until laboratory analysis.

Aqueous THg concentration was determined following U.S. EPA method 1631, by bromine monochloride (BrCl) oxidation, tin (II) chloride ($SnCl_2$) reduction, two-stage gold amalgamation and gas-phase detection with a Tekran 2600 Cold-Vapour Atomic Fluorescence Spectrometer (CVAFS) (Tekran Instruments Corporation). The analytical detection limit was 0.04 ng L^{-1}, calculated as three times the standard deviation (SD) of ten blanks. New standards (0.5 ng L^{-1}) were run after each set of 12 samples to test for analytical stability (mean recovery 102.5 ± 9.0%, n = 79). All water samples were run in duplicate or triplicate with a Relative Standard Deviation (RSD) of usually <10% for THg.

Aqueous MeHg concentration was determined following U.S. EPA method 1630, by acid-distillation to remove matrix interferences, derivatization by aqueous-phase ethylation, purging on Tenax (Tenax Corporation) and separation by gas chromatography, before detection with either a Tekran 2500 or Tekran 2700 CVAFS (Tekran Instruments Corporation). The analytical detection limit was 0.02 ng L^{-1} and 0.01 ng L^{-1} respectively for the Tekran 2500 and Tekran 2700, calculated as three times the SD of ten blanks. New standards (0.5 ng/L) were run after each set of 10-12 samples to test for analytical stability (mean recovery 104.2 ± 17.3%, n = 53). Analyses were accepted when recovery of certified trace metal reference materials was in the certified range (152 ± 13 ng/g for TORT-2 lobster hepatopancreas, National Research Council of Canada) and the mean (± SD) recovery was 99.5 ± 8.4% (n = 97). All water samples were run in duplicate with a Relative Standard Deviation (RSD) of <12% for MeHg. Hg analyses met the criteria of a Canadian Association for Laboratory Accreditation (CALA) inter-calibration

exercise and an Interlaboratory Quality Assurance Program administered by the Northern Contaminants Program (Government of Canada) (see SI).

Statistical analysis. For all statistical analyses, among-year averages were calculated for each site (from 2008-2011 for Bylot and 2006-2013 for Kuujjuarapik) although not all variables were measured at each site for each year. All of the variables were normalized in order to reduce skewness and the effects of outliers using either log transformations (Temp, pH, Cond, DOC, Chla, Cl, Fe, Mg, Mn, Na, SO_4^{2-}, TN, TP, THg, MeHg, %MeHg,), square root transformations (Ca, K) or power transformations (square) (DO). Inorganic Hg(II) concentrations were estimated by the difference between THg and MeHg concentrations at each site. Normalized data were used to perform all analyses with the R statistical package (R Development Core Team; http://cran.r-project.org). For comparisons of limnological properties and mercury concentrations, the geometric mean (GM) was calculated to better measure the central tendency, calculated as the antilog of the mean of the logarithmic values of the data set. Sites with missing data for multiple variables were not included in the regression analysis, and replacement values were calculated for four sites (each with one missing variable) by imputing the overall variable mean for the type of sample site.

Comparisons of limnological properties and mean mercury concentrations were conducted with one-way ANOVAs followed by post-hoc pairwise comparisons using the Tukey HSD correction ($\alpha < 0.05$). Sensitivity analysis with a non-parametric approach (Kruskal-Wallis chi-squared, χ^2 rank sum tests) was conducted to test the assumptions of the analysis of variance model and the non-parametric tests gave the same conclusions as the analyses of variance (Thabane et al., 2013). Gradients in environmental characteristics were examined by principal component analysis (PCA) using the vegan package in R on centered and scaled data (n=40). A non-parametric multivariate analysis of variance (MANOVA) was also run to determine whether samples sites differed significantly in terms of measured environmental variables (Adonis test, Vegan package in R) (Oksanen et al., 2013). Due to high collinearity between many of the variables, multiple regression models were difficult to interpret and therefore only simple linear regression models are presented for the most highly correlated environmental variables.

TABLE 1: Comparison of limnological properties from sampled sites on Bylot Island and near Kuujjuarapik-Whapmagoostui. Surface water geometric mean values (bold) and ranges (min – max) are shown. One-way ANOVA results and post-hoc pairwise comparisons between the 3 groups (Tukey's HSD) are given ($\alpha < 0.05$). *P*-values were corrected for multiple tests (Holm correction) and non-significant tests are shown by n.s. Several variables were not available for the Bylot lakes and for taiga/rock ponds (na) yet with *p*-values for the entire model.

Bylot	a) Trough Ponds (n=18)		b) Polygonal Ponds (n = 9)		c) Lakes (n = 7)		F	*P* - value	Post-Hoc
Temp (°C)	**12.5**	(8.0 – 19.2)	**13.5**	(11.9 – 15.8)	**9.4**	(6.1 – 16.1)	*n.s.*	*n.s.*	*n.s.*
pH	**6.8**	(5.9 – 7.6)	**8.0**	(6.5 – 8.7)	**6.9**	(6.6 – 7.6)	14.54	< 0.001	b > a; b > c
Cond (µS cm^{-1})	**95**	(43 – 448)	**78**	(51 – 119)	**18**	(9 – 90)	15.87	< 0.001	a > c, b > c
DO (mg L^{-1})	**8.90**	(3.81 – 12.25)	**10.46**	(6.75 – 12.09)	**11.52**	(10.43 – 12.85)	*n.s.*	*n.s.*	*n.s.*
a_{320} (m^{-1})	**37.8**	(18.4 – 269.4)	**16.3**	(8.2 – 77.9)	**3.3**	(1.3 – 6.3)	29.34	< 0.001	a > b > c
DOC (mg L^{-1})	**12.4**	(7.7 – 33.0)	**9.0**	(6.6 – 15.2)	**2.3**	(1.0 – 5.3)	36.32	< 0.001	a > c, b > c
CO_2 (µM)	**108.4**	(24.3 – 609.1)	**20.6**	(9.1 – 280.1)	**na**	na	8.206	< 0.01	a > b
CH_4 (µM)	**5.59**	(2.09 – 19.90)	**1.70**	(0.68 – 5.05)	**na**	na	11.58	< 0.001	a > b
SO_4^{2-} (mg L^{-1})	**1.26**	(0.07 – 3.59)	**1.49**	(0.40 – 6.08)	**1.21**	(0.66 – 2.47)	*n.s.*	*n.s.*	*n.s.*
Fe (µg L^{-1})	**90.4**	(11.2 – 1637.5)	**52.9**	(28.68 – 352.4)	**19.9**	(6.06 – 881.6)	38.87	< 0.001	a > c, b > c
Mn (µg L^{-1})	**10.5**	(2.05 – 556.1)	**1.75**	(0.58 – 13.94)	**na**	na	*n.s.*	*n.s.*	*n.s.*
TP (µg L^{-1})	**43.5**	(14.6 – 359.7)	**19.4**	(12.9 – 46.8)	**4.5**	(3.1 – 8.5)	18.68	< 0.001	a > c, b > c
TN (µg L^{-1})	**743.9**	(268.6 – 4366)	**418.7**	(334.3 – 572.3)	**122.8**	(94.8 – 194.5)	19.82	< 0.001	a > c, b > c
Chl*a* (µg L^{-1})	**1.60**	(0.40 – 26.60)	**0.94**	(0.30 – 2.66)	**1.13**	(0.62 – 1.70)	*n.s.*	*n.s.*	*n.s.*
THg (ng L^{-1})	**2.75**	(1.26 – 21.82)	**1.74**	(1.24 – 2.93)	**1.05**	(0.68 – 1.55)	8.34	< 0.01	a > c
MeHg (ng L^{-1})	**0.72**	(0.14 – 10.58)	**0.21**	(0.08 – 0.34)	**0.03**	(0.00 – 0.06)	45.03	< 0.001	a > b > c
MeHg (%)	**26.0**	(11.1 – 48.5)	**12.0**	(4.9 – 18.7)	**1.5**	(0.0 – 5.8)	64.30	< 0.001	a > b > c
Kuujjuarapik	**a) Thaw ponds Surface Waters (n = 12)**		**b) Thaw Ponds Bottom Waters (n = 9)**		**c) Taiga/Rock Ponds (n=12)**		**F**	***P* - value**	**Post-Hoc**
Temp (°C)	**17.8**	(14.4 – 24.2)	**7.6**	(4.9 – 13.1)	**13.5**	(11.4 – 16.3)	50.95	< 0.001	a > c > b
pH	**6.6**	(5.8 – 7.2)	**6.2**	(5.9 – 6.9)	**6.9**	(5.7 – 7.8)	*n.s.*	*n.s.*	*n.s.*
Cond (µScm^{-1})	**52**	(27 – 204)	**188**	(145 – 265)	**77**	(26 – 514)	8.77	0.001	b > a, b > c
DO (mgL^{-1})	**7.76**	(2.49 – 9.81)	**0.41**	(0.41 – 9.31)	**10.41**	(8.34 – 12.73)	33.73	< 0.001	c > a > b
A_{320} (m^{-1})	**31.1**	(12.9 – 53.7)	**48.3**	(19.7 – 106.9)	**na**	na	*n.s.*	*n.s.*	*n.s.*
DOC (mgL^{-1})	**8.71**	(4.0 – 28.0)	**7.3**	(4.2 – 11.9)	**12.5**	(6.8 – 18.3)	*n.s.*	*n.s.*	*n.s.*
CO_2 (µM)	**61.0**	(33.9 – 141.6)	**376.6**	(106.9 – 815.5)	**na**	na	39.78	< 0.001	b > a
CH_4 (µM)	**0.44**	(0.24 – 1.41)	**42.12**	(0.48 – 311.9)	**na**	na	28.05	< 0.001	b > a
SO_4^{2-} (mgL^{-1})	**0.39**	(0.05 – 12.52)	**0.37**	(0.08 – 12.47)	**2.31**	(0.74 – 12.87)	6.03	< 0.01	c > a, c > b
Fe (µgL^{-1})	**357.9**	(45.9 – 2462.3)	**141.4**	(31.6 – 512.3)	**186.4**	(53.6 – 519.7)	*n.s.*	*n.s.*	*n.s.*
Mn (µgL^{-1})	**6.86**	(1.15 – 32.40)	**8.09**	(0.61 – 30.44)	**5.52**	(1.51 – 47.82)	*n.s.*	*n.s.*	*n.s.*
TP (µgL^{-1})	**53.7**	(15.3 – 237.3)	**184.1**	(48.1 – 431.8)	**14.69**	(5.2 – 65.3)	30.53	< 0.001	b > a > c
TN (µgL^{-1})	**409**	(228 – 2899)	**360**	(267 – 496)	**530**	(208 – 804)	*n.s.*	*n.s.*	*n.s.*
Chl*a* (µgL^{-1})	**5.91**	(1.97 – 14.30)	**52.50**	(7.4 – 203.4)	**1.39**	(0.46 – 4.76)	50.30	< 0.001	b > a > c
THg (ngL^{-1})	**2.12**	(0.75 – 4.35)	**3.66**	(1.38 – 8.56)	**6.50**	(3.47 – 11.16)	16.23	< 0.001	c > b > a
MeHg (ngL^{-1})	**0.14**	(0.02 – 3.56)	**0.99**	(0.13 – 3.07)	**0.33**	(0.11 – 1.24)	9.26	< 0.001	b > a; b > c
MeHg (%)	**6.7**	(2.7 – 81.9)	**27.2**	(6.4 – 78.1)	**5.1**	(1.3 – 12.9)	18.33	< 0.001	b > c, b > a

Results and Discussion

Thermal stratification. The ponds sampled on Bylot Island (trough and polygonal ponds) and near Kuujjuarapik (taiga/rock and thermokarst ponds) varied in their vertical thermal structure. Strong seasonal thermal stratification was not observed in polygonal ponds on Bylot Island. While polygonal ponds had well-mixed water columns, trough ponds showed stratified conditions during a large fraction of the summer due to the surrounding microtopography, their small fetch, and high humic contents (data not presented here). Hence bottom waters of Bylot trough ponds were mainly hypoxic (often < 2 mgL^{-1}) with only occasional mixing of the upper water column.

Taiga/rock ponds sampled near Kuujjuarapik were very shallow (<1 m) and did not show thermal stratification. However, 9 of the 12 thermokarst ponds (1-3 m in depth) sampled near Kuujjuarapik were strongly thermally stratified. Stratification was sufficiently stable over time to cause low oxygen values in bottom waters, ranging from 0.13 – 3.7 mg L^{-1} or less than 2% saturation at most sites (Table 1, Fig. S2). On average, temperature in the hypolimnion (bottom waters) was around 10°C cooler than at the surface and mean dissolved oxygen was only 5% of the surface concentrations for the Kuujjuarapik thermokarst ponds (Table 1). Oxygen depletion in bottom waters is caused by very limited mixing of the water column, including in spring, and large microbial respiration (Rautio et al., 2011, Laurion et al., 2010, Breton et al., 2009). Thermokarst ponds in this region are often formed as a result of lithalsa degradation and are therefore prone to stable thermal stratification and long water residence time due to high turbidity and low percolation in silty clay soils (Jolivel and Allard, 2013).

Limnological properties and dissolved gases. Geometric means (± standard deviation, GM ± SD) of limnological properties were compared among sites. Trough and polygonal thaw ponds on Bylot Island showed higher nutrient and DOC levels compared to the (ultra)oligotrophic sites more commonly studied in polar regions (Table 1). Nutrient and DOC concentrations for High Arctic lakes and ponds are typically low, with reported means of 148 – 289 μg L^{-1} for TN, 1.3 – 12.0 μg L^{-1} for TP and 1.5 to 2.2 mg L^{-1} for DOC (Lim and Douglas, 2003, Michelutti et al., 2002, Hamilton et al., 2001, Antoniades et al., 2000). Compared to mean concentrations from 204 lakes across the Canadian Arctic Archipelago, mean nutrient (TN, TP) levels were roughly

2 to 4 times higher for Bylot polygonal and trough ponds respectively, whereas DOC levels were 2 to 3 times higher (Hamilton et al., 2001).

Bylot thaw ponds also had significantly higher concentrations of solutes than sampled lakes, with higher geometric means for conductivity (μS cm^{-1}), chlorine (Cl), and iron (Fe) (ANOVA, Table 1). Trough ponds, in particular, had higher DOC concentrations and significantly darker water colour (a_{320}) than either polygonal ponds or lakes ($p < 0.05$). This supports our field observations of more active peat slumping in trough ponds. Bottom water was not collected in Bylot ponds, but profiles indicated higher specific conductivity and lower oxygen and pH in trough pond bottom waters. Higher levels of lateral erosion in trough ponds result from ice-wedge melting and soil subsidence on the edge of peat polygons leading to higher inputs of organic material. Indeed, a slightly larger fraction of old carbon available for microbial degradation was observed in trough ponds (Negandhi et al., 2013). Polygonal ponds typically show fewer signs of erosion and had lower DOC concentrations (Negandhi et al., 2013, Fortier and Allard, 2004, Allard, 1996).

Concentrations of dissolved gases (CH_4, CO_2) were also significantly higher in trough ponds when compared to polygonal ponds (respectively 3 and 5 times higher, Table 1). High levels of CO_2 and CH_4 in trough ponds compared with polygonal ponds likely reflect anoxic conditions promoting fermentation and methanogenesis, which may occur in biofilms, sediments or surrounding anaerobic soils (Paytan et al., 2015, Negandhi et al., 2013). High levels of dissolved gases also indicate strongly reducing conditions in sediments at these sites, leading to the remineralisation and remobilization of ions (such as Mn) from anoxic sediments.

Subarctic thermokarst ponds similarly displayed higher nutrient and DOC concentrations than neighbouring lakes. Lakes sampled near Kuujjuarapik had mean TN of 267 ± 50.5 μg L^{-1}, mean TP of 6.83 ± 3.33 (TP) μg L^{-1} and mean DOC of 4.98 ± 1.38 mgL^{-1} (GM ± SD, G. MacMillan, n = 7, unpublished data 2012). The average concentrations were therefore 1.5 times (TN), 1.7 times (DOC) and 7 times (TP) higher in the surface waters of Kuujjuarapik thermokarst ponds (Table 1). The bottom waters of these thaw ponds also showed distinct water chemistry, with much higher mean specific conductivity (3×), TP (4×), Chla (8×), CO_2 (6×) and CH_4 (95×) than at the surface (ANOVA, Table 1). The low oxygen measured in the bottom waters of these sites may have caused the remobilization of ions from anoxic sediments and therefore led to higher

conductivity. Higher concentrations of dissolved CO_2 and CH_4 in Kuujjuarapik bottom waters also indicates anoxic conditions suitable for microbial gas formation, similar to Bylot trough ponds.

Taiga/rock ponds had the highest average concentrations of Na^+, Cl^-, and sulfate (SO_4^{2-}) but had lower TP and Chla than Kuujjuarapik thermokarst ponds. Concentrations of DOC and nutrients (TN, TP) were roughly twice as high as in neighboring lakes, yet TP was significantly lower than in thermokarst ponds. Taiga/rock ponds also showed higher conductivity likely related to their coastal locations and marine aerosol influence from Hudson Bay.

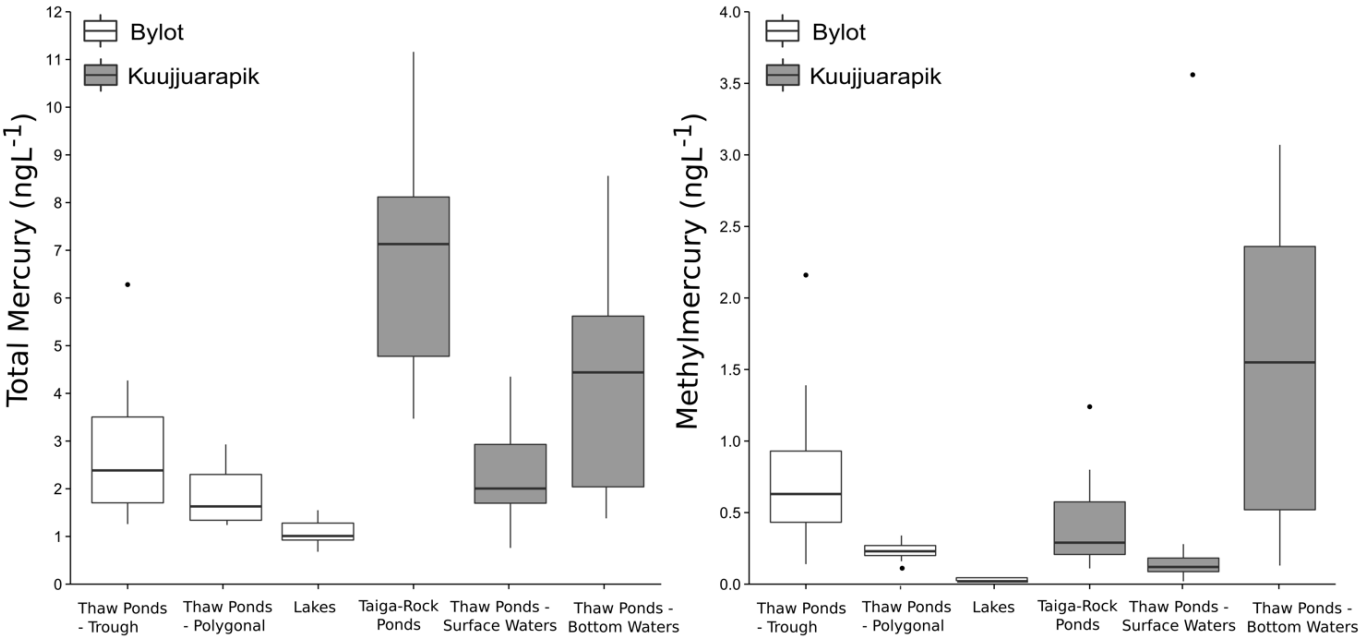

FIGURE 1: Box plots showing concentrations in ng L^{-1} (median ± SD; dots are outliers) for total mercury on the left panel, and methylmercury on the right panel for trough ponds (n=18), polygonal ponds (n=9) and lakes (n=7) on Bylot Island, and for taiga/rock ponds (n=12), thermokarst surface waters (n=12) and thermokarst bottom waters (n=9) near Kuujjuarapik-Whapmagoostui. One trough pond outlier (BYL63) was not included in this figure due to extreme values (21.82 ngL^{-1} for THg, 10.58 ngL^{-1} for MeHg).

Total mercury and methylmercury levels. On Bylot Island, trough ponds had the highest mean (and median) water concentrations of both THg and MeHg (Table 1, Fig. 1). Geometric mean concentrations of THg from trough ponds were 1.5 times the average found in polygonal ponds and 2.6 times the average in lakes (although the difference was not significant for polygonal ponds). Mean MeHg concentrations were highest in trough ponds, being approximately 3.5 times the average in polygonal ponds and 24 times the average found in larger water bodies. Statistical tests showed differences in MeHg concentrations between trough ponds, polygonal ponds and lakes (Table 1, $p < 0.05$). The percentage of THg in the form of MeHg (or %MeHg) was also significantly higher in both types of thaw pond (26.0 ± 9.0% in trough ponds and 12.0 ± 5.1% in polygonal ponds) when compared to the lakes at 1.5 ± 9.5% (GM ± SD). It should be noted that maximum values reported here for Bylot thaw ponds are very high due to the sampling of one extreme site (BYL63) over two consecutive years (reaching 30.2 ng L^{-1} THg and 18.2 ng L^{-1} MeHg in 2009, and respectively 13.4 and 2.97 ng L^{-1} in 2010). However, median values of THg and MeHg followed the same trends among pond types as the means (SI: Table S1) and statistical tests still showed differences between all groups without these extreme values ($p < 0.05$).

Higher levels of MeHg measured in Bylot thaw ponds (particularly trough ponds) may either originate from a) *in situ* methylation in sediments by microorganisms or b) transport from surrounding peaty soils. Our results suggest that *in situ* methylation may be an important source of MeHg in these systems, as high MeHg concentrations combined with high %MeHg often indicates high net methylation rates (Gilmour et al., 1998). A strong positive correlation between MeHg and inorganic Hg(II) concentrations at these sites ($R^2adj = 0.53$, $p < 0.01$) suggests that they are suitable aquatic systems for *in situ* production of MeHg and are limited by the availability of inorganic Hg(II) (Fig. 2).

On the other hand, MeHg may accumulate in these systems due to high rates of production and transport from surrounding anaerobic soils. Mercury binds strongly to DOC, enhancing the mobilization and transport of this metal within a watershed (Ravichandran, 2004, Watras et al., 1995). However, recent studies in the High Arctic have found variable and relatively low methylation potentials of wetland soils and low export of MeHg to downstream lakes (Oiffer and Siciliano, 2009, Loseto et al., 2004). Reported methylation rates and %MeHg in Arctic soils

are also low compared to the MeHg levels measured in Bylot thaw ponds. Since few data are currently available on methylation rates in Arctic soils (and on the soils surrounding our sample sites in particular), the source of MeHg in these Bylot thaw ponds may therefore be either transport from surrounding soils or *in situ* methylation.

For stratified Kuujjuarapik thermokarst ponds, both THg and MeHg concentrations were significantly higher in bottom waters than at the surface (Table 1, $p < 0.05$). Bottom water mean concentrations were about 1.7 times higher for THg and 7 times for MeHg compared to surface water concentrations. Taiga/rock ponds showed the highest mean concentrations of THg (6.50 ± 2.47 ng L^{-1}) and relatively high concentrations of MeHg (0.33 ± 0.33 ng L^{-1}), although MeHg was much lower than in thermokarst pond bottom waters (Fig. 1). Statistical tests showed differences between all groups for THg and higher MeHg in bottom waters of stratified thermokarst ponds relative to other groups ($p < 0.05$, Table 1). The %MeHg was also significantly higher in the bottom waters of stratified thermokarst ponds (27.2 ± 24%) when compared to surface waters (6.7 ± 22%) or to taiga/rock ponds (5.1 ± 3.7%). It should be noted that one shallow thermokarst pond sampled in 2013 (SAS-1G) showed much higher concentrations of THg (4.35 ± 0.24 ng L^{-1}) and MeHg (3.56 ± 0.11 ng L^{-1}), as well as higher %MeHg (82%) than neighbouring sites. Statistical tests still showed differences between all groups without these extreme values ($p < 0.05$).

Strong thermal stratification in Kuujjuarapik thermokarst ponds results in low oxygen or anoxic conditions, which are highly conducive for microbial Hg(II) methylation (Eckley and Hintelmann, 2006). Other studies have even suggested that year-round stable stratification potentially allows for ongoing microbial activity (hence potentially methylation) in bottom waters during the winter months (Rautio et al., 2011). Moreover, dark bottom waters in these turbid thermokarst ponds precludes photodemethylation losses at depth (Watanabe et al., 2011). Bottom waters in these ponds have a combination of high MeHg concentrations and high %MeHg suggesting that, as for the Bylot trough ponds, these sites may have high net methylation rates (Gilmour et al., 1998). However, the lack of correlation between Hg(II) and MeHg at these sites ($p > 0.05$) either suggests that 1) MeHg production is not limited by the availability of inorganic Hg(II) or 2) measured Hg(II) concentrations do not reflect the Hg(II) bioavailable to methylating microorganisms (Fig. 2). As for Bylot Island, there are limited data

available for MeHg production and transport from Subarctic peatlands. However, high MeHg and %MeHg in strongly stratified bottom waters of Kuujjuarapik thaw ponds suggests *in situ* methylation at these sites.

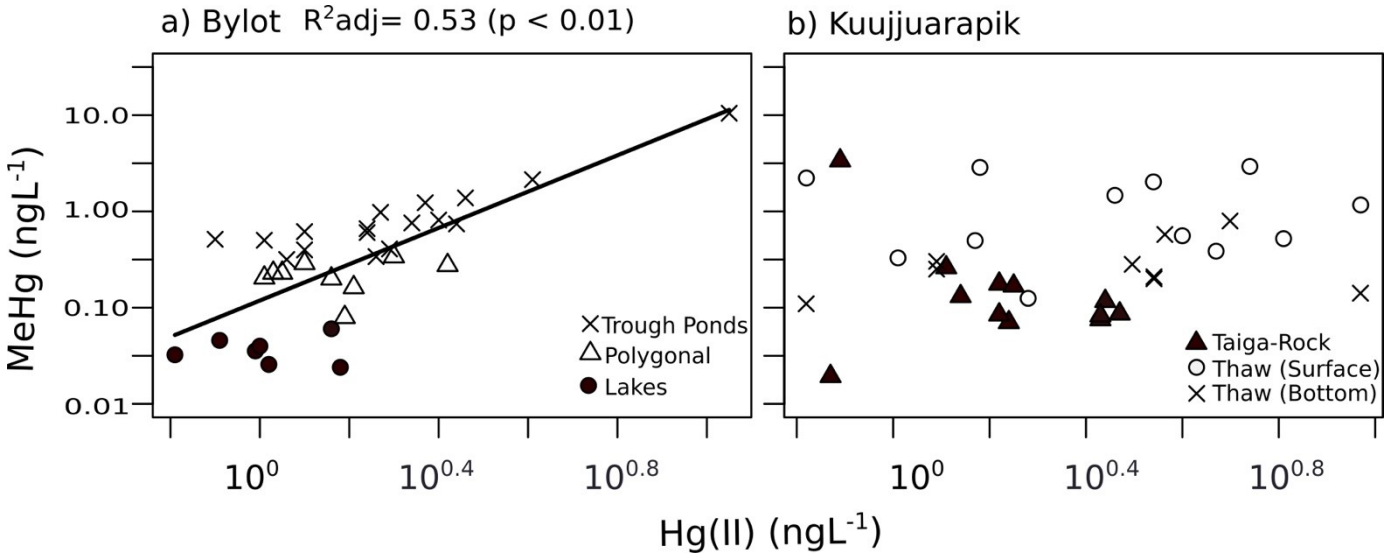

FIGURE 2: Correlations between inorganic Hg(II) and MeHg concentrations in surface and bottom waters from a) Bylot Island (R^2adj = 0.53, $p < 0.001$) and b) Kuujjuarapik-Whapmagoostui ($p > 0.05$).

Shallow Kuujjuarapik taiga/rock ponds had high THg concentrations and relatively high MeHg concentrations compared to the surface waters of thermokarst ponds (Fig. 1). Proximity of these ponds to the coast of Hudson's Bay may lead to marine inputs of MeHg (St. Pierre et al., 2015). However, the %MeHg was quite low which suggests that these sites may have lower rates of Hg(II) methylation than thaw ponds. The lack of stratification (and therefore reducing conditions for Hg(II) methylation) combined with low organic matter inputs due to little or no peripheral vegetation may help explain the lower %MeHg found at these sites. Higher rates of bio- or photodemethylation may also explain the low %MeHg found in well-lit taiga/rock ponds despite the large pool of potentially bioavailable inorganic Hg.

Unfiltered concentrations of THg and MeHg were measured at all sites over all sampling years. For a subset of sites, dissolved (filtered at 0.45 µm) concentrations were also measured at least

once over the extended sampling period (2006 to 2013). Overall, both THg and MeHg were primarily in the dissolved phase, with mean ± SD values of 79.0 ± 16.7% for THg and 83.8 ± 25.6% for MeHg on Bylot (n=11), and of 87.0 ± 8.6% for THg and 83.9 ± 10.4% for MeHg in the Kuujjuarapik area (n=16). This suggests that the Hg measured at these sites is mobile, with a higher potential for lateral transport into other aquatic systems than Hg bound to settling particles. Concentrations of MeHg found in the dissolved phase are also more bioavailable for uptake by lower trophic levels (algae) (Le Faucheur et al., 2014).

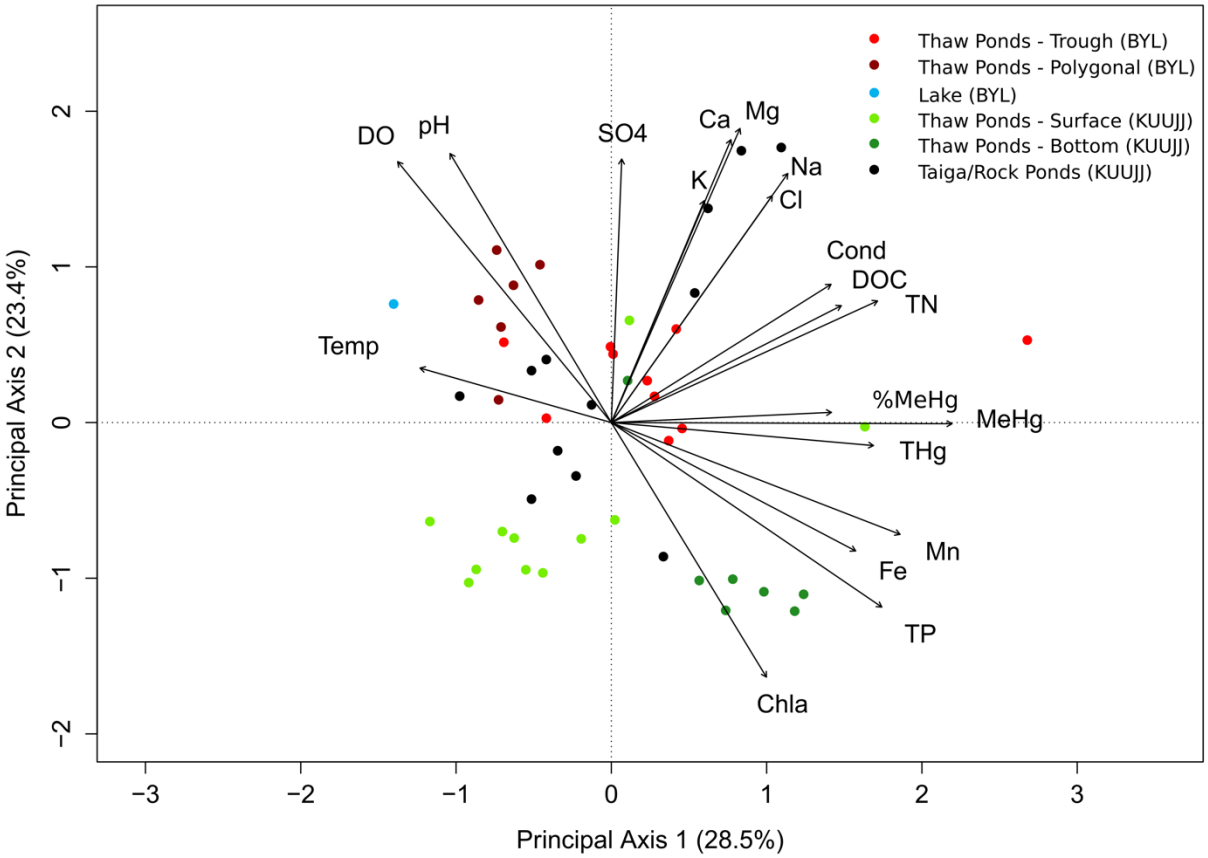

FIGURE 3: Principal Component Analysis (PCA) correlation biplot showing 47 sample sites (coloured points) and 21 physicochemical/environmental variables (black arrows) for Bylot and Kuujjuarapik. Site name abbreviations in the legend are BYL for Bylot sample sites and KUUJJ for Kuujjuarapik sites. The PCA accounts for 51.9% of the total variation among sites (Axis 1: 28.5% and Axis 2: 23.4%). The PCA identified the dominant environmental gradient related to THg, MeHg, TN, TP Mn, Fe and DOC concentrations (axis 1) and a secondary gradient of variables including pH, DO, Chla and major ion concentrations (axis 2).

Environmental drivers of methylmercury concentrations in Arctic and Subarctic ponds. PCA was used to identify the dominant environmental gradients in the dataset (Fig. 3). The PCA biplot accounted for 51.9% of the total variation among sites from both study areas (Axis 1: 28.5% and Axis 2: 23.4%). The remaining unexplained variability (48%) can be attributed to a number of different factor, for example, local and regional climatic variation (precipitation, temperature), sedimentation rates, heterogeneity in microbial communities and analytical variability. On the correlation biplot, environmental variables are represented by black arrows, whereas sites are represented by coloured points. The angles relative to axis 1 and 2 show the weight of the variable in determining the construction of the ordination axis, and the angles between the arrows are representative of the degree of correlation between variables (Legendre and Legendre, 1998).

Based on the PCA scores, the distribution of the sites along axis 1 was most strongly driven by environmental gradients in THg, MeHg, TP, TN, Mn, Fe, and DOC. The dominant gradients detected in axis 2 of the PCA were for pH, DO, Chla, SO_4^{2-} and major ions (Ca, Mg, Na, Cl). The Subarctic sites tended to be more productive (higher planktonic Chla) than Bylot sites (Fig. 3), although polygonal ponds had thick cyanobacterial mats (Vézina and Vincent, 1997). Overall, the PCA analysis shows a clustering of the different types of ponds based on distinct water chemistry conditions and the positive association of mercury (THg, MeHg and %MeHg) with environmental variables indicating inputs of organic matter (DOC, Fe), high nutrients (TN, TP) and reducing conditions in the sediments (Mn, Fe, TP). Strongly reducing conditions in sediments or bottom waters leads to the remobilization of ions (such as Hg and P) bound to Fe and Mn oxides back into the water column (Borch et al., 2009). Differences in environmental variables among sample sites (trough, polygonal, Subarctic thermokarst and taiga/rock) were evaluated using a permutational MANOVA (Adonis function, Vegan package in R) which showed that physico-chemical characteristics of the water differed between sample sites (np-MANOVA, $F = 20.47$, $R^2 = 0.71$, $p < 0.01$, 999 permutations).

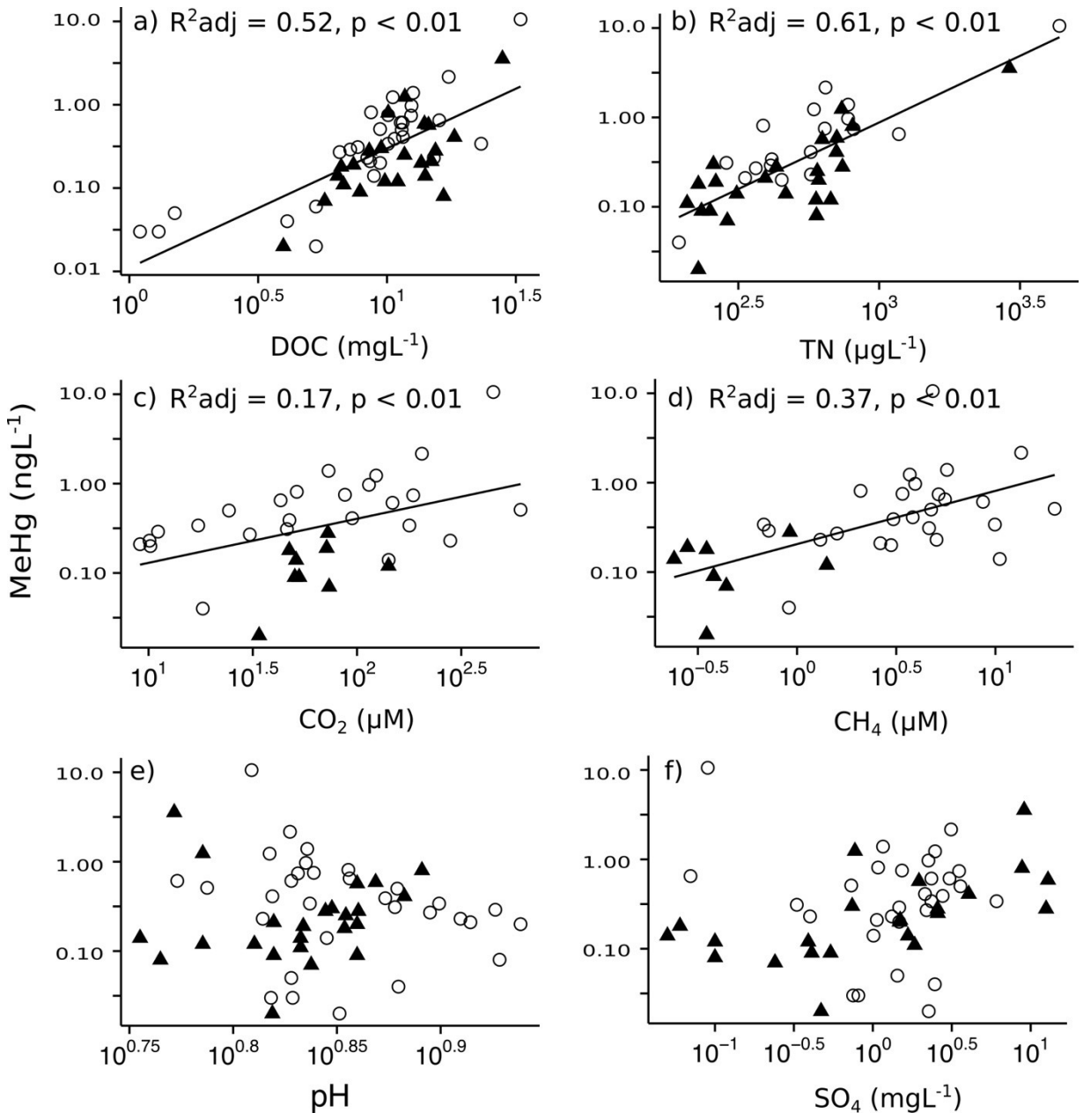

FIGURE 4: Correlations between MeHg concentrations (ngL^{-1}) for surface waters of all samples sites (n = 58) showing significant positive correlations for a) DOC (mgL^{-1}), and b) TN (µgL^{-1}) and no significant correlations for c) pH and d) SO_4^{2-}(mgL^{-1}). All axes are shown on logarithmic scales and regressions were performed on log-transformed data. Bottom waters for stratified Kuujjuarapik thaw ponds were not included to preserve independence of observations. Open circles represent Bylot sites and dark triangles represent Kuujjuarapik sites.

Simple linear regression models were also calculated for THg and MeHg with the most highly correlated environmental variables (SI: Table S4). Surface water THg was significantly correlated with water colour (a_{320}: R^2adj = 0.57, $p < 0.01$), DOC (R^2adj = 0.45, $p < 0.01$), Fe (R^2adj = 0.26, $p = 0.02$) and TN (R^2adj = 0.33, $p = 0.01$). MeHg was most highly correlated with TN (R^2adj = 0.61, $p < 0.01$), DOC (R^2adj = 0.57, $p < 0.01$), water colour (a_{320}: R^2adj = 0.39, $p < 0.01$) and CH_4 (R^2adj = 0.37, $p < 0.01$) (Fig. 4). Some regressions showed high leverage due to outlying sample sites, however these relationships were still found to be highly significant when these sample sites were excluded (SI: Fig. S3). Simple linear regression models were also calculated separately for each region (either Bylot: n = 34 or Kuujjuarapik: n = 24) and on a subset of data from the bottom waters of stratified ponds (n = 9). Overall, concentrations of THg and MeHg were correlated with similar (collinear) environmental variables for these data subsets (for R^2adj and *p*-values, see SI: Table S4).

Many of the explanatory variables were collinear and the relative importance of specific correlations is therefore difficult to interpret. For example, DOC, Fe and water colour (log a_{320}) were correlated with each other, as both Fe and DOC concentrations are known to affect water colour (Kritzberg and Ekström, 2012). DOC concentrations were also strongly correlated to CO_2, TN, and Mn concentrations in surface waters. Concentrations of Fe and Mn were auto-correlated and were negatively correlated with pH and dissolved oxygen (DO), as these metals are only soluble under anoxic, reducing conditions. This notwithstanding, these correlations indicate that MeHg concentrations are strongly correlated with environmental variables indicating high inputs of organic matter (DOC, a_{320}, Fe), high nutrients (TP, TN), microbial activity (dissolved CO_2 and CH_4 gases) and reducing conditions in the sediments (Mn, Fe, TP) at these sites.

This study confirms our hypothesis that permafrost thaw ponds may be sources of MeHg in the Canadian Arctic and Subarctic. High concentrations of MeHg (ng L^{-1}) and %MeHg were measured in Bylot trough ponds (0.72 ± 2.37, 26% ± 9.0) and in the bottom waters of Kuujjuarapik thaw ponds (0.99 ± 1.17, 27% ± 24). These values are well above the levels typically found in freshwater ecosystems in the Arctic where average MeHg concentrations generally remain below 0.1 ng L^{-1} (and less than 15% of total Hg) with a few exceptions (i.e. Ellesmere Island ponds) (Chételat et al., 2015, Lehnherr et al., 2012a, Lehnherr et al., 2012b).

Thaw pond MeHg concentrations were also high in comparison with temperate lakes and rivers in northeastern North America (n = 277) where they were found to range from 0.01 to 3.12 ng L^{-1} with a mean of 0.30 ng L^{-1} (Dennis et al., 2005). Interestingly, Bylot polygonal ponds had lower MeHg (0.21 ± 0.08 ng L^{-1}) and %MeHg (12% ± 5.1) than neighbouring trough ponds. This is may be due to more oxic water columns, lower levels of lateral erosion (and hence inputs of OM and nutrients) and/or lower sediment surface area to water volume ratio in polygonal ponds which leads to greater dilution of MeHg from the sediments. Surface waters from Kuujjuarapik thermokarst ponds also showed much lower levels of MeHg than bottom waters (0.14 ± 3.34, 6.7% ± 2.7). This indicates that thermal stratification and anaerobic bottom waters create favourable conditions for microbial Hg(II) methylation at these sites. High concentrations of MeHg combined with high %MeHg also support the hypothesis of high net methylation rates in Kuujjuarapik thermokarst pond bottom waters (Gilmour et al., 1998).

Furthermore, this study highlights differences in the major environmental variables explaining among-site differences in MeHg levels in small Arctic and Subarctic aquatic systems when compared to more temperate systems. The major variables controlling MeHg production at temperate latitudes are typically temperature, pH, redox conditions, sulfate and DOM (Lehnherr, 2014, Mitchell et al., 2008). Similarly, MeHg concentrations in the present study were positively correlated with inputs of organic matter (DOC) and low redox (anaerobic) conditions in sediments or bottom waters. Positive correlations between MeHg and DOC in freshwaters may indicate the export of Hg bound to DOM from surrounding soils or alternatively that organic matter limits microbial activity in lake sediments, thus *in situ* methylation rates (Dennis et al., 2005, Watras et al., 1998, Wang and Driscoll, 1995, Winfrey and Rudd, 1990). Anoxic bottom waters or sediments also favour both Hg release from sediments and increased microbial Hg(II) methylation (Eckley and Hintelmann, 2006, Ullrich et al., 2001). Yet THg and MeHg concentrations were not correlated with water column temperature, pH, or SO_4^{2-} at these sites, variables which control MeHg production at more temperate latitudes (Fig. 4) (Lehnherr, 2014, Mitchell et al., 2008). The production of MeHg typically increases at warmer temperatures due to increased microbial activity, yet we found no association between surface water temperature and MeHg concentration. Elevated MeHg concentrations were found in thaw ponds from both study areas, despite their difference in latitude (~20°N) and climate regimes. Lack of correlation

between MeHg and SO_4^{2-} concentrations in surface waters may be due to low sulfate concentrations (<10 mg L^{-1} or <100 μM), which limit the activity of sulfate-reducing bacteria. Future studies should focus on relationships between sulfate water concentrations and sulfide pore-water concentrations to identify links between the sulfur and mercury cycles at these sites. Lack of correlation between MeHg and SO_4^{2-} may also indicate that other types of bacteria are responsible for Hg(II) methylation in sediments or bottom waters, such as iron-reducing bacteria or methanogens (Hamelin et al., 2011, Kerin et al., 2006, Ullrich et al., 2001)

Unlike for temperate aquatic systems, strong positive correlations were found in these Arctic and Subarctic ponds between MeHg, and higher nutrients (TN, TP) and dissolved greenhouse gases (CO_2, CH_4). Only a few previous studies have found positive relationships between MeHg and lake nutrient status and the exact relationship between methylation, nutrient status and N availability remains unclear (Braaten et al., 2014, Tjerngren et al., 2012). A previous study in High Arctic ponds also found positive correlations for MeHg concentrations with nitrogen (ratio of ammonium to nitrate, NH_4^+:NO_3^-) and dissolved CH_4 concentrations (Lehnherr et al., 2012b). These results were explained as indicating the relative importance of anaerobic microbial activity on Hg(II) methylation and higher ratios of methylation to demethylation rates. Other recent studies performed at the same sites near Kuujjuarapik show that thermokarst ponds are methanotroph-rich ecosystems, indicating that methane is a potentially important energy source for microorganisms at these sites (Crevecoeur et al., 2015, Rossi et al., 2013). In the present study, the lack of correlation between sulfate and MeHg concentrations and the strong correlations found between dissolved CH_4 and MeHg levels may indicate that methane-producing microorganisms (methanogenic archaea) contribute to the production of MeHg in the sample sites, as has been observed in other aquatic systems (Hamelin et al., 2011). These novel correlations highlight the importance of investigating the role of organic matter erosion and nutrient inputs on the stimulation of anaerobic microbial activity, and hence potential *in situ* methylation by methanogenic archaea, in these ubiquitous aquatic systems.

Ecological significance. Our findings contrast with the lack of stimulatory effects observed for retrogressive thaw slumps of clay-rich tills entering lakes in western Canadian Arctic (Deison et al., 2012), highlighting that permafrost degradation can affect the mercury cycle differently across the Arctic landscape. Permafrost thaw ponds are now considered the most common

freshwater aquatic system at circumpolar latitudes and the impacts of thermokarst thawing on Arctic aquatic ecosystems is increasing rapidly with climate warming (Kokelj and Jorgenson, 2013, Breton et al., 2009, Schuur et al., 2008). Our study strongly suggests that increasing inputs of organic matter and nutrients into Arctic surface waters can have potentially major consequences for the transport and/or *in situ* production of MeHg, particularly in these abundant ponds (Stern et al., 2012, Bowden et al., 2008, Guo et al., 2007, McNamara et al., 1999). Small permafrost thaw ponds may play an important role in controlling the local and regional fluxes of contaminants in the warming Eastern Canadian Arctic.

MeHg in thaw ponds may enter aquatic food webs through feeding on zooplankton by migratory bird population or through downstream transport to larger water bodies. On Bylot Island, large-scale thermal erosion has led to drainage of the terrain into a nearby river (Godin et al., 2014, Fortier et al., 2007). In ice-rich permafrost areas, thawing may lead to the coalescence of trough and polygonal ponds into larger lakes, which can then be catastrophically drained into nearby rivers by thermal erosion (Jorgenson and Shur, 2007, Allard, 1996, Billings and Peterson, 1980). In the Subarctic, there are also signs that rapidly degrading discontinuous permafrost can increase hydrological connectivity and potentially the transport of MeHg to the hydrological network. In the Sheldrake River catchment north of Kuujjuarapik, the thermokarst pond area has increased by 96% over the past 50 years, whereas stream and channel drainage has increased by 18% (Jolivel and Allard, 2013). Sediment and organic material from the degrading permafrost in this area have been tracked many kilometers distant into Hudson Bay, demonstrating the potential for the export of Hg from ponds to coastal waters. On the other hand, Subarctic thaw ponds can be ephemeral and disappear through 'terrestrialization' (encroaching peat cover) over a relatively short time frame, which may not lead to mercury export (Vallée and Payette, 2007). Further studies are required in order to understand the large-scale ecological implications of high MeHg concentrations found in thaw ponds in the eastern Canadian Arctic, especially in the context of a rapidly warming North.

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Supporting Information consists of 15 pages including detailed materials and methods, interlaboratory calibrations for aqueous THg and MeHg concentrations. Total of 4 tables and 3 figures.

Supporting Information

High Methylmercury in Arctic and Subarctic Ponds is Related to Nutrient Levels in the Warming Eastern Canadian Arctic

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Supporting Information consists of 15 pages including detailed materials and methods, interlaboratory calibrations for aqueous THg and MeHg concentrations. Total of 4 tables and 3 figures.

MATERIALS AND METHODS

Study sites. Bylot Island is a polar oasis located above the Arctic Circle, where conditions are cold and dry, with long-term averages of -34 °C in February and 6 °C in July, and average yearly precipitation of 191 mm. Kuujjuarapik-Whapmagoostui is located in the Subarctic region of Quebec on the eastern shore of Hudson Bay, with long-term average temperatures of -23 °C in February and 11 °C in July, and with average yearly precipitation of 649 mm (EC, 2015, Bouchard et al., 2011).

Bylot thaw ponds are part of a dynamic network of syngenetic ice-wedge polygons that developed in the outwash plain of glacier C-79 after 6000 BP, modified by the accumulation of wind-blown and organic sediments that began after 3670 ± 110 BP and now reaching 2-3 m deep (Fortier and Allard, 2004). Bylot Island thaw ponds can be classified into two types: 1) low-center polygonal ponds created by the rise of peat polygon ridges generating cuvettes that fill with water and offer a stable environment for the establishment of thick microbial mats; and 2) trough ponds that form over melted ice wedges between the polygon mounds, an elongated aquatic system featuring peat erosion and higher turbidity therefore classified as thermokarstic (Laurion et al., 2010). Both types of ponds examined were no more than a few meters in diameter and generally less than 1.5 m in depth. At this site, the active soil layer is approximately 40 to 60 cm deep (Fortier and Allard, 2004). A few lakes were also sampled at this site, two kettle lakes formed on glacier ice melt depressions of about 11 m deep (named BYL36 and BYL37), a thermokarst lake 4.5 m deep (BYL66; Fig 2b), and some nearby oligotrophic lakes on rocky substrate (BYL39, BYL40, BYL49, BYL50; not shown). These seven larger aquatic systems on Bylot were categorized as “lakes” for this study, given their much larger surface area and depth than the polygonal and trough ponds.

The Subarctic sample sites included thermokarst, taiga/rock basin ponds sampled near the village of Kuujjuarapik-Whapmagoostui. At the Kwakwatanikapistikw lithalsa peatland (or “KWK”) and Sasapimakwananisikw palsa bog (“SAS”) (local Cree names of nearby rivers), thermokarst thaw ponds develop in depressions left after the ice has melted below mineral (KWK) or besides organic (SAS) permafrost mounds (Bhiry et al., 2011, Breton et al., 2009). The ponds are surrounded by dense vegetation, mainly shrubs, small trees and mosses. They are 10 to 30 m in diameter and have a maximum depth of 3.5 m. The taiga/rock basin ponds are

formed on granite or carbonate-derived bedrock respectively and are 10-20 m in diameter with a maximum depth of 1 m.

Physico-chemical sampling. DOC concentrations were measured using a Shimadzu TOC-5000A carbon analyzer (2006-2011) or an IO Aurora 1030 carbon analyzer (2012-2013), calibrated with potassium biphthalate. To measure the optical properties of DOM, water samples were filtered through pre-rinsed cellulose acetate filters (0.2 µm pore size; Advantec Micro Filtration Systems), and scanned from 250 to 800 nm on a spectrophotometer (Varian Cary 300). The absorption coefficient at 320 nm (a_{320}) was used as a proxy to quantify the water colour.

Total nitrogen was measured by flow injection analysis (Lachat Instruments) on unfiltered samples fixed by H_2SO_4 (0.15% final concentration) and digested with potassium persulfate. Using the same water samples as above for TN, total phosphorus (TP) was measured by spectrophotometry (2006-2011) or by flow injection analysis (Astoria) (2012-2013) (Strainton et al., 1977).

To measure Chla concentration, water samples were passed through glass fiber filters (0.7 µm nominal pore size; Advantec MFS) and kept frozen at -80 °C until the extraction of pigments in 95% boiling ethanol (Mush, 1980). The fluorescence was measured with a spectrofluorometer (Varian Cary Eclipse) before and after acidification (to correct for interference by pheophytin) and the Chla concentration calculated as in Jeffrey and Welschmeyer (1997).

Water samples for anion and cation analysis were filtered through pre-rinsed cellulose acetate filters or pre-combusted glass-fibre filters (0.7 um pore size, Whatman GF-F), and they were preserved with HNO_3 (0.15% final concentration). Anions were quantified using ion chromatography (either Dionex Corp. or Waters, IC-Pak A and C columns). Cations were analyzed with inductively coupled plasma optical emission spectrometry (ICP-OES, Varian VISTA AX CCD) in 2006-2011, or with an atomic absorption spectrophotometer (AAS, Agilent) in 2012-2013. Water samples for major metals were filtered and preserved with HNO_3 (2%) before analysis by inductively coupled plasma mass spectrometry (ICP-MS, Perkin-Elmer NexION 300x).

Dissolved CO_2 and CH_4 were determined following Hesslein et al. using the equilibration of 2 liters of water into 20 mL of ambient air for 3 min (Hesslein et al., 1991). The headspace was

sampled in duplicated vials (red stopper Vacutainer®) previously flushed with helium and vacuumed. Gas samples were taken within 5 minutes after collecting the water and were kept at 4 °C until analysis by gas chromatography (Varian 3800 with a COMBI PAL head space injection system and a CP-Poraplot Q 25 m × 0.53 mm column and flame ionization detector).

Aqueous THg and MeHg concentrations

Table A: Results for the CALA Laboratory Intercalibration for THg in 2014.

Matrix	Analyte	Units	Assigned Value	Assigned Uncertainty	Reported Value	S -Value	Z-Score	PT-Score	Summary
Water	Mercury	µg L^{-1}	0.67	0.01	0.63	0.11	-0.364		
Water	Mercury	µg L^{-1}	1.75	0.02	1.62	0.20	-0.650		
Water	Mercury	µg L^{-1}	2.47	0.03	2.33	0.27	-0.519		
Water	Mercury	µg L^{-1}	4.47	0.05	4.24	0.45	-0.511	92	Acceptable

Table B: Results for the Northern Contaminants Interlaboratory Quality Assurance Program (NCP III QA/QC Program 2014-2015)

Matrix	Analyte	Units	Reported Value	Design	Median	SD	n	%RECUP
Water	THg	ng L^{-1}	5053	5000	5200	342	15	101%
Water	MeHg	ng L^{-1}	935	1000	960	26.2	4	93.5%

TABLE S1. Mercury concentrations and physicochemical characteristics, including temperature (Temp), conductivity (Cond), dissolved oxygen (DO), dissolved organic carbon (DOC), chlorophyll *a (Chla)*, total mercury (THg) and methylmercury (MeHg), of a) trough ponds, b) polygonal ponds and c) lakes on Bylot Island.

Site	Year Sampled	Temp (°C)	pH	Cond ($\mu S\ cm^{-1}$)	DO ($mg\ L^{-1}$)	a_{320} (m^{-1})	DOC ($mg\ L^{-1}$)	CO_2 (μM)	CH_4 (μM)	Ca ($mg\ L^{-1}$)	Mg ($mg\ L^{-1}$)	K ($mg\ L^{-1}$)
a) Trough Ponds (n = 18)												
BYL24	2009 - 2010	14.52	7.17	43	11.97	32.4	8.67	51.4	2.09	4.82	2.87	0.65
BYL27	2008 - 2010	10.50	6.90	67	10.46	32.4	10.10	87.5	3.40	4.64	3.59	1.52
BYL33	2009	13.31	7.55	100	10.05	18.4	7.70	46.1	4.63	10.15	8.56	1.49
BYL38	2008 - 2010	9.17	6.57	51	8.07	54.3	10.53	123.5	3.70	3.37	2.52	1.12
BYL47	2008 - 2010	12.06	6.84	95	10.17	37.9	12.45	114.1	3.94	6.37	4.73	1.68
BYL48	2009 - 2010	15.32	6.59	79	10.87	32.5	11.53	94.8	3.83	7.13	4.76	1.24
BYL59	2009 - 2010	8.72	6.78	62	9.14	47.4	12.40	186.0	5.17	3.66	2.93	1.36
BYL63	2009 - 2010	12.99	6.44	139	3.81	269.4	33.00	450.7	4.83	17.21	10.16	2.20
BYL64	2009 - 2010	13.68	7.18	61	10.80	44.7	15.95	43.0	5.57	4.89	3.59	1.23
BYL67	2009 - 2010	13.16	6.85	56	11.61	50.0	12.63	73.0	5.70	5.06	3.43	1.10
BYL68	2009	8.03	5.93	62	5.55	25.7	11.30	-	-	4.19	3.27	1.16
BYL69	2009	11.38	6.13	233	4.50	19.1	9.40	609.1	19.90	18.63	10.59	2.23
BYL70	2009	13.55	6.87	448	9.81	41.6	23.20	178.4	9.94	20.37	17.87	2.01
BYL71	2009	14.20	7.47	100	10.97	20.6	10.70	47.4	3.06	8.11	5.15	1.63
BYL72	2009	14.45	7.57	141	12.25	21.5	11.40	24.3	4.74	12.48	7.41	2.77
BYL74	2009 - 2010	11.43	6.72	85	8.22	76.3	17.35	204.8	13.49	10.07	5.90	1.56
BYL75	2009	15.64	6.73	125	10.04	38.1	11.50	148.0	8.66	15.64	7.21	1.69
BYL76	2009	18.16	7.00	116	9.21	24.9	8.90	141.8	10.52	13.66	6.52	1.81
	Mean	12.79	6.85	115	9.30	49.30	13.26	154.4	6.66	9.47	6.17	1.58
	Median	13.24	6.85	90	10.05	35.19	11.45	114.1	4.83	7.62	4.95	1.54
	Std dev	2.60	0.44	95	2.45	56.89	6.12	153.9	4.58	5.58	3.83	0.50
	Min	8.03	5.93	43	3.81	18.43	7.70	24.3	2.09	3.37	2.52	0.65
	Max	18.16	7.57	448	12.25	269.45	33.00	609.1	19.90	20.37	17.87	2.77
b) Polygonal Ponds (n = 9)												
BYL01	2008 - 2010	13.32	8.44	68	12.06	10.2	7.20	11.1	0.72	4.39	3.24	2.00
BYL22	2008 - 2010	12.14	7.85	51	11.17	16.0	6.55	30.6	1.59	2.41	1.51	2.07
BYL31	2009	14.32	8.21	119	9.98	19.8	8.60	9.1	2.63	13.30	9.71	1.78
BYL44	2008 - 2010	11.89	8.12	56	10.70	11.0	8.38	10.1	1.31	5.42	3.62	1.74
BYL51	2008 - 2010	12.07	8.68	86	12.09	14.2	9.40	10.2	2.98	6.05	3.95	2.37
BYL61	2009	14.82	8.48	70	10.65	8.2	-	-	-	-	-	-
BYL65	2009	14.32	7.93	85	11.46	15.4	10.10	17.3	0.68	8.39	5.11	2.38
BYL73	2009	15.77	6.52	119	6.75	77.9	15.20	280.1	5.05	15.86	6.67	1.21
BYL78	2010	-	-	-	-	-	-	-	-	-	-	-
	Mean	13.58	8.03	82	10.61	21.6	9.35	52.7	2.14	7.98	4.83	1.94
	Median	13.82	8.17	78	10.93	14.8	8.60	11.1	1.59	6.05	3.95	2.00
	Std dev	1.45	0.67	26	1.72	23.1	2.85	100.6	1.56	4.91	2.68	0.41
	Min	11.89	6.52	51	6.75	8.2	6.55	9.1	0.68	2.41	1.51	1.21
	Max	15.77	8.68	119	12.09	77.9	15.20	280.1	5.05	15.86	9.71	2.38
c) Lakes (n =7)												
BYL36	2009	16.12	7.58	90	10.88	6.29	4.1	18.22	0.91	4.54	2.80	1.30
BYL37	2010	-	-	-	-	-	5.3	-	-	-	-	-
BYL39	2008	6.35	6.58	9	11.93	3.94	1.3	-	-	0.80	0.29	-
BYL40	2008	6.08	6.73	15	12.85	3.56	1.5	-	-	1.29	0.49	-
BYL49	2008	8.89	6.95	12	12.02	3.40	1.5	-	-	5.79	4.23	-
BYL50	2008	13.34	6.74	13	11.19	1.34	1.0	-	-	1.21	0.46	-
BYL66	2009	-	7.1	-	10.43	-	5.3	-	-	-	-	-
	Mean	10.16	6.95	28	11.55	3.71	2.86	-	-	2.73	1.65	-
	Median	8.89	6.85	13	11.56	3.56	1.50	-	-	1.29	0.49	-
	Std dev	4.43	0.36	35	0.88	1.77	1.96	-	-	2.28	1.78	-
	Min	6.08	6.58	9	10.43	1.34	1.00	-	-	0.80	0.29	-
	Max	16.12	7.58	90	12.85	6.29	5.30	-	-	5.79	4.23	-

TABLE S1 *continued*

Site	Na (mg L^{-1})	Cl (mg L^{-1})	SO_4 (mg L^{-1})	Fe (µg L^{-1})	Mn (µg L^{-1})	TP (µg L^{-1})	TN (µg L^{-1})	Chl*a* (µg L^{-1})	THg (ng L^{-1})	MeHg (ng L^{-1})	%MeHg (MeHg/THg)
a) Trough Ponds (n = 18)											
BYL24	2.99	2.75	1.08	101.25	2.99	31.8	387.3	1.46	3.34	0.81	24.3
BYL27	4.46	7.36	1.53	90.50	2.58	26.3	641.2	1.17	2.96	0.75	25.3
BYL33	1.99	2.35	0.33	48.23	2.05	14.5	286.8	0.40	1.45	0.31	21.4
BYL38	3.79	5.92	2.48	385.03	6.55	63.0	586.8	0.99	3.59	1.23	34.3
BYL47	5.19	8.44	2.25	97.79	9.47	45.3	775.5	1.38	3.46	0.97	28.0
BYL48	5.28	6.03	2.14	164.59	5.43	24.3	571.6	1.99	2.36	0.41	17.4
BYL59	4.30	5.93	3.52	109.38	11.36	50.8	811.4	26.60	3.52	0.74	21.0
BYL63	10.49	12.60	0.09	1637.50	556.14	359.8	4366.3	1.89	21.82	10.58	48.5
BYL64	5.17	7.20	0.07	154.00	12.00	31.9	1174.9	1.23	2.41	0.65	27.0
BYL67	3.84	4.79	1.16	220.29	5.34	49.4	776.0	3.71	4.27	1.39	32.6
BYL68	4.57	6.68	3.06	53.03	6.95	-	-	-	2.35	0.61	26.0
BYL69	18.84	28.60	0.73	27.80	140.95	-	-	0.80	1.30	0.51	39.2
BYL70	60.15	56.43	2.35	46.89	20.52	-	-	2.50	2.16	0.34	15.7
BYL71	7.17	9.76	2.77	11.25	3.68	-	-	1.30	1.65	0.39	23.6
BYL72	9.43	13.64	3.59	40.65	4.25	-	-	3.20	1.53	0.50	32.7
BYL74	2.28	1.50	3.13	270.38	20.31	-	645.0	1.29	6.28	2.16	34.4
BYL75	3.74	1.64	2.35	94.88	16.67	-	-	0.70	1.87	0.61	32.6
BYL76	4.06	2.04	1.01	12.13	10.39	-	-	0.90	1.26	0.14	11.1
Mean	8.76	10.20	1.87	198.09	46.54	69.72	1002.1	3.03	3.75	1.28	27.5
Median	4.52	6.36	2.20	96.34	8.21	38.64	645.0	1.30	2.39	0.63	26.5
Std dev	13.42	13.16	1.15	372.18	131.05	102.95	1139.8	6.14	4.68	2.37	9.0
Min	1.99	1.50	0.07	11.25	2.05	14.55	286.8	0.40	1.26	0.14	11.1
Max	60.15	56.43	3.59	1637.50	556.14	359.75	4366.3	26.60	21.82	10.58	48.5
b) Polygonal Ponds (n = 9)											
BYL01	4.12	5.13	1.47	29.94	0.71	17.1	412.0	1.32	1.55	0.29	18.7
BYL22	2.15	5.01	2.19	55.75	1.13	46.8	364.7	1.66	2.93	0.27	9.2
BYL31	2.86	2.08	1.06	43.64	4.62	12.9	334.3	0.60	1.24	0.21	16.9
BYL44	3.69	4.69	1.32	32.51	1.07	15.3	572.3	2.66	1.31	0.23	17.6
BYL51	5.10	7.02	1.47	28.58	0.58	15.6	450.9	1.46	1.66	0.20	12.0
BYL61	-	-	-	-	-	-	-	0.40	1.63	0.08	4.9
BYL65	3.49	4.65	6.08	48.79	1.56	21.4	415.8	1.00	2.33	0.34	14.6
BYL73	3.47	3.21	0.40	352.36	13.94	-	-	0.30	1.34	0.23	17.2
BYL78	-	-	-	-	-	-	-	-	2.30	0.16	7.0
Mean	3.55	4.54	2.00	84.51	3.37	21.5	425.0	1.18	1.81	0.22	13.1
Median	3.49	4.69	1.47	43.64	1.13	16.3	413.9	1.16	1.63	0.23	14.6
Std dev	0.93	1.56	1.88	118.55	4.86	12.72	83.05	0.78	0.58	0.08	5.1
Min	2.15	2.08	0.40	28.58	0.58	12.9	334.3	0.30	1.24	0.08	4.9
Max	5.10	7.02	6.08	352.36	13.94	46.8	572.3	2.66	2.93	0.34	18.7
c) Lakes (n = 7)											
BYL36	6.82	13.29	2.47	6.06	1.30	8.5	194.5	1.7	1.01	0.04	4.0
BYL37	-	-	-	-	-	-	-	-	1.49	0.06	4.0
BYL39	-	0.31	0.75	9.61	-	3.14	105.9	1.67	1.07	0.03	2.8
BYL40	-	0.42	1.43	7.78	-	4.73	104.5	0.91	0.86	0.05	5.8
BYL49	-	0.56	0.66	881.57	-	3.82	137.0	1.19	0.99	0.00	0.0
BYL50	-	0.69	0.81	7.85	-	3.67	94.8	0.62	0.68	0.03	4.4
BYL66	-	8.33	2.26	-	-	-	-	-	1.55	0.02	1.3
Mean	-	3.93	1.40	182.57	-	4.77	127.3	1.22	1.09	0.03	3.2
Median	-	0.63	1.12	7.85	-	3.82	105.9	1.19	1.01	0.03	4.0
Std dev	-	5.55	0.80	390.75	-	2.16	40.8	0.47	0.32	0.02	2.0
Min	-	0.31	0.66	6.06	-	3.14	94.8	0.62	0.68	0.00	0.0
Max	-	13.29	2.47	881.57	-	8.50	194.5	1.70	1.55	0.06	5.8

TABLE S2. Mercury concentrations and physicochemical characteristics (see abbreviations in Table S1) of a) the surface and b) bottom waters of thermokarst ponds and c) in tundra and rock ponds near Kuujjuarapik-Whapmagoostui.

Site	Year Sampled	Temp (°C)	pH	Cond (µS cm^{-1})	DO (mg L^{-1})	A_{320} (m^{-1})	DOC (mg L^{-1})	CO_2 (µM)	CH_4 (µM)	Ca (mg L^{-1})	Mg (mg L^{-1})	K (mg L^{-1})
a) Thaw Ponds: Surface Waters (n = 12)												
Kwk1	2006, 2009	19.09	6.60	46	9.59	42.2	7.85	52.8	0.38	1.12	1.09	0.88
Kwk2	2006, 2009	16.07	6.88	38	8.56	26.3	5.73	73.5	0.44	0.88	0.95	0.59
Kwk6	2006, 2009	17.65	6.59	61	9.81	12.9	3.96	33.9	0.35	1.67	1.77	1.16
Kwk11	2006, 2009	17.80	6.10	27	9.40	53.7	11.01	141.6	1.411	1.41	0.96	0.56
Kwk12	2006, 2009	18.57	6.80	36	9.08	26.5	6.43	51.0	0.24	0.63	0.81	0.43
Kwk16	2006, 2009	24.25	7.24	53	9.25	38.9	7.86	50.3	0.38	1.24	1.41	0.94
Kwk19	2013	16.57	6.46	37	6.52	-	9.81	-	-	1.75	2.09	1.96
Kwk20	2006, 2009	17.98	6.82	-	9.17	42.2	7.41	71.5	0.28	0.88	1.04	0.87
Kwk23	2009	19.14	7.14	48	9.21	32.1	6.64	47.3	0.35	1.06	1.23	0.94
Kwk38	2009	19.72	7.25	204	9.43	25.1	8.53	72.5	0.92	5.50	7.40	2.17
SAS1G	2013	14.76	5.91	84	2.49	-	28.06	-	-	8.70	3.34	1.01
SAS2A	2013	14.35	5.82	49	5.78	-	16.58	-	-	2.56	1.32	0.13
	Mean	17.99	6.63	61	8.19	33.3	9.99	66.0	0.53	2.29	1.95	0.97
	Median	17.89	6.70	48	9.19	32.1	7.85	52.9	0.38	1.33	1.28	0.91
	Std dev	2.60	0.49	47	2.19	12.2	6.52	31.4	0.39	2.40	1.85	0.59
	Min	14.35	5.82	27	2.49	12.9	3.96	33.9	0.24	0.63	0.81	0.13
	Max	24.25	7.25	204	9.81	53.7	28.06	141.6	1.41	8.70	7.40	2.17
b) Thaw Ponds: Bottom Waters (n = 9)												
Kwk1	2009	7.75	6.11	155	0.23	44.2	8.30	405.0	93.8	2.78	1.65	0.99
Kwk2	2009	8.28	6.24	200	0.28	47.9	6.12	-	-	2.49	1.80	0.96
Kwk6	2009	9.06	6.30	265	0.14	19.7	4.17	421.8	145.2	-	-	-
Kwk11	2009	-	-	-	9.31	53.9	11.93	131.3	1.24	0.67	0.90	0.44
Kwk12	2009	7.35	6.08	247	0.19	63.1	7.45	761.2	259.0	3.37	1.93	1.17
Kwk16	2009	4.88	5.94	163	0.19	44.8	7.21	476.9	114.9	1.81	1.54	0.93
Kwk20	2009	5.25	6.14	145	0.15	106.9	9.27	815.5	311.9	3.62	2.08	1.30
Kwk23	2009	13.13	6.87	209	0.18	87.6	7.47	570.1	131.6	2.56	1.79	1.18
Kwk38	2009	7.75	6.11	155	3.69	24.0	6.28	106.9	0.479	5.54	7.45	2.14
	Mean	7.93	6.22	192	1.60	54.7	7.58	461.1	132.3	2.85	2.39	1.14
	Median	7.75	6.13	182	0.19	47.9	7.45	449.4	123.3	2.67	1.79	1.08
	Std dev	2.54	0.28	46	3.12	28.1	2.18	258.2	110.1	1.42	2.07	0.48
	Min	4.88	5.94	145	0.14	19.7	4.17	106.9	0.479	0.67	0.90	0.44
	Max	13.13	6.87	265	9.31	106.9	11.93	815.5	311.9	5.54	7.45	2.14
c) Taïga and Rock Ponds (n = 12)												
R104	2012 - 2013	14.07	6.10	26	8.34	-	11.73	-	-	1.06	0.81	0.57
R202	2012 - 2013	13.09	7.39	189	11.13	-	13.98	-	-	8.22	5.40	1.09
R206	2012 - 2013	12.18	7.63	280	11.46	-	18.27	-	-	12.53	8.25	1.66
R301	2012 - 2013	12.55	7.24	131	9.34	-	14.49	-	-	7.75	3.31	1.40
T102	2012 - 2013	16.30	7.24	55	11.47	-	13.58	-	-	6.99	2.17	0.29
T104	2012 - 2013	14.64	7.15	61	10.55	-	11.69	-	-	8.59	1.56	0.70
T107	2012 - 2013	13.32	6.99	39	11.10	-	15.42	-	-	3.29	1.35	0.41
T207	2012 - 2013	12.83	6.80	61	10.91	-	6.78	-	-	7.04	1.28	0.71
R217	2013	12.84	7.78	514	12.73	-	10.11	-	-	2.90	5.29	3.32
Km2.5	2013	13.71	5.69	26	9.36	-	14.07	-	-	4.55	1.33	0.50
Km4	2013	16.01	7.04	50	10.32	-	9.49	-	-	0.93	0.62	0.35
WP2	2013	11.43	6.60	42	9.03	-	14.88	-	-	3.28	1.19	0.29
	Mean	13.58	6.97	123	10.48	-	12.87	-	-	5.59	2.71	0.94
	Median	13.20	7.09	58	10.73	-	13.78	-	-	5.77	1.45	0.63
	Std dev	1.47	0.60	145	1.25	-	3.08	-	-	3.49	2.39	0.87
	Min	11.43	5.69	26	8.34	-	6.78	-	-	0.93	0.62	0.29
	Max	16.30	7.78	514	12.73	-	18.27	-	-	12.53	8.25	3.32

TABLE S2 *Continued*

Site	Na (mg L^{-1})	Cl (mg L^{-1})	SO_4 (mg L^{-1})	Fe (µg L^{-1})	Mn (µg L^{-1})	TP (µg L^{-1})	TN (µg L^{-1})	Chl*a* (µg L^{-1})	THg (ng L^{-1})	MeHg (ng L^{-1})	%MeHg (MeHg/THg)
a) Thaw Ponds: Surface Waters (n = 12)											
Kwk1	3.13	3.89	0.54	477.32	7.55	43.1	251	3.91	3.05	0.09	3.0
Kwk2	2.76	3.80	0.24	293.69	5.90	35.6	289	4.30	1.80	0.07	4.1
Kwk6	2.86	4.23	0.47	136.13	11.00	34.9	228	8.20	0.76	0.02	2.7
Kwk11	3.57	3.82	0.10	271.61	4.16	43.2	597	8.72	3.36	0.12	3.4
Kwk12	2.74	3.72	0.05	234.93	4.67	24.3	312	2.76	1.53	0.14	8.9
Kwk16	2.94	3.57	0.41	462.17	8.01	74.7	234	8.56	1.74	0.09	5.1
Kwk19	4.79	3.54	0.39	930.11	7.79	96.3	673	10.40	2.89	0.12	4.2
Kwk20	3.15	-	-	45.884	1.146	80.0	263	9.65	2.07	0.19	9.2
Kwk23	3.08	4.17	0.06	303.48	11.12	70.2	228	12.71	1.94	0.18	9.3
Kwk38	7.34	4.03	12.52	500.68	8.70	69.9	431	3.67	1.57	0.28	17.7
SAS1G	6.14	5.38	9.09	2462.28	32.40	237.3	2899	4.67	4.35	3.56	81.9
SAS2A	6.85	5.26	0.10	492.22	5.06	15.3	599	1.97	2.79	0.08	2.9
Mean	4.11	4.13	2.18	550.87	8.96	68.73	584	7.01	2.32	0.41	12.7
Median	3.14	3.89	0.39	382.83	7.67	56.56	301	6.43	2.01	0.12	4.7
Std dev	1.72	0.63	4.34	643.05	7.92	58.56	747	4.06	0.99	0.99	22.2
Min	2.74	3.54	0.05	45.88	1.15	15.30	228	1.97	0.76	0.02	2.7
Max	7.34	5.38	12.52	2462.28	32.40	237.31	2899	14.30	4.35	3.56	81.9
b) Thaw Ponds: Bottom Waters (n = 9)											
Kwk1	3.07	4.89	0.62	83.98	11.82	175.9	267	66.4	7.03	0.55	7.8
Kwk2	3.29	5.18	0.25	250.75	30.44	341.5	496	180.2	8.56	3.07	35.9
Kwk6	-	-	0.24	105.70	na	197.7	389	87.2	2.02	0.52	25.7
Kwk11	3.07	3.68	0.08	31.61	0.61	48.1	409	14.6	2.04	0.13	6.4
Kwk12	3.03	5.17	0.25	286.48	22.61	207.1	448	158.9	3.02	2.36	78.1
Kwk16	2.63	3.37	0.30	131.75	11.27	167.1	399	22.4	4.44	1.55	34.9
Kwk20	3.99	6.60	0.28	512.29	17.37	377.0	289	203.4	5.62	2.13	37.9
Kwk23	3.13	4.55	0.17	410.61	15.07	431.8	267	37.1	4.53	3.01	66.4
Kwk38	7.34	4.03	12.47	40.37	1.26	75.4	351	7.4	1.38	0.35	25.4
Mean	3.69	4.68	1.63	205.95	13.81	224.6	368	86.4	4.29	1.52	35.4
Median	3.10	4.72	0.25	131.75	13.44	197.7	389	66.4	4.44	1.55	34.9
Std dev	1.52	1.03	4.07	170.47	10.07	132.3	81	75.9	2.45	1.17	24.0
Min	2.63	3.37	0.08	31.61	0.61	48.1	267	7.4	1.38	0.13	6.4
Max	7.34	6.60	12.47	512.29	30.44	431.8	496	203.4	8.56	3.07	78.1
c) Taïga and Rock Ponds (n = 12)											
R104	3.97	4.66	0.77	491.27	7.80	43.5	736	4.76	10.62	1.24	11.7
R202	16.69	34.14	12.87	278.78	9.33	15.1	707	2.05	4.59	0.59	12.9
R206	23.73	34.07	4.05	371.34	22.88	12.2	705	0.96	5.14	0.41	8.0
R301	10.96	15.64	1.96	313.66	4.91	19.7	628	1.53	7.80	0.57	7.4
T102	3.79	4.41	1.48	67.43	1.51	11.8	610	1.16	7.22	0.20	2.7
T104	3.87	5.50	2.58	78.20	2.17	7.8	603	1.57	4.71	0.25	5.2
T107	4.18	12.00	2.57	103.42	3.41	24.8	741	2.99	7.04	0.28	3.9
T207	3.78	5.03	1.84	53.64	1.53	5.2	208	0.98	3.47	0.11	3.2
R217	52.01	56.31	8.82	519.68	8.97	65.3	804	1.74	9.07	0.80	8.8
Km2.5	4.28	4.78	1.67	164.91	5.51	12.4	466	1.33	11.16	0.14	1.3
Km4	3.55	5.13	0.74	281.19	47.82	5.3	258	0.46	4.80	0.30	6.2
WP2	4.27	5.42	1.49	156.91	2.43	12.6	394	0.62	7.22	0.21	2.9
Mean	11.26	15.59	3.40	240.03	9.86	19.6	572	1.68	6.90	0.42	6.2
Median	4.23	5.46	1.90	221.84	5.21	12.5	619	1.43	7.13	0.29	5.7
Std dev	14.37	16.91	3.69	162.12	13.33	17.8	197	1.18	2.47	0.33	3.7
Min	3.55	4.41	0.74	53.64	1.51	5.2	208	0.46	3.47	0.11	1.3
Max	52.01	56.31	12.87	519.68	47.82	65.3	804	4.76	11.16	1.24	12.9

TABLE S3. GPS Coordinates (dd°mm'ss") from trough ponds, polygonal ponds and lakes on Bylot Island (Nunavut), and thaw ponds and tundra/rock ponds near Kuujjuarapik-Whapmagoostui (Nunavik, QC).

Bylot	Site	Latitude (°N)	Longitude (°W)	Kuujjuarapik-Whapmagoostui	Site	Latitude (°N)	Longitude (°W)
Trough Pond	BYL24	73°09'25	79°58'42	Thaw Pond	Kwk1	55°19'51	77°30'09
	BYL27	73°09'20	79°59'14		Kwk2	55°19'50	77°30'10
	BYL33	73°15'11	80°04'12		Kwk6	55°19'56	77°30'06
	BYL38	73°09'19	79°59'04		Kwk11	55°19'49	77°30'13
	BYL47	73°09'37	79°58'50		Kwk12	55°19'48	77°30'14
	BYL48	73°09'23	79°59'13		Kwk16	55°19'47	77°30'11
	BYL59	73°09'23	79°59'02		Kwk19	55°19'47	77°30'16
	BYL63	72°52'55	79°52'58		Kwk20	55°19'56	77°30'08
	BYL64	72°52'55	79°53'01		Kwk23	55°19'57	77°30'06
	BYL67	73°09'15	79°59'14		Kwk38	55°19'58	77°29'58
	BYL68	na	na		SAS1G	55°13'09	77°42'29
	BYL69	73°08'39	80°04'05		SAS2A	55°13'35	77°41'49
	BYL70	73°09'59	80°05'57	Taiga/ Rock Ponds	R104	55°17'48	77°45'18
	BYL71	73°08'56	80°02'49		R202	55°18'41	77°44'41
	BYL72	73°09'25	80°00'51		R206	55°18'39	77°44'46
	BYL74	73°10'46	79°52'15		R301	55°18'44	77°44'26
	BYL75	73°11'08	79°50'46		T102	55°16'35	77°44'08
	BYL76	73°11'02	79°48'29		T104	55°16'39	77°49'00
Polygonal Pond	BYL01	73°09'28	79°58'50		T107	55°16'39	77°44'08
	BYL22	73°09'28	79°58'44		T207	55°16'54	77°43'44
	BYL31	73°15'11	80°04'17		R217	55°18'37	77°44'49
	BYL44	73°09'28	79°58'46		Km2.5	55°18'37	77°44'49
	BYL51	73°09'26	79°59'11		Km4-1	55°19'27	77°42'55
	BYL61	73°15'11	80°04'17		WP2	55°16'58	77°44'07
	BYL65	73°09'40	79°58'04				
	BYL73	na	na				
	BYL78	73°06'28	80°07'53				
Lake (Bylot)	BYL36	73°09'34	79°58'13				
	BYL37	73°09'19	79°58'29				
	BYL39	73°02'48	79°25'34				
	BYL40	73°02'40	79°25'45				
	BYL49	73°00'47	79°28'51				
	BYL50	73°00'48	79°27'14				
	BYL66	73°09'14	79°59'34				

TABLE S4. Simple linear regression models for the most highly correlated environmental variables for surface waters of all data (n=58), separately for each region (Bylot: n = 34 or Kuujjuarapik: n = 24) and on a subset of data from the bottom waters of stratified ponds (n = 9).

Sample Site	n	Modeled Variable	Independent Variables	*p*-value	Adjusted R^2
All Sites: Surface Waters	58	THg	a320	< 0.01	0.57
			DOC	< 0.01	0.45
			TN	0.01	0.33
			Fe	0.02	0.26
		MeHg	TN	< 0.01	0.61
			DOC	< 0.01	0.57
			a320	< 0.01	0.39
			CH_4	< 0.01	0.37
Bylot Island Surface Waters	34	MeHg	Fe	< 0.01	0.65
			TP	< 0.01	0.84
			Mn	< 0.01	0.37
			Hg(II)	< 0.01	0.53
Kuujuarapik Surface Waters	24	MeHg	DOC	< 0.01	0.45
			TN	< 0.01	0.54
			Hg(II)	>0.01	ns
Kuujuarapik Bottom Waters	9	MeHg	Mn	0.01	0.84
			TP	< 0.05	0.79
			Fe	< 0.01	0.85
			CO_2	< 0.05	0.71
			CH_4	< 0.05	0.56
			DO	0.02	0.49

FIGURE S1. Map of the study area, showing Kuujjuarapik-Whapmagoostui (Quebec, Canada) and Bylot Island (Nunavut, Canada).

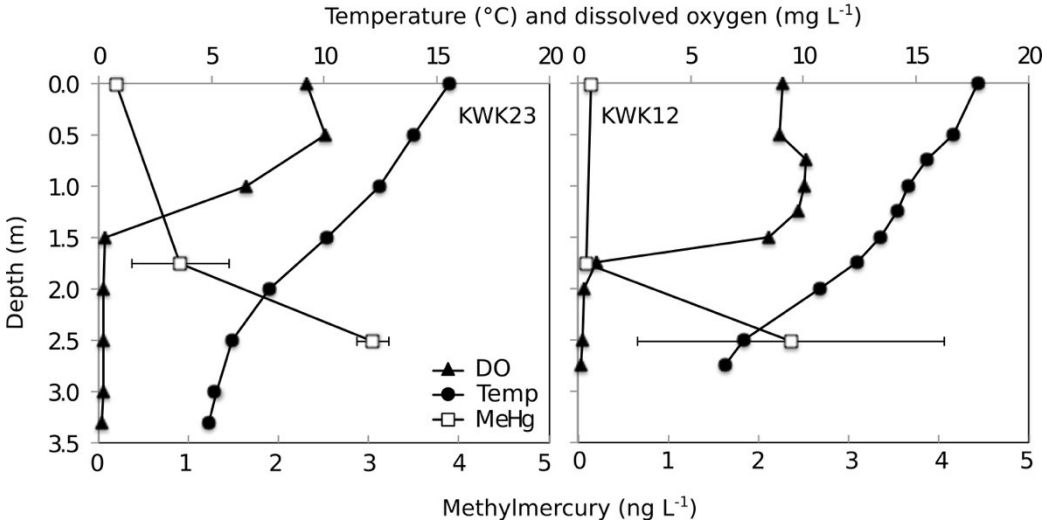

FIGURE S2. Vertical profiles of dissolved oxygen concentrations (DO, mg L^{-1}), temperature (Temp, °C) and MeHg concentrations (ng L^{-1}) for two stratified thermokarst ponds sampled near Kuujjuarapik-Whapmagoostui in August 2009.

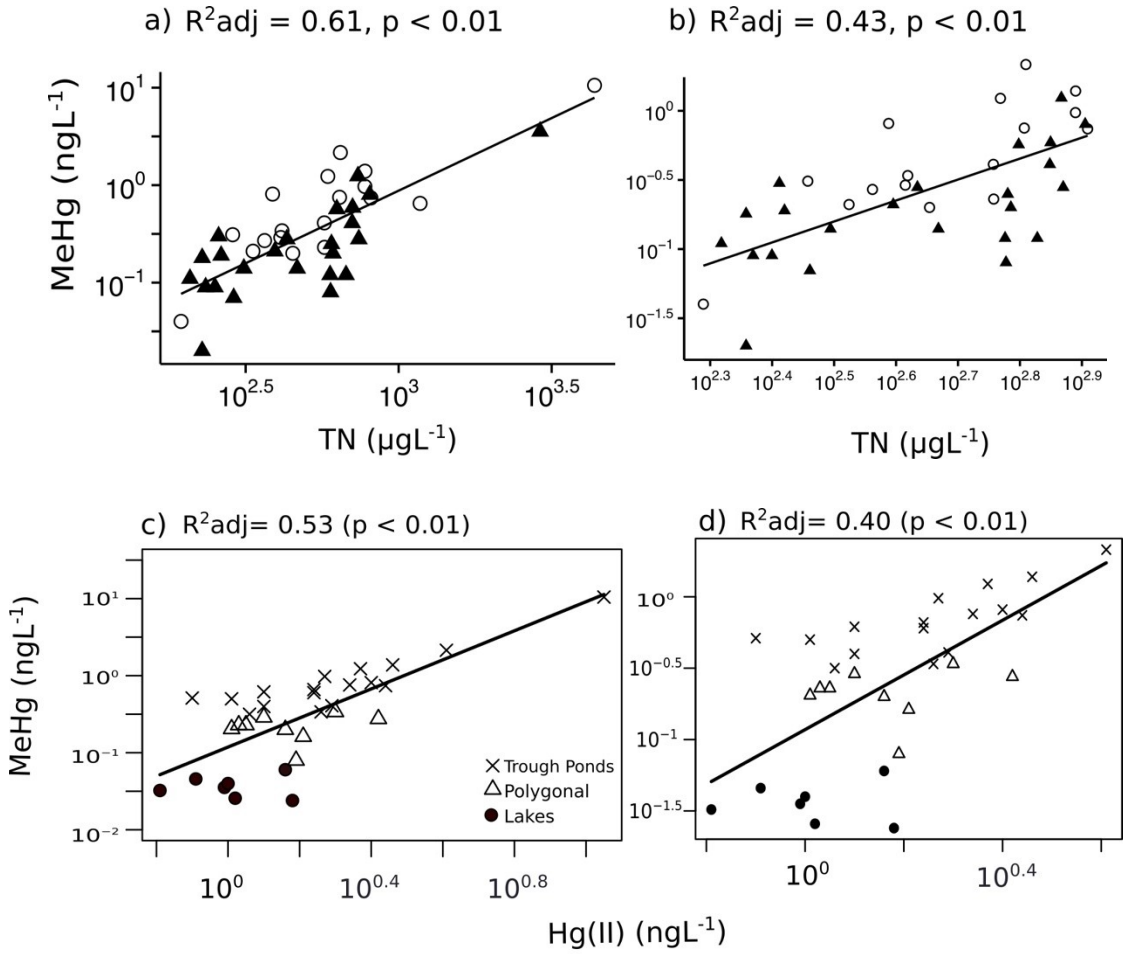

FIGURE S3. Correlations between MeHg concentrations (ngL^{-1}) showing significant positive correlations for a) all sample sites for TN (μgL^{-1}), n = 58 and b) a subset of sample sites for TN (μgL^{-1}) without 3 outliers, n = 55. Open circles represent Bylot sites and dark triangles represent Kuujjuarapik sites fpr a) and b). Correlations between MeHg concentrations (ngL^{-1}) showing significant positive correlations for c) all Bylot sample sites for Hg(II (ngL^{-1}), n = 34 and d) all sites on Bylot Island without the outlier, n = 33. All axes are shown on logarithmic scales and regressions were performed on log-transformed data.

CHAPITRE 2: Effets de la stœchiométrie nutritive sur la bioaccumulation de Hg dans le zooplancton d'eau douce de l'Arctique

Influence of nutrient stoichiometry on mercury bioaccumulation in Arctic freshwater zooplankton

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Abstract

This study examined the role of aquatic productivity and nutrient stoichiometry on mercury bioaccumulation in Arctic aquatic ecosystems. In the context of rapid climate change, an understanding of productivity influences on mercury bioaccumulation at the base of the food web is crucial to monitor long-term shifts in mercury dynamics in the Arctic. Consistent with previous findings at temperate latitudes, we hypothesized that higher algal biomass in Arctic lakes and more rapid zooplankton growth from the consumption of high-quality food, would reduce MeHg concentrations in zooplankton through biodilution. To test these hypotheses, we sampled a gradient in ecosystem productivity in the eastern Canadian Arctic and measured mercury bioaccumulation and the carbon:nutrient ratios (C:N, C:P) in seston and zooplankton from each water body. We did not find negative correlations among seston MeHg concentrations and water chlorophyll, phosphorus or nitrogen concentrations, nor did seston nutritional quality (seston %P, and C:N, CP ratios) influence zooplankton MeHg concentrations as predicted by biodilution theory. Bulk zooplankton (57 ± 45 ng g^{-1}) and *Daphnia* MeHg concentrations (101 ± 86 ng g^{-1}) were positively correlated with water MeHg concentrations and only weakly negatively correlated to water nutrient concentrations (TN, TP). Our results therefore suggest aqueous MeHg exposure is the dominant factor controlling MeHg uptake at the base of the food web and biodilution and nutritional quality are not important drivers of MeHg concentrations of seston or zooplankton within unproductive Subarctic and Arctic waterbodies.

Introduction

The transport and environmental fate of mercury will be affected by rapid climate change with important implications for human and ecosystem health (Stern et al. 2012). It remains challenging to predict future changes in the Arctic mercury cycle because of the influences of multiple drivers operating simultaneously and often antagonistically (Krabbenhoft and Sunderland, 2013). Arctic ecosystems can act as important indicators of future changes, as northern regions are warming at two to three times the global annual average (IPCC, 2018). Arctic ecosystems are also vulnerable to mercury pollution because of high atmospheric deposition and uptake by vegetation, coupled with high rates of biomagnification in unproductive food webs (Obrist et al., 2017, Lavoie et al., 2013, Steffen et al., 2007). Mercury is a research priority in the Arctic because methylmercury (MeHg), an organic chemical form of this metal, can bioaccumulate and biomagnify to potentially toxic levels within aquatic food webs. This issue is of particular concern for northern Indigenous communities who often depend on fish or marine mammals for subsistence food (Wheatley and Wheatley, 2000).

Climate change-induced permafrost thawing can affect mercury cycling in freshwater ecosystems (MacMillan et al., 2015, Rydberg et al., 2010, Macdonald et al., 2005). Climate models predict dramatic near-surface permafrost degradation by 2100 (~ 95%) under both high and low emission scenarios (Lawrence and Slater, 2005). The thawing of permafrost may increase transport of historically-accumulated mercury from soils and peatlands into aquatic systems through increased leaching and hydrological connectivity (Manasypov et al., 2015, Vonk et al., 2015). The release of nutrients and organic carbon from previously-frozen soils may also lead to higher aquatic ecosystem productivity in Arctic lakes (Rautio et al., 2011). These lakes are typically unproductive (or oligotrophic) with low levels of nutrients and algal biomass, and increasing productivity may have important implications for the mercury cycle. Increased aquatic productivity can affect the mercury cycle by influencing rates of MeHg bioaccumulation, as bioaccumulation is usually greater in biota from unproductive lakes when compared to more productive systems (Chételat et al., 2018, Kidd et al., 2012, Kidd et al., 1999). Although permafrost thaw may initially lead to increased mobility of mercury into aquatic systems, the bioavailability of metals in these systems will ultimately depend on other chemical and biological ecosystem changes.

Ecological stoichiometry is a conceptual framework which examines how different organisms can influence, and can be influenced by the balance of energy and chemical elements in their environment (Balseiro et al., 2008, Sterner and Elser, 2002). Studies in this area focus on stoichiometric constraints of the biologically important macronutrients (C, N, P) and their influence on energy, nutrient fluxes and trophic relationships. Laboratory studies have shown a strong interaction between nutrient stoichiometry and metal accumulation (Karimi et al., 2007, Wang and Dei, 2006), yet the relationship between these two variables has not been adequately tested *in situ* in natural lakes. MeHg uptake in biota at the base of food webs, such as phytoplankton and macrozooplankton, strongly influences the transfer of MeHg to higher trophic levels, e.g. fish. In fact, the largest step in methylmercury bioaccumulation is found between water and algae, with from 10 to 10^4 times more methylmercury found in seston than water (Watras et al., 1998). Seston includes all suspended particles in the water column, mainly small floating phytoplankton, bacteria and organic detritus. Zooplankton are also key vectors for the transfer of energy and contaminants from lower to upper trophic levels and some species (e.g. *Daphnia*) accumulate high levels of mercury (Chételat and Amyot, 2009, Pickhardt et al., 2005). Seston and zooplankton are potentially susceptible to the stoichiometric controls of mercury uptake into the food web.

Zooplankton have different stoichiometric requirements for macronutrients compared to other groups of aquatic biota (Karimi and Folt, 2006, Elser and Hassett, 1994). The C:N:P ratios of zooplankton are often close to the Redfield ratio of 106:16:1, although the ratio can vary between species and individual organisms based on body size and growth status (Karimi et al., 2010, Andersen and Hessen, 1991). The growth rate hypothesis states that rapid growth and development in an individual leads to allocation of phosphorus to RNA to meet protein synthesis demands, affecting the transfer efficiency of energy and other elements (e.g. Hg) through food webs (Karimi et al., 2007, Sterner and Elser, 2002). Karimi et al. (2007) examined the effects of stoichiometric food quality constraints on mercury bioaccumulation in the common crustacean zooplankton, *Daphnia pulex*. This laboratory study found that high food quality (i.e. low C:N and C:P ratios) led to a reduction in the concentrations of bioaccumulated mercury due to rapid growth of *D. pulex*. This form of biodilution is called somatic growth dilution and occurs

due to a greater proportional gain in total biomass relative to the intake of MeHg from ingesting high-quality food (Karimi et al., 2010, Karimi et al., 2007)

A second form of biodilution, referred to as algal bloom dilution, has also been observed in temperate aquatic food webs (Pickhardt et al., 2005, Pickhardt et al., 2002). This hypothesis states that greater algal biomass in a lake, often through stimulation from nutrient loading, results in less mercury uptake in individual algal cells. Both forms of biodilution lead to lower concentrations of MeHg at the bottom of the food web. Biodilution of mercury has been confirmed in laboratory studies, and it has been observed in productive ecosystems at temperate latitudes (Hill and Larsen, 2005, Pickhardt et al., 2002). Our field study examined for the first time the potential for mercury algal and growth biodilution at higher latitudes where lakes are less productive, yet vulnerable to climate-induced changes in primary production.

We tested the importance of mercury biodilution in Arctic freshwater ecosystems by examining the empirical relationships between the quantity and quality of food resources and mercury bioaccumulation. Our objectives were to a) characterize the nutritional quality and status of freshwater seston and zooplankton along a climate gradient in the Arctic and b) determine if mercury biodilution was occurring in lakes with higher seston biomass or greater nutrient availability. We hypothesized that greater aquatic productivity in Arctic lakes results in more algal biomass and more rapid zooplankton growth from the consumption of high-quality food, thereby reducing MeHg concentrations in zooplankton. To test these two hypotheses, we sampled lentic ecosystems along 20° of latitude in the eastern Canadian Subarctic and Arctic that ranged in size and productivity. From 2012-2014, we sampled a total of 47 lakes and ponds located near Kuujjuarapik-Whapmagoostui (Quebec), Iqaluit (Nunavut), and Resolute (Nunavut). We measured MeHg concentrations and the carbon:nutrient ratios (C:N, C:P) in both seston and zooplankton from each water body. Our findings test the applicability of current theory on mercury biodilution for Arctic freshwater ecosystems and provide predictions for potential impacts of climate change on mercury bioaccumulation.

Methods

Study sites. From 2012 to 2014, 47 lakes and ponds were sampled in the mid-summer (July-August) from three geographic areas in the eastern Canadian Subarctic and Arctic. In 2012, 7 lakes and 17 ponds were sampled near Kuujjuarapik-Whapmagoostui (K-W) in the Subarctic taiga south of the treeline in Nunavik, Quebec (55°N, 77°W). In 2013, 12 lakes were sampled in the Arctic tundra on Baffin Island near Iqaluit, Nunavut (64°N, 68°W), and 11 lakes were sampled in 2014 near Resolute, Nunavut (74°N, 94°W) in the high Arctic polar desert. A subset of this dataset was previously published in two articles which had different objectives than the current study (Chételat et al., 2018, MacMillan et al., 2015). Water bodies were categorized as either lakes or ponds for this study based on surface area and depth. Coastal waterbodies in the study regions were often relatively small systems and therefore lakes were categorized separately from ponds based on a surface area greater than 0.01 km^2. Lake size ranged from 0.03 to 4.5 km^2 (median 0.13) with mean lake depths ranging from 0.60 to 12 m (median of 1.9 m for all sites). Ponds near K-W ranged from 2.5 to 30 m in diameter with average depths of 1.0 m. Twelve of the 16 ponds were taiga/rock ponds (pooled into one group) which were formed on granite or carbonate-derived bedrock respectively. The four other ponds were thermokarst thaw ponds, or ponds which develop in depressions left after the ice had melted below mineral or organic (SAS) permafrost mounds (Breton et al., 2009).

Field sampling for water, seston, zooplankton. All study lakes were sampled for *in situ* water temperature, pH, specific conductivity, and dissolved oxygen with a YSI probe (YSI 600QS, YSI Inc., Yellow Springs, Ohio, USA). None of the lakes showed thermal stratification during the mid-summer sampling periods (N = 30). However, the thaw ponds were deeper than the taiga/rock ponds (with a maximum depth of 3.5 m) and showed thermal stratification with anoxic bottom waters (Matveev et al., 2016, MacMillan et al., 2015). At each site, duplicate surface water samples were collected with sub-surface hand grabs in HDPE bottles for water chemistry analysis, including dissolved organic carbon (DOC), major ions (Ca, Mg, K, Na, Cl, SO_4), chlorophyll *a* (Chla), total nitrogen (TN), and total phosphorus (TP). PETG bottles were used for aqueous Hg and MeHg concentrations (total and dissolved) (Lewis and Brigham, 2004). Surface water samples for Hg/MeHg were collected from shore or from a raft in duplicate using a peristaltic pump with an acid-washed Teflon line. Samples were filtered either using a) an

acid-washed (HCl 10%) Teflon filtration tower with pre-combusted glass-fibre filters (0.7 um pore size, Whatman GF-F) or b) a peristaltic pump with acid-washed Teflon tubing (HCl 10%) and a High Capacity In-Line Groundwater Sampling Capsule (0.45 um pore size, GWV, Pall Corporation, Port Washington, NY). Both filtration apparatuses were flushed with site water before sampling. Samples were collected using the clean hands, dirty hands sampling protocol for trace metals. All Hg samples were preserved within 24h of sampling with ultrapure hydrochloric acid to 0.4% final concentration and kept at -4°C until laboratory analysis.

Bulk samples of plankton were collected in two size fractions to examine seston (0.7 µm to 53 µm) and macrozooplankton (larger than 200 µm). Note that seston samples may have included small-sized zooplankton (i.e. rotifers). However, we assumed that the majority of the biomass in these size fractions was representative of two different trophic levels (Dobberfuhl and Elser, 2000). Surface water for seston analysis was pre-filtered using 53 µm nitex mesh and then filtered onto pre-combusted glass-fibre filters (0.7 um pore size, Whatman GF-F) either a) directly in the field with a peristaltic pump for sites in Iqaluit and Resolute or b) in the lab on the same day of water collection using a Teflon filtration tower for K-W sites. All equipment for seston filtration (mesh, filters, tubing) was acid-washed prior to use with 10% HCl. Seston filters were frozen at -20°C before analysis for elemental composition, stable isotope ratios and MeHg. From 5 to 7 seston filters were collected at each site in order to have enough material for duplicate filters of a) MeHg analysis, b) C and N content and stable isotope ratios and c) P content analysis. Since only 5 filters were sampled in 2012 at the Subarctic lakes near K-W, analysis for P content was not possible (N = 8). Extra filters were taken from a subset of sites in Iqaluit and Resolute and were used as triplicate samples for MeHg analysis.

Bulk zooplankton were sampled by horizontal surface hauls at depths of 1 to 2 m using a large diameter net (200 µm mesh). Duplicate or triplicate bulk samples were filtered, rinsed with ultrapure Milli-Q water, and frozen at -20°C before analysis without a depuration step. Sub-samples were taken from each bulk sample and preserved in ethanol (70%) for taxonomic analysis. Whenever feasible, zooplankton were live-sorted in the field for a few taxonomic groups of interest (N = 37 sites). Sorted zooplankton species included *Daphnia* (N = 33), *Chaoborus* (N = 13), and *Anostraca* (N = 6) and sub-samples of live individuals were preserved

in sterile, RNase/DNase free cryovials with RNA*later* solution (Ambion, Inc., Austin, Texas) for nucleic acid analysis and stored at -20°C until analysis.

Laboratory analysis for water, seston, zooplankton. For water chemistry, dissolved organic carbon (DOC) was measured with a Pt-catalyzed Shimadzu TOC 5000 analyzer, total nitrogen (TN) was determined as nitrate after potassium persulfate alkaline digestion, total phosphorus (TP) was determined by flow injection analysis (Astoria II, Astoria-Pacific, U.S. EPA method 365-3) and chlorophyll-a (Chla) was measured by spectrophotometer after ethanol extraction. Anions were quantified using ion chromatography (either Dionex Corp. or Waters, IC-Pak A and C columns) and cations were analyzed with either inductively coupled plasma optical emission spectrometry (ICP-OES, Varian VISTA AX CCD, in 2011) or with an atomic absorption spectrophotometer (AAS, Agilent, in 2012-2014). Aqueous THg concentration was determined by bromine monochloride (BrCl) oxidation, tin (II) chloride ($SnCl_2$) reduction, two-stage gold amalgamation and gas-phase detection with a Tekran 2600 Cold-Vapour Atomic Fluorescence Spectrometer (CVAFS) (Tekran Instruments Corporation, U.S. EPA method 1631). Aqueous MeHg concentration was determined by acid-distillation to remove matrix interferences, derivatization by aqueous-phase ethylation, purging on Tenax (Tenax Corporation) and separation by gas chromatography, before detection with either a Tekran 2500 or Tekran 2700 CVAFS (Tekran Instruments Corporation, U.S. EPA method 1630).

Dried seston and zooplankton were analysed for MeHg at the Laboratoire de biogéochimie environnementale (Université de Montréal, Montreal, Canada). For those samples, MeHg was extracted from sample masses of 0.5–2 mg for seston or 3-30 mg for zooplankton by digestion in 4 M HNO_3 at 55°C for 16 h, derivatized by aqueous ethylation using sodium tetraethylborate, trapped with Tenax and measured with a Tekran 2700 CVAFS. Seston filters and zooplankton samples (bulk and sorted) were freeze-dried and weighed into tin capsules to be analysed for carbon and nitrogen stable isotope ratios ($\delta^{13}C$, $\delta^{15}N$) as well as percent carbon (%C) and percent nitrogen (%N) using an elemental analyser interfaced with an isotope ratio mass spectrometer (IR-MS, Thermo Delta Advantage) at the G.G. Hatch Stable Isotope Laboratory (University of Ottawa, Ottawa, Canada). Before C/N analysis, seston filters were exposed to an acid atmosphere (30% HCl) for 24 hours to remove inorganic carbon. C/N analyses for Subarctic seston samples were run using ten filter punches and samples mass was calculated based on

surface area as a percent of total filter mass. Arctic and high Arctic seston samples were analysed for C/N using the whole filter which was homogenized prior to analysis. Stable isotope ratios are reported in Delta (δ) notation, the units are parts per thousand (‰) and defined as δX= ((Rsample-Rstandard))/Rstandard) x 1000 where X is ^{15}N or ^{13}C, and R is the ratio of the abundance of the heavy to the light isotope.

Digested seston and zooplankton samples were analyzed for total phosphorus content (%P) based on analysis for molybdate/ascorbic acid reactive orthophosphate with a segmented flow system (Astoria-Pacific, Astoria II, U.S. EPA method 365-3). Digested samples were prepared using two different methods which gave similar results (see Quality assurance and control below). The first method used a pre-combustion step at 550ºC for 1 hour, followed by acid-digestion (1M HCl) at 300ºC for 20 minutes. The second method used a persulfate digestion in glass tubes in the autoclave at 121ºC for 45 minutes. Nucleic acid content (RNA and DNA) of whole *Daphnia* were analysed for samples from sites near K-W and Iqaluit in 2012 and 2013. A pool of individual *Daphnia* from a sample (N = 3 - 45 individuals) were weighed in a vial and homogenized in buffer using a bead mill. DNA and RNA were extracted from tissue homogenates using spin column kits from Qiagen (DNeasy Blood and Tissue Kit or miRNeasy Microkit; Qiagen Inc., Montreal, Canada). Purified solutions of RNA and DNA were quantified by absorption on a Nanodrop spectrophotometer and normalized to sample tissue mass.

Zooplankton taxonomic composition was examined under a dissecting microscope (x10 - 40 magnification) in order to determine the dominant taxon present in each bulk sample. Zooplankton were classified into major groups (Order or Genus) using taxonomic keys (Haney et al., 2013, Thorp et al., 2009), specifically cladocerans, copepods, and chaoborids. Duplicate taxonomic samples were analysed from each site and a minimum of 200 individuals were identified in each replicate. Duplicate samples were then compared graphically to ensure consistency between replicates and the replicate samples were pooled together for analysis. The relative contribution of each taxon or group (e.g. % daphnia, %calanoid, % cladoceran, % copepod etc.) was calculated by dividing the number of individuals from each taxonomic group by the total number of individuals. The average body length (mm) of *Daphnia* in sorted samples was measured under the microscope from top of the eye to the base of the tail spine for 25 individuals from each sample when applicable.

Quality assurance and control. Standard recovery is reported here as the mean ± SD. For aqueous total Hg concentrations, the analytical detection limit was 0.04 ngL^{-1} and was calculated as three times the standard deviation (SD) of ten blanks. All water samples were run in duplicate with a Relative Standard Deviation (RSD) of <3% for THg. New standards (0.5 ng L^{-1}) were run after each set of 12 samples to test for analytical stability (recovery 103.2 ± 4.8 %, N = 41). Average recovery of a matrix spike for MeHg was 86.8 ± 7.2 % (N = 8). For MeHg concentrations in surface water and solids, the analytical detection limit was 0.01 ng L^{-1} and was calculated as three times the SD of ten blanks. New standards (0.5 ng/L) were run after each set of 10-12 samples to test for analytical stability (recovery 98.8 ± 10.6 %, N = 52). All water samples were run in duplicate with a Relative Standard Deviation (RSD) of <6% for MeHg in water samples. Average RSD for MeHg concentrations in zooplankton was 13% (N = 55). There was insufficient sample to do analytical duplicates for seston MeHg analyses. MeHg analyses were accepted when recovery of certified trace metal reference materials was in the certified range for TORT-2 (152 ± 13 ng/g, lobster hepatopancreas, National Research Council of Canada) and recovery for TORT-2 was 102 ± 8.3 % (N = 33).

Quality assurance for carbon and nitrogen stable isotope ratios included triplicate analyses of an internal standard (analytical precision of 0.2‰) and duplicate analyses of 10% of samples (coefficient of variation or CV < 5%). For total phosphorus analyses, blanks and standards of 25 ug L^{-1} were run every 10 samples with a mean recovery of 104 ± 3.8 % (N = 15). Apple leaves were used as standard reference material (SRM) for total phosphorus analyses in solids (NIST 1515, National Institute of Standards and Technology). Standard recovery for TP was 93.6 ± 10.8% (N = 8) for seston analyses and 88.0 ± 11.7 % (N = 11) for zooplankton analyses. To compare analysis methods for phosphorus in solids, certified standards (NIST 1515) and duplicate zooplankton samples were run with both methods and similar results were achieved (CV of 3% for duplicate samples). Quality assurance for the quantification of nucleic acids in Daphnia was based on an internal reference material (IRM) (fish muscle) that was run on each day of analysis to ensure consistency over time. CV for the IRM and sample duplicates for DNA content was 13.7% (N = 9) and for RNA content was 13.2% (N = 20). Spike recovery was also used to estimate recovery with this method and was measured at 86 ± 6 % for DNA (N = 8) and

59 ± 11 % for RNA (N = 13). We can therefore assume consistent but only partial recovery of RNA using this method.

Data handling and statistical analyses. Dissolved surface water concentrations of MeHg were used for statistical analyses. Geometric means (or GM) were calculated for all variables due to skewed distributions of the data, as well as either standard deviation (SD) or standard error (SE). Concentrations of MeHg, %C, %N and %P in seston and zooplankton are reported on a dry weight basis. Seston MeHg concentration was calculated based on the volume of surface water filtered on the sample filter (ng MeHg/L of seston). For seston samples found to be below detection limits for MeHg (N = 9), half of the detection limit (or 0.005 ng/L) was used. Seston biomass for each site was calculated (in mg/L) as the mean dry sample mass on filters divided by the total filtered water volume. DNA and RNA contents of Daphnia are presented based on wet weight basis. For zooplankton samples, elemental ratios of C:N:P were calculated as the ratio of elemental carbon to nitrogen to phosphorus content in seston or zooplankton on a molar basis. All statistical analyses were performed in R version 3.3.1 (R Core Development Team, 2016). Graphics were created with the '*ggplot2*' package (Wickham, 2016). All of the variables were tested for normality and transformed, if required, to reduce skewness and outlier influence. All variables were normalized using $\log_{10}$ transformations (N = 15), except for pH, logKd, seston C:N:P ratios and %P, zooplankton MeHg and %P (no transformation) and %cladoceran or %daphnia (square root transformations).

Simple linear regressions were calculated to predict relationships between seston biomass, Chla and seston MeHg concentrations. Multivariate analyses were conducted on three dependent variables to examine which environmental variables influence MeHg concentration in 1) seston, 2) bulk zooplankton and 3) sorted *Daphnia*. Multiple regressions were calculated using LASSO (Least Absolute Shrinkage and Selection Operator) analyses with the R package '*lars*' (Hastie and Efron, 2013). This technique resembles forward selection approaches in linear regression but it limits the sum of the regression coefficients using a tuning parameter (lambda, λ). The technique is well-suited to small datasets with collinear variables (Efron et al., 2002, Tibshirani, 1996). Model selection was based on the model with the lowest Mallow's Cp value. Mallow's Cp is a statistic used for subset selection which is similar to the Akaike information criterion (AIC) or Bayesian information criterion (BIC) (James et al., 2013). The '*selectiveInference'*

(Tibshirani et al., 2017) package in R was used to estimate the significance of each independent variable (p) in the models using its corresponding λ value. Table 2 shows LASSO model results including the model coefficients and fixed inference p-values for independent variables at the given level of the penalty parameter (lambda or λ). Lasso path plots are shown in Figures S3 to S7.

Results

Lake trophic status. Lake trophic status indicators measured in this study included aqueous TN, TP, Chla, and seston biomass. Average concentrations were 243 ± 440 µg L^{-1} for aqueous TN, 8.3 ± 37 µg L^{-1} for aqueous TP (Table 1, Table S1), indicating that the trophic status of study sites ranged from oligotrophic to eutrophic. Most of the lakes were ultra-oligotrophic or oligotrophic (68% of all sites) and ponds were mesotrophic (10 ponds) or eutrophic (5 ponds) following Canadian guidelines (Cloutier and Sanchez, 2007). Seston biomass (or suspended particulate matter) ranged from 0.07 - 9.37 mg dry wt L^{-1} among sites. Particulate organic carbon ranged from 167 - 1517 ug L^{-1} and Chla ranged from 0.09 - 10.4 ug L^{-1} among sites. Seston biomass was positively related to aqueous TN, aqueous TP, and Chla concentrations (R^2 = 0.53, 0.41 and 0.26 respectively, $p < 0.001$, log-scaled variables). The weaker relationship between seston biomass and Chla concentration was influenced by sites near Resolute which, unlike the other regions, did not show a clear trend between these variables (Fig. 1a).

Seston and zooplankton characterisation To determine the contribution of algal biomass to total particulate carbon, we calculated a linear regression for surface water particulate carbon (ug/L) to Chla (ug/L). The regression shows variable contribution of detrital carbon to suspended particulate matter among sites (log-scaled, Fig. 1b). For lakes across all regions, the majority of zooplankton communities were dominated by copepods, with the exception of a few small lakes near Resolute that were almost entirely composed of *Anostraca* (fairy shrimp) and *Daphnia* (Figure S1, S2). The relative abundance of cladocerans in sample sites averaged 44 ± 36 % and Daphnia averaged 19 ± 25 %. Rotifers were not collected in the samples as the net mesh size was too large, but they may have been present in seston samples. The presence of chironomid larvae (benthic invertebrates) in bulk zooplankton samples from some shallow sites

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Nutrient stoichiometry for seston and zooplankton. Average nutrient content for seston samples was 31 ± 17 %, 4.9 ± 3.8 % and 0.3 ± 0.2 % for C, N and P respectively (Figure 2). Average nutrient content for bulk zooplankton samples was higher than for seston at 40 ± 6.6 %, 7.6 ± 2.0 % and 0.9 ± 0.3 % for C, N and P respectively (% of dry weight, GM ± SD) (Figure 2 and Table 1, S1). P content is often more variable than C or N in zooplankton from the field, however this was not apparent in this study as coefficients of variation (CV) were 6.2, 4.0 and 3.4 % for C, N, and P respectively. Average nutrient content for sorted *Daphnia* was slightly higher than bulk samples, averaging 42 ± 6.6 % and 8.3 ± 1.4 % for C and N (Table S1). There was insufficient biomass to measure % P in sorted *Daphnia* samples from this study, however we calculated the ratio of RNA to DNA content as a proxy for growth rate in *Daphnia* (similar to % P content in bulk samples). For sorted *Daphnia*, RNA:DNA ratios ranged from 0.8 – 4.9 (average of 1.9 ± 0.9). Average seston nutrient molar ratios were 7.4 ± 1.9 for C:N, 236 ± 100 for C:P, and 32.5 ± 20 for N:P. Although seston samples were far from the Redfield ratios of 106 and 16, bulk zooplankton samples were less variable and closer to Redfield ratios. Average nutrient molar ratios were 6.1 ± 1.5 for C:N, 117 ± 48 for C:P and 19.2 ± 4.6 for N:P for bulk zooplankton (Table 1, S1). Average C:N molar ratios were lower for sorted *Daphnia* samples (5.1 ± 0.5) .

Mercury concentrations for seston and zooplankton. Seston MeHg concentrations ranged from below detection limits at <0.005 to 16.3 ng MeHg L^{-1} of surface water (or to 9.29 ng MeHg g^{-1} d.w). Average seston MeHg across all sites was 0.53 ± 3.6 ng L^{-1} or 0.66 ± 2.2 ng g^{-1} (N = 44) and were not significantly correlated with seston biomass ($p > 0.05$). Bulk zooplankton MeHg concentrations were roughly 100 times higher than those in seston. Zooplankton MeHg ranged from 8.6 - 192 ng MeHg g^{-1} and averaged 57 ± 45 ng MeHg g^{-1} d.w (N = 47). MeHg

concentrations in sorted *Daphnia* samples were higher than those measured in bulk samples, ranging from 13 - 414 ng g^{-1} and averaging 101 ± 86 ng g^{-1} (N = 32). Compared with bulk zooplankton from the same waterbody, *Daphnia* had on average 1.5 fold higher MeHg concentrations (GM ± SE: 1.5 fold difference, range: 0.4 - 9.0).

Relationships between nutrient stoichiometry and mercury bioaccumulation. Multivariate analyses including a range of lake properties revealed that water pH and seston biomass were the main explanatory variables of MeHg concentration in seston across all sites (N = 43, Model 1) (Table 2). DOC was also a significant variable in the full dataset model for seston MeHg concentration ($p = 0.031$). Together, these variables explained 52% of the variance in seston MeHg levels among water bodies. Multivariate analyses were also run on a subset of sites to include seston phosphorus content (C:P) as an input variable (N =35, Model 2). Similarly, the significant explanatory variables for seston MeHg concentrations in this model were pH and seston biomass ($p < 0.01$). Unlike with Model 1, DOC was not a significant contributor to the second model. This may be due to the exclusion of higher DOC lakes from K-W where no seston P data were available (N = 8). Seston C:P ratios were significantly negatively related to seston MeHg concentrations. For both models, water MeHg concentration, Chla, and seston %P, and seston C:N ratios did not explain seston MeHg concentrations.

Bulk zooplankton MeHg concentrations were strongly positively correlated with surface water dissolved MeHg concentrations (N = 40, Model 3, Table 2). Aqueous pH, Chla, seston biomass, seston C:P ratios and zooplankton C:N ratios were also contributors to the model, however model coefficients were not statistically significant. Together these parameters explained 60% of the variance in bulk zooplankton MeHg concentrations. Multivariate analyses were also run for zooplankton MeHg concentrations on a subset of sites in order to include seston C:P ratios as an input variable (N = 32, Model 4). Similar to Model 3, the MeHg in bulk zooplankton was best predicted by aqueous MeHg concentration, with many other variables contributing (non-significantly) to the model. Aqueous TN concentrations were negatively related to zooplankton MeHg in this model (Model 4, $p < 0.001$).

Multivariate analyses were also used to explain MeHg concentrations in sorted *Daphnia* from study sites (Model 5 & 6, Table 2). As with models for bulk zooplankton, MeHg concentrations in *Daphnia* were best explained by dissolved MeHg concentrations ($p < 0.01$) for all sites and

for a subset of sites with seston P content data. Aqueous TP concentrations also contributed significantly to both models. Seston MeHg was significantly positively correlated with *Daphnia* MeHg in Model 6 (but not Model 5). Other variables were included in the models, including pH, DOC, seston and *Daphnia* C:N, and RNA/DNA ratios, but with non-significant p-values ($p > 0.05$).

Discussion

Environmental factors controlling seston MeHg. Seston biomass in this study was low, reflecting that the majority of sample lakes were (ultra-) oligotrophic. However, seston biomass was within the range of seston density reported for nine temperate lakes in northeastern United States (Adams et al., 2009). Mean seston MeHg concentrations (0.66 ± 2.2 ng g^{-1}) were also much lower than previously reported for temperate lakes (33 ± 14 ng g^{-1}) (Watras et al., 1998) and for a meta-analysis of temperate and tropical pelagic food webs (1.7 - 410 ng g^{-1}, N = 39) (Wu et al., 2018). Lack of correlation between seston and water MeHg indicates that the supply of MeHg from the water column is not the strongest driver of MeHg partitioning at the base of the food web. It is not unusual to find a lack of correlation between water MeHg and seston MeHg concentrations (Wu et al., 2018), although positive relationships have been shown between total dissolved Hg and seston Hg (Adams et al., 2009). A negative relationship between seston MeHg and DOC concentrations suggests that DOC plays a role in MeHg partitioning to seston across sample lakes. Seston MeHg concentrations in this study also showed a positive trend with pH, where previous studies on Hg partitioning in seston show a slight inverse relationship (Watras et al., 1998). This positive correlation water pH may partly reflect regional differences in pH, as the ultra-oligotrophic sites had higher seston MeHg and were also more alkaline sites. Negative correlations were not found among seston MeHg concentrations and key indicators of trophic status, including aqueous TN, TP and Chla concentrations. However, positive trends with TN and TP may indicate that seston biomass is a good indicator of lake trophic status across these sites. Multivariate regressions showed that greater seston biomass was strongly linked to higher seston MeHg concentrations across sample sites (Table 2, Fig 1c).

TABLE 1: Geometric means (± SD) for surface water physico-chemical measurements and the methylmercury concentrations and nutrient stoichiometry of seston and bulk zooplankton from lakes and ponds at subarctic, arctic and high arctic sites (N = 47).*

		Lakes			Ponds
		K-W	Iqaluit	Resolute	K-W
	N	7	12	11	17
Surface Water	Temp (°C)	14 ± 2.1	6.4 ± 2.3	4.6 ± 2.5	14 ± 2.2
	Cond (µScm)	49 ± 33	38 ± 22	286 ± 246	69.7 ± 125.4
	pH	7.3 ± 0.6	7.1 ± 0.4	8.2 ± 0.2	6.8 ± 0.7
	DOC (mg/L)	5.0 ± 1.4	1.9 ± 0.7	1.5 ± 1.0	11.5 ± 5.2
	Chla (µg/L)	1.9 ± 0.6	0.4 ± 0.3	0.4 ± 0.6	2.1 ± 2.9
	TN (µg/L)	267 ± 51	93.7 ± 45.2	170.4 ± 97.3	573.7 ± 596.3
	TP (µg/L)	6.4 ± 2.2	4.6 ± 2.4	5.2 ± 4.9	18.8 ± 57.9
	TN:TP (molar)	92 ± 27	45 ± 25	72 ± 66	67 ± 47
Seston	Biomass (mg/L)	1.1 ± 0.5	0.34 ± 0.25	1.2 ± 1.3	2.0 ± 9.0
	MeHg (ng/L)	0.84 ± 0.67	0.04 ± 0.17	6.05 ± 4.6	0.3 ± 1.3
	C (%)	33 ± 6	50 ± 16	17 ± 16	33 ± 12
	N (%)	4.2 ± 0.9	9.9 ± 7.2	2.6 ± 2.4	5.2 ± 2.9
	P (%)	- ± -	0.48 ± 0.19	0.22 ± 0.14	0.37 ± 0.17
	C:N (molar)	9.1 ± 1.4	6.2 ± 1.3	7.7 ± 1.5	7.5 ± 2.3
	C:P (molar)	- ± -	268 ± 106	204 ± 88.6	239 ± 102
	N:P (molar)	- ± -	43.1 ± 25.3	26.6 ± 10.1	30.5 ± 19.5
Zooplankton	MeHg (ng/g)	91.8 ± 30.5	57.0 ± 40.7	48.9 ± 42.1	50.5 ± 53.1
	C (%)	43 ± 2.1	46 ± 4.7	41 ± 3.7	35 ± 6.9
	N (%)	9.3 ± 0.8	8.8 ± 1.3	8.5 ± 1.0	5.9 ± 2.3
	P (%)	1.0 ± 0.13	0.88 ± 0.25	1.0 ± 0.28	0.74 ± 0.28
	C:N (molar)	5.4 ± 0.3	6.1 ± 0.5	5.6 ± 0.7	6.3 ± 0.9
	C:P (molar)	107 ± 11.9	135 ± 44.8	101 ± 28	114 ± 28.0
	N:P (molar)	19.9 ± 1.9	22.2 ± 5.4	18.2 ± 3.13	17.8 ± 5.1

* K-W = Kuujjuarapik-Whapmagoostui, Temp = temperature, Cond = specific conductivity, Chla = chlorophyll *a*, DOC = dissolved organic carbon, TN = total nitrogen, TP = total phosphorus, TN:TP = molar ratio of TN to TP, MeHg = methylmercury, C = carbon, N = nitrogen, P = phosphorus (note: C, N and P measured as % of dry mass basis).

TABLE 2: Summary of multivariate regression analyses examining the influence of environmental variables describing the surface water MeHg, lake trophic status, seston quality and zooplankton nutritional status on seston, bulk zooplankton and Daphnia MeHg bioaccumulation across all sample sites. Table shows model coefficients and p-values.*

Dependent Variable				**Model Metrics**			**Independent Variables**												
Seston [MeHg]	N	df	Cp	R^2	λ		MeHg (aq)	pH	DOC	Chla	TN (aq)	TP (aq)	Seston Biomass	Seston C:N					
Model 1	43	4	11.3	0.517	4.03	*Coefficient*	0	0.40	-0.23	0	0	0	0.40	0					
						p-value	--	**0.003**	**0.031**	--	--	--	**<0.001**	--					
Seston [MeHg]	N	df	Cp	R^2	λ		MeHg (aq)	pH	DOC	Chla	TN (aq)	TP (aq)	Seston Biomass	Seston C:N	Seston C:P				
Model 2	35	4	5.74	0.559	2.86	*Coefficient*	0	0.59	0	0	0	0	0.26	0	-0.22				
						p-value	--	**<0.001**	--	--	--	--	**0.007**	--	**0.028**				
Zooplankton [MeHg]	N	df	Cp	R^2	λ		MeHg (aq)	pH	DOC	Chla	TN (aq)	TP (aq)	Seston Biomass	Seston [MeHg]	Seston C:N	--	Zoop C:N	Zoop C:P	Clado %
Model 3	40	8	12.0	0.604	4.62	*Coefficient*	2.93	0.25	0	0.14	-2.3	0	-0.31	0	0	--	-0.47	0	0.47
						p-value	**<0.001**	0.263	--	0.573	0.085	--	0.376	--	--	--	0.067	--	0.101
Zooplankton [MeHg]	N	df	Cp	R^2	λ		MeHg (aq)	pH	DOC	Chla	TN (aq)	TP (aq)	Seston Biomass	Seston [MeHg]	Seston C:N	Seston C:P	Zoop C:N	Zoop C:P	Clado %
Model 4	32	8	6.92	0.640	3.34	*Coefficient*	3.50	0.36	0	0	-2.79	0	-0.38	0	0	0.06	-0.36	0	0.63
						p-value	**<0.001**	0.298	--	--	**<0.001**	--	0.327	--	--	0.870	0.257	--	0.100
Daphnia [MeHg]	N	df	Cp	R^2	λ		MeHg (aq)	pH	DOC	Chla	TN (aq)	TP (aq)	Seston Biomass	Seston [MeHg]	Seston C:N	--	Daphnia C:N		
Model 5	23	8	6.72	0.736	14.7	*Coefficient*	254	18.0	0	0	-46.8	-231	0	26.9	-6.6	--	-3.9		
						p-value	**0.009**	0.159	--	--	0.221	**<0.001**	--	0.233	0.607	--	0.668		
Daphnia [MeHg]	N	df	Cp	R^2	λ		MeHg (aq)	pH	DOC	Chla	TN (aq)	TP (aq)	Seston Biomass	Seston [MeHg]	Seston C:N	RNA: DNA	Daphnia C:N		
Model 6	18	9	11.1	0.876	12.0	*Coefficient*	133	38.2	5.5	0	0	-187	0	61.8	-13.0	8.5	-13.1		
						p-value	**0.006**	0.158	0.761	--	--	**<0.001**	--	**0.007**	0.197	0.415	0.103		

*DOC = dissolved organic carbon, MeHg (aq) = dissolved aqueous MeHg, Chla = chlorophyll a, TN = total aqueous nitrogen, TP = total aqueous phosphorus, Clado = Cladoceran, Daph = Daphnia

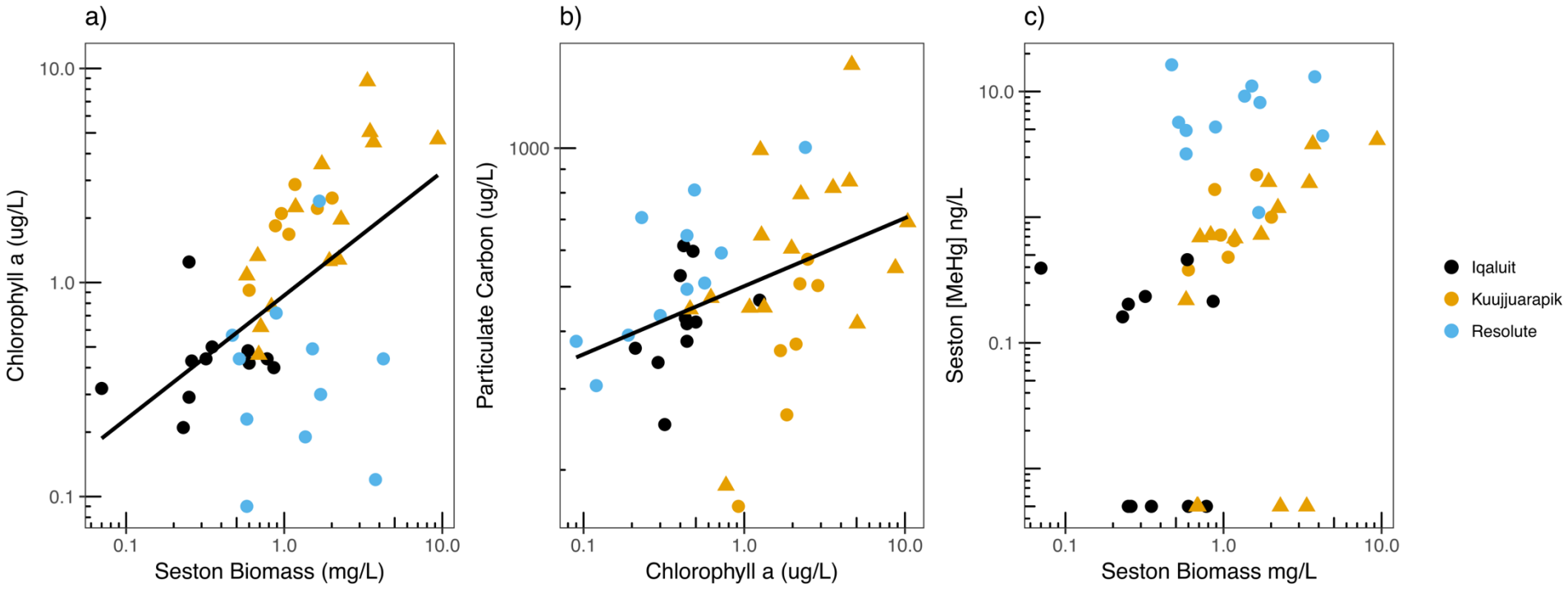

FIGURE 1. Simple linear regressions between a) chlorophyll-a concentration (ug/L) and seston biomass (mg/L) (log y = -0.6 + 0.57 log x, $R^2 = 0.26$, $p < 0.001$); b) particulate carbon concentrations (ug/L) and chlorophyll-a concentration (ug/L) (log y = 2.7 + 0.15 log x, $R^2 = 0.15$, $p = 0.018$); and c) seston methylmercury (MeHg) concentrations (ng/L) and seston biomass (mg/L) ($p > 0.05$). All variables are log-scaled. Circles represent lakes and triangles represent ponds.

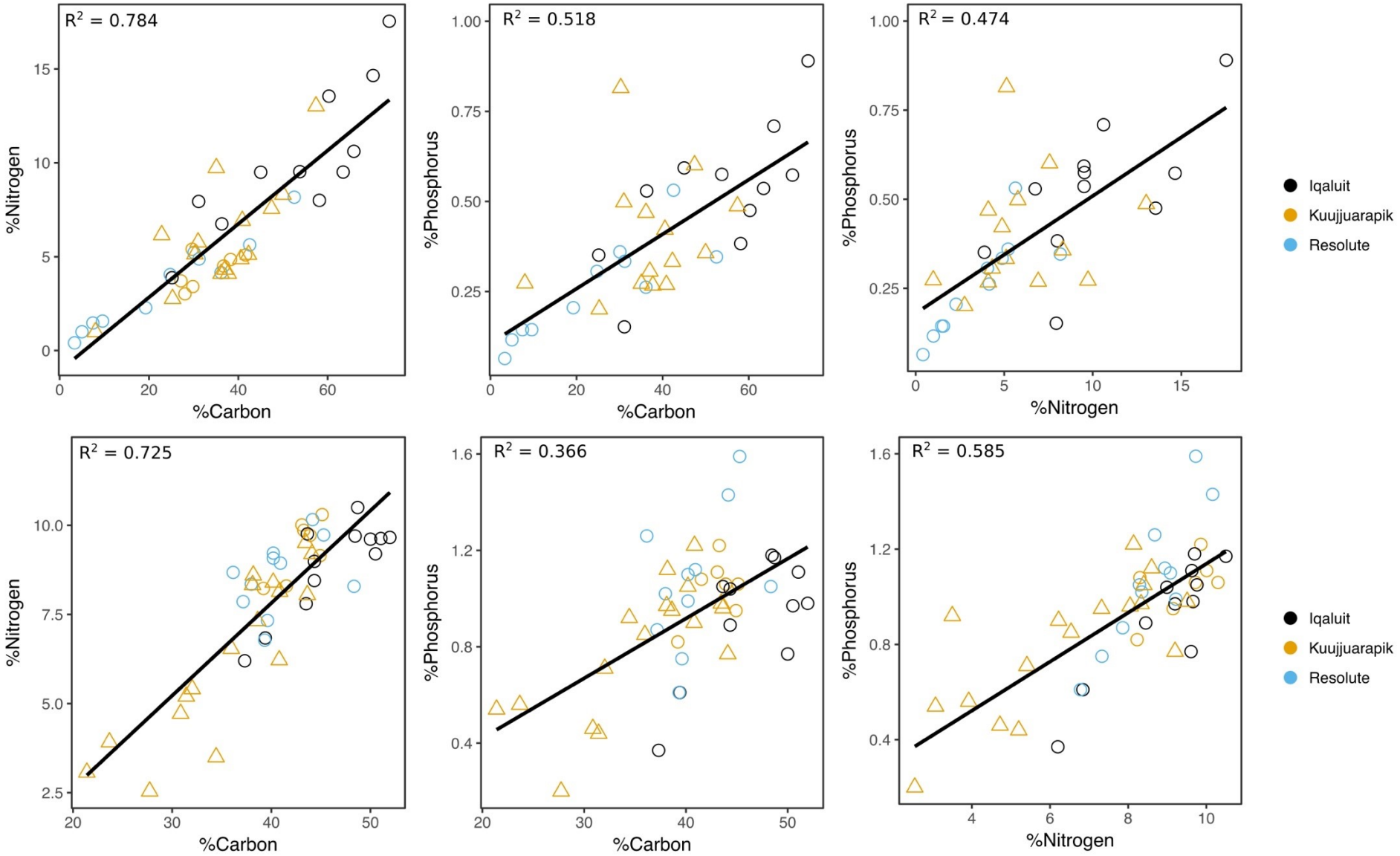

FIGURE 2. Relationships between carbon, nitrogen and phosphorus (as % of dry mass) in seston (top row) and bulk zooplankton (bottom row) from lakes and ponds at subarctic, arctic and high arctic sites. (All regressions are $p < 0.01$). Circles represent lakes and triangles represent ponds.

Based on algal growth dilution theory, we hypothesized that greater aquatic productivity in Arctic lakes would mean higher seston biomass and therefore a reduction in MeHg concentrations in seston. We found, however, the opposite trend where seston biomass was positively correlated with MeHg levels (Table 2). Results with seston C:P also showed the opposite trend as expected with biodilution theory, where seston with higher nutritional status (i.e. with lower C:P ratios) had higher MeHg levels. Seston C:P ratio is a major determinant of energy transfer in aquatic food webs and sestonic C:P ratios in this study were comparable to those reported for Norwegian lakes with a mean of 250 (min - max: 24 - 1842, N = 112) (Hessen, 2006). The relative proportion of biotic and abiotic particles in seston across sites likely influenced seston MeHg concentrations and nutrient stoichiometry. The relatively weak relationship ($R^2 = 32$) between seston biomass and Chla, specifically for Resolute sites, indicates that samples had variable composition of algal and non-algal suspended particles. The wide range of C:Chla ratios for seston in this study may reflect differences in photoacclimation, nutrient deficiency or the contribution of heterotrophic organisms and C-enriched detritus to seston biomass (North et al., 2012, Wienke and Cloern, 1987).

Environmental factors controlling zooplankton MeHg. Bulk zooplankton MeHg concentrations were lower, but comparable, to results from a recent meta-analysis of pelagic food webs which reported a range of 2.7 to 2600 ng MeHg g^{-1} d.w. (Wu et al., 2018). In this study, both bulk zooplankton (57 ± 45 ng g^{-1}) and *Daphnia* MeHg concentrations (101 ± 86 ng g^{-1}) were most strongly positively correlated with dissolved MeHg concentrations. We also found no indication that food quality (i.e. seston nutritional status) influenced either bulk zooplankton or *Daphnia* MeHg concentrations. Growth rate, as measured by % P in bulk zooplankton samples or the RNA:DNA ratio in sorted *Daphnia*, also did not significantly predict MeHg bioaccumulation in zooplankton. We also did not find any significant relationships between taxonomic composition (e.g. % daphnia, % copepod) and MeHg concentrations in bulk zooplankton samples (Table 2).

We hypothesized that more rapid zooplankton growth due to the consumption of high-quality food would reduce MeHg concentrations in zooplankton from Arctic lakes. However, we found only weak evidence to support this hypothesis. We found no significant relationship between zooplankton MeHg and seston biomass or Chla. In some models, negative trends were found

between aqueous TN and bulk zooplankton MeHg, as well as between aqueous TP and *Daphnia* MeHg (Table 2). These results are consistent with biodilution theory and may indicate links between lake trophic status (or nutrient limitation) and MeHg bioaccumulation for a subset of sites (Model 4, without lakes from Kuujjuarapik) or for *Daphnia* only.

Conclusions. In this study, the highest seston MeHg concentrations were found in alkaline lakes with high seston biomass and the highest bulk zooplankton and *Daphnia* MeHg concentrations were found in lakes with high MeHg concentrations in surface waters. Indicators of lake trophic status (Chla, TN, TP, seston biomass) and seston nutritional quality (seston %P and C:N, CP ratios) did not influence seston MeHg concentrations as predicted by the biodilution theory. Although weak negative relationships were found with aqueous TN and TP concentrations, seston nutritional quality (seston %P, and C:N, CP ratios) did not influence zooplankton MeHg concentrations as predicted by biodilution theory. Thus far, biodilution has only been observed in highly productive systems and never in oligotrophic waterbodies such as those examined in this study (Pickhardt et al., 2002, Kidd et al., 1999). Biodilution theory may not universally applicable to all waterbodies, as the extent of predicted changes in Arctic aquatic productivity may also not be sufficient to cause biodilution, and shifts in zooplankton community structure and body size can confound the theory (Todorova et al., 2015).

Arctic lakes are mostly oligotrophic and climate warming may lead to increased productivity due to greater inputs of organic material and nutrients. This increase in productivity has important implications for nutrient stoichiometry and mercury bioaccumulation, however, until the present study, there have been very few measurements of either MeHg or nutrient stoichiometry in Arctic seston. Our results suggest that aqueous MeHg exposure is the dominant factor controlling MeHg uptake at the base of the food web and biodilution and nutritional quality may not be important drivers of MeHg in seston or zooplankton within Subarctic and Arctic waterbodies. Climate change impacts on aqueous methylmercury production are therefore more likely to be key drivers MeHg bioaccumulation in Subarctic and Arctic waterbodies.

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Author contributions. GM, JC, MR, and MA conceived and designed the study. GM MR, and JC performed the field data collection. Data and statistical analysis was done by GM. GM wrote the manuscript and all authors edited and give final approval to the manuscript.

Supporting Information consists of 6 pages including 1 table and 8 supporting figures.

Supporting Information:

Influence of nutrient stoichiometry on mercury bioaccumulation in Arctic freshwater zooplankton

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Supporting Information consists of 6 pages including 1 table and 8 supporting figures

Table S1: GPS Coordinates, surface water physicochemical variables, nutrient stoichiometry (C,N,P) and MeHg in biota for all samples sites (N = 47).

					Surface Water							Seston					Bulk Zooplankton				*Daphnia*		
Region	Site	Year	Lat	Long	Temp	Cond	pH	DOC	TN	TP	Chla	Density	MeHg	C	N	P	MeHg	C	N	P	MeHg	C	N
					C	µs/cm		mg/L	µg/L	µg/L	µg/L	mg/L	ng/L	%	%	%	ng/g	%	%	%	ng/g	%	%
K-W	KJ1	2012	55.320	-77.711	13.0	104	8.1	6.01	309	8.11	1.84	0.88	1.66	29.7	5.4	-	155	41.5	8.30	1.08	279	44.4	8.42
	KJ2	2012	55.369	-77.618	11.0	102	7.9	4.17	215	3.09	0.92	0.60	0.38	27.2	3.7	-	111	39.2	8.23	0.82	148	47.5	10.1
	KJ4	2012	55.334	-77.625	13.0	43	7.1	4.01	206	4.66	1.68	1.07	0.48	36.7	4.5	-	63.9	43.1	10.0	1.11	126	50.7	10.1
	KJ5	2012	55.291	-77.719	17.0	56	7.4	7.58	338	7.91	2.22	1.62	2.17	29.8	3.4	-	77.2	45.1	10.3	1.06	-	43.8	9.52
	KJ6	2012	55.320	-77.642	16.0	19	6.6	4.39	306	8.65	2.87	1.17	0.65	41.6	5.1	-	81.9	44.9	9.15	0.95	78.6	45.9	9.86
	KJ7	2012	55.334	-77.597	14.0	46	7.3	5.81	281	8.67	2.48	2.01	1.00	28.0	3.0	-	78.9	43.3	9.86	1.22	135	46.7	10.6
	KJ8	2012	55.337	-77.612	16.0	31	6.6	3.87	245	6.31	2.10	0.96	0.72	38.3	4.8	-	100	43.9	9.72	1.06	202	46.7	10.0
Iqaluit	IQ1	2013	63.797	-68.546	7.3	20	6.7	2.11	108	5.71	0.44	0.32	0.23	65.9	10.6	0.71	80.8	48.7	10.5	1.17	146	44.6	9.41
	IQ2	2013	63.758	-68.444	4.9	60	6.9	2.62	102	4.48	1.25	0.25	0.20	63.5	9.5	0.54	74.7	43.6	9.76	1.05	114	45.7	8.48
	IQ4	2013	63.798	-68.538	5.3	28	6.9	1.23	45	3.74	0.32	0.07	0.39	73.8	31.3	0.89	76.4	50.5	9.20	0.97	84.6	45.5	7.48
	IQ5	2013	63.749	-68.398	3.0	45	6.8	1.70	58	4.12	0.21	0.23	0.16	70.2	14.6	0.57	31.9	48.5	9.70	1.18	45.2	-	-
	IQ6	2013	63.916	-68.573	6.0	44	6.5	1.18	76	3.75	0.29	0.25	<0.01	45.0	9.5	0.59	35.3	43.5	7.80	-	-	-	-
	IQ7	2013	63.685	-68.376	6.9	92	7.2	3.01	173	9.61	0.42	0.60	<0.01	36.3	6.7	0.53	25.5	50.0	9.61	0.77	-	-	-
	IQ8	2013	63.825	-68.604	4.0	63	7.3	1.64	97	5.30	0.43	0.26	<0.01	53.8	9.5	0.58	35.8	51.0	9.63	1.11	13.0	-	-
	IQ9	2013	63.767	-68.538	10.1	39	7.3	2.96	186	9.80	0.44	0.78	<0.01	25.2	3.9	0.35	63.0	37.3	6.20	0.37	101	42.8	8.60
	IQ10	2013	63.757	-68.479	7.1	25	7.3	2.08	78	4.88	0.40	0.86	0.21	31.1	7.9	0.15	173	44.3	8.99	1.04	168	45.8	9.37
	IQ11	2013	63.765	-68.518	8.4	19	6.8	1.71	148	3.98	0.50	0.35	<0.01	60.3	13.5	0.47	91.7	44.3	8.45	0.89	92	39.5	6.90
	IQ12	2013	63.783	-68.540	8.9	50	7.6	2.60	97	5.30	0.48	0.59	0.46	58.1	8.0	0.38	70.4	39.4	6.84	0.61	124	45.3	8.36
	IQ13	2013	63.875	-68.478	9.7	22	8.0	1.03	61	1.16	-	-	-	-	-	-	35.1	52.0	9.66	0.98	-	-	-
Resolute	RZ1	2014	74.690	-94.990	3.0	239	8.1	2.04	174	6.63	0.57	0.47	16.31	42.5	5.6	0.53	74.0	48.3	8.29	1.05	-	-	-
	RZ2	2014	74.721	-94.862	8.0	130	8.2	0.75	73	4.61	0.12	3.78	13.10	5.0	1.0	0.12	74.4	40.2	9.08	1.10	-	-	-
	RZ3	2014	74.684	-94.989	2.3	850	8.0	0.97	132	1.08	0.09	0.58	4.90	19.2	2.3	0.21	61.3	36.1	8.68	1.26	-	-	-
	RZ4	2014	74.759	-95.060	3.8	346	8.0	2.25	186	4.07	0.44	0.52	5.69	52.5	8.2	0.35	14.5	39.6	7.33	0.75	-	-	-
	RZ5	2014	74.777	-95.096	3.4	125	8.2	0.88	229	4.05	0.30	1.70	8.17	7.4	1.5	0.14	9.6	39.3	6.78	0.61	-	-	-
	RZ6	2014	74.688	-94.943	3.4	399	8.1	1.11	103	3.53	0.23	0.58	3.19	31.2	4.9	0.33	26.0	40.9	8.94	1.12	-	-	-
	RZP2	2014	74.735	-94.962	10.2	389	8.3	2.00	165	5.59	0.44	4.24	4.44	3.3	0.4	0.06	61.9	37.2	7.86	0.87	-	-	-
	RZP3	2014	74.744	-94.955	7.8	156	8.3	1.08	122	5.26	0.19	1.36	9.18	9.6	1.6	0.14	154	40.2	9.22	0.99	-	-	-
	RZP4	2014	74.707	-95.003	5.6	232	8.5	4.32	430	17.51	2.40	1.67	1.09	36.1	4.2	0.26	40.6	45.3	9.73	1.59	34.0	32.9	6.98
	RZP5	2014	74.737	-94.893	3.7	217	8.3	2.54	259	14.32	0.72	0.89	5.22	30.1	5.2	0.36	76.9	44.2	10.2	1.43	-	-	-
	RZP6	2014	74.680	-94.914	5.5	761	7.9	1.55	213	5.57	0.49	1.51	11.06	24.7	4.1	0.31	106	38.0	8.35	1.02	414	-	-
Ponds	KJ3	2012	55.304	-77.716	10.0	130	8.0	4.06	242	3.09	0.77	0.83	0.72	22.8	6.2	-	76.6	32.0	5.41	0.71	-	-	-
	R1-04	2013	55.297	-77.756	15.6	31	6.0	11.40	736	43.53	5.05	3.49	1.87	47.4	7.6	0.60	192	43.6	8.05	0.96	201	45.6	8.70
	R2-02	2013	55.311	-77.744	17.0	199	7.5	11.62	707	15.14	3.57	1.73	0.73	50.0	8.3	0.36	114	31.4	5.20	0.44	267	34.2	7.14
	R2-06	2013	55.311	-77.746	15.1	279	7.6	17.30	665	12.18	1.28	2.21	1.19	25.3	2.8	0.20	101	23.7	3.92	0.56	249	28.2	4.99
	R3-01	2013	55.312	-77.741	12.8	119	7.2	11.03	628	19.67	-	-	-	-	-	-	47.1	30.8	4.72	0.46	106	37.5	7.59
	T1-02	2013	55.276	-77.736	17.9	48	7.2	11.44	610	11.77	1.26	1.93	1.91	37.0	4.3	0.31	76.7	43.5	9.51	0.98	89.9	41.7	9.56
	T1-04	2013	55.277	-77.750	13.9	67	7.1	11.95	603	7.79	2.25	1.18	0.68	37.7	4.1	0.27	17.9	27.7	2.54	0.20	160	-	-
	T1-07	2013	55.277	-77.736	15.5	37	6.9	12.84	741	24.79	4.52	3.67	3.81	40.5	4.9	0.42	22.1	34.4	3.50	0.92	48.5	-	-
	T2-07	2013	55.282	-77.729	12.2	63	7.2	5.97	208	5.21	1.08	0.58	0.22	42.3	5.1	0.33	97.9	36.0	6.54	0.85	109	34.4	6.19
	R2-17	2013	55.310	-77.747	12.8	514	7.8	10.11	804	65.32	1.74	-	-	-	-	-	73.8	21.4	3.07	0.54	127	37.8	6.80
	Km2.5-01	2013	55.324	-77.715	13.7	26	5.7	14.07	466	12.41	1.33	0.68	<0.01	57.4	13.0	0.49	26.9	40.8	6.22	0.90	44.3	43.9	9.34
	Km4-01	2013	55.333	-77.695	16.0	50	7.0	9.49	258	5.29	0.46	0.69	<0.01	35.1	9.7	0.27	152	44.1	9.20	0.77	177	-	-
	WP2	2013	55.283	-77.735	11.4	42	6.6	14.88	394	12.57	0.62	0.71	0.69	31.0	5.8	0.50	120	38.6	7.32	0.95	120	44.2	7.32
	KWK11	2013	55.319	-77.504	17.8	27	6.1	11.01	597	43.19	8.72	3.36	<0.01	30.3	5.1	0.81	18.7	38.1	8.33	0.97	41.7	-	-
	KWK19	2013	55.330	-77.505	16.6	37	6.5	9.81	673	96.26	10.4	36.1	2.14	8.0	1.0	0.27	11.7	38.2	8.60	1.12	-	-	-
	SAS1G	2013	55.219	-77.708	14.8	84	5.9	28.06	2899	240.3	4.67	9.37	4.12	36.1	4.1	0.47	56.6	40.8	8.14	1.22	61.1	40.8	8.08
	SAS2A	2013	55.226	-77.697	14.4	49	5.8	16.58	599	15.30	1.97	2.29	<0.01	40.9	6.9	0.27	8.58	40.2	8.40	1.05	14.7	40.4	8.38
				min	2	19	5.7	0.75	45	1.08	0.09	0.07	<0.01	3.3	0.4	0.06	8.6	21.4	2.5	0.20	13.0	28.2	5.0
				max	18	850	8.5	28.1	2899	240	10.4	36.1	16	74	31	0.89	192	52.0	10.5	1.59	414	50.7	10.6
				max/min	8.0	45	1.5	37	65	222	122	514	3262	22	75	14	22	2.4	4.1	7.8	32	1.8	2.1

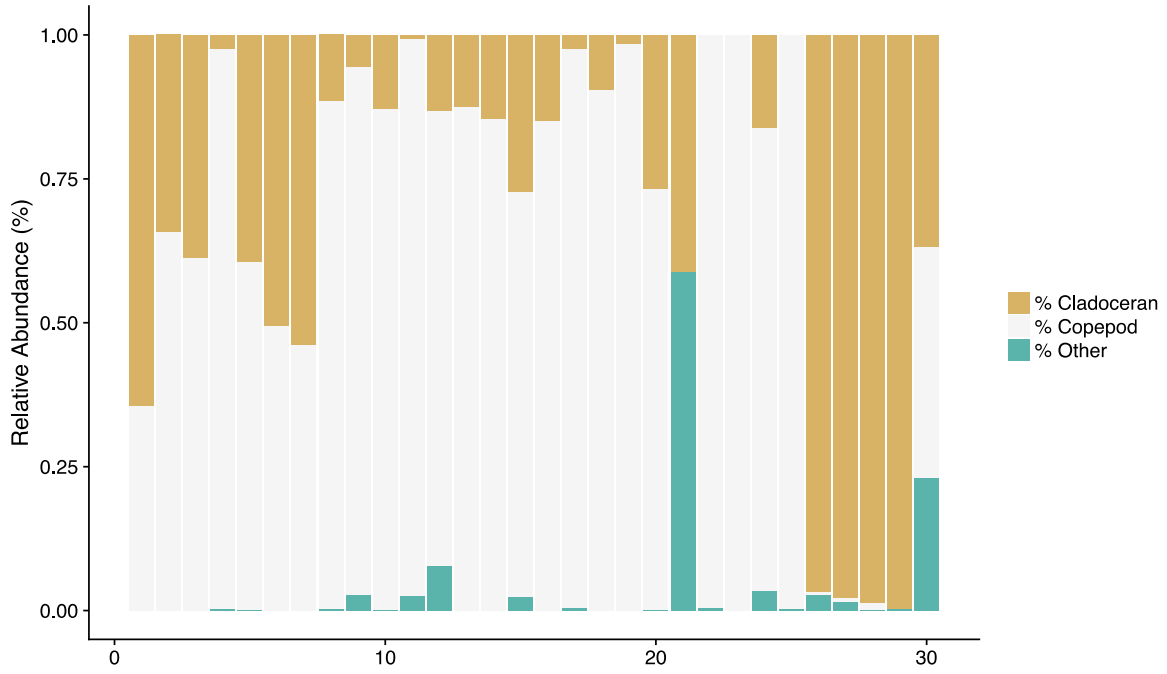

FIGURE S1. Relative abundances of major zooplankton groups for lakes sample sites across all regions (K-W, Iqaluit, and Resolute). Note: the "Other" category includes the groups *Chaoborus*, *Chironomid*, and *Hydracarina*. On the x-axis: Sites # 0-7 = K-W, Sites # 8 - 19 = Iqaluit, Sites # 20 - 30 = Resolute.

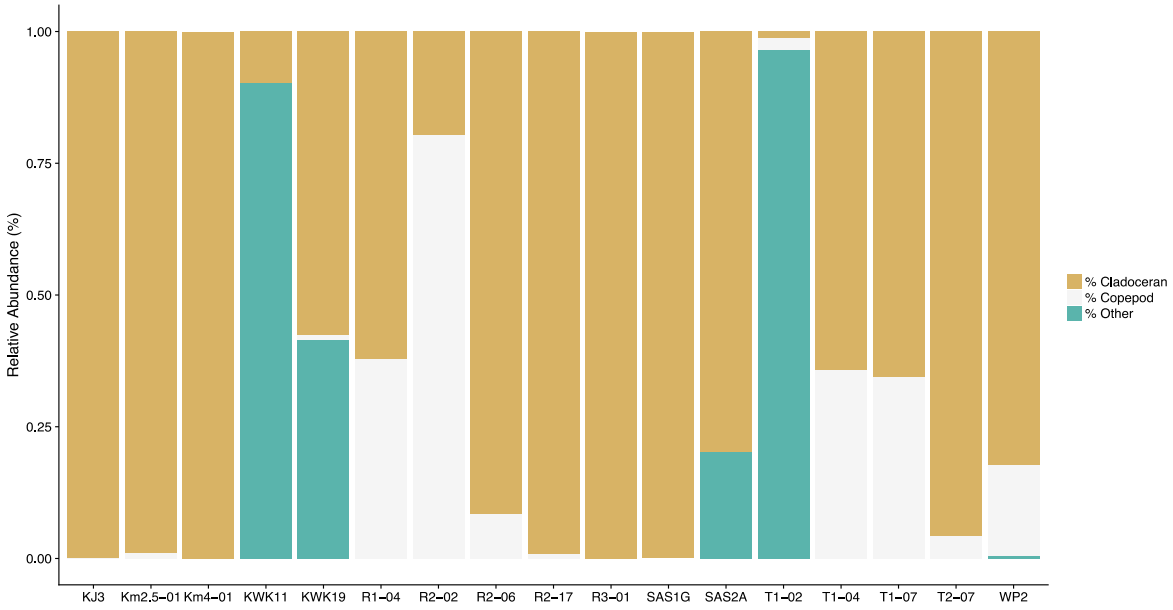

FIGURE S2. Relative abundances of major zooplankton groups for each sample site across all sample regions (K-W, Iqaluit, and Resolute). Note: the "Other" category includes the groups *Chaoborus*, *Chironomid*, and *Hydracarina*.

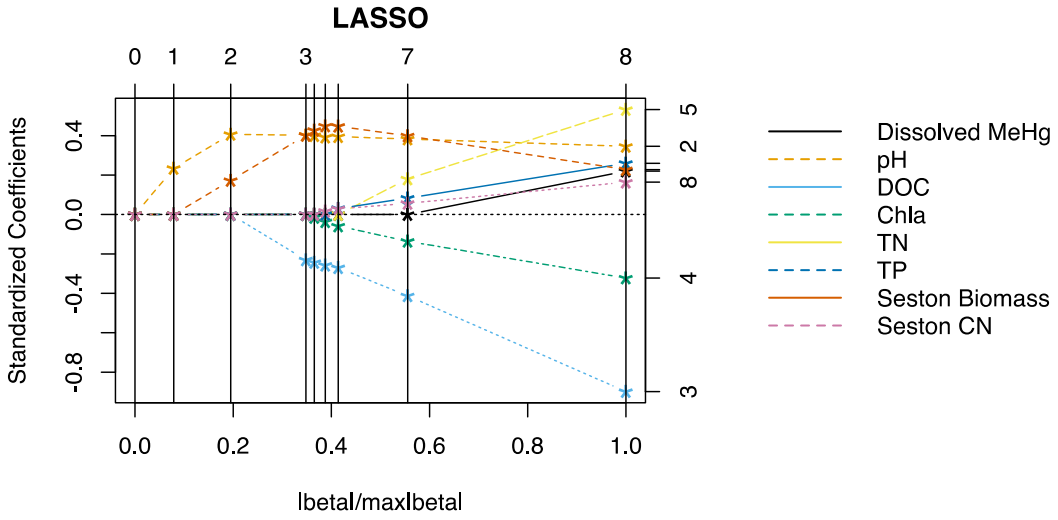

FIGURE S3: Path plots for Model 1 (Table 2) showing the standardized regression coefficients of independent variables included in LASSO models of seston MeHg concentrations across all lakes (N = 43).

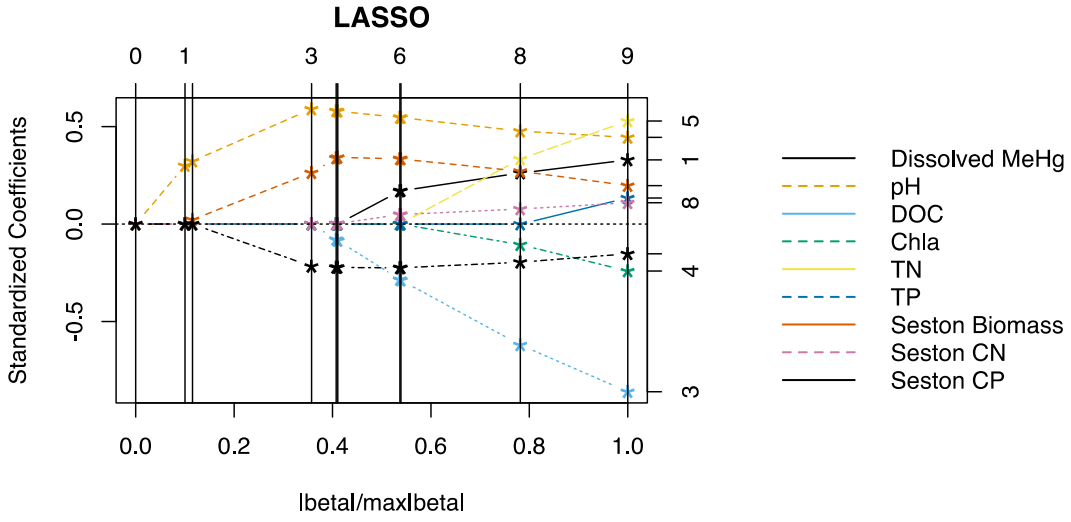

FIGURE S4: Path plots for Model 2 (Table 2) showing the standardized regression coefficients of independent variables included in LASSO models of seston MeHg concentrations across all lakes (N = 35).

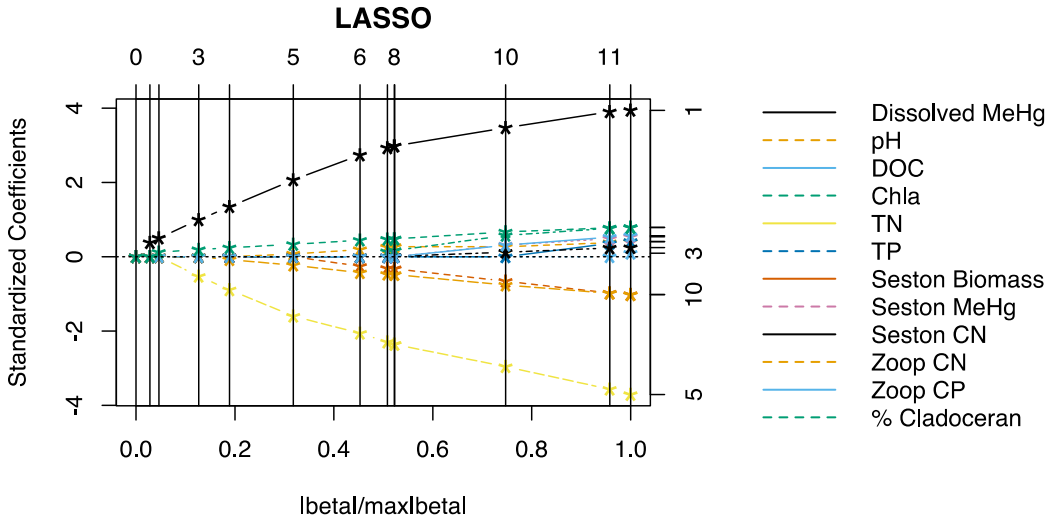

FIGURE S5: Path plots for Model 3 (Table 2) showing the standardized regression coefficients of independent variables included in LASSO models of bulk zooplankton MeHg concentrations across all lakes (N = 40).

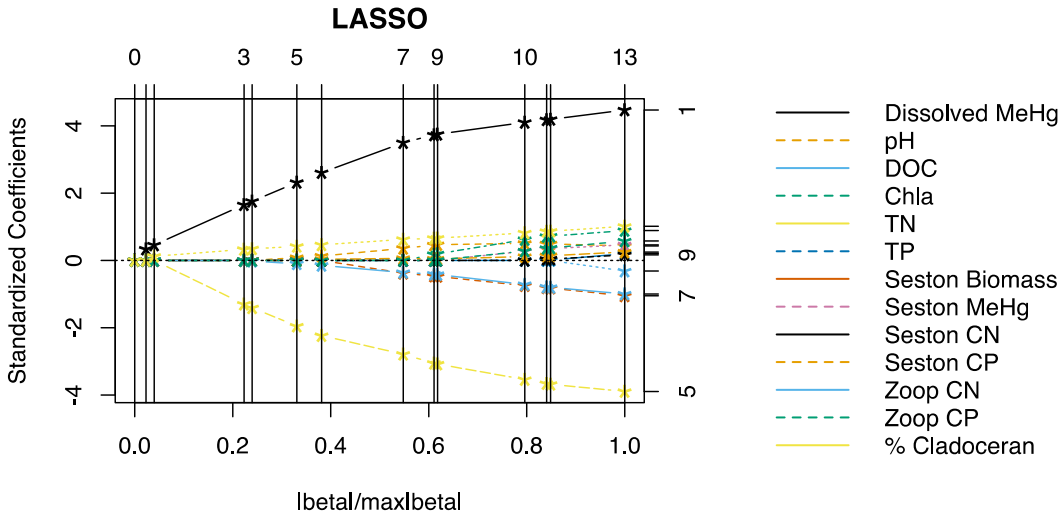

FIGURE S6: Path plots for Model 4 (Table 2) showing the standardized regression coefficients of independent variables included in LASSO models of bulk zooplankton MeHg concentrations across all lakes (N = 32).

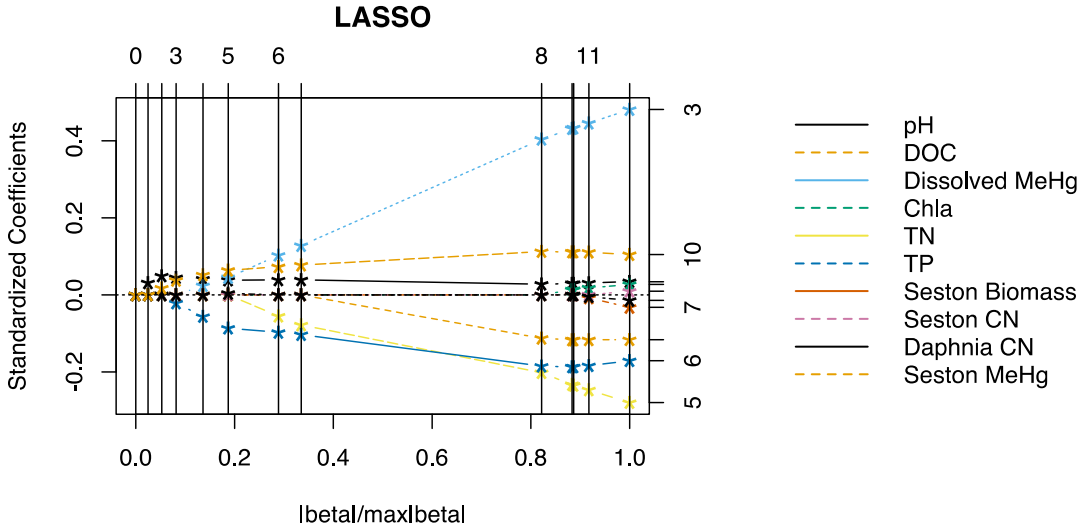

FIGURE S7: Path plots for Model 5 (Table 2) showing the standardized regression coefficients of independent variables included in LASSO models of *Daphnia* MeHg concentrations across all lakes (N = 23).

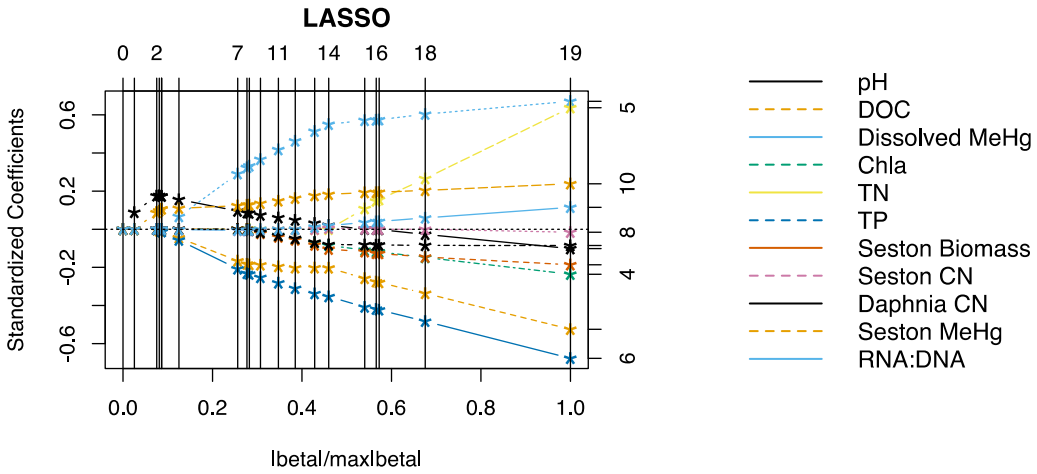

FIGURE S8: Path plots for Model 6 (Table 2) showing the standardized regression coefficients of independent variables included in LASSO models of *Daphnia* MeHg concentrations across all lakes (N = 18).

CHAPITRE 3: Bioaccumulation de terres rares dans les écosystèmes marins, terrestres, et d'eau douce dans l'est de l'Arctique canadien

Rare earth elements in freshwater, marine, and terrestrial ecosystems in the eastern Canadian Arctic

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Abstract. Few ecotoxicological studies exist for rare earth elements (REEs), particularly field-based studies on their bioaccumulation and food web dynamics. REE mining has led to significant environmental impacts in several countries (China, Brazil, U.S.), yet little is known about the fate and transport of these contaminants of emerging concern. Northern ecosystems are potentially vulnerable to REE enrichment from prospective mining projects at high latitudes. To understand how REEs behave in remote northern food webs, we measured REE concentrations and carbon and nitrogen stable isotope ratios (∂^{15}N, ∂^{13}C) in biota from marine, freshwater, and terrestrial ecosystems of the eastern Canadian Arctic (N=339). Wildlife harvesting and tissue sampling was partly conducted by local hunters through a community-based monitoring project. Results show that REE generally follow a coherent bioaccumulation pattern for sample tissues, with some anomalies for redox-sensitive elements (Ce, Eu). Highest REE concentrations were found at low trophic levels, especially in vegetation and aquatic invertebrates. Terrestrial herbivores, ringed seal, and fish had low total REE levels in muscle tissue ($\sum$REE for 15 elements <0.1 nmolg^{-1}), yet accumulation was an order of magnitude higher in liver tissues. Age- and length-dependent REE accumulation also suggest that REE uptake is faster than elimination for some species. Overall, REE bioaccumulation patterns appear to be species- and tissue-specific, with limited potential for biomagnification. This study provides novel data on the behaviour of REE in ecosystems and will be useful for environmental impact assessment of REE enrichment in northern regions.

Environmental Impact Statement. Rare earth elements (REEs) are contaminants of emerging concern and are increasingly exploited around the globe for use in the high-tech sector. Knowledge of the fate of REEs and their impact on natural ecosystems is needed as emissions to the environment increase. Field-based studies on REE bioaccumulation and food web transfer are rare, especially in remote northern ecosystems which are vulnerable to REE enrichment from mining. This study examined species- and tissue-specific REE bioaccumulation patterns in marine, freshwater and terrestrial ecosystems, focusing on wildlife of importance to Northerners. We found that REEs bioaccumulate more in biota near the base of the food chain (plants, invertebrates) with limited biomagnification potential. This pattern was consistent across all REEs examined. This study provides critical new information on the bioaccumulation of REEs in food webs of vulnerable northern environments.

Introduction

Rare earth elements (REEs) are a chemically-similar group of emerging contaminants, which includes the 15 trivalent lanthanide metals, as well as scandium (Sc) and yttrium (Y). Not particularly rare, REEs are increasingly exploited for critical uses in high-tech industries, including electronics, medicine, clean energy, and agriculture (Gonzalez et al., 2014, Barry and Meehan, 2000). REEs are used for magnets, metal alloys, catalysts, fertilisers and ceramics, as well as for eutrophication management in freshwaters (Copetti et al., 2016, GC, 2014). Increasing emissions have led to significant release of REEs into the environment, yet knowledge of their fate and impact on natural ecosystems is limited. Most existing studies use REEs to trace geochemical processes in natural systems and few studies have examined the ecotoxicology and/or environmental impacts of these metals. The majority of existing REE ecotoxicity studies are laboratory-based, whereas field measurements of natural background levels, environmental behaviour and bioaccumulation potential in food webs are extremely rare (Weltje et al., 2002, Yang et al., 1999).

Mining and processing of rare earth ore is known to have major environmental impacts, mainly the production of atmospheric pollution, acidic wastewater, and radioactive tailings (Zhou et al., 2015, Liang et al., 2014, EPA, 2012). However, significant REE enrichment in water, soil and vegetation near mining sites in China has also led to recent concerns about the environmental impacts of REEs themselves (Li et al., 2010, Wang et al., 2010, Zhang et al., 2010, Liang et al., 2005). Rivers located near rare earth mines in the Yellow River region of China, for example, have dissolved REE concentrations three orders of magnitude higher than unperturbed rivers (Liang et al., 2014). A lack of key ecotoxicological data renders environmental impact assessment of REEs difficult and hinders the creation of environmental guidelines or thresholds (Gonzalez et al., 2014). REEs were historically considered as low risk to environmental or human health because they are lithophilic, hence largely insoluble and immobile (i.e. not bioavailable) in soils (Šmuc et al., 2012, Hedrick, 1995). In fact, REEs have been widely used in plant fertilizers and feed additions for farm animals in China and Europe, showing positive physiological effects (Pang et al., 2002) On the other hand, recent laboratory studies show the potential for both bioaccumulation and toxicity of REEs in many species, including microorganisms and phytoplankton (Balusamy et al., 2012, Wang et al., 2012, Tai et al., 2010),

aquatic plants (Xu et al., 2012, Weltje et al., 2002), terrestrial plants (Brioschi et al., 2012, Thomas et al., 2014, Turra et al., 2011, Hu et al., 2004, Sneller et al., 2000), terrestrial and aquatic invertebrates (Li et al., 2010, Zhang et al., 2010, Borgmann et al., 2005, Barry and Meehan, 2000), as well as in fish and humans (Mayfield and Fairbrother, 2015, Cui et al., 2012, Zaichick et al., 2011, Hongyan et al., 2002, Chen et al., 2001). REEs may therefore follow a hormetic dose response with positive physiological effects at low doses (e.g. increased chlorophyll or growth) and toxic effects at high doses (Pagano et al., 2015). Based on one study, maximum permissible concentrations for REEs range from 1.8 to 22 ugL^{-1} in fresh surface waters and from 1.8 to 18.8 gkg^{-1} d.w. in lake sediments (Sneller et al., 2000). However, further research is required to better estimate toxicity thresholds and long-term effects of REE exposure, as toxicity can occur for any metal accumulating to high levels in organs via long-term exposure (Haraguchi, 2004).

Rising demand for REEs, and decreasing export from China, have recently led to many new REE mining ventures around the world (EPA, 2012). Although no REE production or refining currently occurs in Canada, more than 200 exploration projects are under development, including 11 in an advanced stage. The majority of these projects are found in northern Canada, including five projects in northern Quebec and two in the Northwest Territories (GC, 2014). Accelerated warming combined with significant pressure to exploit natural resources mean that Arctic ecosystems are vulnerable to rapid industrial and environmental change. Climate change is occurring more rapidly at high latitudes and has been shown to affect contaminant cycling, including for metals (Vonk et al., 2015). It is therefore important to consider the environmental impacts of REE enrichment at high latitudes, as anthropogenic REE enrichment near mining sites could lead to significant REE accumulation in biota. However, there are only limited data available for REE environmental behaviour in northern ecosystems.

The aim of this field-based study was to evaluate the potential for bioaccumulation and trophic transfer of REEs in freshwater, marine, and terrestrial food webs of the eastern Canadian Arctic. Biological samples were collected in 2012, 2014 and 2015 from marine, terrestrial, and freshwater ecosystems near Kuujjuarapik-Whapmagoostui (Nunavik, Quebec). Wildlife harvesting and tissue sampling were conducted by local hunters through a community-based monitoring project. The objectives of this study were a) to assess REE levels in biota of different

trophic levels found in freshwater, marine and terrestrial ecosystems in the Arctic, focusing on taxa of importance to Northerners, b) to evaluate the species- and tissue-specific bioaccumulation of REEs in key taxa and c) to trace the trophic transfer of REEs within northern ecosystems using carbon and nitrogen stable isotope measurements of food web structure. Quantifying and tracing REE behaviour in these ecosystems will allow us to better evaluate the potential environmental impact of REE enrichment in the northern environment.

Materials and Methods

Study sites. Marine, freshwater (lakes and a river) and terrestrial ecosystems were sampled near Kuujjuarapik-Whapmagoostui (K-W), a community located in the Subarctic taiga in Nunavik, Quebec, Canada (55° 16' 30'' N, 77° 45' 30'' W). This region encompasses marine, freshwater and terrestrial ecosystems of importance to Northerners, including southeastern Hudson Bay, the Great Whale River, and numerous coastal lakes underlain by discontinuous, scattered permafrost (Bhiry et al., 2011). All samples were collected within a relatively restricted geographic radius (< 70 km) around K-W. No documented rare earth element deposits or exploitation activities currently exist in this region and our study provides baseline environmental data for REE in the eastern Canadian Arctic.

Lake sampling. In 2012, replicate samples of benthic invertebrates (N = 17), zooplankton (N = 19), and fish (N = 60) were collected from 8 lakes for the analysis of REE concentrations and stable isotope ratios of nitrogen and carbon (∂15N, ∂13C). Bulk zooplankton were sampled by horizontal surface hauls with a large net (1 m diameter, 200 µm mesh). Benthic invertebrates were sampled along the shoreline with a kick net (500 µm mesh), or by Ekman grab for deeper water, and were live-sorted into broad taxonomic groups without depuration. Undepurated animals (i.e. with gut contents) were used in this study because gut contents are consumed by predators. However, the reported REE concentrations in benthos (and possibly zooplankton) should be considered upper limits, as a recent publication reported an average ratio of 1.75 ± 0.05 REEs in undepurated versus depurated invertebrates (Amyot et al., 2017). Different species of benthic invertebrates were pooled together to compare broad taxonomic groups, including amphipods, caddisflies, anisoptera, and corixidae. Brook trout (*Salvelinus fontinalis*), the only

large-bodied fish species at these sites, were captured with a gill net from 5 of the 8 lakes. Ancillary data collected for the brook trout included total length, fork length, mass, sex and age (estimated by annuli counting of otoliths using the crack and burn method). Surface water and surface sediment (top 1-2 cm, by Ekman grab) were also collected for REE analysis from an inflatable raft with an electric motor. Ultra-trace sampling techniques were used to quantify REE concentrations.

Marine, river, and terrestrial sampling. In 2014 and 2015, wildlife harvesting by hunters was organized by the Sakkuq Landholding Corporation of Kuujjuarapik. Local hunters collected tissue samples from biota in Hudson Bay, the Great Whale River and terrestrial ecosystems near K-W. Species were chosen to reflect taxa of importance to local communities as well as a variety of representative trophic levels and ecosystems. The skills, experience and traditional knowledge of hunters were critical for the animal collections, particularly related to the distribution and seasonal movements of local populations. Record sheets were used to record data on the location, size, and sex of harvested animals. Ancillary data collected for ringed seals included length, and axial and maximum girth.

Marine sampling included tissue collection (muscle, liver) of a top marine predator, the ringed seal (N = 23, *Phoca hispida*), as well as a benthic molluscivore, the common eider (N = 16, *Somateria mollissima*). Marine invertebrates were also collected from coastal sites: a planktonic feeder, the blue mussel (N = 9 pools of 10 individuals, *Mytilus edulis*, all tissues without shell) and a benthic feeder, the sea urchin (N = 5 pools of 10 individuals, order Echinoida, gonads). For the river samples, anadromous freshwater fish were collected from the mouth of the Great Whale River, including brook trout (N = 6, *Salvelinus fontinalis*) and lake whitefish (N = 22, *Coregonus clupeaformis*). Terrestrial sampling included tissue collection (muscle, liver) from three terrestrial herbivores: snowshoe hare (N = 6, *Lepus americanus*), willow ptarmigan (N = 9, *Lagopus lagopus*), and caribou (N = 6, *Rangifer tarandus*). Sampled terrestrial vegetation included above-ground tissues (stems and leaves) from 1) vascular plants (N = 8): crowberry (*Empetrum nigrum*), Labrador tea (*Rhododendron* sp.), and bearberry (*Arctostaphylos alpina*), and 2) non-vascular plants (N = 9): lichens (fruticose type, ground and tree) and moss (*Spagnum* sp.). The surfaces of plant samples (e.g., leaves) were not cleaned with ultra-pure water and therefore, REE measurements represent both internal accumulation and external adsorption on

surfaces, which is relevant for estimating metal exposure to grazing herbivores. Terrestrial vegetation was pooled together into either vascular or non-vascular plants for comparison within ecosystems.

Rare earth element analysis. Sediment and biological samples were stored at -20°C, freeze-dried, and homogenized before analysis for REEs by inductively coupled plasma mass spectrometry (ICP-MS, Perkin-Elmer NexION 300x) following microwave digestion. From 0.07 - 0.20 g (median 0.10 g) of sample was weighed into pre-washed Teflon tubes (HNO_3 45%, HCl 5%) and digested with 3 mL of trace metal grade HNO_3 (70%) for 15 minutes at 170°C. Two more 15 minute cycles were completed after adding 0.5 - 1.0 mL of OPTIMA grade hydrogen peroxide (30% H_2O_2) before each cycle. Digested samples were diluted with ultra-pure water (MilliQ, 18.2 MΩ•cm) to a volume of 50 mL and then re-diluted (1:2) into trace metal clean polypropylene tubes. Surface water samples were filtered on a clean Teflon filtration tower (HCl 10%) and preserved with HNO_3 (2%) before analysis. Vegetation samples were digested using longer cycles (30 min) with more H_2O_2 (1.0 mL each cycle) to permit a more complete digestion of tough plant material. Samples with low biomass (benthic invertebrates, 0.005 - 0.015g) were digested over a longer period at a lower temperature (room temperature for 24h, hot plate for 2h at 80°C) using equivalent volumes of HNO_3 (70%) and H_2O_2 and diluted to 10 mL with ultra-pure water.

ICP-MS detection limits were sufficiently low (0.0001 - 0.0022 $nmolg^{-1}$) to quantify samples with low REE concentrations (Supporting Information, Table S1). Detection limits were calculated as three times the standard deviation of 10 blanks. REE digestions included analytical blanks and appropriate reference standards, including sediment (STSD-1, stream sediment, CCRMP, CANMET), animal tissues (BCR 668 mussel tissue, IRMM) and plants (BCR 670 aquatic plant, IRMM). Average uncertainty of the method was ± 10% for samples with high concentrations and ± 40% for samples with low concentrations close to detection limits (calculated as the coefficient of variation or CV). Average (min-max) recovery of reference material was 87% (79 - 101%) for animal tissue, 84% (67 – 117%) for plant tissue, and 70% (40 – 99%) for sediment (SI Table S2). These values are consistent with average recoveries reported in the literature (Mayfield and Fairbrother, 2015, Dolegowska and Migaszewski, 2013, Weltje et al., 2002). It is important to note that sediment certified values are classified as “total”

concentrations and use multi-acid dissolution (HNO_3, HF). Some of the variability in analytical recovery for sediments could be explained by the less aggressive or "partial" extraction methods used in this study to estimate the labile, bioavailable REE concentration in samples (Snape et al., 2004).

Stable isotope analysis. Dry sediment and biological samples were weighed into tin capsules and analyzed for stable isotope ratios ($\delta^{13}C$, $\delta^{15}N$) using an elemental analyser interfaced with an isotope ratio mass spectrometer (IR-MS, Thermo Delta Advantage) at the G.G. Hatch Lab (U. of Ottawa). Samples were pooled in the same manner as for REE analyses. Only the muscle tissues from the vertebrate samples were analysed for stable isotopes. Only $\delta^{15}N$ values of sediments were analyzed because samples were not acidified to remove carbonates. Stable isotope ratios are reported in Delta (δ) notation, the units are parts per thousand (‰) and defined as $\delta X = ((R_{sample}-R_{standard}))/R_{standard}) \times 1000$ where X is ^{15}N or ^{13}C, and R is the ratio of the abundance of the heavy to the light isotope. For freshwater lakes, nitrogen stable isotope ratios ($\delta^{15}N$) were adjusted for among lake differences in baseline values using $\delta^{15}N$ values from lake sediment. The adjusted value ($\delta^{15}N_{adj}$) allows for comparison between lakes by accounting for variation in baseline $\delta^{15}N$ across different ecosystems (Cabana and Rasmussen, 1996). Sediment $\delta^{15}N$ values varied from -0.4 to 2.2 between the sampled lakes and raw $\delta^{15}N$ values are shown in Table S5. For marine samples, baseline $\delta^{15}N$ signatures were not adjusted as samples were collected from the same area. Quality assurance included triplicate analyses of an internal standard (analytical precision of 0.2 ‰) and duplicate analyses of 10% of samples.

Data handling. In this study, 15 of the 17 REEs were used to calculate the sum of all detected REE ($\sum$REE) in nmol/g (biota and sediments) or nmol/mL (water). Promethium (Pm) was not included as it does not occur naturally and results for scandium (Sc) were excluded due to analytical interference. Previous studies have found that Sc ($^{45}Sc^{+}$) had false high readings due to interference with sample organic content (Barton and Miskelly, 2006, Reed et al., 1994) and that Sc is not strongly correlated with other REE (Mayfield and Fairbrother, 2015). Detection frequencies were variable for the 15 REEs and different taxonomic groups in this study. Non-detected elements were often from the heavy REE group, except for Y which was the most widely-detected element (90% of samples). Y, La, and Nd were detected in over 80% of samples, whereas Tm and Lu were detected in < 50% of samples. 100% of elements were

detected in the aquatic invertebrate and plant samples, but low detection frequencies (< 30% of elements) were found in samples from aquatic vertebrates (seal, eider fish) (SI Table S3).

For data analysis, we divided REEs into two groups based on physicochemical parameters, the light REEs (LREE) from La-Gd and the heavy REEs (HREE) from Tb-Lu and Y. Other authors divide REE into three groups and the specific elements placed in each group vary between studies (Mayfield and Fairbrother, 2015, Long et al., 2010, Sneller et al., 2000). Geometric means (the antilog of the mean of the logarithmic values of the data set) were used to calculate average ∑REE within taxonomic groups to measure central tendency with high intra-group variation. Analytical blank values were subtracted from the sample values for each element. Sample measurements of REEs below detection limits (<DL) were estimated as the concentration of half the detection limit value, except when applying normalisation as in Fig. 2 and Figures S2-S3. All tissue concentrations are presented on a dry-weight basis.

To graphically compare REE abundances from different samples, individual element concentrations were normalised based on their geological abundance using a standard (Post Archean Australian Shale or PAAS) (Pourmand et al., 2012) and using mean sediment concentrations. Normalisation eliminates the Oddo-Harkins effect (or saw-tooth pattern) and deviations from a horizontal line after normalization indicate natural or anthropogenic enrichments (or depletions) of elements (or anomalies). Eu and Ce anomalies (∂Eu and ∂Ce) were calculated by $\partial Eu = Eu_{PAAS} / (Sm_{PAAS} \times Gd_{PAAS})^{0.5}$ and $\partial Ce = Ce_{PAAS} / (La_{PAAS} \times Pr_{PAAS})^{0.5}$ where PAAS indicated Post Archean Shale Standard normalized values.(Yang et al., 2016)

Statistical analyses. All statistical analysis was performed in R version 3.3.1 (R Core Development Team, 2016). Significance levels were $\alpha < 0.05$. Concentration data (muscle, liver) for REEs (individual elements and ∑REE) were $\log_{10}$ transformed to reduce skewness and the influence of outliers. Stable isotope, age, and size (length, girth) values followed normal distributions. Pearson product-moment correlation coefficients were calculated to assess the relationships between the 15 REE concentrations in tissue samples (R: *corrplot* package). Significant values for Pearson's r were calculated with Holm correction to control for the experiment-wise error rate. Pearson's correlation analysis was conducted to assess the relationship between LREE and HREE concentration using all available data (N=339). Comparisons of $\log_{10}$-ΣREE concentrations between different taxonomic groups and tissue

types for each distinct ecosystem (marine, terrestrial and freshwater) were conducted using Welch's analysis of variance (ANOVA) and Games-Howell post-hoc tests. This is a nonparametric approach that does not assume equal variance or sample size between groups (R: *userfriendlyscience* package).

Linear mixed effects model analyses (LMM) were performed on brook trout (lakes only, N=58) and ringed seal (N=23) datasets using R package *lme4* (Bates et al., 2015). This approach evaluated whether tissue REE concentration varied with animal size and sex, while controlling for habitat (lake ID) and year collected. Only liver concentrations were used in the models as muscle concentrations were close to detection limits. Variables were standardized (centered, reduced) and were excluded from models when highly collinear (Pearson's product-moment correlation coefficients > 0.8). Random intercepts, slopes and interaction terms were tested and removed when removal improved (or did not significantly change) model fit using the Akaike information criterion (AICc, R: *AICcmodavg* package). A brook trout outlier was excluded to improve model fit. Marginal R^2 (variance explained by fixed factors) and conditional R^2 (variance explained by fixed and random effects) were obtained from the models fitted through restricted maximum likelihood analysis (Nakagawa and Schielzeth, 2013). Model validation for all linear models was performed by visual inspection of residual plots, which did not show deviation from homoscedasticity or normality.

Results and Discussion

REE behaviour in northern ecosystems. Concentration patterns show that all 15 REEs are highly correlated with each other in tissue samples. Significant positive correlations were found between many elements (r = 0.94 to 1.0 for vegetation and invertebrates; r = 0.2 to 1.0 for vertebrate muscle and liver tissues; $p < 0.05$, Fig. S1). Correlation analysis of LREE versus HREE concentrations (log-scaled $nmolg^{-1}$) in biota showed that concentrations of heavy and light elements were strongly and positively correlated in tissues (Fig 1). Correlation coefficients were significant for vertebrate muscle and liver tissues (r = 0.81, $p < 0.001$), for plants and invertebrates (r = 0.97, $p < 0.001$) and for the combined datasets (r = 0.90, $p < 0.001$). Almost all individual samples were found below the 1:1 slope line (dotted line) on the scatterplot,

demonstrating that LREE were consistently more concentrated than HREE in tissues (Fig. 1). On average, LREE comprised 86 ± 19% (mean ± SD) of the total REE content in biota. The dominant individual REEs (>10% of ∑REE) found in sampled taxa were La, Ce, Nd and Y.

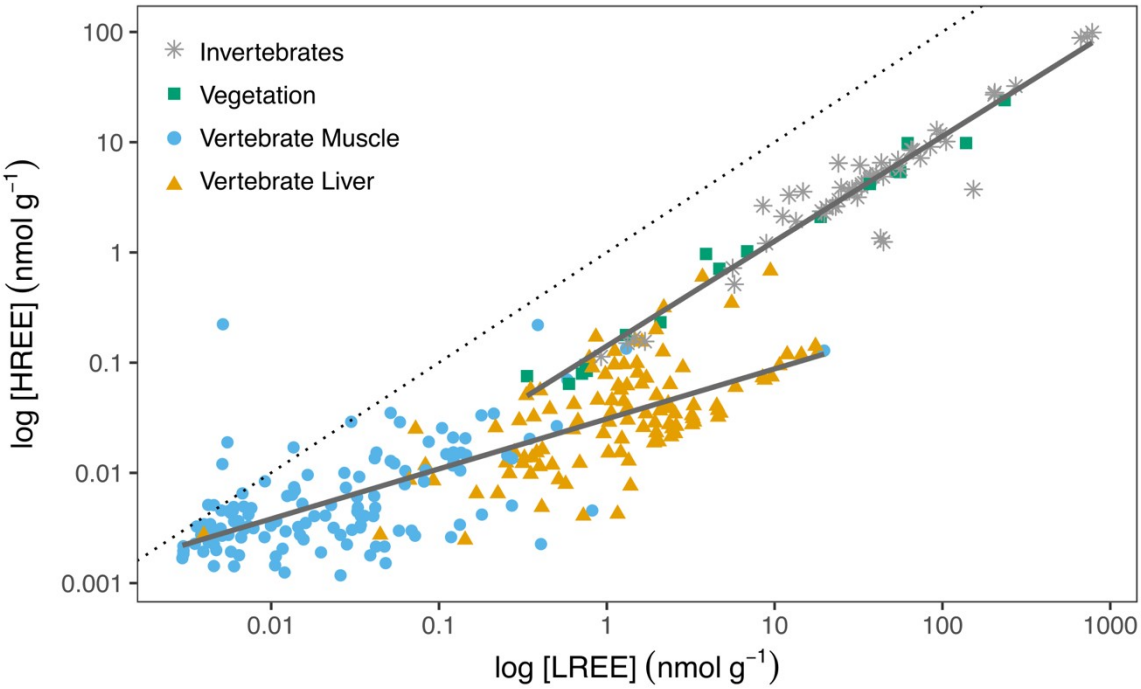

FIGURE 1: Relationship between LREE and HREE concentrations (log-scaled nmolg^{-1}) in biota (N=339) from all ecosystems (vertebrate muscle and liver: N = 256, r = 0.81, p < 0.001, invertebrates and vegetation: N = 69, r = 0.97, p < 0.001). Dotted line shows 1:1 slope. Points show individual samples of invertebrates (marine, freshwater), vertebrate liver and muscle (marine, freshwater, terrestrial), and vegetation (terrestrial: vascular plants, moss, lichen).

REEs are known to be a strongly coherent and predictable group of elements in surface waters, soils and rocks based on chemical similarities (trivalent, electropositive, poorly soluble) and geochemical behaviour. However, information is scarce on REE behaviour when undergoing bioaccumulation in living organisms. Most previous studies have focused only on bioaccumulation patterns of 3 or 4 elements (mainly LREE) (Gonzalez et al., 2014). By examining all 15 REEs, we have identified a relatively uniform trend of REE bioaccumulation among a wide variety of taxonomic groups in northern ecosystems. Due to strong covariance

between all 15 REEs, the ∑REE (sum of all REEs) will be used in the main text to display trends in REE bioaccumulation. Detailed individual element data are available in the Supporting Information (SI). Different slopes for LREE vs. HREE concentrations between taxonomic groups (Fig. 1) may be due to analytical variability at low concentrations (e.g. in vertebrate muscle) or may indicate finer scale differences in REE bioaccumulation patterns between vertebrate tissues and invertebrates/plants.

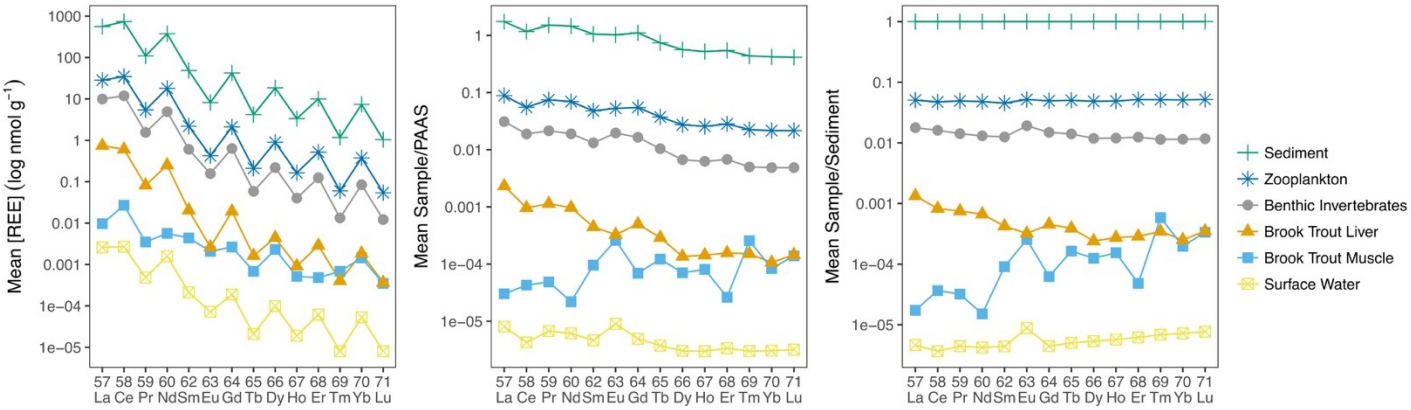

FIGURE 2: Concentration of REEs versus atomic number for biotic and abiotic component from freshwater ecosystems. Left panel shows mean [REE] (log-scaled geometric means: nmol/g for biota and sediments; nmol/mL for water) showing the pattern of log-linear or saw-tooth decrease with atomic number. Middle panel shows PAAS-normalized REE concentrations (log-scaled geometric means: $nmolg^{-1}$/PAAS $nmolg^{-1}$). Right panel shows sediment-normalized REE concentrations (log-scaled geometric means: $nmolg^{-1}$/sediment $nmolg^{-1}$). Points show element means for each taxonomic group, water and sediment. Samples below detection limits were excluded from figure.

REE bioaccumulation in biota typically display a saw-tooth pattern or "REE pattern" following Oddo-Harkins rule (Weltje et al., 2002). This pattern is due to a) log-linear decrease in concentration with atomic number and b) higher concentrations in even-numbered elements over adjacent odd-numbered ones. Finding this pattern mirrored in tissues (Fig. 2, Fig. S2 left panels) indicates that REE bioaccumulation mirrors REE crustal abundance, which are strongly conserved in soils, sediments, and water relative to the Earth's crust. The normalisation of individual element concentrations to a shale standard (PAAS) can reveal differences in the relative abundance of individual elements. For most taxa, little deviation from a horizontal line

indicates that bioaccumulation patterns were relatively uniform across the REE series in our dataset (Fig. 2 middle panel, SI Fig. S2 and S3). Even less deviation from the horizontal was apparent with normalisation to sediment concentrations for freshwater ecosystems (Fig. 2, right panel). Normalised data for vertebrate muscle tissues showed a lot of scatter and should be interpreted with care because concentrations were highly variable and close to detection limits. However, PAAS and sediment-normalised liver concentrations showed a clear downward slope with LREE enriched relative to HREE (Fig. S3). This trend has also been noted in human organs (aorta, liver and bone) but the mechanisms driving this pattern remain uncertain (Chen et al., 2001).

Positive Eu anomalies (∂Eu) were detected for surface water samples (1.9 ± 0.83) and some benthic invertebrates (1.3 ± 1.2), yet not for sediment or zooplankton (geometric mean ± SD) (Fig. 2, right panel). Positive anomalies (values > 1) indicate increased uptake of the element relative to other REEs. The ∂Eu anomaly may be linked to the reduction of Eu^{3+} to the more mobile Eu^{2+} under anoxic conditions in the water column (Weltje et al., 2002), which may then be transferred along the food web to benthic invertebrate (but not zooplankton or fish). Strong positive ∂Eu were also found for all vascular plants (Fig. S3). However, despite many studies reporting similar positive ∂Eu in vegetation samples (Censi et al., 2017, Chiarenselli et al., 2001), it is possible that these anomalies may be analytical artifacts from BaO interference on the ICP-MS (Stille et al., 2009). Negative Ce anomalies (∂Ce) ranging from 0.3 to 0.8 were detected in many of the aquatic samples (including lake surface water) possibly indicating oxidation of Ce^{3+} to the less soluble Ce^{4+} in these systems (SI Fig. S4).

Novel trends were found between carbon stable isotope ratios ($\partial^{13}C$, ‰) and Ce anomalies (∂Ce) for brook trout from sample lakes. ∂Ce for brook trout were all negative (<1) indicating decreased uptake of this element relative to other REEs, likely related to negative ∂Ce values in the water or sediments of sample lakes. A significant positive correlation was found for $\partial^{13}C$ and ∂Ce values in brook trout liver ($N=60$, $R^2_{adj} = 0.67$, $p < 0.001$) (SI Fig. S4). $\partial^{13}C$ analysis can be used as a proxy for food carbon source (i.e benthic or pelagic) but also varies with lake size and productivity (Post, 2002). This positive correlation appears to be driven by differences in baseline $\partial^{13}C$ values between the 5 sample lakes rather than trends within lakes, indicating that REE bioaccumulation may vary with lake productivity (SI Fig. S4). Overall, the exact

mechanisms driving REE anomalies in biota remain largely unknown and more research is needed to better understand the relationship between geology, internal physiological processes, food sources and ecosystem status on REE bioaccumulation.

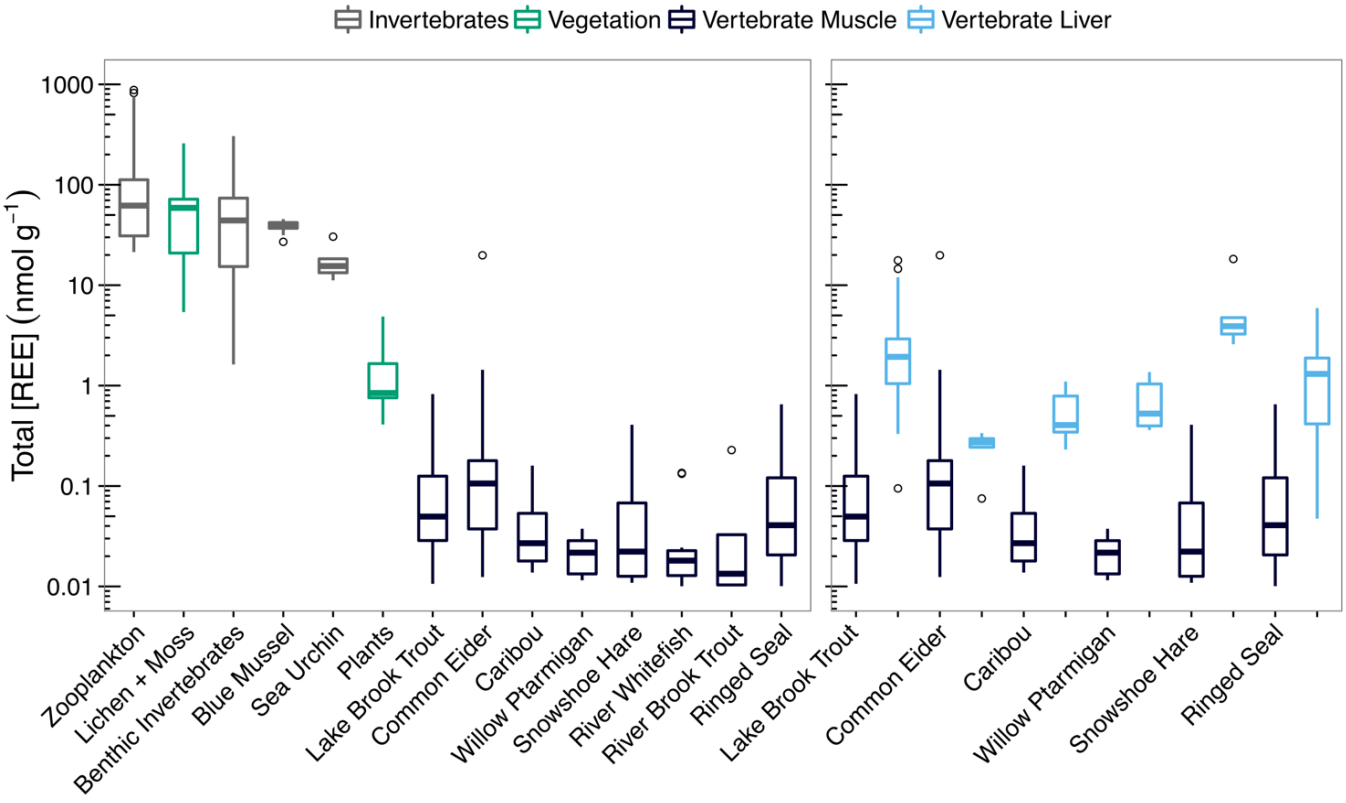

FIGURE 3: Boxplot of ∑REE concentrations (log-scaled nmolg^{-1}) showing median ± SD; dots are outliers (N = 5 - 60 see Table S4). Left panel shows ∑REE concentrations in descending order for each taxonomic group (only vertebrate muscle tissues). Right panel shows vertebrate ∑REE concentrations in muscle compared to liver tissues from the same animals. Differences in mean ∑REE between taxonomic groups were compared using Welch's ANOVA with Games-Howell post-hoc tests.

REE bioaccumulation and biomagnification. Little information exists on REE concentrations in biota from natural ecosystems. In this study, mean ∑REE concentrations varied widely from 0.013 to 103 nmolg^{-1} dry weight (geometric mean or GM) (Fig. 3, SI Table S4 and S5). The highest ∑REE concentrations were found in biota at the base of the food web, especially in lichen/moss (42 ± 81), marine invertebrates (sea urchins 17 ± 7.6; blue mussels 38 ± 5.9), and

freshwater invertebrates (benthic invertebrates 33 ± 85, zooplankton 103 ± 484) (GM ± SD, $nmolg^{-1}$). Analysis of variance between taxa from the same ecosystem showed that biota at the base of the food web (vegetation, invertebrates) had significantly higher ∑REE concentrations than vertebrate muscle samples from the same ecosystem (Welch's ANOVA, $F = 108.3$, $p < 0.001$). These differences were less pronounced when comparing the base of the food web to vertebrate liver concentrations, yet were still significant for marine and freshwater systems (Welch's ANOVA, $p < 0.001$). In the terrestrial environment, vertebrate liver concentrations were not significantly different than REE levels measured in vascular plants (Welch's ANOVA, $F = 63.39$, $p > 0.05$), yet were lower than ΣREE values from pooled lichen/moss. Lichen/moss samples were greater than 35 times more concentrated than in vascular plants from the same general area (GM of 41.5 versus 1.12 $nmolg^{-1}$) (Welch's ANOVA, $F = 81.8$, $p < 0.001$) (Fig 3).

Vascular plants from this study had a mean ΣREE concentration of 1.12 $nmolg^{-1}$ or 0.15 $mgkg^{-1}$ (SI Table S5), which falls at the lower end of the range of previous reported values for above-ground tissue concentrations for the same 15 REE (0.06 to 1.6 $mgkg^{-1}$) (Censi et al., 2013, Chiarenselli et al., 2001, Markert and Zhang, 1991). Plants usually reflect the REE distribution and exchangeable (i.e. soluble) soil concentrations in substrate soils, with higher bioaccumulation in plants on low pH soils (Thomas et al., 2014). Previous studies showed that lichens accumulate two-fold higher concentrations of REEs than vascular plants (Anawar et al., 2012), whereas our results show that natural REE levels can be an order of magnitude higher for lichens (and moss). Unlike vascular plants, lichens accumulate elements from atmospheric deposition (rainfall, dust), which may be a pathway for greater REE bioaccumulation than the uptake of REEs by root systems in vascular plants (Chiarenselli et al., 2001). Moss uptake nutrients from atmospheric deposition and from soils, where acidic soil conditions may lead to higher bioavailability of these metals (Feng-Fu et al., 2004, Akagi et al., 2002, Wen et al., 2002). Sources of REEs for low-lying vegetation may also include the adsorption of dust particles and metals to external surfaces. One study found that REE levels in plant leaves versus the atmospheric dust trapped on leaf surfaces was similar for both concentration and composition (Censi et al., 2017).

Although it is known that REE are bioavailable to lichens and plants (Weltje et al., 2002, Hao et al., 1996, Yang et al., 1999), our results suggest that REE are also widely bioavailable to

aquatic invertebrates (both freshwater and marine). A handful of marine studies have previously reported relatively high levels (> 1.0 $mgkg^{-1}$) for individual REE in plankton (Strady et al., 2015), flying squid (Pernice et al., 2009), and scallops (Bustamante and Miramand, 2005), and two studies have previously measured elevated REE levels in freshwater invertebrates (Amyot et al., 2017, Weltje et al., 2002). Higher REE levels in invertebrates may be due to increased uptake and surface adsorption of metals to the carapace. Overall, vegetation and aquatic invertebrates should therefore be considered good bio-indicators of REE contamination (Bonnail et al., 2017).

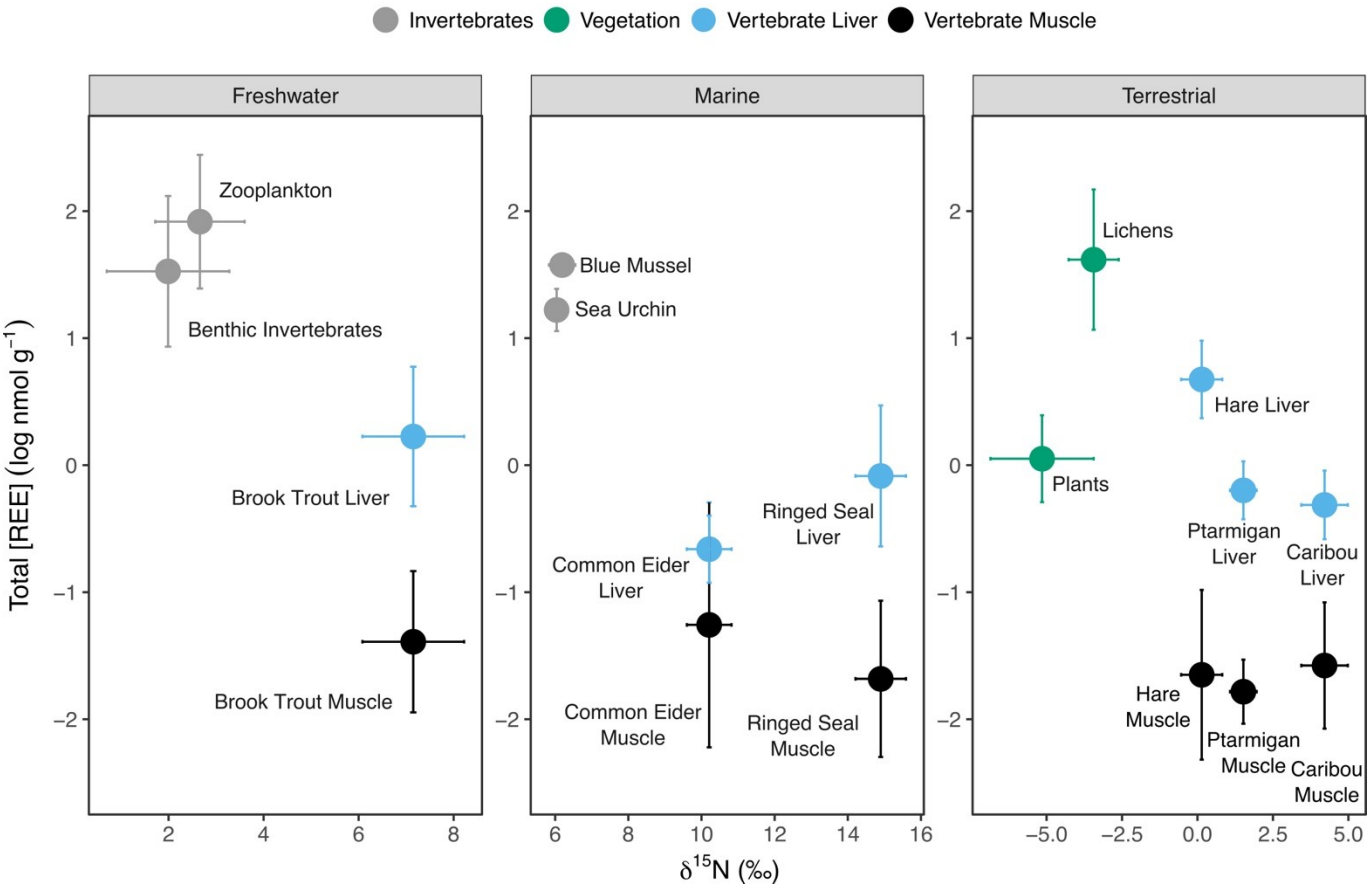

FIGURE 4: Relationship between mean ∂15N (‰) and mean ∑REE concentrations (log_{10} $nmolg^{-1}$) by taxonomic groups in freshwater (lakes only), marine and terrestrial ecosystems. Values shown are mean ± standard deviation. ∂15N values were adjusted for baseline ∂15N variation in freshwater lakes using ∂15N sediment values ($\partial 15N_{adj}$). Sample size (N) varies from 5 to 60 (Table S4).

Comparisons between REE concentrations and $\delta^{15}N$ showed that ∑REE decrease with increasing trophic level across marine, freshwater and terrestrial ecosystems (Fig. 4). When compared to lower trophic levels, ∑REE values were roughly an order of magnitude lower in vertebrate liver tissues and 2 orders of magnitude lower in muscle. A decrease in concentration with $\delta^{15}N$ demonstrates that there is limited potential for biomagnification of REEs in these northern ecosystems. Previous laboratory studies have shown that many REEs bioaccumulate (e.g. La, Ce, Pr, Nd, Sm, Eu, Gd) but do not appear to biomagnify within aquatic or terrestrial microcosms (Gonzalez et al., 2014, Weltje et al., 2002, Yang et al., 1999). Laboratory studies, however, may not accurately represent REE behaviour within natural ecosystems, because they are simplified systems within a limited range of parameters. To our knowledge, only three studies have measured REE levels in coexisting organisms found at different lower trophic levels within natural food webs (Amyot et al., 2017, Strady et al., 2015, Weltje et al., 2002). Our field-based research confirms the limited potential for REE biomagnification within three different northern ecosystems.

Tissue-specific REE bioaccumulation. Vertebrates from all ecosystems had REE muscle concentrations that were orders of magnitude lower than ∑REE concentrations in biota near the base of the food web (Fig. 3, right panel). Previous research has also found that REE are commonly not detected or found at trace levels in fish muscle (Yang et al., 2016, Mayfield and Fairbrother, 2015). Like fish, common eider, ringed seal, caribou, ptarmigan, and snowshoe hare in this study had low mean REE muscle concentrations, less than 0.1 $nmolg^{-1}$ (or 0.01 $mgkg^{-1}$). To the best of our knowledge, this is the first published dataset for REE concentrations in terrestrial and marine vertebrates (other than humans) (Zaichick et al., 2011). It is important to note that ∑REE concentrations in liver were consistently higher (approx. 4 - 200 times) than in muscles for all vertebrates (Fig. 3). These differences were statistically significant for willow ptarmigan, ringed seal and brook trout (lakes only) (Welch's ANOVA, $F = 43.5$, $p < 0.001$). Other comparisons were likely not significant due to small sample size and high inter-group variability (Welch's ANOVA, $p > 0.05$). Regression analysis comparing muscle and liver ∑REE concentrations of all vertebrates showed only a weak correlation, with very low explanatory power ($N=108$, $R^2_{adj} = 0.04$, $p = 0.03$). For brook trout from lakes, however, muscle and liver concentrations showed a weak positive correlation ($N=59$, $R^2_{adj} = 0.13$, $p < 0.01$).

Determining the primary organs where REEs accumulate is important for understanding the potential modes of toxic action of these contaminants of emerging concern. Previous studies on aquatic vertebrates have similarly shown that REEs are more concentrated in internal organs (liver, kidney, intestine, gills) compared to muscle (Amyot et al., 2017, Copetti et al., 2016, Mayfield and Fairbrother, 2015, Pernice et al., 2009, Bustamante and Miramand, 2005). For a marine squid, however, REE concentrations did not significantly differ between organs and muscle (Pernice et al., 2009). There is currently little available information on the cellular mechanisms of tissue-specific REE bioaccumulation. Studies on humans have shown that our livers are often enriched in REEs and associated with proteins in intracellular complexes (Chen et al., 2001). REEs have a strong affinity for the mineral and organic components of the skeleton (Vidaud et al., 2012). Molecular level studies are clearly needed to identify common modes of action and the biochemical effects of REEs. Future research should evaluate REE concentrations in internal organs and whole organism concentrations (including bones) as muscle concentrations may not provide accurate estimates of REE exposure.

Size and sex-dependent REE bioaccumulation. For ringed seal, no evidence was found for an effect of sex (fixed effect) or year of collection (random effect) on liver REE concentrations. Seal age was not measured. A low sample size and unbalanced design may contribute to the lack of an effect in this model because a small number of female seals were sampled (N = 6). The best fit model was a simple linear regression with seal length as a significant predictor of liver REE concentration (logREE ~ Length, $R^2_{adj} = 0.51$, $p < 0.001$) (Fig. 5). Seal girth (axial, total) was highly collinear with seal length ($r = 0.90$) and was also positively correlated with liver REE concentration (logREE ~ Girth, $R^2_{adj} = 0.61$, $p < 0.001$).

For brook trout, there was a statistically significant relationship between age, sex and liver REE concentration (Fig. 5). The best fit LMM included the fixed effects (sex, age) and a random intercept (lake ID) (logREE ~ Sex + Age + (1|Lake)). Fixed effects explained 25.0% of the variation in liver REE concentration (marginal R^2) and the full model explained 72.3% (conditional R^2); thus 47.3% of the variance was associated with the random effect, i.e. habitat or lake. The random intercept indicated that the influence of sex and age on liver REE concentration varied among fish from different lakes. There was a weak positive correlation between fish age and REEs, with REE levels increasing at approximately 1.15 $nmolg^{-1}$ per year

in fish livers. On average, male fish had liver concentrations 2.5 times higher than female fish ($p < 0.001$, Fig. 5). No significant overall effect of length on REE concentration was found for fish liver in this dataset, although fish length and age were only weakly related across lakes ($N = 58$, $r = 0.31$, $p = 0.02$). Overall, the model suggests that sex and age influenced REE bioaccumulation in brook trout but that site-specific exposure was more important.

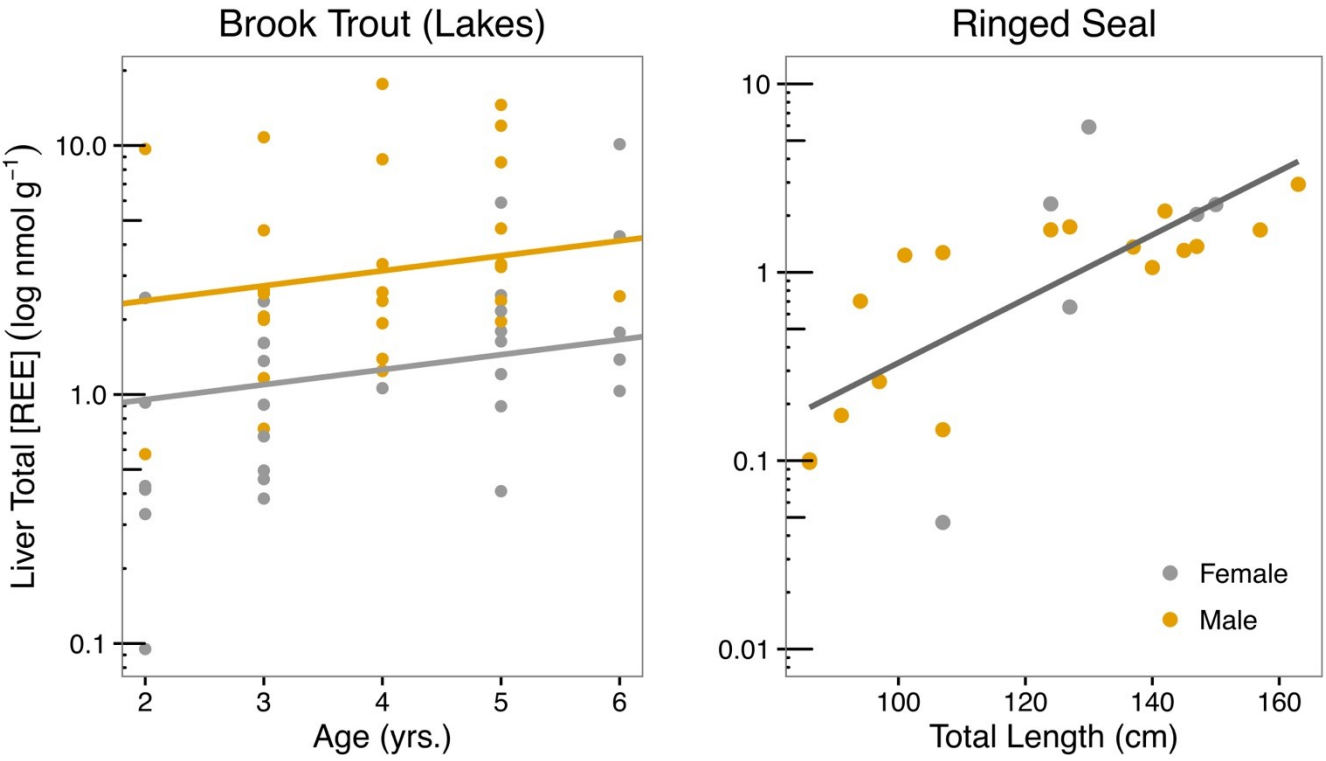

FIGURE 5: Relationships between sex, size and age of brook trout and ringed seal and liver REE concentrations (log-scaled nmolg^{-1}). Linear mixed effects models (LMM) indicate that sex ($p < 0.001$) and age ($p = 0.03$) were significant predictors of liver REE concentration for brook trout (N=58, sex coefficient ± SE: *female* = -0.14 ± 0.17, t value = -0.82; *male* = 0.26 ± 0.06, t value = 6.34; age coefficient (coef) ± SE: age = 0.06 ± 0.03, t value = 2.28). No significant effect of length was found for liver REE concentration in brook trout. For ringed seals, LMM showed no effect of sex on liver REE concentrations. Simple linear regression indicates that seal length (cm) was a significant predictor of liver REE concentration for ringed seal (N=23, $p < 0.001$).

Metal bioaccumulation occurs due to uptake from different sources (water, food or air) coupled with slower rates of elimination (Wiener et al., 2003). Our results indicate that REE bioaccumulation is greater than elimination over time for ringed seal and brook trout. Similar results were also reported by Mayfield and Fairweather (2015) for rainbow trout (also in the family *Salmoninae*) with concentrations of Sc, La, Ce, Nd and Y increasing weakly (and not always significantly) with fish age, size and weight. However, these authors also found that sucker species showed significant negative correlations with age, mass and length which indicates that REE bioaccumulation patterns vary with species, possibly due to differences in migratory and foraging behaviours. In the present study, an effect of sex was found only for the brook trout. Since no significant differences in length or weight were observed between male and female fish, lower liver REE concentrations in female fish could be due to metal depuration during egg production, differences in foraging behaviour, or dimorphism in liver function (but not size dimorphism) (Robinson et al., 2012). Increasing REE bioaccumulation with size (length or weight) and age may also indicate changes in diet over time. Although the relationship between $\partial^{13}C$ (an indicator of dietary carbon source) and fish age was not significant, seal length was positively correlated with $\partial^{13}C$ indicating a change in diet with seal growth in this study ($r = 0.53$, $p = < 0.01$).

Conclusions

This study greatly improves our understanding of REE bioaccumulation and trophic transfer in remote Arctic ecosystems. The bioaccumulation of REEs showed a predictable and coherent pattern of log-linear decrease with atomic number for most tissues. The normalization of individual REE concentrations revealed species- and tissue-specific anomalies for individual elements. This study also showed that REE bioaccumulate in a wide variety of biota from marine, freshwater and terrestrial ecosystems and that primary producers and consumers are good bio-indicators of REE pollution in the environment. REE levels decreased with trophic position, which indicated limited potential for biomagnification. Low levels of REEs in vertebrate muscle indicate that consumption of this tissue is unlikely to be an important exposure route for humans in northern regions unaffected by mining activities. Low levels of naturally-

occurring REEs in northern biota suggest that adverse effects on biota should only be expected under extreme conditions (contamination, low pH). Future research should focus on REE concentrations in internal organs and whole organism concentrations because low muscle REE concentrations may not provide accurate estimates of environmental exposure to total REEs. The findings on REE behaviour and bioaccumulation patterns from this study provide critical new information for assessing the potential toxicity pathways of REEs in vulnerable northern environments.

Acknowledgements. This study is an example of fruitful research that can be completed through cooperation between the scientific and indigenous communities in the Arctic. Special thanks to all the hunters of Kuujjuarapik-Whapmagoostui: Jimmy Paul Angatookalook, Charlie Angatookalook, Michael Angatookalook, Daniel Audla, Joanna Fleming, Jordan Kroonenberg, Willie Novalinga, Simionie Papayluk, Eddy Tookoo, Samson Tooktoo, Vincent Tooktoo, and Alec Tuckatuck. We are grateful to the three anonymous reviewers for their careful reading of this manuscript and their insightful comments. We would also like to thank Tania Perron, Dominic Bélanger and Murray Richardson for their help in the field and in the lab. Many thanks to Catherine Girard, Meredith Claydon, Emmanuelle Chrétien and Zofia Ecaterina Taranu for help with statistical analyses and with R.

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Supporting Information consists of 8 pages including 5 tables and 4 supporting figures.

Supporting Information

Rare earth elements in freshwater, marine, and terrestrial ecosystems in the eastern Canadian Arctic

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Supporting Information consists of 8 pages including 5 tables and 4 supporting figures.

TABLE S1: Mean detection limits for REEs based on 4 separate ICP-MS analytical runs.

Element	ICP-MS Detection Limits		
	µg/L	ng/g	nmol/g
Y	0.0002	0.1976	0.0022
La	0.0001	0.1442	0.0010
Ce	0.0001	0.1452	0.0010
Pr	0.0001	0.0604	0.0004
Nd	0.0003	0.2684	0.0019
Sm	0.0003	0.2576	0.0017
Eu	0.0001	0.1125	0.0007
Gd	0.0001	0.1398	0.0009
Tb	0.0000	0.0449	0.0003
Dy	0.0002	0.1540	0.0009
Ho	0.0000	0.0325	0.0002
Er	0.0000	0.0478	0.0003
Tm	0.0000	0.0315	0.0002
Yb	0.0001	0.0825	0.0005
Lu	0.0000	0.0143	0.0001

TABLE S2: REE concentrations in certified reference materials (with uncertainty) and measured values in standards (with standard deviations).

	STSD-1 (Creek Sediment)				**BCR 668 (Mussel Tissue)**				**BCR 670 (Aquatic Plant)**			
	nmolg-1 d.w.				pmolg-1 d.w.				pmolg-1 d.w.			
	Certified		**Measured (n=16)**		**Certified**		**Measured (n=16)**		**Certified**		**Measured (n=10)**	
Element	Mean	CI	Mean	SD	Mean	CI	Mean	SD	Mean	CI	Mean	SD
Y	472	± na	273	± 23	662	± 58	584	± 25	5196	± 776	4068	± 167
La	216	± na	163	± 16	578	± 48	476	± 35	3506	± 338	2705	± 284
Ce	364	± na	271	± 29	633	± 83	496	± 45	7044	± 443	5631	± 547
Pr	-	±	45	± 4.4	87	± 8.5	71	± 5.5	859	± 106	667	± 45
Nd	194	± na	183	± 18	378	± 41	321	± 27	3279	± 208	2764	± 229
Sm	40	± na	36	± 3.4	74	± 6.7	67	± 5.1	626	± 67	566	± 39
Eu	11	± na	7.5	± 0.7	18	± 1.6	16	± 1.2	153	± 16	177	± 6.0
Gd	-	±	37	± 3.1	82	± 6.0	82	± 8.2	622	± 85	622	± 26
Tb	8	± na	4.8	± 0.4	10	± 1.1	9.8	± 0.7	88	± 10	77	± 3.4
Dy	34	± na	25	± 2.0	55	± 3.7	45	± 3.1	486	± 54	406	± 24
Ho	-.	±	4.8	± 0.4	11	± 3.6	9.2	± 0.7	96	± 16	74	± 3.0
Er	-	±	14	± 1.2	27	± 2.9	24	± 2.0	263	± 27	218	± 14
Tm	-	±	1.8	± 0.2	2.8	± 0.4	2.5	± 0.4	34	± 5.5	27	± 1.0
Yb	23	± na	12	± 1.0	16	± 2.9	14	± 1.1	231	± 25	175	± 10
Lu	5	± na	1.9	± 0.2	2.2	± 0.2	2.1	± 0.2	36	± 3.9	24	± 0.9

TABLE S3: Detection frequencies for 15 individual REEs are shown by sampled taxonomic group. Mean detection frequencies for all elements by group are also shown. Sample sizes (N) and tissues are shown. Tissues include gonads (GON), muscle (MU), liver (LIV), and kidney (KID).

		Marine						**Terrestrial**							
		Sea Urchin	Blue Mussel	Common Eider		Ringed Seal		All Plants	Snowshoe Hare		Willow Ptarmigan		Caribou		
	N	5	9	16	16	23	23	17	6	6	9	9	5	6	6
	Tissue	GON	All	MU	LIV	MU	LIV	Leaves	MU	LIV	MU	LIV	MU	LIV	KID
LREE	La	1	1	0.25	1	0.52	0.96	1	0.83	1	0.78	1	0.80	1	0.83
	Ce	1	1	0.25	1	0.48	0.96	1	0.33	1	0.56	1	0.40	1	0.83
	Pr	1	1	0.25	1	0.39	0.96	1	0.50	1	0.67	1	0.60	1	0.83
	Nd	1	1	0.25	1	0.52	0.96	1	0.67	1	0.56	1	0.80	1	0.67
	Sm	1	1	0.25	1	0.13	1	1	0.33	1	-	1	0.40	1	0.67
	Eu	1	1	0.13	1	0.04	0.91	1	-	1	-	0.89	-	1	0.83
	Gd	1	1	0.25	0.50	0.52	0.96	1	0.50	1	0.33	1	0.20	1	1
HREE	Y	1	1	0.94	1	0.57	0.96	1	0.83	1	0.78	1	1	1	0.83
	Tb	1	1	0.25	0.94	0.04	0.96	1	0.33	1	0.11	1	-	1	0.67
	Dy	1	1	0.25	0.75	0.17	0.83	1	-	1	-	1	0.40	1	0.50
	Ho	1	1	0.19	0.31	0.09	0.78	1	-	0.83	-	0.78	-	0.83	0.17
	Er	1	1	0.25	0.88	0.17	0.87	1	0.33	1	-	1	0.20	0.83	0.67
	Tm	1	1	0.06	0.50	-	0.57	1	0.17	0.50	-	0.22	-	0.17	0.17
	Yb	1	1	0.25	0.69	0.13	0.83	1	0.17	0.67	0.33	0.67	-	0.50	0.67
	Lu	1	1	0.25	0.19	0.17	0.70	0.94	0.33	0.50	-	0.22	-	0.50	0.17
	Mean	1	1	0.27	0.78	0.26	0.88	1	0.44	0.90	0.51	0.85	0.32	0.86	0.63

		Freshwater (River)		**Freshwater (Lake)**				
		Brook Trout	Whitefish	Benthos	Zooplankton	Brook Trout		
	N	6	22	17	19	60	60	
	Tissue	MU	MU	All	All	MU	LIV	Mean
LREE	La	0.33	0.45	1	1	0.85	0.98	0.83
	Ce	-	0.18	1	1	0.73	0.98	0.74
	Pr	0.50	0.41	1	1	0.77	0.98	0.79
	Nd	0.50	0.50	1	1	0.80	0.98	0.81
	Sm	0.50	0.27	1	1	0.28	0.97	0.73
	Eu	0.17	0.14	1	1	0.13	0.90	0.64
	Gd	-	0.23	1	1	0.42	0.97	0.72
HREE	Y	0.83	0.55	1	1	0.78	0.95	0.90
	Tb	-	0.23	1	1	0.28	0.97	0.63
	Dy	-	0.23	1	1	0.23	0.87	0.68
	Ho	-	0.14	1	1	0.27	0.83	0.58
	Er	-	0.23	1	1	0.45	0.95	0.66
	Tm	0.17	0.09	1	1	0.13	0.68	0.44
	Yb	-	0.18	1	1	0.17	0.82	0.55
	Lu	-	0.09	1	1	0.23	0.57	0.48
	Mean	0.20	0.26	1	1	0.44	0.89	

TABLE S4: Geometric means of individual elements ($nmolg^{-1}$) and total REE concentrations (∑REE, $nmolg^{-1}$ and ngg^{-1}) for tissues of sampled taxonomic group from marine, terrestrial, and freshwater ecosystems. ∑REE concentrations are the sum of all REE, except scandium. Tissue type (muscle, liver) and samples sizes (N) are shown. Geometric means measure central tendency with high intra-group variation and are calculated as the antilog of the mean of the logarithmic values. Non-detected elements were included using values of 1/2 of the detection limit.

			nmol/g															nmol/g		mg/kg	
Ecosystem	**Tissue**	**N**	**Y**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	∑REE	SD	∑REE	SD
Marine																					
Sea Urchin	Gonad	5	2.929	5.017	4.323	0.699	2.392	0.331	0.053	0.353	0.035	0.164	0.032	0.098	0.012	0.074	0.011	16.67	7.57	2.21	0.99
Blue Mussel	Bulk	9	3.409	10.029	14.013	1.683	5.927	0.841	0.131	0.829	0.077	0.327	0.059	0.179	0.020	0.128	0.020	37.70	5.89	5.17	0.81
C. Eider	Muscle	16	0.005	0.007	0.013	0.002	0.005	0.003	0.001	0.003	0.000	0.001	0.000	0.000	0.000	0.001	0.000	0.055	4.938	0.008	0.693
C. Eider	Liver	5	0.009	0.129	0.102	0.012	0.044	0.007	0.001	0.005	0.000	0.001	0.000	0.000	0.000	0.001	0.000	0.332	0.304	0.046	0.043
Ringed Seal	Muscle	23	0.002	0.002	0.003	0.000	0.002	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.021	0.142	0.003	0.019
Ringed Seal	Liver	23	0.020	0.196	0.297	0.033	0.115	0.016	0.003	0.014	0.001	0.003	0.000	0.001	0.000	0.001	0.000	0.823	1.284	0.115	0.180
Terrestrial																					
Plants	Above ground	8	0.112	0.228	0.424	0.044	0.152	0.023	0.060	0.021	0.002	0.009	0.002	0.006	0.000	0.004	0.001	1.124	1.478	0.154	0.199
Lichen	Above ground	9	3.323	8.969	17.645	1.883	6.575	0.937	0.191	0.909	0.089	0.364	0.066	0.196	0.023	0.143	0.019	41.48	81.37	5.71	11.25
S. Hare	Muscle	6	0.003	0.004	0.002	0.001	0.002	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.022	0.160	0.003	0.023
S. Hare	Liver	6	0.030	1.723	2.119	0.181	0.551	0.048	0.006	0.049	0.002	0.004	0.000	0.003	0.000	0.001	0.000	4.729	5.995	0.663	0.841
Ptarmigan	Muscle	9	0.001	0.002	0.002	0.000	0.003	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.016	0.011	0.002	0.001
Ptarmigan	Liver	9	0.009	0.199	0.266	0.028	0.102	0.010	0.001	0.011	0.001	0.001	0.000	0.001	0.000	0.000	0.000	0.634	0.390	0.089	0.055
Caribou	Muscle	5	0.002	0.004	0.003	0.001	0.007	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.027	0.064	0.004	0.009
Caribou	Liver	6	0.012	0.135	0.211	0.023	0.076	0.010	0.002	0.010	0.001	0.002	0.000	0.001	0.000	0.001	0.000	0.487	0.367	0.068	0.052
River																					
Brook Trout	Muscle	6	0.006	0.001	0.001	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.016	0.089	0.002	0.008
Whitefish	Muscle	22	0.002	0.001	0.001	0.001	0.002	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.013	0.036	0.002	0.005
Lakes																					
Benthos	Bulk	17	2.280	9.943	11.886	1.552	4.912	0.605	0.157	0.634	0.059	0.219	0.040	0.125	0.013	0.085	0.012	33.54	85.05	4.62	11.67
Zooplankton	Bulk	19	9.187	28.349	34.786	5.383	17.980	2.190	0.423	2.106	0.210	0.896	0.164	0.519	0.060	0.376	0.054	103.8	484.6	14.24	66.30
Brook Trout	Muscle	60	0.003	0.006	0.010	0.002	0.004	0.001	0.000	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.041	0.153	0.006	0.021
Brook Trout	Liver	60	0.035	0.659	0.539	0.075	0.229	0.018	0.002	0.017	0.001	0.003	0.001	0.003	0.000	0.001	0.000	1.683	3.700	0.234	0.519

TABLE S5. Summary of total rare earth elements concentrations [ΣREE, geometric means] and stable nitrogen isotope values ($\delta^{15}N$ and adjusted $\delta^{15}N$ or $\delta^{15}N_{adj}$*) in biota from marine, terrestrial, and freshwater Subarctic ecosystems in Nunavik, Quebec. ΣREE concentrations are the sum of all REE, except scandium.

Ecosystem	[ΣREE] (nmol/g)				[ΣREE] mg/kg)				$\delta^{15}N$ (‰)				$\delta^{15}N_{adj}$ (‰)*			
	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max
Marine																
Sea Urchin	16.67	7.57	11.18	30.44	2.21	0.99	1.47	4.01	6.04	0.22	5.72	6.34				
Blue Mussel	37.70	5.89	27.05	45.49	5.17	0.81	3.71	6.23	6.19	0.36	5.67	6.79				
Common Eider	0.055	4.938	0.005	19.85	0.008	0.693	0.001	2.786	10.21	0.61	9.61	11.47				
Ringed Seal	0.021	0.142	0.005	0.651	0.003	0.019	0.001	0.088	14.90	0.69	13.62	16.36				
Terrestrial																
Plants	1.124	1.478	0.410	4.870	0.154	0.199	0.056	0.657	-5.15	1.71	-7.64	-2.42				
Lichen	41.48	81.37	5.395	258.7	5.71	11.25	0.737	35.7	-3.44	0.83	-4.78	-1.92				
Snowshoe Hare	0.022	0.160	0.007	0.407	0.003	0.023	0.001	0.057	0.14	0.68	-0.80	0.73				
Ptarmigan	0.016	0.011	0.007	0.038	0.002	0.001	0.001	0.005	1.51	0.44	0.97	2.15				
Caribou	0.027	0.064	0.008	0.160	0.004	0.009	0.001	0.022	4.21	0.77	3.33	5.25				
River																
Brook Trout	0.016	0.089	0.006	0.228	0.002	0.008	0.001	0.021	14.69	0.21	14.42	14.96				
Whitefish	0.013	0.036	0.005	0.135	0.002	0.005	0.001	0.018	11.81	0.84	9.92	12.97				
Lakes																
Benthos	33.54	85.05	1.624	305.4	4.62	11.67	0.223	41.89	2.61	0.98	1.02	4.58	1.99	1.29	0.16	4.97
Zooplankton	103.8	484.6	22.75	1395	14.24	66.30	3.12	190.8	3.41	0.72	2.14	4.24	2.61	0.86	1.53	4.26
Brook Trout	0.041	0.153	0.005	0.823	0.006	0.021	0.001	0.116	8.16	0.85	5.82	10.25	7.15	1.07	5.21	9.39

*See "Methods" for an explanation of $\delta^{15}N$ adjustment.
**SD = standard deviation; SD is shown only for results where $n \geq 3$.

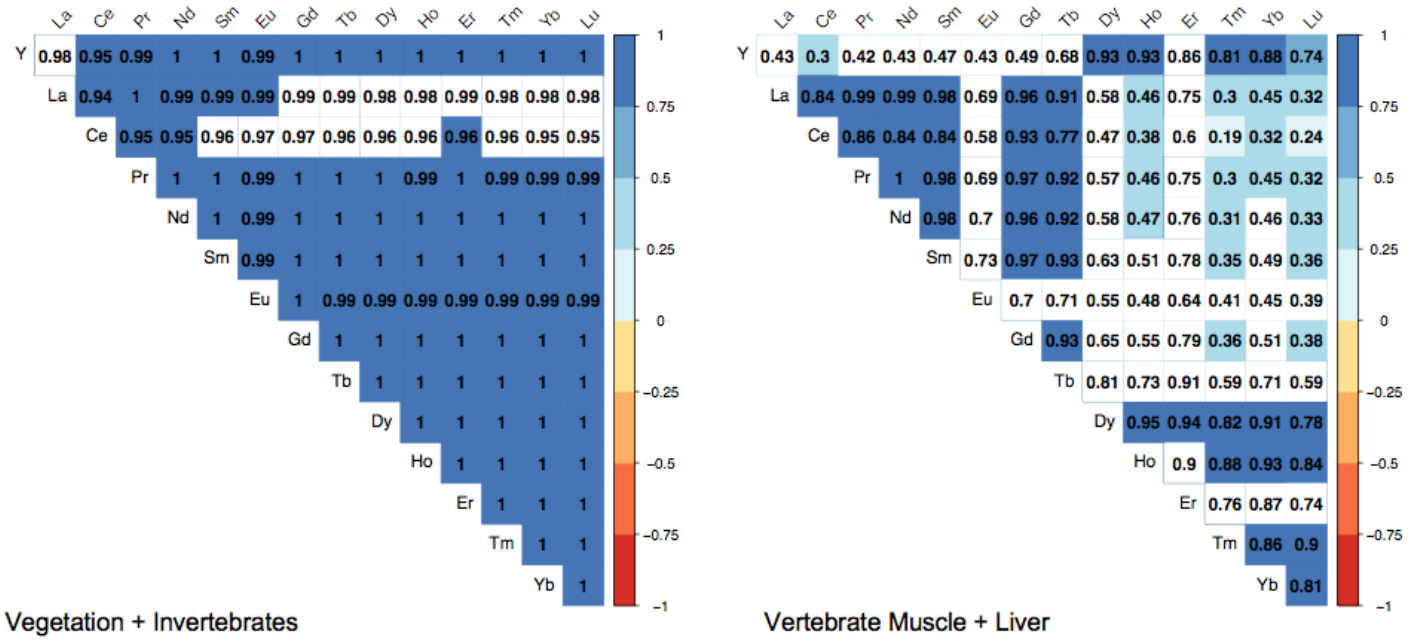

FIGURE S1: Pearson correlation matrices with Holm adjusted probabilities. Positive correlations are shown in blue, negative correlations in red, and colour intensity is proportional to the correlation coefficients (which are shown in black). Non-significant correlations are shown in white ($p > 0.05$).) Samples are from vegetation and invertebrates (left panel, N = 70) and vertebrate muscle and liver tissues (right panel, N = 256).

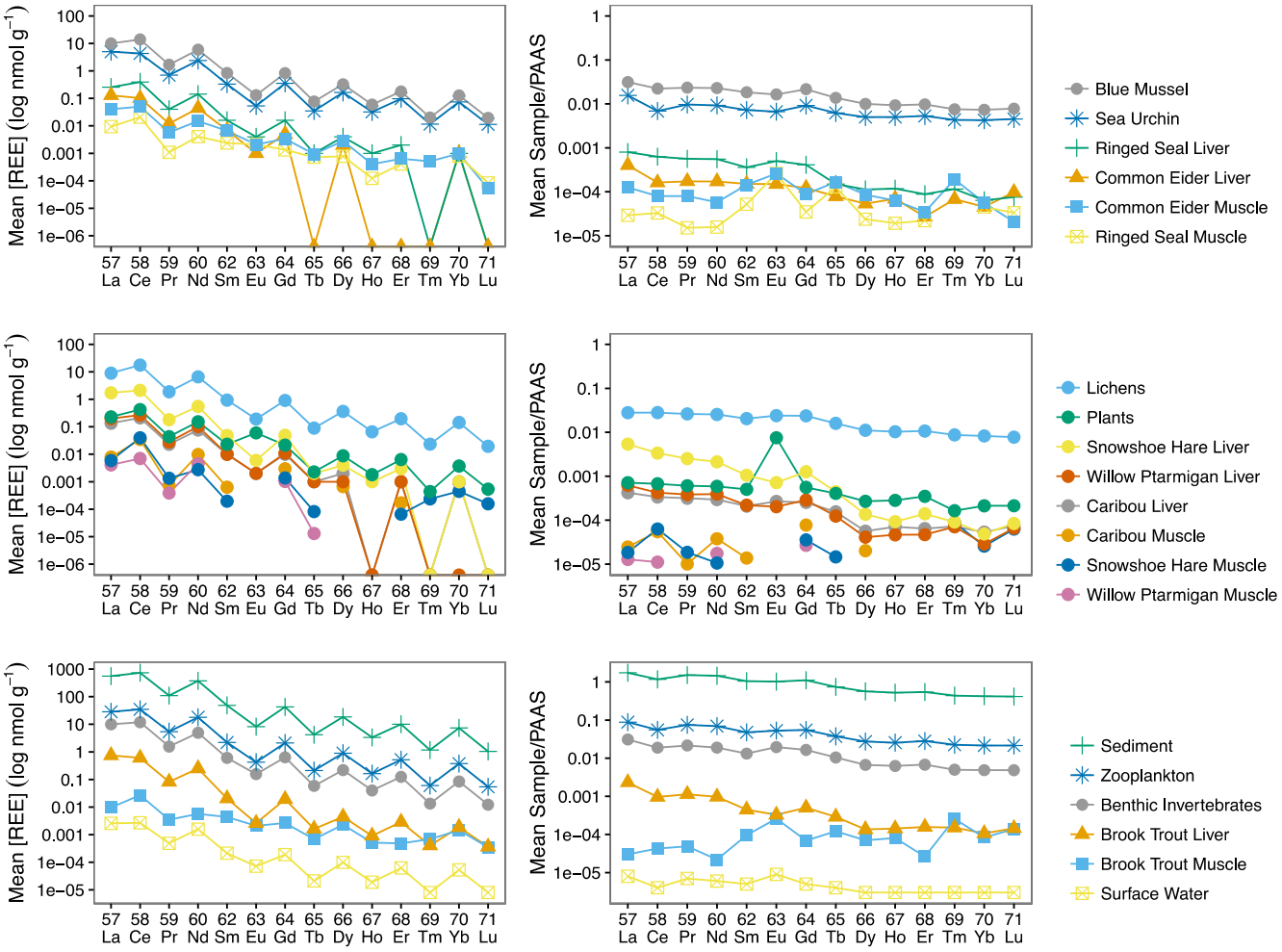

FIGURE S2: REE concentration versus atomic number for biotic and abiotic component from all ecosystems. Left panels are mean [REE] (log-scaled geometric means, nmolg^{-1}) showing the pattern of log-linear or saw-tooth decrease with atomic number. Right panels are PAAS-normalized REE concentrations (log-scaled, geometric means nmolg^{-1}/PAAS nmolg^{-1}). Points show element means for each taxonomic group and samples below detection limits were excluded from figure (e.g. muscle tissues).

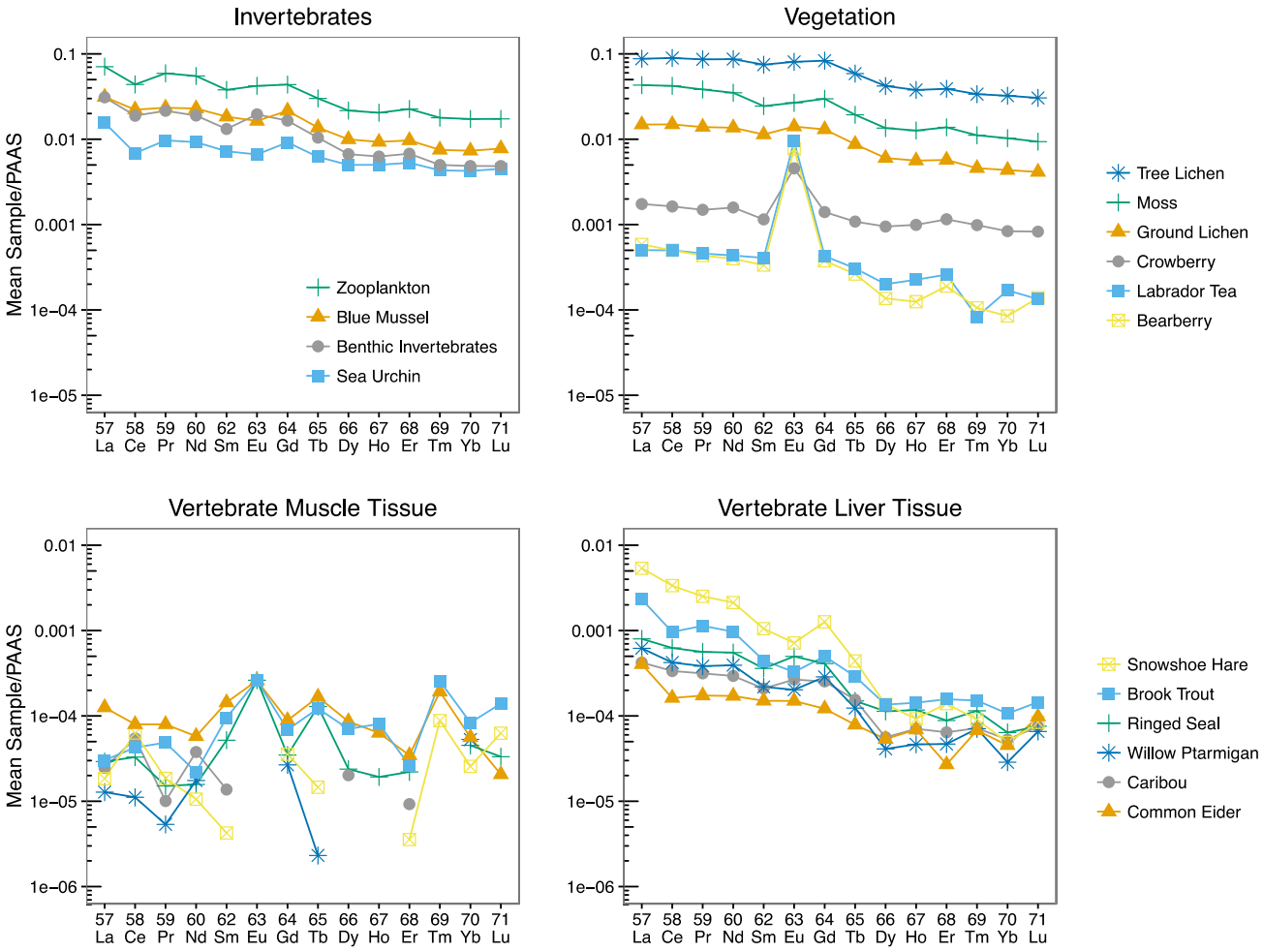

FIGURE S3: PAAS-normalized REE concentrations (geometric means, log nmolg^{-1}) versus atomic number for biotic components from all ecosystems including invertebrates, vegetation, vertebrate muscle and vertebrate liver tissues. Points show element means for each taxonomic group and samples below detection limits were excluded from the figure (e.g. muscle tissues).

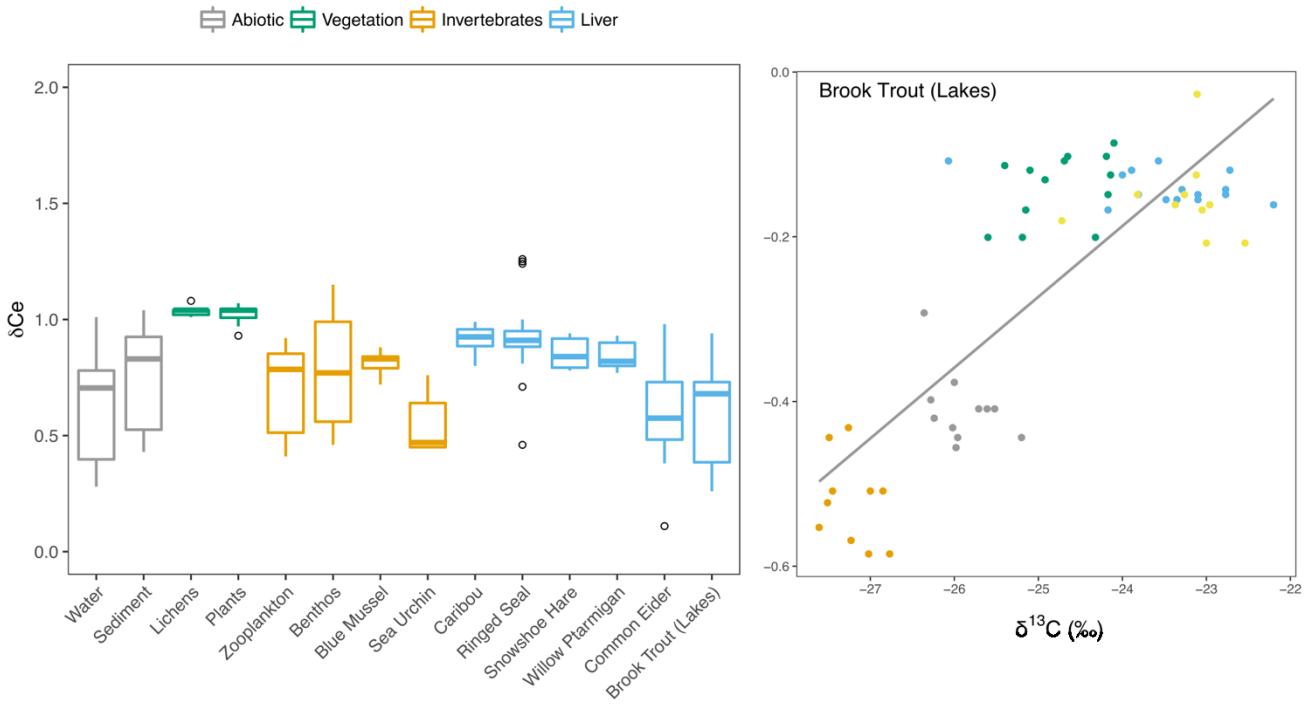

FIGURE S4: Boxplots showing the measured Ce anomaly in biota (∂Ce) by taxonomic group (left panel). Values close to 1 indicate no significant anomaly. Simple linear regression between ∂Ce (log_{10} - scaled) and carbon stable isotope ratios ($\partial^{13}C$, ‰) for freshwater brook trout: N = 54, $R^2_{adj} = 0.66$, $p < 0.001$. Coloured points indicate different sample lakes (geometric mean of 5 lakes). ∂Ce is calculated as $Ce_{PAAS} / (La_{PAAS} \times Pr_{PAAS})^{0.5}$ where PAAS indicated Post Archean Shale Standard normalized values.

CHAPITRE 4: Les facteurs environnementaux qui influencent la bioaccumulation de terres rares dans le zooplancton d’eau douce

Environmental drivers of rare earth element bioaccumulation in freshwater zooplankton

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Abstract

Human activities have resulted in significant release of rare earth elements (REEs) into the environment. However, the pathways of REEs from waters and soils into freshwater food webs remain poorly understood. Recent studies suggest that aquatic invertebrates, may be good biomonitors for REEs, yet there is little information on factors that control REE bioaccumulation in these organisms. Our goal was to study the environmental drivers of REE levels in zooplankton, a key component in plankton food webs, across lakes from geographic areas with different bedrock geology. From 2011 to 2014, bulk zooplankton samples were collected for REE analysis from 39 lakes in eastern Canada. We observed a more than 200 fold variation in surface water REE concentrations and a 10 fold variation in sediment REE concentrations. These concentration gradients were associated with a range of more than an order of magnitude in zooplankton REE concentrations ($\sum$REEY 3.2 - 210 nmol g^{-1}). We found higher REE bioaccumulation in zooplankton from lakes with lower pH and higher REE to dissolved organic carbon ratios. Bioaccumulation was also strongly linked to the free ion concentrations of REEs (REE^{3+}) in surface waters. Our study suggests that zooplankton REE bioaccumulation is an excellent predictor of bioavailable REEs in freshwaters.

Introduction

Global demand for rare earth elements (REEs) is rapidly increasing because these metals are essential in many high-tech industries, notably electronics, medicine and renewable energy.(Alonso et al., 2012) Industrial activities have led to significant release of REEs into the environment from mining, municipal and electronic waste, and agricultural sources,(EPA, 2012) yet the bioavailability and environmental risks of REEs have not received much attention.(Gonzalez et al., 2014) Compared to other trace metals with well-documented environmental impacts,(Dudka and Adriano, 1997) there are far fewer field-based studies examining REE bioavailability in freshwater aquatic ecosystems.(MacMillan et al., 2017, Amyot et al., 2017, Mayfield and Fairbrother, 2015, Weltje et al., 2002, Twiss and Campbell, 1998) REEs are 17 metals of emerging concern which are grouped together because they have very similar chemical and toxicological properties. REEs are predominantly trivalent cations (M^{3+}) with similar ionic radii and include the 15 lanthanide metals (La to Lu), as well as scandium (Sc) and yttrium (Y). Only "rare" because they do not concentrate into easily exploitable mineral deposits, the abundance of REEs in the Earth's crust is comparable to other trace metals, including copper, lead and zinc.(Taylor and McClennan, 1985) Site-specific field data from freshwater ecosystems are needed to support environmental impact assessment of REEs and establish baseline environmental guidelines.

Pathways of REE movement into freshwater biota from water, soils and sediments are not well studied. Poorly soluble in the natural environment, REEs are found at very low or trace concentrations (< 0.01 ug L^{-1}) in waters of most uncontaminated aquatic systems.(Gonzalez et al., 2014) REEs are lithophile elements, forming strong complexes with organic and inorganic ligands (including carbonate and phosphate ions), and hence the majority of REEs are bound to sediments or suspended particles in the water column.(Herrmann et al., 2016, Davranche et al., 2015) As with other trace metals, the major natural sources of REEs to lake surface waters are atmospheric deposition, inputs from watersheds, and diffusion or resuspension from the lake sediments. Atmospheric particles are a major source of REEs to the ocean,(Tachikawa et al., 2003, Goldstein et al., 1984) but may not be the dominant natural source for small lakes with large watershed to lake surface area ratios. Geologic REE inputs to lakes may vary with geographic region due to the lithology of their catchments, with different geological structures and chemical composition of the

rocks.(Long et al., 2010) Soil REE content is influenced by the presence of REE-bearing minerals, carbonates and organic matter, as well as soil weathering, pH, particle size, and clay content.(Buda et al., 2010, Tyler, 2004)

Only a fraction of the total concentrations of REEs is available to enter living organisms and this bioavailable metal fraction has the capacity to be solubilized and released from environmental compartments, i.e. soils, sediments, and particles.(Caussy et al., 2003) The bioavailability of trace metals in aquatic ecosystems is controlled by their chemical speciation in water, which is strongly influenced by environmental factors, including pH, the presence of other cations (i.e. H^+, Ca^{2+}, Mg^{2+}) and competition with other metals for complexation with inorganic and organic ligands. Given the influence of environmental factors, models are widely used to predict trace metal speciation and bioavailability based on site-specific water chemistry. The free ion activity model (FIAM) and the biotic ligand model (BLM) predict that bioavailability is most strongly associated with the free ionic form of the metal (M^{z+}) in surface waters, as well as with the influence of chemical competitors at biological uptake sites.(Campbell, 1995) Estimating free ion metal concentrations typically involves the use of computer software (e.g. MINEQL$^+$, PHREEQC, WHAM) because the analytical methods for detecting low ambient M^{z+} concentrations are challenging. These computational algorithms are based on equilibrium binding constants that describe reactions of metals with a variety of inorganic and organic ligands.

It is well-established that REEs naturally bioaccumulate in vegetation, especially in lichen and moss,(Weltje et al., 2002, Chiarenselli et al., 2001, Hao et al., 1998) and recent studies suggest that REEs bioaccumulate to similar levels in aquatic invertebrates, such as freshwater zooplankton.(MacMillan et al., 2017, Amyot et al., 2017) Similar to other trace metals, REEs can be adsorbed to outside surfaces, or they can be taken up into invertebrates from the surrounding water and from food.(Hare, 1992) Although not commonly used in biomonitoring, zooplankton assemblages are good candidate biomonitors for freshwater ecosystems as they are widespread, abundant, relatively easy to sample, and play important ecological roles.(Zhou et al., 2008, Croteau et al., 1998) However, using species assemblages for biomonitoring, such as periphyton or zooplankton, requires careful characterisation of assemblage composition.

This study examined environmental drivers that determine REE concentrations in freshwater zooplankton in four geographic regions (in five geological provinces) from temperate to high arctic

environments in Eastern Canada. From 2011 to 2014, unsorted (bulk) zooplankton samples were collected for REE analysis from 39 lakes during the summer. We determined a) REE concentrations in water, sediment and bulk zooplankton, b) the influence of REE speciation and free ion concentration on REE bioaccumulation in zooplankton and c) the influence of watershed characteristics and within-lake environmental factors on REE concentrations in zooplankton. This study generated important baseline data on REE bioaccumulation in zooplankton across five geological provinces in eastern Canada.

Methods

Study Sites. From 2011 to 2014, 39 lakes were sampled during July or August from different geographic areas including temperate, subarctic, arctic and high arctic ecosystems in eastern Canada (Fig. 1, Table S1). In 2011 and 2012, 14 lakes were sampled near Montreal, Quebec (45°N, 73°W), hereafter referred to as temperate lakes. In 2012, 8 lakes were sampled near Kuujjuarapik-Whapmagoostui (K-W) in the subarctic taiga south of the treeline in Nunavik, Quebec (55°N, 77°W). In 2013, nine lakes were sampled in the arctic tundra near Iqaluit, Nunavut (64°N, 68°W) and 8 more lakes were sampled in 2014 in the polar desert near Resolute, Nunavut (74°N, 94°W). The 39 study lakes were selected to represent a gradient in geology, lake and watershed size, water chemistry, trophic status, as well as food web composition (Tables S1, S2). Study lakes were situated in five geological provinces: the Appalachian Orogen and Grenville provinces (Montreal), the Superior Province (Kujjuarapik-Whapmagoostui), Churchill Province (Iqaluit) and the Arctic Platform (Resolute Bay). Surficial geology differs within each of these provinces and among the four sampling regions (Fig. 1).(Fulton, 1995)

All study lakes were sampled for *in situ* water temperature, pH, specific conductivity, and dissolved oxygen with a YSI probe (YSI 600QS, YSI Inc., Yellow Springs, Ohio, USA). All sample lakes were relatively small in size (ranging from 0.1 to 4.7 km^2 with a median of 0.27 km^2) and were shallow with mean depths of 0.3 to 12 m (Table S1). None of the subarctic or arctic lakes (N = 25) showed thermal stratification during the mid-summer sampling periods. All of the temperate lakes near Montreal showed thermal stratification (N =14), with the thermocline from 2.5 to 6.0 m. Note that a subset of this data was previously published in two articles with different research objectives from the current study (MacMillan et al., 2017, Amyot et al., 2017). There is currently no REE mining or exploitation in the study regions and therefore none of these lakes

were considered to be contaminated, i.e. there are no known metal point sources within their watersheds. However, the temperate lakes are located in watersheds influenced by agricultural activities.

Physical Lake and Watershed Characteristics. For all sites, lake area and watershed area were computed in ArcGIS (ESRI 2011, ArcGIS) using digital elevation models (DEM) and standard terrain analysis methods (with SAGA GIS for northern sites).(Conrad et al., 2015) Average lake depth was estimated using the formula 0.46*depthmax (where depthmax is maximum measured lake depth). This formula is commonly used to estimate average lake depth in the absence of complete bathymetric surveys and is based on the assumption of an elliptic sinusoidal lake morphometry.(Wetzel, 2001) Lake volume for temperate sites was estimated as lake area multiplied by average depth. For northern sites, bathymetric surveys were conducted at all lakes using a small inflatable raft and sounder that recorded water depth, latitude and longitude (Lowrance Elite-5 HDI fish finder). Lake volumes were calculated from the average depth of the interpolated grid and the lake area. Several of the Resolute lakes were covered with a large ice pan and therefore average depth and volume were calculated with the formula used for temperate sites.

Water, Sediment, and Zooplankton Sampling. Ultra-trace sampling techniques were used to collect the environmental samples. Surface water (N = 39), surface sediment (N = 34) and zooplankton (N = 34) were collected for trace metals and REE analysis from a boat with an electric motor. Surface sediment was sampled in the deepest zone of the lake by Ekman grab. Water was carefully removed from the top of the samples and 1-2 cm of intact sediment was collected in triplicate and then frozen at -20°C in plastic bags until digestion and analysis. Duplicate surface water samples were collected with sub-surface hand grabs (at 10 - 20 cm below the surface) in HDPE bottles for water chemistry analysis, including dissolved organic carbon (DOC), major ions (Ca, Mg, K, Na, Cl, SO_4), chlorophyll *a* (Chla), total nitrogen (TN), total phosphorus (TP). Chla, TN and TP were not measured at temperate sites (N = 14; Table S1). Water samples for trace metals and REEs were also collected at 10 - 20 cm sub-surface using either hand grabs or an acid-washed (HCl 10%) peristaltic pump with Teflon tubing.

Water samples for metals and REEs were filtered either using an acid-washed (HCl 10%) Teflon filtration tower with a pre-combusted glass-fiber filter (0.7 µm pore size, Whatman GF-F) which was flushed with site water, or a peristaltic pump with a High Capacity In-Line Groundwater

Sampling Capsule with a 0.45 µm pore size membrane (Pall Corporation, Port Washington, NY). Blanks of Milli-Q water (18.2 MΩ·cm) filtered on glass-fiber filters showed slight increases after filtration for Y, La, Ce, and Eu (< 0.02 µg L^{-1}) and negligible increases of ~ 0.005 µg L^{-1} for all other REEs. Filtered Milli-Q blanks using the peristaltic pump and in-line filter capsule had concentrations < 0.005 µg L^{-1} for all REEs. These levels were negligible compared to measured REEs at most sites, except at some lakes in Resolute where measurements were closer to detection limits. Analytical blank values were subtracted from surface water concentrations for each element (when detected) and filtered blanks were not subtracted. All water samples for trace element analysis were stored in trace-metal clean falcon tubes, acidified with ultrapure HNO_3 (2% v/v, Omnitrace grade), and stored at 4°C.

At temperate sites, integrated zooplankton samples from the first 6 m of the water column were collected with a large plankton net (1 m diameter, 200 µm mesh). For northern sites, zooplankton were sampled by horizontal surface hauls at depths of 1 to 2 m with the same net. Sub-samples were taken from each site and preserved in ethanol (70% v/v) for taxonomic analysis. Replicate zooplankton samples (N = 2-3) were filtered (200 µm), rinsed with ultrapure Milli-Q water and frozen at -20°C in acid-washed (HCl 10%) 500 mL HDPE jars without a depuration step. In 2018, an additional experiment was conducted to assess the influence of depuration (i.e. removal of gut contents) on REE concentrations in pelagic zooplankton. Zooplankton concentrations of individual REEs declined by 27% ± 7% after 8h of depuration in filtered lake water (N=3). Reported REE concentrations in this study should therefore be considered upper limits for pelagic zooplankton.

Sample Preparation and Analysis. DOC in surface waters was measured as non-purgeable organic carbon by adding H_3PO_4, followed by persulfate digestion, with an Aurora 1030 TOC analyzer (OI Analytical, Texas). TN was determined as nitrate after potassium persulfate alkaline digestion and TP was determined by spectrophotometer using the ascorbic acid/molybdenum blue method. Chla was measured by spectrophotometer after ethanol extraction. Anions were quantified using ion chromatography (either Dionex Corp. or Waters, IC-Pak A and C columns) and cations were analyzed with either a) inductively coupled plasma optical emission spectrometry (in 2011, ICP-OES, Varian VISTA AX CCD) or b) with an atomic absorption spectrophotometer (in 2012 - 2014, AAS, Agilent).

Sediment organic matter content was estimated by loss on ignition (LOI). Sediment particle size distribution was estimated using sieving techniques for the coarse fraction (> 2 mm) and laser diffraction for the smaller fractions (< 2 mm) on both unprocessed and processed samples (LS 13 320, Beckman Coulter, Indianapolis, USA). To determine particle size distribution, sediment was digested using HCl and H_2O_2 to remove carbonates and organic components, respectively. Note: sediment digestions for trace metal analysis were conducted separately (see below). Unprocessed sediment was sieved and run unaltered. Calculations for light diffraction used the Fraunhofer optical model.(Donato et al., 2009, Van Hengstum et al., 2007, Murray, 2002) Particle size is expressed in volume percentage where clay was from 0.24 - 2.0 μm, silt was from 2.0 - 63 μm, and sand was from 63 - 1000 μm.

Dry sediment and zooplankton were weighed in tin capsules and analyzed for carbon and nitrogen stable isotope ratios ($\delta^{13}C$, $\delta^{15}N$) as well as percent carbon (%C) and percent nitrogen (%N) using an elemental analyser interfaced with an isotope ratio mass spectrometer (IR-MS, Thermo Delta Advantage) at the G.G. Hatch Stable Isotope Laboratory (University of Ottawa, Ottawa, Canada). Stable isotope ratios are reported in Delta (δ) notation; the units are parts per thousand (‰) and defined as $\delta X = ((Rsample-Rstandard))/Rstandard) \times 1000$ where X is ^{15}N or ^{13}C, and R is the ratio of the abundance of the heavy to light isotope. For more information on data handling for stable isotope ratios, see Supporting Information (SI).

Taxonomic composition of zooplankton was examined using a dissecting microscope (x10 - 40 magnification) and zooplankton were classified into major groups (Order or Genus) using taxonomic keys(Thorp et al., 2009, Haney et al., 2013) Duplicate taxonomic samples were analysed from each study lake and a minimum of 200 individuals were identified in each replicate. Replicate samples were compared and then pooled together for analysis (N = 400-500 individuals per lake). The relative contribution of each major group (e.g. % cladocerans, % copepods, and % chaoborids) was calculated by dividing the number of individuals in each taxonomic group by the total number of individuals.

Trace Metal and REEs Analysis. Water samples were analysed for trace metals and REEs by inductively-coupled plasma mass spectrometry (ICP-MS, PerkinElmer; NexION 300X) using an ^{115}In internal standard to correct for instrumental drift. A 6 or 7-point multi-element calibration curve was acquired every 20 samples and blank and quality control samples were run every 10

samples. Analyzed trace metals included Al, Mn, Ni, Cu, Zn, As, Se, Cd, Pb, and Fe, and REEs included La-Lu, Sc and Y. Detection limits for temperate lake analyses were previously published in Amyot *et al.* (2017). Detection limits were calculated as three times the standard deviation of 10 analytical blanks for northern lakes and are reported in Table S3. Homogenized sediment and zooplankton were freeze-dried and 0.01 to 0.18 g (median 0.10 g) of sample was weighed into pre-washed (HNO_3 45%, HCl 5%) Teflon tubes and digested with 3 mL of trace metal grade HNO_3 (70% m/v) for 15 minutes at 170°C in a microwave. Two more 15 minute cycles were completed after adding 0.5 - 1.0 mL of OPTIMA grade hydrogen peroxide (30% H_2O_2) before each cycle. Digested samples for trace metal analysis were diluted with ultra-pure water (MilliQ, 18.2 MΩ•cm) to a volume of 50 mL, re-diluted (1:2) into trace metal clean falcon tubes, and analyzed by ICP-MS. Sediment samples were centrifuged prior to analysis by ICP-MS to remove any residues remaining after sample digestion. Partial sediment extractions were used in this study to measure REE concentrations because they were considered more representative of the labile, bioavailable metal fraction. (Snape et al., 2004)

Quality Assurance. Quality assurance for carbon and nitrogen stable isotope ratios included triplicate analyses of an internal standard (analytical precision of 0.2 ‰) per run and duplicate analyses of 10% of samples (CV < 5%). Quality assurance for trace metals and REEs included a) the analysis of analytical and field blanks, b) the analysis of certified reference materials and analytical sample duplicates and c) an inter-laboratory calibration with the Centre d'expertise en analyse environnementale (CEAEQ, Government of Québec, Quebec City). Quality control for REEs in surface waters was assured through an inter-laboratory calibration with CEAEQ of four unfiltered subarctic water samples (Table S5). For digestions, average (min-max) recovery for REEs in reference material was 87% (79 - 101%) for mussel tissue, 84% (67 – 117%) for plant tissue, and 70% (40 – 99%) for sediment (Table S6). These values are consistent with average recoveries reported in the literature.(Mayfield and Fairbrother, 2015, Dolegowska and Migaszewski, 2013, Weltje et al., 2002) Coefficients of variation (CV) were calculated for analytical and field duplicates to estimate analytical precision and were approximately ± 13% for water, ± 7% for sediment and ± 21% for zooplankton. Details on quality assurance are found in the SI (Tables S3 to S6).

Data Handling. REEs have very similar geochemical behaviour, and therefore total REE concentrations (instead of single element concentrations) were used to present the majority of

results.(Amyot et al., 2017) For comparison with the published literature, two sums were calculated, a) ∑REE, or the sum of 14 lanthanides (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and b) ∑REEY, the sum of 14 lanthanides plus yttrium (Y). Promethium (Pm) was not included because it does not occur naturally and scandium (Sc) results were excluded due to analytical interference. Some results are shown using lanthanum (La) as a representative single element, because it is the second most abundant REE (after Ce) and does not have variable oxidation states.

Surface water dissolved REE concentrations are reported in nmol L^{-1} while sediment and biota concentrations are reported in nmol g^{-1} on a dry weight basis (d.w.). Bioaccumulation factors (BAFs, L Kg^{-1}, log10-transformed) were calculated as the ratio of zooplankton ∑REEY (nmol Kg^{-1}) to surface water ∑REEY (nmol L^{-1}) using field data. Sediment-water partition coefficients (Kd in L Kg^{-1} or log Kd in log L Kg^{-1}) were calculated for study lakes based on individual element and ∑REEY concentrations in dry surface sediment (nmol Kg^{-1}) divided by surface water concentrations (nmol L^{-1}). Note that Kd was calculated using partial extractions for ∑REEY levels in sediment samples. Ratios of REEs to DOC concentrations in surface waters were calculated for each study lake by dividing surface water ∑REEY or single element concentrations (M) by site-specific DOC concentrations (mg L^{-1}).

Free ion concentrations of REEs were calculated with the Windermere Humic Aqueous Model software (WHAM 7.0.5).(Tipping et al., 2011) Model inputs were field-measured temperature, pH, inorganic and organic ligands concentrations (including DOC, major ions and trace metals as listed previously). Total carbonates were assumed to be at equilibrium with the atmosphere and were defined with a value of 3.09×10^{-4} (atm) for all sites. Field measurements of DOC were used to estimate fulvic acid concentrations for WHAM models, calculated using the following equation: 1 mg C L^{-1} is equal to 1.3 mg fulvic acid L^{-1}. This equation assumes that organic matter is composed of 50% carbon and that 65% of organic matter is composed of complex-forming fulvic acids.(Bryan et al., 2002) The database used for the models was not changed for this study and precipitation was not allowed (see Table S7 for WHAM equilibrium constants). Competition of calcium (Ca^{2+}) and hydrogen ions (H^{+}) with free ionic REE^{3+} at zooplankton uptake sites were considered using competition models described in Croteau *et al.* (1998) and Hare and Tessier (1998) (Hare and Tessier, 1998, Croteau et al., 1998).

Statistical analyses. All statistical analyses were performed in R version 3.3.1 (R Core Development Team, 2016). Graphics were created with the '*ggplot2*' package.(Wickham, 2016) All data were tested for normality and transformed, if required, to reduce skewness and outlier influence. All REE concentrations and lake physico-chemistry variables were $\log_{10}$ transformed, with the exception of mean depth, sediment %N and %OM (square root transformation), sediment silt % (power of 2 transformation), and TP (aq), sediment $\delta^{15}N$, and sediment Al concentrations (no transformation, normal distributions). ΣREEY concentrations were compared between different regions using Welch's analysis of variance (ANOVA) with Games-Howell post-hoc tests because this test is designed for cases where variance is heterogeneous and sample size is small (R: *userfriendlyscience* package).(Peters, 2018)

Simple linear regressions were used to compare REE concentrations between water, sediment, and zooplankton. Visual inspection of linear model residual plots did not show deviation from homoscedasticity or normality. Multivariate analyses were conducted to examine which environmental variables influence both ∑REEY and La concentrations in a) surface water b) surface sediment, and c) log Kd and d) bulk zooplankton. Multiple regressions were calculated using LASSO (Least Absolute Shrinkage and Selection Operator) analyses with the R package '*lars*'.(Hastie and Efron, 2013) This technique limits the sum of the regression coefficients using a tuning parameter (lambda, λ) to ensure models are parsimonious and is well-suited to small datasets with many collinear variables.(Tibshirani, 1996, Efron et al., 2002) The best model was chosen as that with the lowest Mallow's Cp value, a statistic for subset selection similar to the Akaike information criterion (AIC) or Bayesian information criterion (BIC).(James et al., 2013) The '*selectiveInference'* (Tibshirani et al., 2017) package in R was used to estimate the significance of each independent variable (p) in the models using its corresponding λ value. See SI for more information on LASSO methods, regression results and path plots (Fig. S5 to S9).

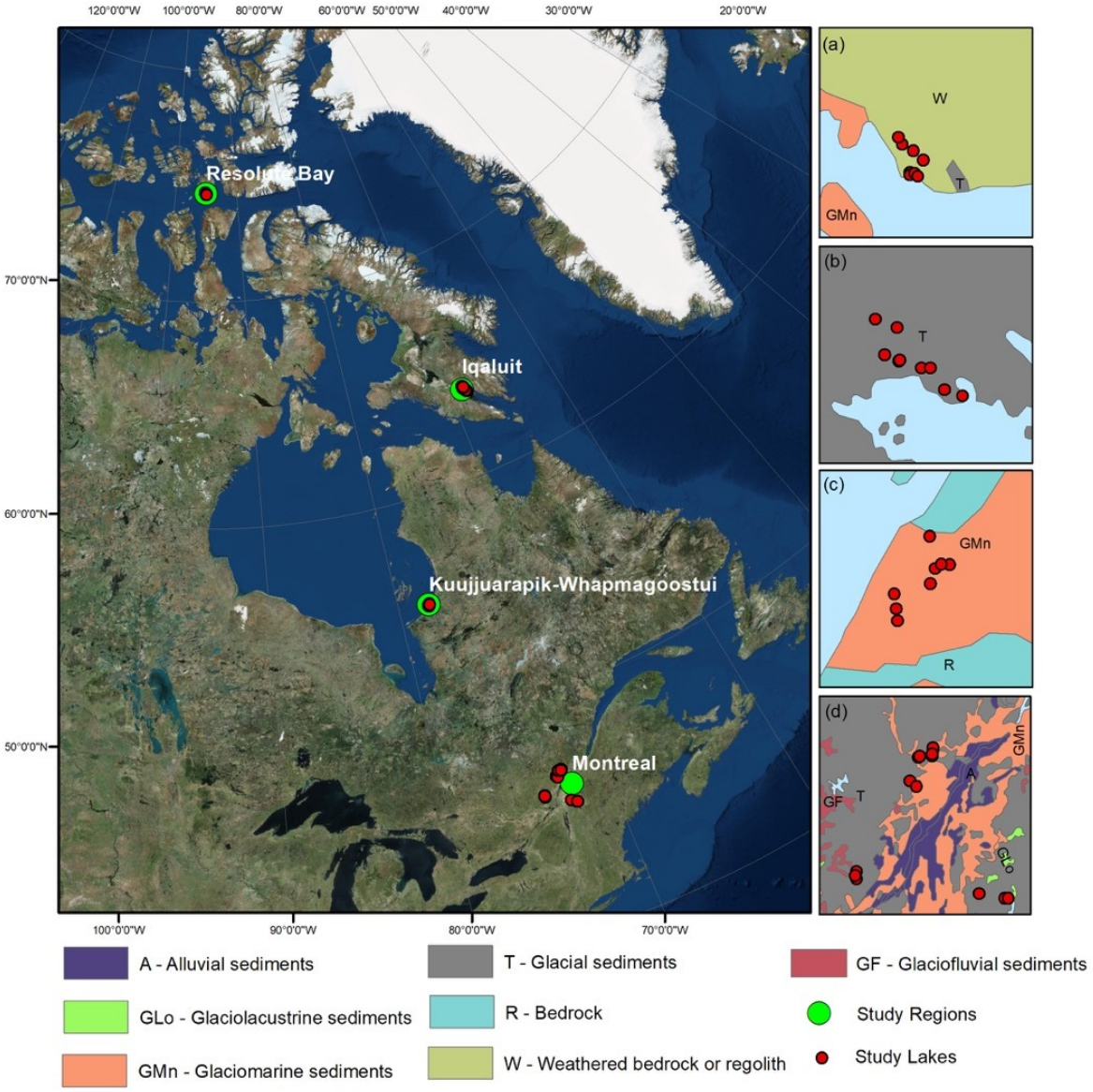

FIGURE 1: Map of the sampling regions in Eastern Canada. Large scale inset panels on right show surficial geology deposits (Fulton 1995) for lakes sampled near (a) Resolute Bay (N = 8); (b) Iqaluit (N = 9); (c) Kuujjuarapik-Whapmagoostui (N = 8); and (d) Montreal (N = 14). The geological provinces of sample lakes from north to south respectively are (a) Arctic Platform, (b) Churchill Province, (c) Superior Province, and (d) Appalachian & Grenville Provinces.

Results and Discussion

Water, Sediment and Zooplankton Regional Variation in REEs. Large regional variation was observed for REE concentrations in water, sediment and bulk zooplankton. ∑REEY concentrations in surface water and sediments varied across regions by up to 2 orders of magnitude, with maximum to minimum ratios for ∑REEY of 11 in sediments and 230 in surface waters (Fig. 2, Tables S1, S2). Analyses of variance among the four geographic regions showed significant differences in surface water, sediment, and zooplankton ∑REEY concentrations, as well as for the sediment-water partition coefficient or Kd (Welch's ANOVA, $p < 0.001$). Surface water ∑REEY concentrations were significantly different among all regions (Games-Howell post-hoc tests, $p < 0.01$), except for Montreal and Resolute ($p > 0.05$). ∑REEY sediment levels in Resolute were significantly lower than for all other regions ($p < 0.01$), and ∑REEY levels in zooplankton were significantly lower in Montreal than all other regions ($p < 0.05$). Kd was significantly higher in Montreal ($p < 0.05$) and lowest in Kuujjuarapik-Whapmagoostui (K-W) ($p < 0.001$). Study lakes were located in five geological provinces and this may play a role in explaining the regional differences in abiotic and biotic REE concentrations among these lakes (Fig. 1). REEs are often used as tracers to study the source of suspended particles and sediments in rivers because they can conserve the geochemical signature of parent materials (bedrock and soils).(Condie, 1991, Leybourne and Johannesson, 2008, Taylor and McClennan, 1985, Goldstein and Jacobsen, 1988) However, more data on local REE mineralisation and solubility in the study regions are required to accurately quantify the effect of geological region.

Surface water ∑REEY concentrations ranged from 0.1 - 21 nmol L^{-1} (or 0.01 - 2.8 μg L^{-1}) across all lakes. These levels are comparable with other published datasets in freshwater ecosystems, although minimum values for ∑REE, La and Yb were lower in this study than previous studies (Table 1). For example, reports from a proposed REE mine in northern Canada show that background REE concentrations in downstream lakes were lower than detection limits for all elements (< 0.05 μg L^{-1}), except for Sc and Y.(Morantz and Hoos, 2013) This observation is consistent with our study where the majority of individual REEs were < 0.05 μg L^{-1} (and all elements were < 0.05 μg L^{-1} in 28 of 39 sites). Our broad geographic survey indicates that detection limits lower than 0.05 μg L^{-1} are required to accurately assess background REE levels in surface water.

Surface sediment ∑REEY concentrations ranged from 314 to 3391 nmol g^{-1} (or 42 to 463 μg g^{-1}) (Fig. 2). These levels are similar to other published datasets for freshwater sediments (Table 1). This partitioning (high Kds; Figures 2c) reflects the low solubility of REEs and the strong binding of REEs to soils and sediments. One recent study measured REEs in river sediments from a prospective mining area in southern Quebec and found a median ∑REE value of 111 μg g^{-1} (min - max: 71 - 185).(Romero-Freire et al., 2018) Another study found mean values ∑REE of 86.9 ± 26.8 μg g^{-1} in river sediments from a watershed in Mexico with an iron ore mine.(Marmolejo-Rodríguez et al., 2007) The values from these two studies are comparable to sites from this study which had median ∑REEY values of 163 μg g^{-1} (Table 1).

Zooplankton ∑REEY levels ranged from 3.2 - 210 nmol/g (or 0.42 to 28 μg g^{-1}) (Fig. 2). In the absence of published data for REEs in freshwater zooplankton, we compared our results to those found for marine invertebrates. Marine studies reported relatively high levels (> 1.0 μg g^{-1}) for plankton, squid and scallops.(Pernice et al., 2009, Bustamante and Miramand, 2005) One study found concentrations of 8.5 pmol g^{-1} (1.15 ng g^{-1}) for ∑REE in marine plankton > 200 μm, (Strady et al., 2015) which is lower than zooplankton ∑REEY measured in this study. Bioaccumulation factors (BAFs) for zooplankton ∑REEY in this study ranged from 3.4 to 5.3, with a median of 4.5 (L Kg^{-1}, log10-transformed). BAF values for individual elements are shown in Fig. S2. The taxonomic composition of bulk zooplankton varied considerably between sample lakes and, we compared the composition to zooplankton ∑REEY values for a subset of samples (N = 22). We found no relationship between the relative abundance of major taxa (e.g. % cladoceran, % copepod, % chaoborids) and zooplankton ∑REEY across sample sites ($p > 0.05$). Future studies could examine the influence of taxonomic composition on REE bioaccumulation at a finer scale, focusing on sites with similar geology and environmental conditions.

Sediment-water partition coefficients (Kd, L Kg^{-1}) were calculated for study lakes based on individual and ∑REEY concentrations in dry surface sediment versus surface water. Median Kd for study sites was 1.3×10^6, ranging from 1.2×10^5 to 8.6×10^6 L Kg^{-1} (N = 34). These results are similar to Weltje *et al.* (2002) where individual element Kd values varied from 1×10^5 to 3×10^6 L Kg^{-1} for five industrialized freshwater sites in the Netherlands. As with this study, Kd values were consistently lower for Eu but did not show any discernable patterns for other elements (Fig. S1), which may be due to the variable oxidation states of Eu compared to other REEs.(Weltje et

al., 2002) As reported above, Kd values were higher and more variable at temperate sites, with a median of 3.4×10^6 compared to 7.9×10^5 for northern sites. This difference may be due to lake stratification and decreased transport of REEs from sediments into surface waters in these systems.

Relationships between REEs in Environmental Compartments. ∑REEY levels in sediments and surface waters were strongly positively correlated ($R^2 = 0.49$, $p < 0.01$, $N = 34$) (Fig. 3a). Mobilization of REEs from aquatic sediments may be an important source of REEs to the water column. Significant positive relationships were found between ∑REEY in bulk zooplankton and surface waters ($R^2 = 0.46$, $p < 0.01$), and to a lesser extent with surface sediments ($R^2 = 0.16$, $p = 0.03$) (Fig. 3b, 3c). These relationships indicate that aqueous REE concentrations were the strongest predictors of REE accumulation in freshwater zooplankton. There was also a strong negative relationship between Kd and ∑REEY in bulk zooplankton ($R^2 = 0.44$, $p < 0.01$) (Fig. 3d). Higher Kd values suggest that REEs are predominantly bound to sediments, leading to lower uptake by pelagic zooplankton feeding in the upper water column. These relationships are examined in more detail using multivariate analyses below in the section "Influence of Within-Lake Environmental Variables and Watershed Characteristics".

REE Speciation and Zooplankton Bioaccumulation. Simple linear correlations between DOC and ∑REEY in surface water or bulk zooplankton were non-significant ($p > 0.05$). However, the relationship between ∑REEY in bulk zooplankton and surface waters ($R^2 = 0.46$, $p < 0.01$, Fig. 3b) was significantly improved by using the ratio of ∑REEY to dissolved organic carbon concentrations (∑REEY:DOC) in surface waters ($R^2 = 0.63$, $p < 0.01$, Fig. S3). This same result was found when using a representative single element (La) to compare zooplankton La concentrations to surface water La concentrations ($R^2 = 0.44$, $p < 0.001$, Fig. 4a) and to the ratio of La to DOC in surface waters ($R^2 = 0.66$ $p < 0.001$, Fig. 4b). These REE:DOC concentration ratios suggest that the presence of organic matter decreases the bioavailability of REEs for uptake by zooplankton. Although REEs form strong complexes with carbonate and phosphate ions, these inorganic ligands may not compete effectively for REEs when organic ligands are present in circumneutral freshwaters.(Marsac et al., 2011, Tang and Johannesson, 2003, Andersson et al., 2006, Davranche et al., 2015) Our results show that strong positive correlations between aqueous and zooplankton REE concentrations are improved by controlling for site-specific DOC concentrations.(Chételat et al., 2018)

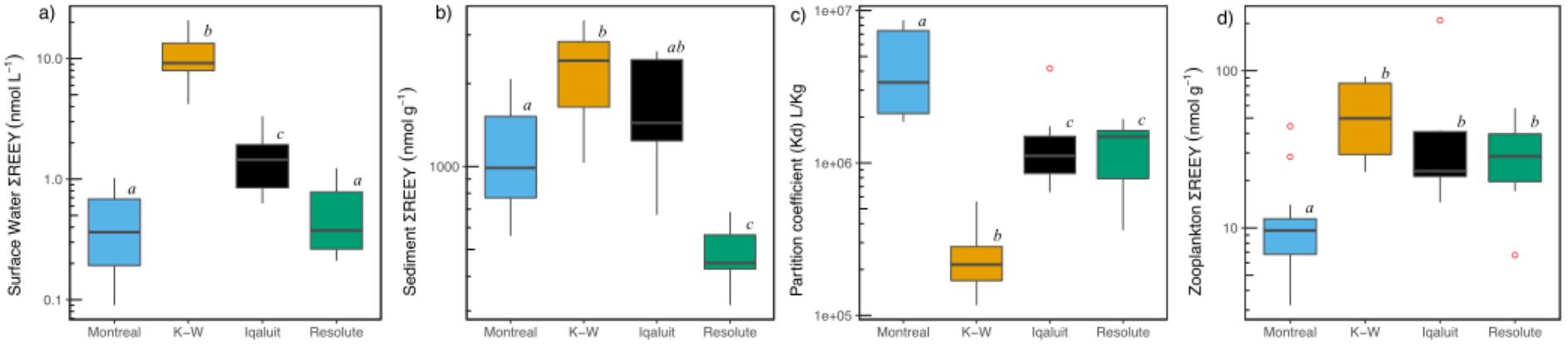

FIGURE 2: Boxplots showing a) ∑REEY concentrations in surface water (log-scaled nmol L^{-1}), b) ∑REEY concentrations in surface sediment (log-scaled nmol g^{-1}), c) sediment-water partition coefficients or Kd (L kg^{-1}) and d) ∑REEY concentrations in bulk zooplankton (log-scaled nmol g^{-1}). Boxplots show the median, interquartile range and ± SD. Red dots are outliers and letters indicate statistically significant differences in concentrations (Welch's ANOVA, Games-Howell post-hoc tests).

TABLE 1: Total REE concentrations (∑REEY, ∑REE) and selected single elements concentrations (La, Yb) from previously published studies on REEs in freshwater environments including surface waters and sediments (for complete references used in this table, see SI).

Freshwater Ecosystems

Surface Waters	Description	pH	Filter µm	∑REEY	∑REE	La	Yb	Units	Reference
Eastern Canada	39 lakes	6.5 - 8.3	0.45, 0.7	0.09 - 20.8	0.06 - 18.2	0.02 - 5.50	0.001 - 0.117	nmol L^{-1}	Current Study
Tuscany (IT)	6 rivers (reference)	4.4 - 7.8	0.45	-	0.34 - 7.81	0.06 - 1.38	0.014 - 0.116	nmol L^{-1}	Protano & Riccobono (2002)*
Tuscany (IT)	4 streams (mining)	3.1 - 5.6	0.45	-	711 - 6494	143 - 1332	6.70 - 40.9	nmol L^{-1}	Protano & Riccobono (2002)
Alpine Regions (FR)	2 alpine streams	7.5	0.45	-	2.26 - 2.74	0.19 - 0.86	0.023 - 0.147	nmol L^{-1}	Aubert *et al.* (2002)
Rotterdam (NL)	5 rivers/ditches	7.3 - 8.7	0.45	-	10 - 25	0.6 - 2.4	0.05 - 0.2	nmol L^{-1}	Weltje *et al.* (2002) †
Northern Canada	1 acidic lake	3.6	0.40	-	68.6	8.56	1.13	nmol L^{-1}	Johannesson & Lyons (1995)
SE Queensland (AU)	19 rivers/streams	5.7 - 7.7	0.22, 0.45	0.88 - 36.5	0.49 - 29.2	0.09 - 8.33	0.014 - 0.232	nmol L^{-1}	Lawrence *et al.* (2006)
Western Siberia (RU)	70 large & small rivers	4.7 - 8.1	0.45	-	0.61 - 24.4ψ	0.10 - 3.67	0.017 - 0.450	nmol L^{-1}	Pokrovsky *et al.* (2016)

Surface Sediments	Description	%POC	%OM	∑REEY	∑REE	La	Yb	Units	Reference
Eastern Canada	34 lakes	-	1.8 - 75.5	314 - 3391	252 - 3049	46 - 1032	2.7 - 25.2	nmol g^{-1}	Current Study
		-	1.8 - 75.5	42 - 463	36 - 433	6.4 - 143	0.47 - 4.36	µg g^{-1}	
Marabasco River (MX)	13 sampling sites	0.1 - 1.7	-	-	318 - 872	62 - 185	4.3 - 13.8	nmol g^{-1}	Marmolejo-Rodríguez *et al.* (2007)
		0.1 - 1.7	-	-	46 - 126	8.6 - 25.7	0.75 - 2.38	µg g^{-1}	
Northern Quebec (CA)	3 rivers/streams	-	7.0 - 73.9	-	-	-	-	nmol g^{-1}	Romero-Freire *et al.* (2018)
		-	7.0 - 73.9	-	71 - 185	-	-	µg g^{-1}	
Europe	Streams	-	-	-	1389	295	18	nmol g^{-1}	Migaszewski & Gałuszka 2015**
		-	-	-	199	41	3.1	µg g^{-1}	

*Original reference values taken from Hoyle et al. (1984) and Keasler & Loveland (1982)
† Values estimated using a web-based software for extracting data from plots (Webplotdigitizer)
ψ Total REE for this study do not include the element terbium (Tb)
** Original values from Salminen *et al.* (2005)

Furthermore, the free ion activity model successfully predicted La, Ce and Dy bioaccumulation in zooplankton. Calculated free ion concentrations of La in our study ranged from 2 x 10^{-16} to 4 x 10^{-13} M (or < than pM) among lakes. Zooplankton La concentrations were proportional to surface water La^{3+} concentrations, as calculated using WHAM speciation modeling ($R^2 = 0.58$, $p < 0.001$, Fig. 4c). The same trend was observed for other REEs (Ce: $R^2 = 0.53$), but was weaker (Dy: $R^2 = 0.28$) or non-significant (Eu: $p > 0.05$) for other elements (Fig. S4). Strady *et al.* (2015) similarly found that REEs in marine plankton correlated well with REE free ions (REE^{3+}). While FIAM has been well-established under laboratory conditions, fewer studies have validated these models under more complex natural conditions, (Lavoie et al., 2012, Ponton and Hare, 2009, Meylan et al., 2004, Mylon et al., 2003, Hare and Tessier, 1996) and their applicability to trivalent metals (M^{3+}), like the REEs.(Weltje et al., 2004, Vukov et al., 2016, El-Akl et al., 2015, Tan et al., 2017, Zhao and Wilkinson, 2015) Our study shows that freshwater zooplankton REE bioaccumulation was linked to the free ion concentrations of REEs (La, Ce, Dy). WHAM calculations also showed that ~99% of REEs were bound to colloidal humic acids in sampled lakes, which is consistent with other studies showing that often > 90% of REEs will form complexes with colloidal organic matter.(Davranche et al., 2015, Andersson et al., 2006) In this study, competition models calculated for calcium Ca^{2+} and H^+ did not improve the relationships between aqueous [La^{3+}] and [La] in zooplankton.(Hare and Tessier, 1998, Croteau et al., 1998) Overall, these results show that bulk zooplankton is an effective biomonitor to evaluate bioavailable REE levels in freshwater lakes.

Influence of within-lake environmental variables and watershed characteristics. Results of multivariate regressions using LASSO models are shown in Tables S8-S9. This modeling showed that surface water ΣREEY was most strongly predicted by ΣREEY concentrations in sediments and by mean lake depth for all sites ($p < 0.001$ for both variables, Table S8). Large model coefficients for these variables indicate that surface water ΣREEY increased significantly with ΣREEY sediment concentrations and decreased with lake depth. After the exclusion of deeper, stratified temperate lakes, lake depth was still negatively related to surface water REE concentrations but relationships were not significant ($p > 0.05$). Similar to the simple regression models reported above, these multivariate results suggest that mobilisation of REEs from sediments is a source of REEs to the water column and that REEs may be less mobilised in deeper stratified lakes. Lake area and aqueous [Fe] also contributed to a lesser extent to the best model

for ΣREEY in surface waters, however these relationships were not statistically significant (Table S8). No significant relationships were found between surface water ∑REEY and water physico-chemistry (temperature, conductivity, DOC, pH) across study sites. Higher water concentrations of REEs are usually associated with low pH, due to the increased solubility of REE^{3+} cations in acidic waters.(Herrmann et al., 2016) Water pH may have not been correlated with aqueous REE concentrations in this study because of the range of pH (6.5 to 8.3) in study lakes, as dissolved REE concentrations tend to increase only when water pH is < 6.5 (Lawrence et al., 2006, Verplanck et al., 2004). We also tested the influence of catchment area to lake area (CA:LA) and lake volume to catchment area (LV:CA) ratios, as proxies for catchment influence and water residence time, respectively, in these models. These ratios were not included in the final models, as they did not improve model predictions over the more parsimonious models shown here.

In sediment, Fe concentration was significantly and positively correlated with ΣREEY concentration ($p = 0.003$, Table S8). Marmolejo-Rodríguez *et al.* (2007) found that the light REEs (La-Gd) correlated with Fe and, inversely, that heavy REEs (Tb-Lu & Y) correlated better with Al in river sediments. The authors hypothesized that dissolved light REEs selectively adsorbed onto iron oxyhydroxides in river sediments. Fe oxyhydroxide adsorption under oxic conditions may explain the positive correlation between REEs and Fe in sediments in the present study, as ΣREEY in sediment samples was mainly light REEs (~78%). Sediment ΣREEY concentrations were not significantly related to sediment properties (% clay, sand, silt, organic matter). Previous studies have found higher REE content in sediments with fine-grain size, low organic matter and high clay content,(Romero-Freire et al., 2018, Herrmann et al., 2016, Marmolejo-Rodríguez et al., 2007) yet no significant trends with these variables were found for sediment [ΣREEY] or [La] among our study lakes ($p > 0.05$). However, LASSO modelling of sediment-water partitioning found that Kd was significantly higher in deeper lakes, with lower clay content and lower Al concentrations in sediments (Table S8). Kd decreased in lakes with higher sediment clay content (%), which contrasts with previous studies where clayey soils had higher REEs and REE oxides were preferentially bound to fine particles.(Zhang et al., 2018, Tyler and Olsson, 2001)

Five models using different subsets of environmental variables were run to evaluate which variables influenced zooplankton ∑REEY and La concentrations (Table S9). For zooplankton ∑REEY concentration, the ratio of aqueous ∑REEY to DOC (Model 1, $R^2 = 0.77$) explained a

greater amount of variability than Kd (Model 2, $R^2 = 0.67$) across study lakes. ∑REEY to DOC ratio was also a stronger predictor than Kd when stratified temperate lakes were excluded from the analysis ($p < 0.01$). Confirming results from simple linear regressions, zooplankton La concentration was strongly related to the ratio of aqueous La to DOC concentrations, Kd for La, and free La^{3+} concentrations (Table S9; Fig. 3, 4). Although surface water REEs were correlated with lake depth, depth did not significantly predict zooplankton ∑REEY concentrations (Table S9). Other environmental variables that did not explain zooplankton ΣREEY and La concentrations in this study included lake area, zooplankton $\delta^{15}N$ and C: N ratios, as well as aqueous Al, Fe and Ca. Lake pH was also a significant predictor of ∑REEY and La concentrations in zooplankton, which was somewhat surprising given that pH was not significantly correlated to aqueous ∑REEY or La, nor to their respective ratios with DOC. Negative regression coefficients for pH indicate that higher REE bioaccumulation occurred in lakes with lower pH.

Environmental Relevance. To our knowledge, this study generated one of the most detailed datasets on natural REE partitioning in lakes and ponds across a large geographic area with varied bedrock geology and environmental conditions. Our results show large regional variation in water, sediment and zooplankton ΣREEY concentrations. We found a more than 200 fold variation in ΣREEY in surface waters and a 10 fold variation in ΣREEY in sediments, which were associated with a range of more than an order of magnitude in zooplankton ΣREEY concentrations. Surface water REEs increased with increasing sediment concentrations, and decreased with lake depth, indicating that REE mobilisation from sediments was a source to the water column and also that REEs were less mobilised in deeper stratified lakes. We found that surface water REE concentrations were strong predictors of REE bioaccumulation in zooplankton over a large exposure gradient. Higher REE bioaccumulation occurred in zooplankton from lakes with higher REE to dissolved organic carbon (DOC) ratios and lower pH. Bioaccumulation was also strongly linked to the free ion concentrations of REEs (REE^{3+}) in surface waters. Overall, this study highlights the utility of zooplankton for the biomonitoring of bioavailable REEs in freshwater ecosystems. concentrations of REEs (REE^{3+}) in surface waters. Overall, this study highlights the utility of zooplankton for the biomonitoring of bioavailable REEs in freshwater ecosystems.

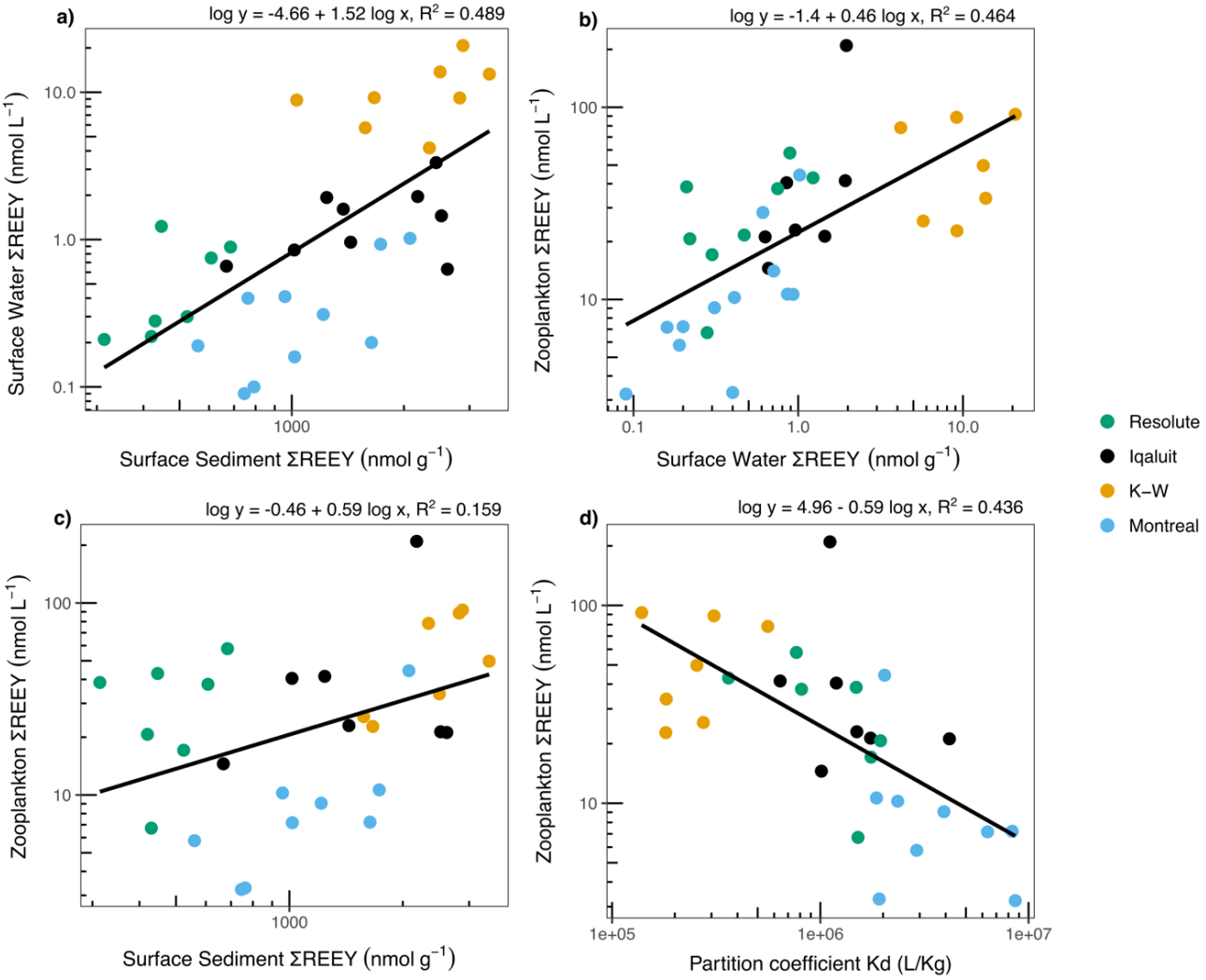

FIGURE 3: Linear regressions for a) surface water ∑REEY as a function of sediment ∑REEY concentrations, b) zooplankton ∑REEY concentrations as a function of surface water ∑REEY and c) zooplankton ∑REEY concentrations as a function of surface sediment ∑REEY and d) zooplankton ∑REEY concentrations as a function of sediment-water partition coefficient or Kd (L kg^{-1}). Data shown for all lakes near Montreal, Kuujjuarapik-Whapmagoostui (K-W), Iqaluit and Resolute ($p < 0.05$). All variables are log-scaled and linear equations are calculated with log-transformed variables.

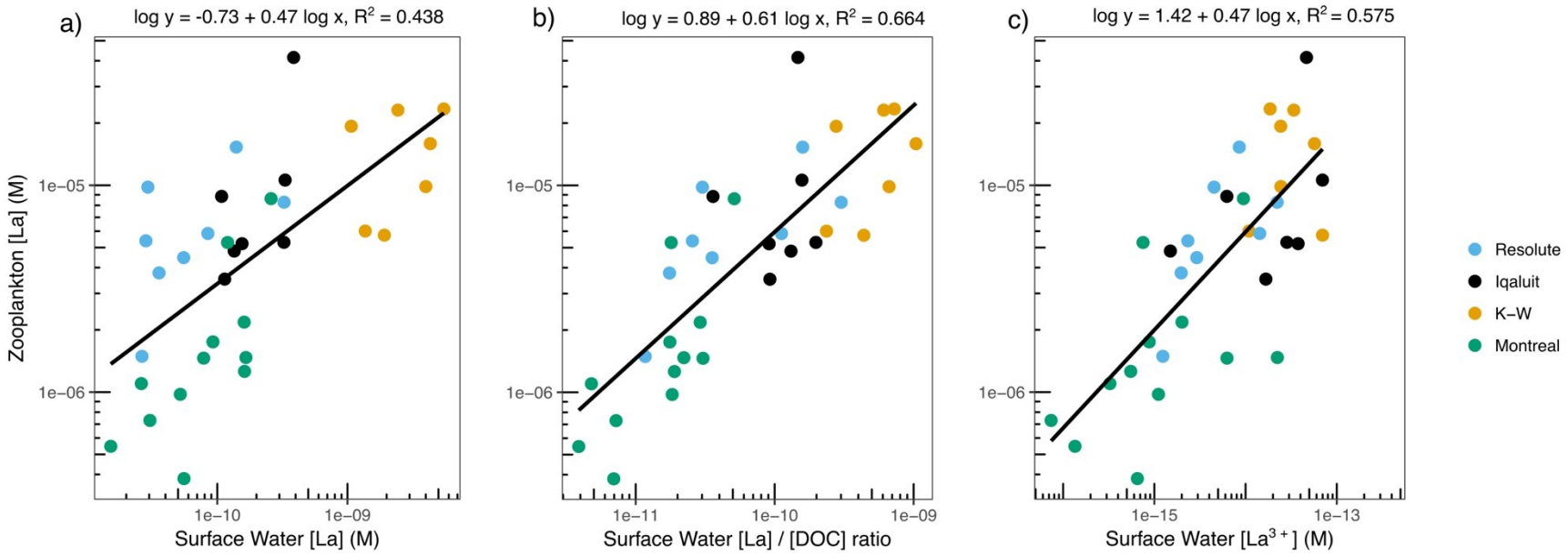

FIGURE 4: Linear regressions for bulk zooplankton La concentrations as a function of 1) surface water La concentrations, 2) ratio of surface water La to DOC concentrations, 3) surface water La free ion (La^{3+}) concentrations for lakes from all study regions ($p < 0.001$). Surface water La^{3+} concentrations were calculated with the Windermere Humic Aqueous Model software (WHAM 7.0.5). All variables on the x- and y-axes are log-scaled. Similar figures for Ce and Dy are shown in SI (Fig. S4).

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Author contributions. GM, MR, JC, TP and MA conceived and designed the study. GM, JC, MR, DP and TP performed the field data collection. Data and statistical analysis was done by GM and MC. GM and MC wrote the manuscript. All authors edited the manuscript and gave their approval to the final version of the manuscript.

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Supporting Information consists of 22 pages including detailed methods for quality assurance, data handling and multivariate analyses, as well as supplementary tables (9) and figures (9).

Supporting Information
Environmental drivers of rare earth element bioaccumulation in freshwater zooplankton

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TABLE S7: Equilibrium Parameters for La, Ce and Dy in the Windermere Humic Aqueous Model (WHAM, version 7.0).

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TABLE S9: Summary of multivariate regression analyses examining the influence of environmental variables on ∑REEY concentrations and La concentrations bulk zooplankton from all samples sites (N = 26-34).* Standardized regression coefficients and p values are shown for each variable.

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FIGURE S1: Partition coefficients (Kd) in log L kg^{-1} based on REE concentrations in dry sediment (nmol Kg^{-1}) versus surface water (nmol L^{-1}) for 34 lakes.

FIGURE S2: Bioaccumulation factors (BAF) calculated as the ratio of REE concentrations in zooplankton (dry weight, nmol/kg) to a) REE concentration in surface water (nmol/L), BAF values are in units of log10-transformed L/kg respectively and are shown versus the atomic number of REE for 34 lakes.

FIGURE S3: Linear regression for bulk zooplankton ∑REEY concentrations (nmol/g) versus ratio of surface water ∑REEY to dissolved organic carbon (DOC) concentrations. All variables shown are log-scaled.

FIGURE S4: Linear regressions for bulk zooplankton Dy and Ce concentrations versus 1) surface water Dy and Ce concentrations, 2) ratio of surface water Dy and Ce to dissolved organic carbon (DOC) concentrations, 3) surface water free ion (Dy^{3+}, Ce^{3+}) concentrations for samples from Montreal, Kuujjuarapik-Whapmagoostui, Iqaluit and Resolute ($p < 0.05$). All variables shown are log-scaled.

FIGURES S5 - S9: Path plots showing the standardized regression coefficients of independent variables included in LASSO models of ΣREEY concentrations across all lakes based on models from Tables S8 and S9.

References for SI

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SI METHODS

Quality assurance. All water, sediment and zooplankton samples were above analytical detection limits for all elements in this study, except for surface waters in temperate lakes where detection frequencies for Ho, Tm, and Lu were 0.98, 0.83, and 0.93, respectively. REE measurements below detection limits were estimated as half of the detection limit value. Analytical blank values were subtracted from samples for each element (when detected). Filtered field blanks were not subtracted from surface water concentrations due to higher variability.

For surface water, standard reference materials were used for quality assurance for trace metals (NIST1640A and QCPE-21) and the average recovery ranged from 93 to 115% (Table S4). Quality control for REEs in surface waters was assured through an inter-laboratory calibration with CEAEQ of four unfiltered subarctic water samples (Table S5). The inter-laboratory calibration also compared metal concentrations in digested samples of sediment (STSD-1, CCRMP/CANMET) and animal tissue (TORT-2; lobster hepatopancreas, NRC). On average, water samples in this study varied by 17% compared to CEAEQ, sediment by 7%, and TORT-2 results by 13% (Table S6).

Certified reference materials (CRM) were also used for quality assurance with digested samples. For trace metal analysis in sediments, a stream sediment CRM (STSD-1) was analysed. Average recovery was compared to partial extraction certified values and was found to be 91% (50 - 129%) for Mn, Ni, Cu, Zn, As, Cd, Pb and Fe (see Table S4). For sediments, recovered metal concentrations were lower than certified values due to differences in extraction methods (full vs. partial extractions). For REEs, sample digestions included three CRM of mussel tissue (BCR 668, Institute for Reference Materials and Measurements or IRMM), plant tissue (BCR 670, IRMM), and stream sediment (STSD-1, Canadian Certified Reference Materials Project or CCRMP). Average (min-max) recovery for REEs in reference material was 87% (79 - 101%) for mussel tissue, 84% (67 – 117%) for plant tissue, and 70% (40 – 99%) for sediment (Table S6). These values are consistent with average recoveries reported in the literature.(Weltje et al., 2002, Mayfield and Fairbrother, 2015, Dolegowska and Migaszewski, 2013) Coefficients of variation (CV) were calculated for analytical and field duplicates to estimate analytical precision and were approximately ± 13% for water, ± 7% for sediment and ± 21% zooplankton.

Data handling for stable isotopes. For northern lakes, zooplankton $\delta^{15}N$ values were adjusted ($\delta^{15}N_{adj}$) for lake-specific baseline signatures by subtracting values of $\delta^{15}N$ in sediment. However, sediment $\delta^{15}N$ was not available for temperate lakes and therefore $\delta^{15}N_{adj}$ could not be calculated for these sites. Only unadjusted $\delta^{15}N$ could therefore be used in analyses with all sample sites pooled together. For analysis on a subset of only northern sites, the $\delta^{15}N_{adj}$ were used. $\delta^{13}C$ values were not measured in sediments because samples were not acidified to remove carbonates. For zooplankton samples, carbon to nitrogen (C:N) ratios were calculated as the ratio of carbon to nitrogen content on a mass basis (percent of sample total dry weight).

Statistical analyses for multivariate analyses. Multivariate analyses were conducted on 8 dependent variables to examine which environmental variables influence both ΣREEY and La concentrations in a) surface water b) surface sediment, and c) sediment-water partition coefficients (log Kd, log L/kg) and d) bulk zooplankton. Models were run for all sites (N = 26 - 34), as well as for only northern sites (N = 20 - 21). Multiple regressions were calculated using LASSO (Least Absolute Shrinkage and Selection Operator) analyses with the R package '*lars*'.(Hastie and Efron, 2013) This technique is formulated for linear models and is similar to forward selection approaches in linear regression. However, LASSO analysis limits the sum of the regression coefficients using a tuning parameter (lambda, λ) which forces the coefficients of variables with low influence on the dependent variable towards zero. This ensures models are parsimonious and do not overfit smaller datasets with collinear variables.(Tibshirani, 1996, Efron et al., 2002) The best model was chosen as that with the lowest Mallow's Cp value, a statistic for subset selection similar to the Akaike information criterion (AIC) or Bayesian information criterion (BIC).(James et al., 2013)

Subsets of environmental variables were included in each LASSO model as independent variables when they were deemed to be 'proximally' related to the dependent variable based on *a priori* information about REE chemistry and transport.(Dormann et al., 2013) Selected independent variables included zooplankton δ13C, δ15N, C:N ratios, surface water pH, ΣREEY/La to DOC ratios, aqueous TP, Ca and Al, as well sediment physico-chemical characteristics. The '*selectiveInference*'(Tibshirani et al., 2017) package in R was used to estimate the significance of each independent variable (p) in the models using its corresponding λ value. Multiple models were used to test key variables on the different dependent variables, as they were not all independent from each other and could not be included in the same model. Tables S8 and S9 show LASSO model results including the model coefficients and fixed inference p-values for independent

variables at the given level of the penalty parameter (lambda or λ). Models with all sites had low Mallow's Cp values which were close to the number of independent variables, indicating models with good fit. Relatively high R^2 values (range: 0.39 - 0.92) for models included indicate strong relationships between ΣREEY or La levels and the environmental variables tested. Models for ΣREEY gave similar results to those calculated for models using a representative single element (La) (Tables S8, S9). Models were also run for a subset of sites (excluding the temperate sites, not shown here). These subset models had higher Cp values and zooplankton models had lower R^2 values, probably due to the smaller sample size of this data subset, but showed similar trends to models with all sites. Lasso path plots for all multivariate analyses are shown in Figures S5 - S9.

TABLE S1: GPS coordinates, water physicochemical characteristics, and surface water DOC, nutrients, ions and trace metals for all sample lakes (N = 39).

Site	Year	Lat	Long	Lake Area	Water -shed	Mean Depth	Temp	Cond	pH	DOC	TN	TP	Ca	Al	Fe	∑REEY	∑REE	∑REEY	∑REE
				km^2	km^2	m	C	µs/cm		mg/L	µg/L	µg/L	µmol/L	µg/L	µg/L	nmol/L	nmol/L	ng/L	ng/L
Subarctic taiga - K-W																			
KJ1	2012	55.320	-77.711	0.08	2.70	0.7	13.0	104	7.9	6.0	309	8.1	186	38.2	43.0	13.75	11.44	1836	1631
KJ2	2012	55.369	-77.618	0.11	3.35	1.0	11.0	102	7.9	4.2	215	3.1	248	24.7	27.4	13.28	11.30	1785	1609
KJ3	2012	55.304	-77.716	0.01	0.62	0.3	10.0	130	7.7	4.1	242	3.1	200	15.6	40.7	8.85	7.35	1180	1047
KJ4	2012	55.334	-77.625	0.29	1.78	1.9	13.0	43	7.1	4.0	206	4.7	100	28.1	24.3	9.15	8.22	1250	1166
KJ5	2012	55.291	-77.719	0.05	1.00	1.3	17.0	56	7.4	7.6	338	7.9	96	65.6	40.2	20.77	18.21	2816	2589
KJ6	2012	55.320	-77.642	0.08	0.39	0.6	16.0	19	6.6	4.4	306	8.7	30	66.2	24.7	9.19	8.10	1249	1152
KJ7	2012	55.334	-77.597	0.39	2.31	0.9	14.0	46	7.3	5.8	281	8.7	110	25.3	58.8	5.74	5.01	777	711
KJ8	2012	55.337	-77.612	0.10	0.19	1.2	16.0	31	6.6	3.9	245	6.3	58	27.3	30.5	4.19	3.71	569	527
Arctic tundra - Iqaluit																			
IQ1	2013	63.797	-68.546	0.03	0.21	1.8	7.3	20	6.7	2.1	108	5.7	106	34.0	17.7	1.93	1.50	257	218
IQ2	2013	63.758	-68.444	0.08	2.00	6.0	4.9	60	6.9	2.6	102	4.5	350	21.0	11.1	1.96	1.45	255	210
IQ3	2013	63.652	-68.297	0.28	4.03	12.0	2.9	34	6.8	2.4	78	4.2	136	22.3	5.5	3.33	2.44	432	352
IQ4	2013	63.798	-68.538	0.09	0.37	5.0	5.3	28	6.9	1.2	45	3.7	131	18.0	3.5	0.66	0.51	87.5	74.4
IQ5	2013	63.749	-68.398	0.36	1.87	6.0	3.0	45	6.8	1.7	58	4.1	235	22.5	5.0	0.96	0.75	128	109
IQ6	2013	63.916	-68.573	0.42	12.50	3.0	6.0	44	6.5	1.2	76	3.7	187	19.2	15.6	1.61	1.16	208	168
IQ7	2013	63.685	-68.376	0.54	3.74	8.0	6.9	92	7.2	3.0	173	9.6	268	17.7	30.3	0.85	0.63	113	93.5
IQ8	2013	63.825	-68.604	0.56	14.20	12.0	4.0	63	7.3	1.6	33	5.3	274	19.7	10.9	1.45	1.07	188	155
IQ13	2013	63.875	-68.478	4.50	41.10	7.5	9.7	22	7.5	1.0	61	1.2	105	2.24	3.05	0.63	0.46	82.2	67.5
Polar desert - Resolute																			
RZ1	2014	74.690	-94.990	0.27	5.18	3.1	3.0	239	7.8	2.0	174	6.6	592	1.82	6.20	0.30	0.18	37.1	26.5
RZ2	2014	74.721	-94.862	0.03	1.51	0.8	8.0	130	8.2	0.8	73	4.6	545	13.04	13.81	0.75	0.52	96.2	75.9
RZ3	2014	74.684	-94.989	0.04	0.42	4.3	2.3	850	7.8	1.0	132	1.1	671	2.22	3.93	0.21	0.14	26.7	20.4
RZ4	2014	74.759	-95.060	0.15	1.56	2.7	3.8	346	8.2	2.3	186	4.1	658	2.27	1.70	0.28	0.16	34.7	23.5
RZ5	2014	74.777	-95.096	0.63	83.7	6.7	3.4	125	8.2	0.9	229	4.0	412	4.58	2.81	0.89	0.61	113	87.7
RZ6	2014	74.688	-94.943	1.21	19.8	9.0	3.4	399	8.1	1.1	103	3.5	613	1.12	1.36	0.22	0.13	26.7	19.3
RZP3	2014	74.744	-94.955	0.04	1.4	0.8	7.8	156	8.3	1.1	122	5.3	498	11.00	4.53	1.23	0.98	163	140
RZP6	2014	74.680	-94.914	0.13	20.8	1.8	5.5	761	8.1	1.6	213	5.6	398	7.84	8.75	0.47	0.36	63.6	54.1
Temperate - Montreal																			
AG	2012	45.308	-72.314	1.10	56.5	7.4	22.2	84	7.5	5.4	-	-	249	15.3	38.5	0.16	0.12	20.9	17.2
CH11	2012	46.801	-72.518	0.92	15.7	9.7	23.1	71	8.0	5.5	-	-	166	54.7	125.8	0.71	0.55	92.9	78.5
CH12	2012	45.428	-72.604	4.70	127.8	4.6	24.7	110	8.0	5.3	-	-	379	28.4	16.0	0.41	0.34	54.8	48.7
CR_MA	2012	46.822	-72.508	1.00	12.4	5.1	22.1	43	6.8	5.1	-	-	114	63.5	69.9	1.02	0.78	132	111
CR_SH	2012	45.990	-74.006	0.23	0.8	5.1	24.7	14	7.1	4.2	-	-	47	32.8	13.3	0.19	0.11	23.6	16.6
GO	2012	46.609	-72.951	0.40	6.2	10.4	23.9	32	7.0	3.4	-	-	86	31.8	30.0	0.33	0.21	41.3	30.7
HE	2012	46.542	-72.891	0.26	2.3	10.6	24.9	40	6.7	2.6	-	-	76	67.2	37.3	0.31	0.25	40.8	35.3
ME	2012	46.789	-72.737	0.35	5.7	3.5	23.2	49	6.9	7.5	-	-	91	331.0	283.2	0.93	0.67	120	97.0
MO	2012	45.928	-74.035	0.31	2.2	9.2	24.3	103	8.1	3.9	-	-	264	30.4	16.6	0.09	0.06	10.9	8.25
OR	2012	45.295	-72.271	1.42	7.5	6.9	22.9	129	8.2	3.5	-	-	215	18.4	13.8	0.10	0.07	13.0	10.3
PE	2012	46.755	-72.561	0.21	0.8	5.5	23.5	57	7.5	2.8	-	-	149	27.6	35.2	0.20	0.16	25.8	22.1
PR12	2012	45.961	-74.041	0.19	7.4	6.4	25.6	38	7.2	8.0	-	-	126	55.1	163.6	0.40	0.23	48.7	34.2
SR	2012	46.791	-72.715	0.59	8.7	9.2	21.2	28	7.4	8.5	-	-	84	86.1	101.0	0.86	0.59	109	84.6
TR	2012	46.769	-72.552	0.10	0.2	11.5	24.2	29	7.1	6.6	-	-	84	43.6	73.3	0.61	0.41	77.0	59.0
			min	0.01	0.19	0.3	2.3	14	6.5	0.8	33	1.1	30	1.12	1.36	0.09	0.06	10.9	8.25
			max	4.70	127	12	26	850	8.3	8.5	338	9.6	671	331	283	20.8	18.2	2816	2589
			max/min	470	673	40	11	61	1.3	11	10	9	22	296	208	240	322	258	314

TABLE S2: Sediment and bulk zooplankton characteristics, stable isotope ratios, and trace elements concentrations for all sample lakes (N=39).

	Surface Sediments													Bulk Zooplankton					
Site	**%N**	**δ15N**	**OM**	**Clay**	**Silt**	**Sand**	**Al**	**Fe**	**∑REEY**	**∑REE**	**∑REEY**	**∑REE**	**Kd**	**δ13C**	**δ15N**	**∑REEY**	**∑REE**	**∑REEY**	**∑REE**
	%	‰	%	%	%	%	mg/g	mg/g	nmol/g	nmol/g	µg/g	µg/g	L/Kg	‰	‰	nmol/g	nmol/g	µg/g	µg/g
Subarctic taiga - K-W																			
KJ1	1.63	0.12	41.7	20.42	64.08	15.51	11.7	16.0	2501	2240	341.4	318.2	1.8E+05	-32.62	2.92	33.63	29.53	4.56	4.20
KJ2	1.39	2.20	46.9	17.12	67.64	15.24	15.0	32.8	3391	3049	463.5	433.0	2.6E+05	-30.71	3.73	49.77	44.51	6.79	6.32
KJ3	1.50	1.02	16.1	10.67	79.49	9.83	4.9	12.0	1031	929	141.1	132.0	1.2E+05	-29.40	2.79	-	-	-	-
KJ4	2.08	0.87	48.8	14.55	67.37	18.08	15.5	24.7	2824	2615	389.2	370.7	3.1E+05	-30.52	3.99	88.62	82.33	12.22	11.66
KJ5	1.45	1.61	49.8	21.24	59.31	16.12	17.9	27.4	2880	2618	394.9	371.7	1.4E+05	-31.94	4.24	91.91	83.49	12.60	11.85
KJ6	2.17	-0.39	75.5	9.72	54.36	35.91	10.5	9.3	1665	1531	228.8	216.8	1.8E+05	-29.17	3.87	22.75	20.82	3.12	2.95
KJ7	1.61	0.90	46.3	25.46	67.45	7.08	13.7	43.1	1575	1449	216.7	205.5	2.7E+05	-29.34	3.64	25.59	23.46	3.52	3.33
KJ8	2.16	0.07	64.4	15.77	70.63	13.61	11.3	19.4	2341	2154	322.0	305.4	5.6E+05	-28.40	2.14	78.29	72.84	10.81	10.32
Arctic tundra - Iqaluit																			
IQ1	0.40	3.03	7.6	8.25	51.83	39.93	4.8	53.1	1241	1002	164.8	143.6	6.4E+05	-32.13	3.87	41.49	37.18	5.66	5.28
IQ2	0.73	4.51	20.8	8.37	71.48	20.16	8.3	105.5	2177	1805	291.2	258.2	1.1E+06	-34.36	4.99	209.53	185.86	28.56	26.46
IQ3	1.24	2.36	19.4	8.80	81.01	10.19	8.7	16.1	2441	1908	321.4	274.0	7.3E+05	-	-	-	-	-	-
IQ4	0.28	3.37	5.1	6.34	53.75	39.91	3.0	9.7	668	572	90.2	81.6	1.0E+06	-33.52	2.52	14.53	12.25	1.95	1.75
IQ5	0.47	3.19	1.8	2.84	30.33	66.83	2.8	9.5	1439	1214	193.5	173.4	1.5E+06	-32.09	3.87	22.98	20.77	3.15	2.95
IQ6	0.52	3.82	22.1	6.18	80.26	13.57	9.1	164.5	1375	1107	182.4	158.6	8.5E+05	-31.21	4.37	-	-	-	-
IQ7	1.45	4.12	42.9	7.01	77.00	15.99	6.0	17.2	1016	824	135.2	118.1	1.2E+06	-34.40	11.67	40.49	34.62	5.46	4.94
IQ8	0.82	4.87	19.8	7.79	79.96	12.07	10.3	54.5	2521	2046	335.2	293.0	1.7E+06	-33.92	4.22	21.33	18.54	2.89	2.64
IQ13	0.28	4.38	-	-	-	-	8.8	47.4	2617	2220	352.1	316.8	4.2E+06	-33.01	4.49	21.16	16.66	2.78	2.38
Polar desert - Resolute																			
RZ1	1.60	5.59	40.8	18.72	78.27	3.23	8.7	26.2	524	408	69.0	58.7	1.8E+06	-30.59	8.32	17.10	14.67	2.30	2.09
RZ2	0.21	5.91	5.7	9.27	89.72	1.01	17.2	28.2	608	484	80.5	69.5	8.1E+05	-24.79	5.70	37.71	30.89	5.03	4.43
RZ3	0.85	4.58	21.0	17.24	76.54	6.22	5.8	9.1	314	252	41.7	36.2	1.5E+06	-30.68	8.27	38.54	34.92	5.27	4.95
RZ4	0.92	2.19	31.0	10.89	68.37	20.74	4.5	6.1	430	354	57.4	50.7	1.5E+06	-33.04	8.90	6.72	5.80	0.91	0.83
RZ5	0.09	10.30	2.5	7.71	78.79	13.51	6.1	10.4	685	578	92.2	82.7	7.7E+05	-32.72	10.64	57.83	53.70	7.97	7.60
RZ6	0.23	8.11	3.8	10.91	85.40	3.70	5.7	8.4	420	346	56.1	49.6	1.9E+06	-31.37	8.21	20.69	19.01	2.84	2.69
RZP3	0.16	3.47	4.1	8.15	87.62	4.22	9.0	12.0	447	369	59.8	52.8	3.6E+05	-28.26	4.04	42.93	36.68	5.79	5.24
RZP6	-	-	-	-	-	-	-	-	-	-	-	-	-	-27.54	5.57	21.64	18.04	2.88	2.56
Temperate - Montreal																			
AG	-	-	19.9	7.17	87.92	4.91	17.7	46.3	1018	859	137.5	123.3	6.4E+06	-32.58	6.44	7.17	5.57	0.94	0.80
CH11	-	-	-	-	-	-	-	-	-	-	-	-	-	-30.74	9.42	14.06	10.28	1.82	1.49
CH12	-	-	17.6	13.29	86.71	-	-	33.6	959	793	128.6	113.8	2.4E+06	-30.21	11.23	10.24	8.73	1.38	1.25
CR_MA	-	-	15.0	8.88	87.68	3.44	-	46.8	2076	1799	281.4	256.8	2.0E+06	-32.61	7.23	44.39	39.93	6.10	5.70
CR_SH	-	-	47.0	7.66	75.46	16.88	15.3	12.5	560	404	72.5	58.6	2.9E+06	-35.63	3.71	5.78	4.35	0.76	0.64
GO	-	-	-	-	-	-	-	-	-	-	-	-	-	-30.33	5.61	-	-	-	-
HE	-	-	54.0	6.54	75.78	17.68	15.5	32.3	1215	987	161.9	141.7	3.9E+06	-30.78	5.87	9.06	7.17	1.20	1.03
ME	-	-	25.0	5.94	86.48	7.56	23.2	24.1	1732	1397	249.7	219.9	1.9E+06	-32.22	3.82	10.63	7.53	1.37	1.09
MO	-	-	32.0	10.31	82.96	6.72	16.0	13.4	746	550	97.0	79.5	8.6E+06	-33.96	10.30	3.22	2.38	0.42	0.34
OR	-	-	13.9	9.84	82.11	8.07	10.9	19.0	792	655	106.2	94.0	7.8E+06	-	-	-	-	-	-
PE	-	-	18.0	7.90	84.82	7.29	17.3	27.2	1637	1398	220.7	199.4	8.3E+06	-29.11	5.77	7.22	5.64	0.96	0.82
PR12	-	-	41.2	8.66	80.44	10.90	17.6	24.4	763	589	100.4	85.0	1.9E+06	-36.16	7.24	3.28	2.49	0.44	0.37
SR	-	-	-	-	-	-	-	-	-	-	-	-	-	-31.37	5.52	10.66	8.57	1.46	1.27
TR	-	-	-	-	-	-	-	-	-	-	-	-	-	-23.43	5.22	28.35	24.05	3.82	3.44
min	0.09	-	1.80	2.84	30.33	1.01	2.80	6.10	314	252	41.7	36.2	1.2E+05	-	-	3.22	2.38	0.42	0.34
max	2.17	-	75.5	25.46	89.72	66.83	23.2	164.5	3391	3049	463.5	433	8.6E+06	-	-	210	186	28.6	26.5
max/min	24	-	42	9.0	3.0	66	8.3	27	11	12	11	12	72	-	-	65	78	68	78

TABLE S3: Average detection limits for REEs and other trace metals in water, sediment and zooplankton for northern sampled sites. Sediment and zooplankton detection limits were calculated with median samples masses (0.13 and 0.08 g respectively). Samples were analyzed in four separate batches by ICP-MS.

Element	Water	Sediment	Zooplankton	Element	Water	Sediment
	ng/L	ng/g	ng/g		µg/L	ng/g
Y	0.2211	0.1701	0.2764	Al	0.023	17.5
La	0.1324	0.1018	0.1655	Mn	0.004	2.76
Ce	0.1594	0.1226	0.1992	Fe	0.073	56.0
Pr	0.0616	0.0474	0.0769	Ni	0.004	2.90
Nd	0.2939	0.2261	0.3674	Cu	0.004	2.91
Sm	0.2317	0.1782	0.2896	Zn	0.024	18.1
Eu	0.1108	0.0852	0.1385	As	0.027	20.6
Gd	0.1268	0.0976	0.1585	Se	0.159	121.9
Tb	0.0449	0.0345	0.0561	Cd	0.005	4.20
Dy	0.1494	0.1149	0.1867	Pb	0.001	0.97
Ho	0.0344	0.0265	0.0430			
Er	0.0385	0.0296	0.0481			
Tm	0.0284	0.0219	0.0355			
Yb	0.0756	0.0582	0.0945			
Lu	0.0211	0.0162	0.0263			

TABLE S4: Percent recovery values for trace metals concentrations in certified reference materials (CRM): NIST1640a and QCPE21-20.

Matrix	% Recovery	Al	Mn	Ni	Cu	Zn	As	Se	Cd	Pb	Fe
Water	NIST1640a	107.2	104.5	115.2	105.3	110.6	115.5	105.6	101.6	102.9	107.9
	NIST1640a	99.1	97.2	97.0	98.8	96.9	100.4	95.5	94.6	96.5	100.2
	NIST1640a	99.0	100.6	98.2	100.1	100.6	105.3	100.8	97.4	99.3	93.0
Water	QCPE21-20	-	100.7	100.4	101.6	103.1	100.6	100.5	99.9	99.8	99.4
	QCPE21-20	-	102.8	101.4	103.3	102.5	100.3	102.5	101.1	102.7	99.9
	QCPE21-20	-	98.7	99.2	101.4	101.4	97.7	101.7	99.3	98.5	99.2
	QCPE21-20	-	95.3	94.7	98.4	96.1	96.3	95.8	98.2	97.7	97.1
Sediment	STSD-1	-	65.8	80.1	72.7	70.9	79.3	-	101.3	74.1	61.5
	STSD-1	-	65.0	72.3	65.7	67.5	77.2	-	-	69.3	62.3
	STSD-1	-	91.5	99.6	93.4	50.0	109.0	-	129.4	97.4	84.5
	STSD-1	-	92.9	97.3	91.4	92.2	107.8	-	125.0	107.5	88.9
	STSD-1	-	91.5	99.2	91.4	90.6	105.8	-	126.5	106.6	88.1
	STSD-1	-	96.6	107.8	94.3	84.5	112.6	-	128.5	100.0	93.4

TABLE S5: Inter-laboratory calibration for REE concentrations (ng/mL) in surface waters for four natural water samples from the subarctic sites (Kuujjuarapik-Whapmagoostui) in this study. The same unfiltered samples were analysed at the CEAEQ (Centre d'expertise en analyse environnementale du Québec) and in the laboratory of this study (UdeM, Université de Montréal).

	KJ4		KJ2		KJ8		KJ10	
Element	CEAEQ	UdeM	CEAEQ	UdeM	CEAEQ	UdeM	CEAEQ	UdeM
Y	0.083	0.083	0.176	0.160	0.042	0.040	0.256	0.240
La	0.339	0.335	0.601	0.555	0.149	0.145	0.687	0.615
Ce	0.452	0.482	0.353	0.332	0.210	0.222	0.444	0.412
Pr	0.063	0.065	0.111	0.110	0.029	0.032	0.135	0.130
Nd	0.208	0.204	0.373	0.344	0.093	0.092	0.459	0.424
Sm	0.026	0.030	0.047	0.042	0.014	0.011	0.063	0.057
Eu	0.019	0.004	0.011	0.008	0.004	0	0.025	0.012
Gd	0.026	0.023	0.044	0.032	0.012	0.011	0.059	0.044
Tb	0.003	0.002	0.005	0.004	0.001	0	0.007	0.006
Dy	0.013	0.012	0.025	0.025	0.006	0.007	0.037	0.035
Ho	0.002	0.002	0.005	0.005	0.001	0	0.008	0.006
Er	0.007	0.007	0.016	0.014	0.004	0.004	0.022	0.023
Tm	0.001	0.001	0.002	0.002	0	0.001	0.003	0.002
Yb	0.007	0.006	0.013	0.012	0.003	0	0.020	0.016
Lu	0.001	0.001	0.002	0.002	0.001	0	0.003	0.003

TABLE S6: REE concentrations in certified reference materials (± uncertainty) with measured values in measured reference materials from this study (± standard deviations). Note: For STSD-1, there are no certified values for Pr, Gd, Ho, Er, Tm. Recovered concentrations for sediments are lower than certified values due to different extraction methods (total vs. partial). Two standards (STSD-1 and Tort-2) show results from an intercalibration for REEs with the laboratory at the CEAEQ (Centre d'expertise en analyse environnementale du Québec).

	BCR 668 (Mussel Tissue) pmol/g d.w.				**BCR 670 (Aquatic Plant)** pmol/g d.w.				**STSD-1 (Creek Sediment)** nmol/g d.w.						**Tort -2 (Lobster hepatopancreas)** ng/g d.w.			
	Certified		Measured (n = 17)		Certified		Measured (n = 11)		Certified		Intercal (n = 2)		Measured (n = 16)		Intercal (n = 2)		Measured (n = 10)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Y	662 ±	58	587 ±	27	5196 ±	776	4102 ±	195	472 ±	na	315 ±	na	273 ±	23	na ±	na	510 ±	46
La	578 ±	48	479 ±	35	3506 ±	338	2716 ±	272	216 ±	na	173 ±	na	163 ±	16	1700 ±	na	1492 ±	137
Ce	633 ±	83	498 ±	45	7044 ±	443	5645 ±	521	364 ±	na	293 ±	na	271 ±	29	1900 ±	na	1337 ±	122
Pr	87 ±	8.5	71 ±	5.8	859 ±	106	671 ±	45	- ±	na	50 ±	na	45 ±	4.4	260 ±	na	183 ±	16
Nd	378 ±	41	322 ±	26	3279 ±	208	2774 ±	220	194 ±	na	194 ±	na	183 ±	18	940 ±	na	731 ±	64
Sm	74 ±	6.7	68 ±	5.5	626 ±	67	569 ±	38	40 ±	na	39 ±	na	36 ±	3.4	160 ±	na	97 ±	6
Eu	18 ±	1.6	16 ±	1.1	153 ±	16	176 ±	6.7	11 ±	na	8.6 ±	na	7.5 ±	0.7	18 ±	na	19 ±	2.0
Gd	82 ±	6	83 ±	8.1	622 ±	85	625 ±	27	- ±	na	36 ±	na	37 ±	3.1	140 ±	na	132 ±	8
Tb	10 ±	1.1	10 ±	0.7	88 ±	10	77 ±	3.7	8 ±	na	4.5 ±	na	4.8 ±	0.4	16 ±	na	13.5 ±	1.0
Dy	55 ±	3.7	46 ±	3.3	486 ±	54	409 ±	24	34 ±	na	29 ±	na	25 ±	2.0	76 ±	na	62 ±	4
Ho	11 ±	3.6	9.2 ±	0.7	96 ±	16	75 ±	3.9	- ±	na	5 ±	na	4.8 ±	0.4	14 ±	na	12.6 ±	1.0
Er	27 ±	2.9	24 ±	1.9	263 ±	27	219 ±	13	- ±	na	16 ±	na	14 ±	1.2	34 ±	na	34 ±	2
Tm	2.8 ±	0.4	2.5 ±	0.4	34 ±	5.5	27 ±	1.3	- ±	na	2 ±	na	1.8 ±	0.2	4 ±	na	3.4 ±	0.4
Yb	16 ±	2.9	14 ±	1.4	231 ±	25	176 ±	10	23 ±	na	16 ±	na	12 ±	1.0	17 ±	na	16 ±	1
Lu	2.2 ±	0.2	2.1 ±	0.2	36 ±	3.9	25 ±	1.5	5 ±	na	1.9 ±	na	1.9 ±	0.2	2 ±	na	2.2 ±	0.3

TABLE S7: Equilibrium Parameters for La, Ce and Dy in WHAM (Windermere Humic Aqueous Model), version 7.0 (Lofts, 2012).

Reactions	$\log_{10}K_o$	delta H_o	Data Source
La[3+] + OH[-] = LaOH[2+]	5.19	-3.04	Klungness, G.D., Byrne, R.H. (2000)
La[3+] + H[+] + CO3[2-] = LaHCO3[2+]	12.67	--	Luo, Y.R., Byrne, R.H. (2004)
La[3+] + CO3[2-] = LaCO3[+]	6.73	--	Luo, Y.R., Byrne, R.H. (2004)
La[3+] + 2CO3[2-] = La(CO3)2[-]	11.3	--	Luo, Y.R., Byrne, R.H. (2004)
La[3+] + SO4[2-] = LaSO4[+]	3.64	4	NIST (2003)
La[3+] + 2SO4[2-] = La(SO4)2[-]	5.3	8	NIST (2003)
La[3+] + 2H[+] + PO4[3-] = LaH2PO4[2+]	21.99	--	NIST (2003)
La[3+] + Cl[-] = LaCl[2+]	0.53	--	NIST (2003)
La[3+] + F[-] = LaF[2+]	3.6	2.8	NIST (2003)
Ce[3+] + OH[-] = CeOH[2+]	5.657	0.3	Klungness, G.D., Byrne, R.H. (2000)
Ce[3+] + CO3[2-] = CeCO3[+]	7.06	--	Luo, Y.R., Byrne, R.H. (2004)
Ce[3+] + 2CO3[2-] = Ce(CO3)2[-]	11.76	--	Luo, Y.R., Byrne, R.H. (2004)
Ce[3+] + SO4[2-] = CeSO4[+]	3.64	4.5	NIST (2003)
Ce[3+] + 2SO4[2-] = Ce(SO4)2[-]	5.1	7.9	NIST (2003)
Ce[3+] + H[+] + CO3[2-] = CeHCO3[2+]	12.64	--	L Luo, Y.R., Byrne, R.H. (2004)
Ce[3+] + PO4[3-] = CePO4[0]	11.73	--	NIST (2003)
Ce[3+] + 2H[+] + PO4[3-] = CeH2PO4[2+]	21.9	--	NIST (2003)
Ce[3+] + Cl[-] = CeCl[2+]	0.57	--	NIST (2003)
Ce[3+] + F[-] = CeF[2+]	3.94	--	NIST (2003)
Dy(3+) + OH[-] = DyOH[2+]	6.41	0.4	Klungness, G.D., Byrne, R.H. (2000)
Dy(3+) + CO3[2-] = DyCO3[+]	7.56	0	Luo, Y.R., Byrne, R.H. (2004)
Dy(3+) + 2CO3[2-] = Dy(CO3)2[-]	12.91	0	Luo, Y.R., Byrne, R.H. (2004)
Dy(3+) + H[+] + CO3[2-] = DyHCO3[2+]	12.83	0	Luo, Y.R., Byrne, R.H. (2004)
Dy(3+) + SO4[2-] = DySO4[+]	3.61	4.8	NIST (2003)
Dy(3+) + 2SO4[2-] = Dy(SO4)2[-]	4.8	9.8	NIST (2003)
Dy(3+) + F[-] = DyF[2+]	4.48	2.2	NIST (2003)

$\log_{10}K_o$ = standard equilibrium (complex formation) constant
delta H_o = standard reaction enthalpy change in kcal/mol ("--" = reaction has no measured enthalpy)

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TABLE S8: Summary of multivariate regression analyses examining the influence of environmental variables on ∑REEY concentrations and La concentrations in surface water, surface sediments from all samples sites (N = 26 - 34).* Standardized regression coefficients and p values are shown for each variable.

Dependent Variable	Model Metrics					Independent Variables										
Surface water	N	DF	Cp	R^2_{adj}	lambda	**REEY (Sed)**	**La (Sed)**	**Lake area**	**WS area**	**Mean depth**	**pH**	**DOC (aq)**	**Ca (aq)**	**Al (aq)**	**Fe (aq)**	
[ΣREEY]	30	5	6.76	0.821	0.644	0.411	na	-0.056	0	-0.320	0	0	0	0	-0.051	
					p	**<0.001**	na	0.328	--	**<0.001**	--	--	--	--	0.246	
[La]	30	4	5.69	0.877	0.921	na	0.510	-0.044	0	-0.28	0	0	0	0	0	
					p	na	**<0.001**	0.379	--	**<0.001**	--	--	--	--	--	
Surface Sediment		DF	Cp	R^2_{adj}	lambda	**OM % (Sed)**	**Clay % (Sed)**	**Al (Sed)**	**Fe (Sed)**	**Lake area**	**WS area**	**Mean depth**				
[ΣREEY]	26	4	0.44	0.529	3.24	0.080	0	0	0.136	0	0	-0.034				
					p	0.088	--	--	**0.003**	--	--	0.429				
[La]	26	4	3.18	0.393	0.82	0.096	0	0	0.145	0	0	-0.073				
						0.130	--	--	**0.017**	--	--	0.215				
Kd	N	DF	Cp	R^2_{adj}	lambda	**OM % (Sed)**	**Clay % (Sed)**	**Al (Sed)**	**[Fe (Sed)**	**Lake area**	**WS area**	**Mean depth**	**pH**	**DOC (aq)**	**Ca (aq)**	**Al (aq)**	**Fe (aq)**
[ΣREEY]	26	11	12.82	0.914	0.136	0	-0.269	0.225	0.054	0.069	-0.304	0.355	0.119	0.086	0	-0.359	0.100
					p	--	**<0.001**	**0.001**	0.205	0.309	**0.007**	**<0.001**	0.054	0.198	--	**<0.001**	0.220
[La]	26	11	10.58	0.908	0.091	0	-0.300	0.174	0.048	0.063	-0.290	0.320	0.105	0.124	0	-0.455	0.144
					p	--	**<0.001**	**0.020**	0.330	0.426	**0.032**	**<0.001**	0.146	0.111	--	**<0.001**	0.134

*Regression analysis technique used was LASSO (or Least Absolute Shrinkage and Selection Operator) from Tibshirani (1996).
Significant p-values ($p < 0.05$) are shown in bold. Variables not included in a model are shown by "na" and zoop: zooplankton, sed: sediment, aq: aqueous, WS: watershed.

TABLE S9: Summary of multivariate regression analyses examining the influence of environmental variables on ∑REEY concentrations and La concentrations bulk zooplankton from all samples sites (N = 26-34).* Standardized regression coefficients and p values are shown for each variable.

Dependent Variable	Model Metrics					Independent Variables											
Zooplankton	N	DF	Cp	R^2_{adj}	lambda	**Zoop $\delta^{15}N$**	**Zoop C:N**	**Lake area**	**WS area**	**Mean depth**	**pH**	**Ca (aq)**	**Al (aq)**	**Fe (aq)**	**REEY to DOC (aq)**	**REEY Kd**	**La^{3+} (aq)**
[REEY] Model 1	34	10	9.24	0.773	0.106	0.071	-0.079	-0.041	0	0.066	-0.145	0.092	-0.093	0.065	0.396	na	na
					p	0.292	0.089	0.411	--	0.271	**0.024**	0.254	0.264	0.395	**<0.001**	na	na
[REEY] Model 2	30	8	6.61	0.669	0.327	0	-0.099	0	0.057	0	-0.228	0.145	-0.062	-0.066	na	-0.325	na
					p	--	0.076	--	0.297	--	**0.003**	0.102	0.503	0.424	na	**<0.001**	na
Zooplankton	N	DF	Cp	R^2_{adj}	lambda	**Zoop $\delta^{15}N$**	**Zoop C:N**	**Lake area**	**WS area**	**Mean depth**	**pH**	**Ca (aq)**	**Al (aq)**	**Fe (aq)**	**La to DOC (aq)**	**La Kd**	**La^{3+} (aq)**
[La] Model 3	34	8	10.4	0.801	0.656	0.062	-0.018	-0.02	0	0	-0.125	0.102	-0.079	0	0.421	na	na
					p	0.165	0.582	0.574	--	--	**0.005**	0.155	0.163	--	**<0.001**	na	na
[La] Model 4	30	8	7.23	0.727	0.527	0	-0.047	0	0.038	0	-0.262	0.182	-0.140	-0.054	na	-0.408	na
					p	--	0.469	--	0.667	--	**0.036**	0.056	0.179	0.641	na	**<0.001**	na
[La] Model 5	34	3	3.59	0.726	1.111	0	0	0	0	0	0	0	-0.026	0	na	na	0.391
					p	--	--	--	--	--	--	--	0.432	--	na	na	**<0.001**

*Regression analysis technique used was LASSO (or Least Absolute Shrinkage and Selection Operator) from Tibshirani (1996).
Significant p-values ($p < 0.05$) are shown in bold. Variables not included in a model are shown by "na" and zoop: zooplankton, sed: sediment, aq: aqueous, WS: watershed.

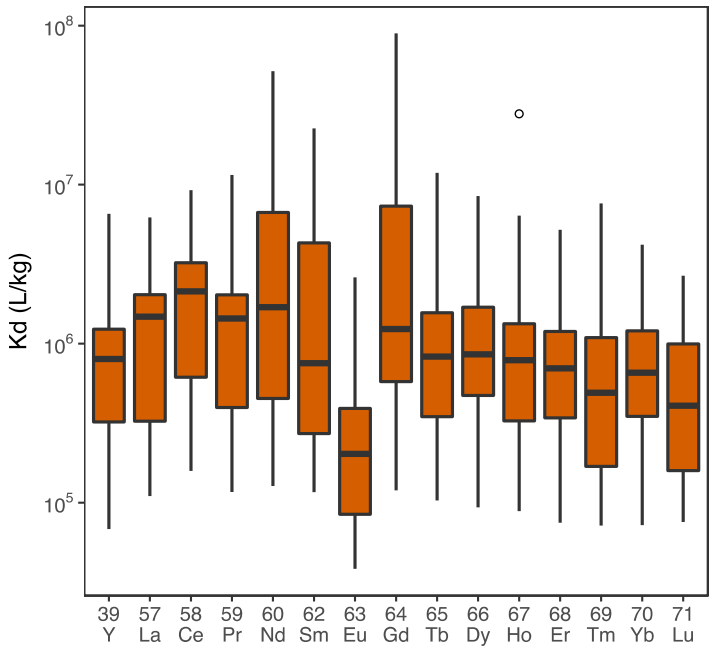

FIGURE S1: Partition coefficients (Kd) in log L kg^{-1} based on REE concentrations in dry sediment (nmol Kg^{-1}) versus surface water (nmol L^{-1}) for 34 lakes.

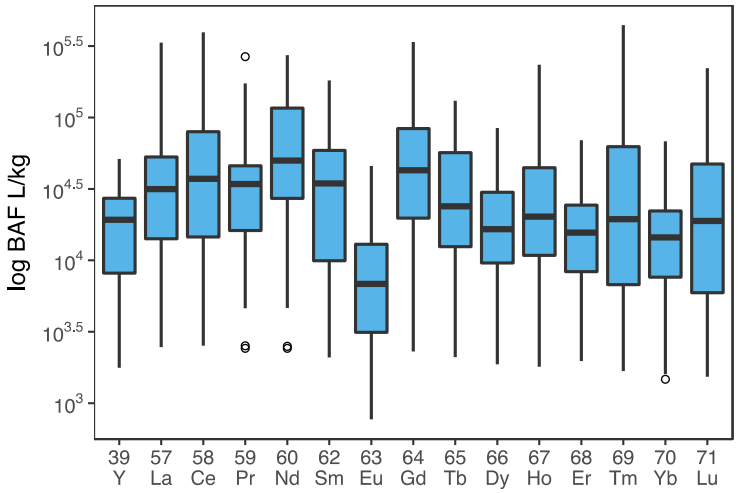

FIGURE S2: Bioaccumulation factors (BAF) calculated as the ratio of REE concentrations in zooplankton (dry weight, nmol/kg) to REE concentration in surface water (nmol/L), BAF values are in units of log10-transformed L/kg respectively and are shown versus the atomic number of REE for 34 lakes.

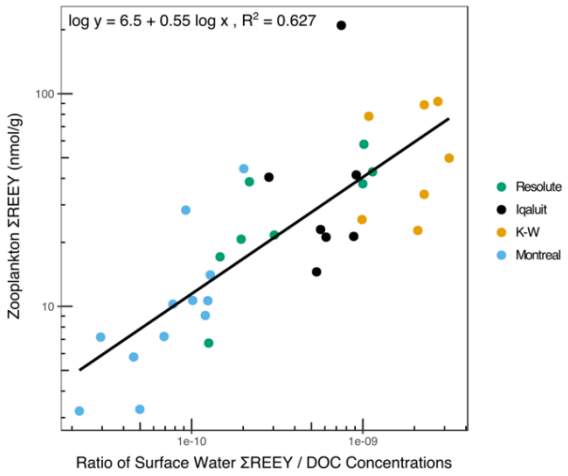

FIGURE S3: Linear regression for bulk zooplankton ∑REEY concentrations (nmol/g) versus ratio of surface water ∑REEY to dissolved organic carbon (DOC) concentrations. All variables shown are log-scaled and linear equations are calculated with log-transformed variables.

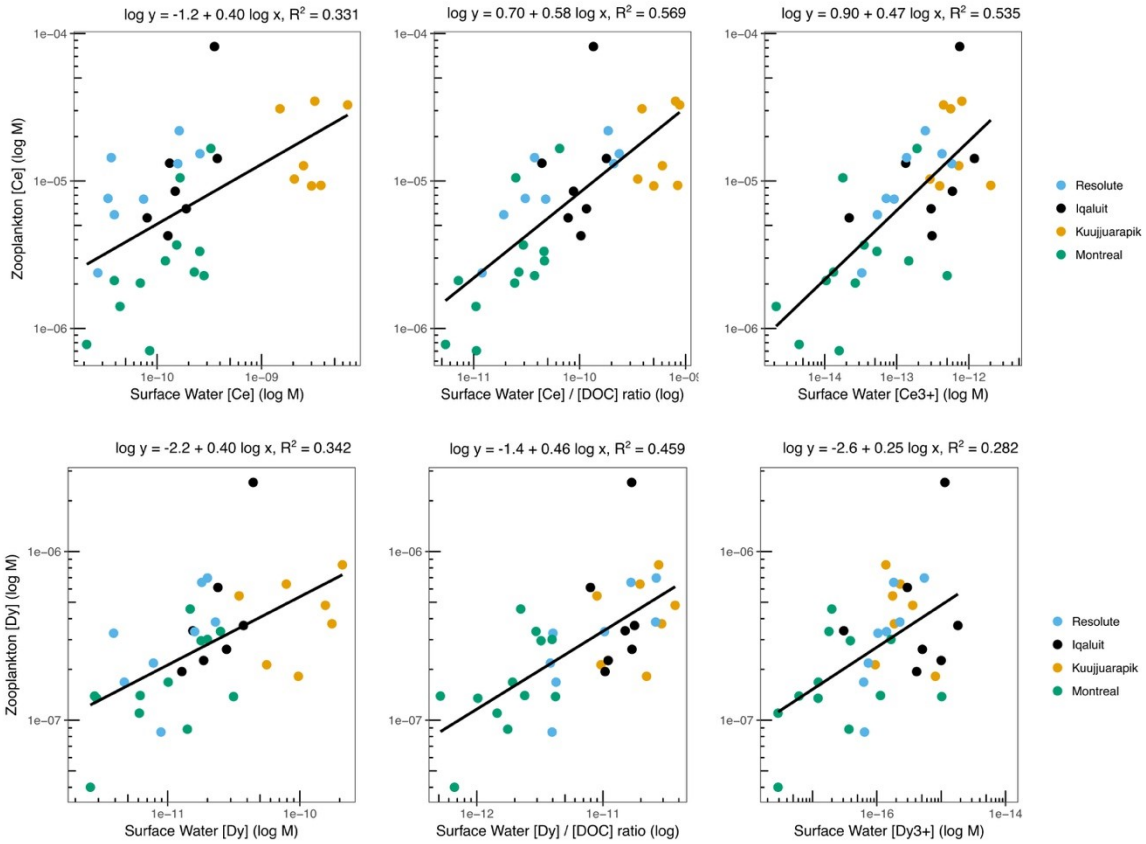

FIGURE S4: Linear regressions for bulk zooplankton Dy and Ce concentrations versus 1) surface water Dy and Ce concentrations, 2) ratio of surface water Dy and Ce to dissolved organic carbon (DOC) concentrations, 3) surface water free ion (Dy^{3+}, Ce^{3+}) concentrations for samples from Montreal, Kuujjuarapik-Whapmagoostui, Iqaluit and Resolute ($p < 0.05$). All variables shown are log-scaled and linear equations are calculated with log-transformed variables.

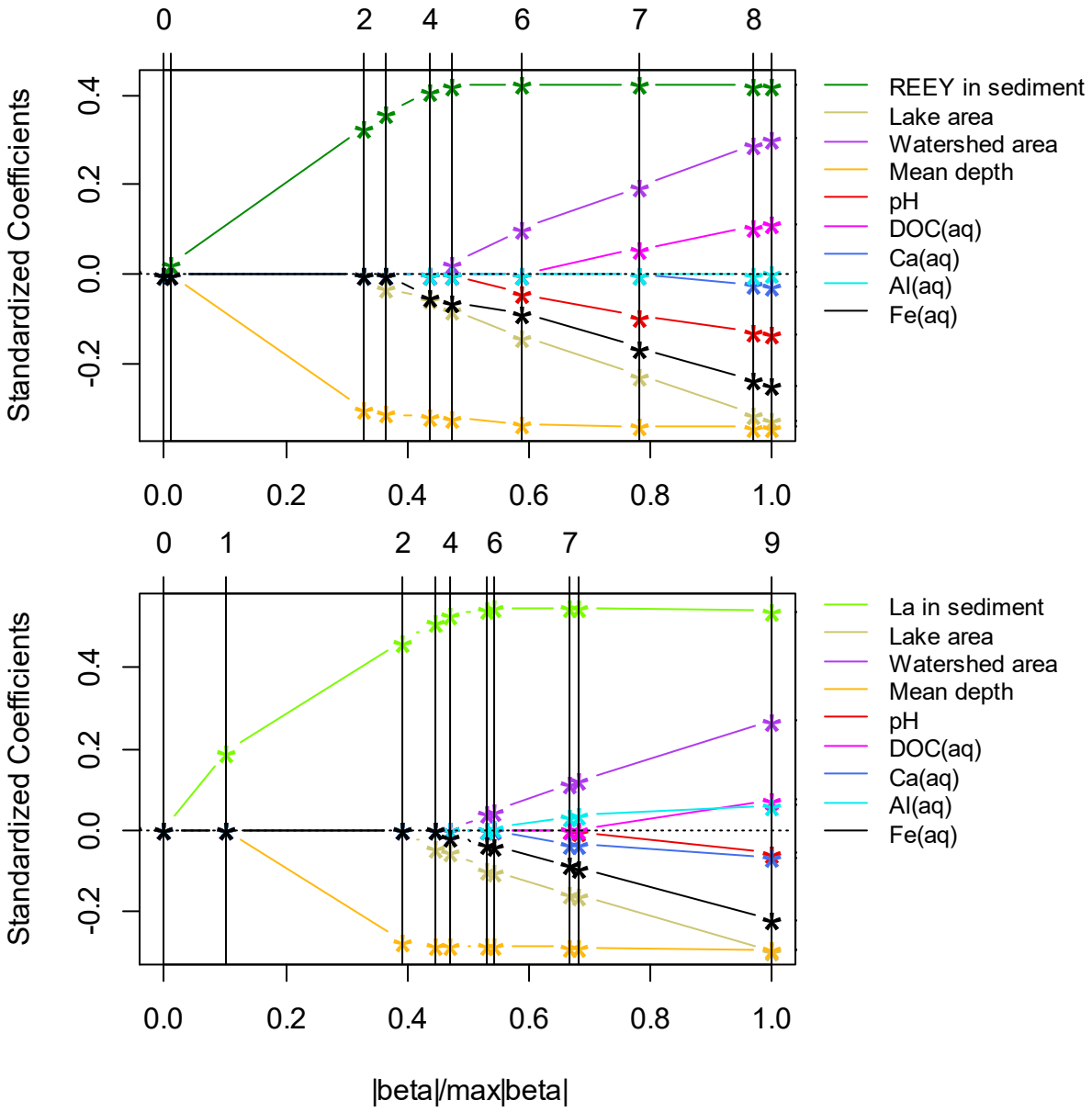

FIGURE S5: Path plots showing the standardized regression coefficients of independent variables included in LASSO models of ΣREEY concentrations (top panel) and La concentrations (bottom panel) in lake surface water across all lakes (N = 30) (Table S8).

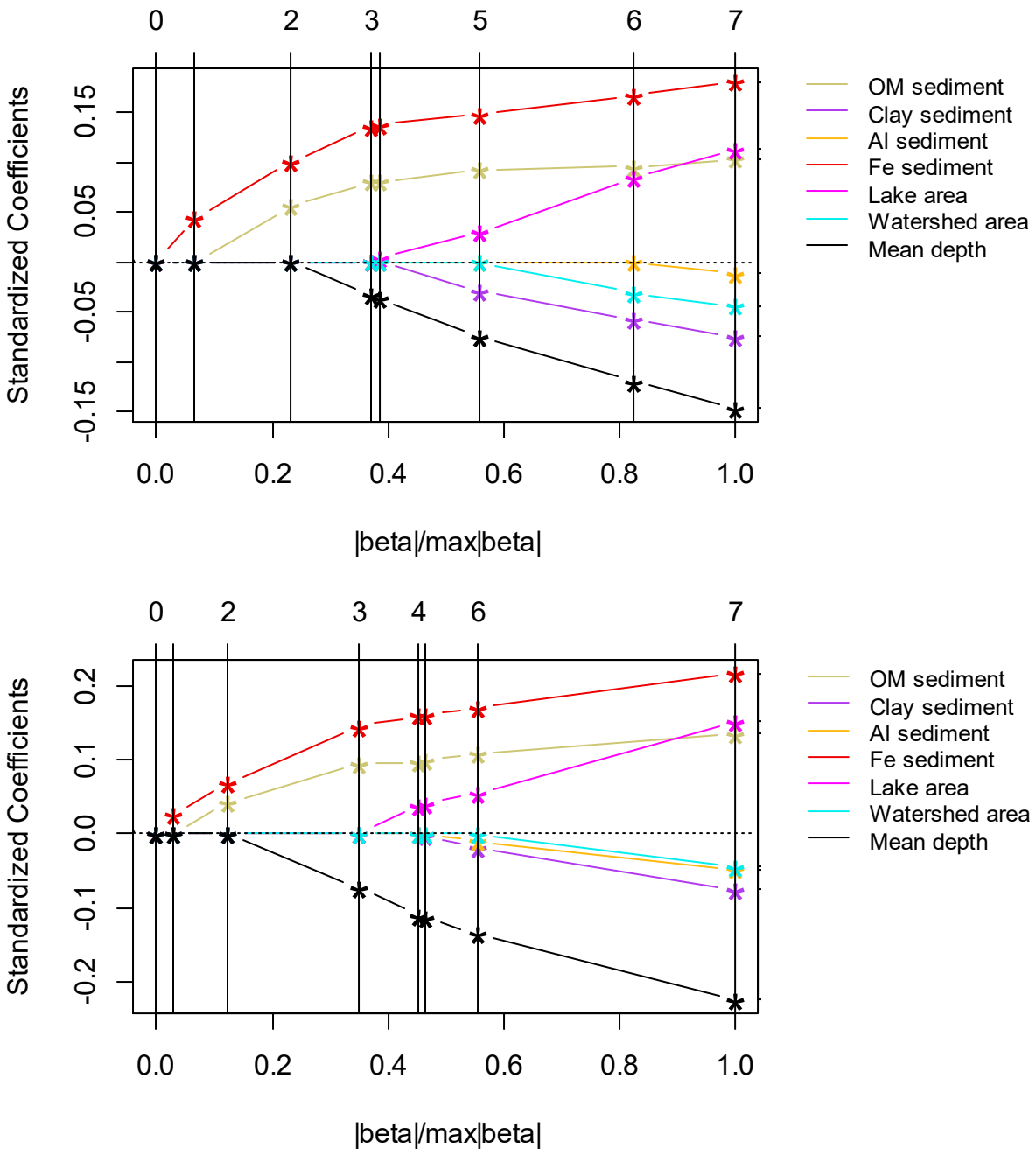

FIGURE S6: Path plots showing the standardized regression coefficients of independent variables included in LASSO models of ΣREEY concentrations (top panel) and La concentrations (bottom panel) in surface sediments across all lakes (N = 26) (Table S8).

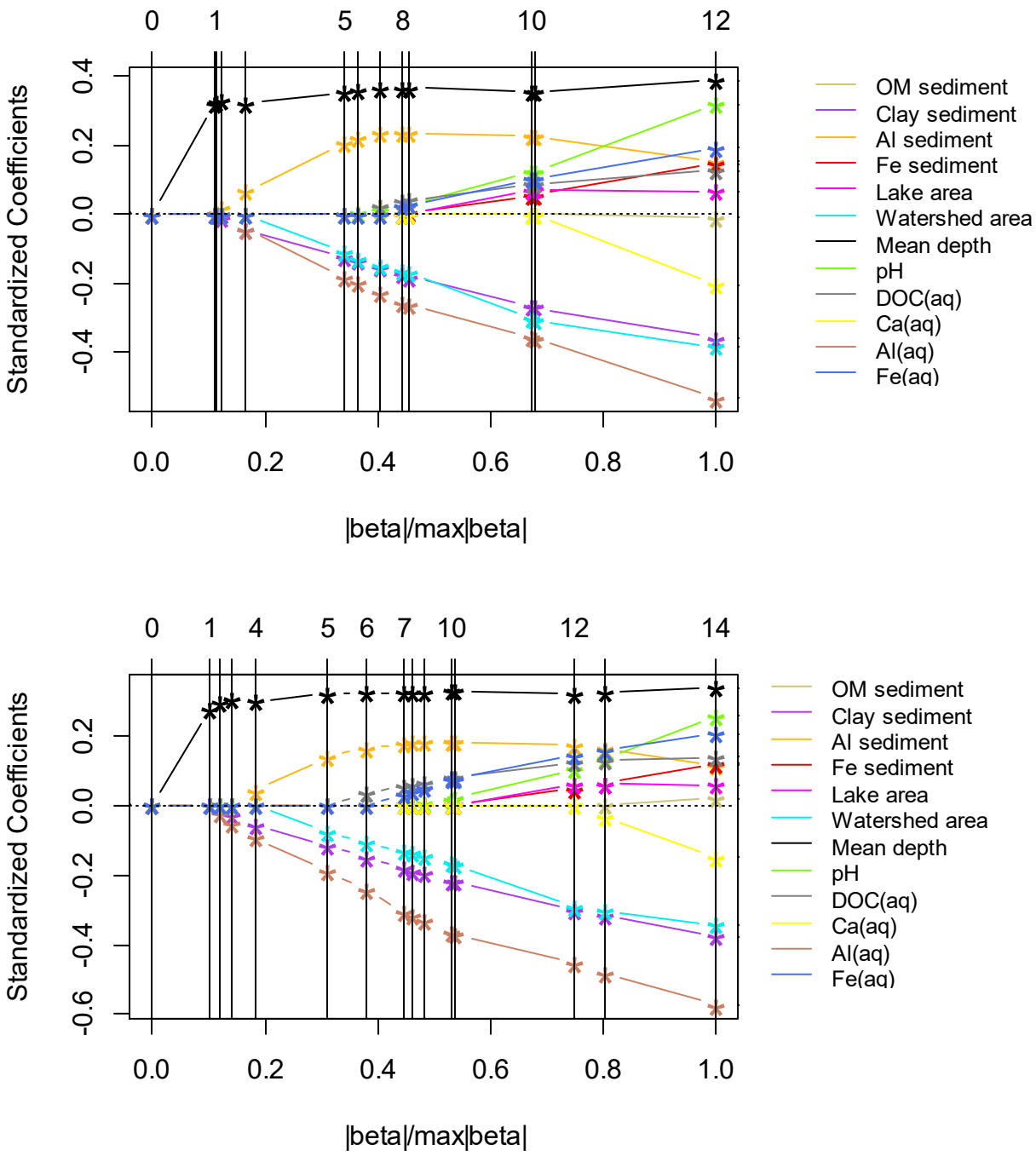

FIGURE S7: Path plots showing the standardized regression coefficients of independent variables included in LASSO models of ΣREEY concentrations (top panel) and La concentrations (bottom panel) in sediment-water partition coefficients (Kd) across all lakes (N = 26) (Table S8).

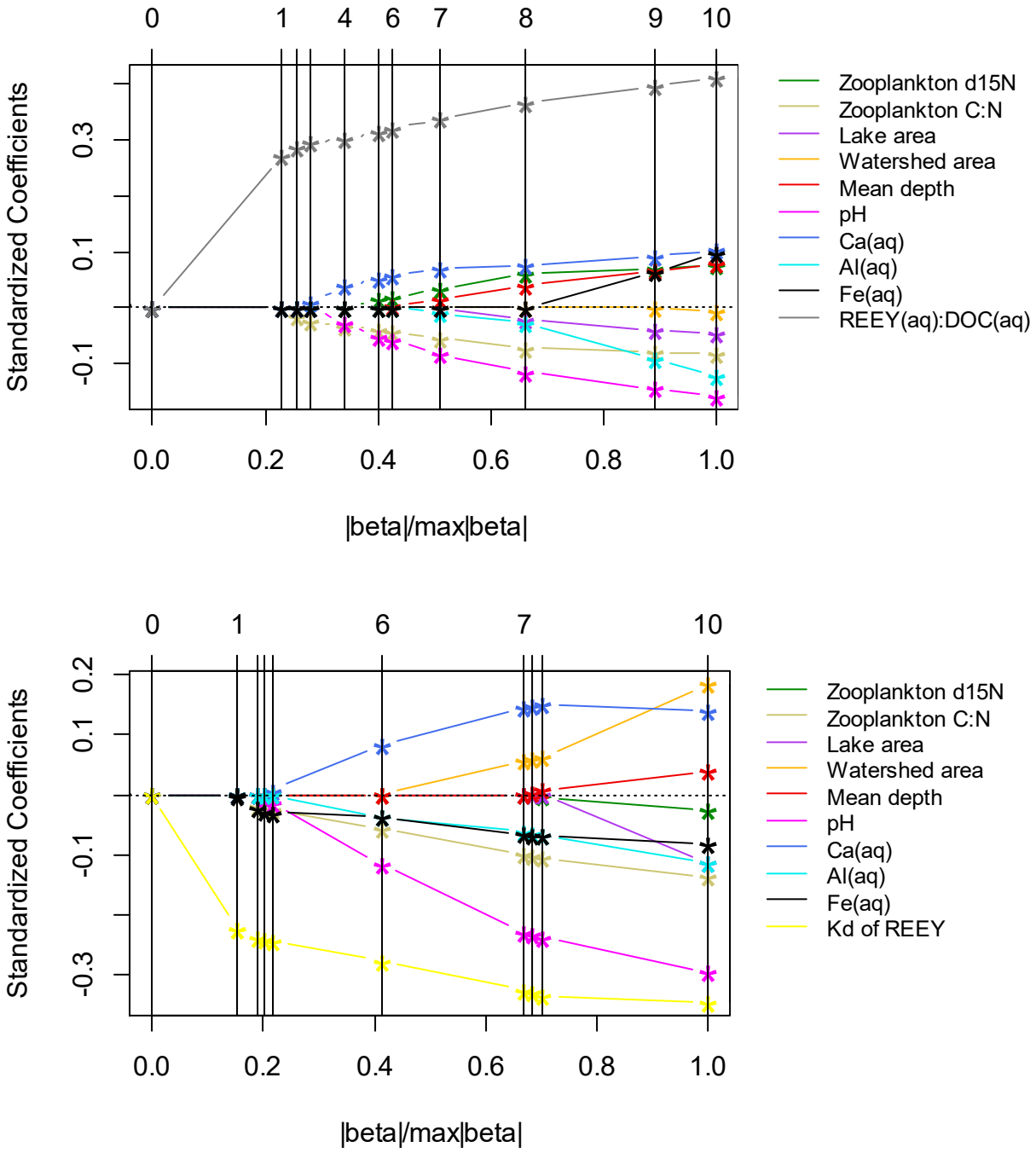

FIGURE S8: Path plots showing the standardized regression coefficients of independent variables included in LASSO models of ΣREEY concentrations in zooplankton across all lakes (N = 34). Plots show two models using different independent variables (see Table S9).

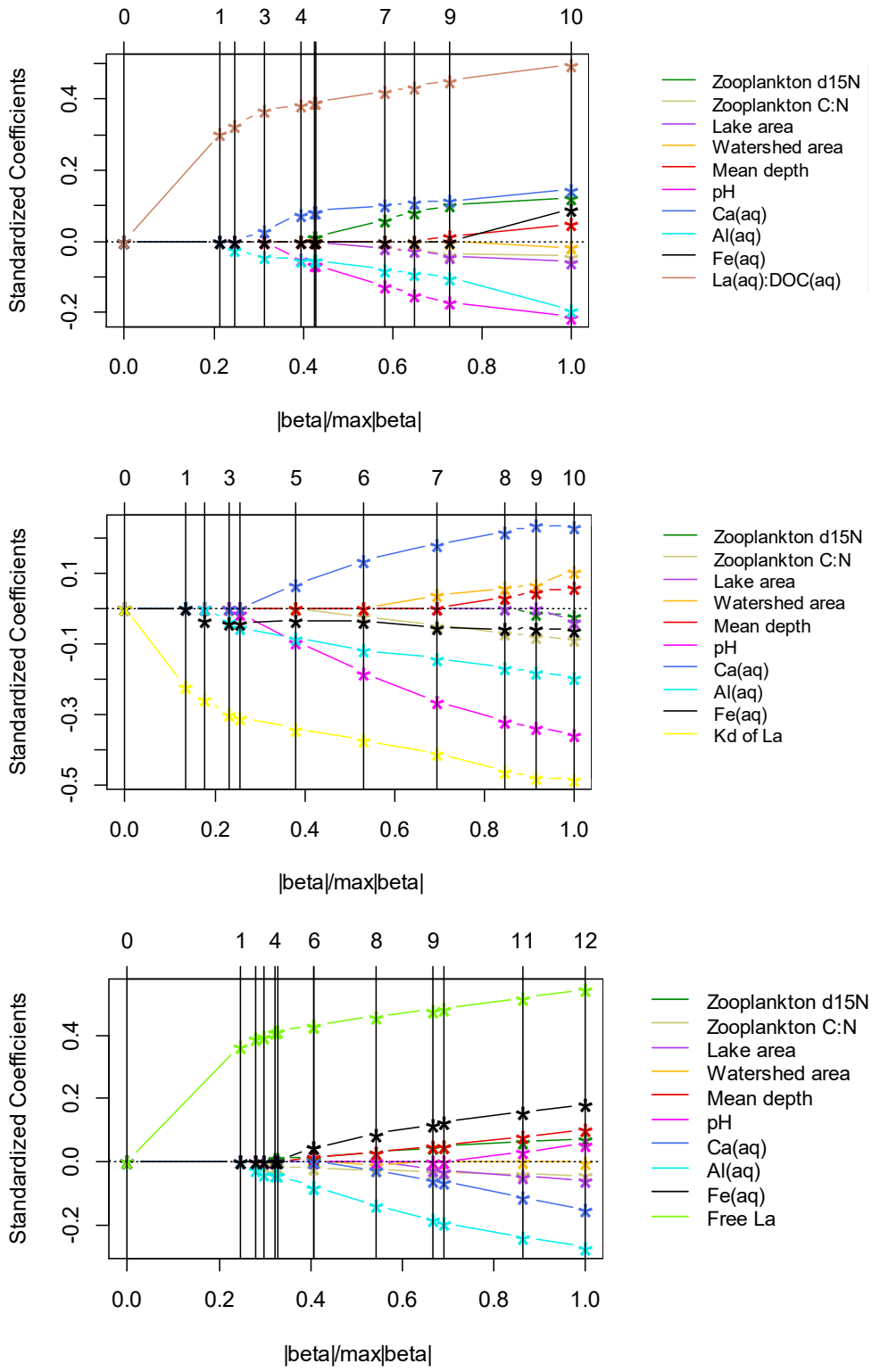

FIGURE S9: Path plots showing the standardized regression coefficients of independent variables included in LASSO models of La concentrations in zooplankton across all lakes (N = 34). Plots show three models using different independent variables (see Table S9).

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SYNTHÈSE

Les écosystèmes arctiques sont d'importants indicateurs des changements globaux futurs, puisque les régions nordiques se réchauffent plus rapidement que les régions tempérées. Ce réchauffement a d'importantes conséquences sur les cycles environnementaux des contaminants et donc sur la santé des écosystèmes et des communautés du Nord. En plus de cette accélération du réchauffement, on assiste à une pression croissante d'exploiter les ressources naturelles en Arctique, contribuant également à la dégradation et à la contamination des écosystèmes nordiques. Au cours de mes travaux de recherche, je suis partie à la chasse aux métaux traces dans le Nord canadien afin d'identifier de grandes tendances dans les écosystèmes complexes. La présente thèse met l'accent sur la biogéochimie du mercure (**Chapitre 1**) et sur les éléments de terres rares (**Chapitre 3**) au sein des écosystèmes arctiques, ainsi que sur leurs dynamiques dans les réseaux trophiques (**Chapitres 2 et 4**). De plus, cette thèse met en lumière l'importance de mener une recherche collaborative avec les communautés autochtones en Arctique (**Annexes 2 à 5**). Par l'entremise de cette thèse, j'ai pu fournir des informations cruciales sur le devenir dans l'environnement des métaux traces, nécessaires à l'évaluation de l'impact de ces changements sur le Nord et sur les communautés qui y vivent.

Changements climatiques : la mobilisation et la bioaccumulation du mercure

Chapitre 1 : Les mares thermokarstiques sont-elles une source potentielle de méthylmercure?

Les mares thermokarstiques sont omniprésentes dans l'Arctique canadien. Cette thèse démontre que les concentrations de méthylmercure mesurées dans ces mares sont bien supérieures aux niveaux retrouvés dans la majorité des écosystèmes d'eau douce de l'Arctique canadien. Les mares de fonte sont considérées comme des *hotspots* d'activité microbienne et, désormais, de mercure dans le Nord. De plus, dans certaines régions, ces mares risquent de proliférer en raison du dégel du pergélisol résultant du réchauffement climatique. En raison de la connectivité hydrologique croissante résultant des changements, les mares thermokarstiques pourraient devenir des sources importantes de méthylmercure vers d'autres cours d'eau nordiques. En effet, dans l'ouest de l'Arctique, les mares de petite taille s'unissent entre elles pour former des lacs plus grands, qui sont ensuite drainés de manière « catastrophique » vers les rivières en réponse à l'érosion thermique. Des cas d'érosion à grande échelle ont aussi été

documentés dans des régions subarctiques menant au drainage du terrain présentant des mares vers des rivières et vers la baie d'Hudson. Pourtant, davantage de travaux de recherche sont nécessaires afin d'évaluer les conséquences écologiques à grande échelle de ces fortes concentrations de méthylmercure dans les mares thermokarstiques.

Chapitre 2 : L'accroissement de la productivité aquatique pourrait-il altérer la bioaccumulation du méthylmercure dans les organismes aquatiques à la base des réseaux trophiques arctiques ?

Il est fort probable que le réchauffement climatique engendrera une augmentation des apports de matière organique et de nutriments vers les lacs et mares arctiques, favorisant la productivité aquatique. Une augmentation de la productivité aquatique peut mener à la biodilution du méthylmercure, causée soit par la forte croissance algale ou alors par la croissance rapide du zooplancton consommateur. Les organismes aquatiques de petite taille se trouvant à la base des réseaux trophiques constituant souvent le point d'entrée pour les métaux traces, une meilleure compréhension des processus de bioaccumulation à ces niveaux de base est nécessaire afin d'élucider la dynamique du mercure. Nos résultats suggèrent que dans ces lacs nordiques peu productifs, les indicateurs de la productivité, tels que la biomasse algale et la stoechiométrie des nutriments, ne sont pas les facteurs contrôlant l'accumulation de mercure à la base des réseaux aquatiques. Plusieurs questions demeurent ouvertes à la suite à cette étude. Les travaux futurs devront porter une attention particulière à la composition et le rôle du seston, en examinant les différentes classes de tailles, la composition taxonomique, la qualité nutritive, ainsi que l'évolution saisonnière du seston dans les lacs oligotrophes du Nord. Ces notions sont d'une importance cruciale, puisque la bioaccumulation du méthylmercure dans les organismes à la base des réseaux trophiques représente une étape déterminante dans le transfert trophique du méthylmercure vers les poissons consommés par d'autres animaux et par les humains.

Terres rares : nouveaux territoires et destin dans l'environnement

Chapitre 3 : Les éléments de terres rares sont-ils bioaccumulables et bioamplifiables dans les réseaux trophiques nordiques?

Malgré un intérêt grandissant en recherche envers les éléments de terres rares et leurs effets potentiels dans l'environnement, peu d'études menées sur le terrain ont été réalisées sur le comportement et le destin de ces contaminants dans les écosystèmes naturels. Bien qu'il soit

établi que les terres rares aient un comportement très cohérent et prévisible dans les compartiments abiotiques (eau, sols, roches), cette thèse démontre des évidences que l'abondance des terres rares en « *dents-de-scie* » est aussi conservée dans les tissus des organismes d'eau douce, marins et terrestres du Grand Nord canadien. Les concentrations de terres rares les plus élevées ont été mesurées dans la végétation et les invertébrés aquatiques, tandis que les herbivores terrestres, les phoques annelés, et les poissons présentaient de faibles niveaux de terres rares dans leurs tissus. Cependant, cette accumulation était d'un ordre de grandeur supérieur dans les tissus du foie. Cette étude démontre que les terres rares suivent des patrons de bioaccumulation spécifiques aux taxons et aux tissus, et que ces contaminants ne sont pas bioamplifiés dans les réseaux trophiques non contaminés du Nord. Les conclusions du ce chapitre sont appuyées par l'article en **Annexe 1**, qui examine le devenir dans l'environnement et le transfert trophique des REEs dans des lacs tempérés. Bien que, de manière générale, les terres rares aient un comportement similaire, des recherches successives seront nécessaires pour mieux comprendre des anomalies observées dans la bioaccumulation de certains éléments de terres rares chez certaines espèces. Les recherches futures devront examiner les anomalies positives et négatives de bioaccumulation et leur lien potentiel avec les conditions environnementales, telles que les conditions d'oxydoréduction et la productivité pour les milieux aquatiques.

Chapitre 4 : Quels facteurs environnementaux expliquent les concentrations d'éléments de terres rares dans les écosystèmes d'eau douce des régions tempérées et arctiques?

Les invertébrés aquatiques, tels que le zooplancton d'eau douce, ont été identifiés comme des biomoniteurs potentiels des concentrations de terres rares dans l'environnement. Cette étude a contribué à un état des connaissances sur les concentrations de référence et sur la bioaccumulation de ces contaminants d'intérêt émergeant, ce qui est important dans le contexte de l'enrichissement potentiel aux latitudes élevées en lien avec les projets d'exploitation minière au Canada. Nous avons identifié les facteurs environnementaux clés qui influencent la bioaccumulation de terres rares dans le zooplancton, incluant le pH, le carbone organique dissous, et la concentration de terres rares sous forme d'ion libre. Nos études soulignent la pertinence du zooplancton dans le suivi biologique de ces contaminants dans les écosystèmes d'eau douce. Puisque nous détenons désormais une meilleure idée du comportement des

éléments de terres rares dans les écosystèmes naturels, il importe d'élargir nos connaissances sur le suivi environnemental et sur les mécanismes de bioaccumulation de ces éléments. De futurs travaux sur les éléments de terres rares devraient examiner les mécanismes d'accumulation, de dépuration, et d'adsorption sur la carapace des REEs chez les invertébrés afin de mieux cibler les avantages et les inconvénients de l'utilisation des invertébrés aquatiques comme biomoniteurs. Il importe aussi d'approfondir nos connaissances sur les mécanismes cellulaires et sur les processus physiologiques internes, en utilisant des techniques de partitionnement subcellulaire, afin de mieux comprendre la bioaccumulation et le transfert trophiques de ces métaux.

Importance de l'intégration d'approches collaboratives avec les communautés

Annexe 2 : Comment bien intégrer des approches collaboratives en écotoxicologie?

Dans le contexte des changements climatiques et du développement au nord du Canada, les avenues de recherches de cette thèse soulèvent aussi des questions d'intérêt pour les communautés qui y vivent, comme en témoigne le projet Imalirijiit, décrit en annexe de cette thèse. Imalirijiit est un mot en inuktitut qui veut dire « *ceux qui étudient l'eau* ». Ce programme de suivi environnemental dans le bassin de la rivière George, au Nunavik, a été co-développé par les membres de la communauté et par les chercheurs afin de répondre aux préoccupations de la communauté suite au développement d'une mine de terres rares sur leur territoire. Les résultats de ce projet démontrent qu'il existe plusieurs défis et avantages à la recherche collaborative avec les communautés du Nord. Ce projet a souligné que certains de ces défis peuvent être surmontés grâce à la création de liens de confiance, à l'établissement d'objectifs et de priorités clairs, à l'intégration du savoir local ainsi qu'en mettant l'accent sur les activités de partage des connaissances et sur l'éducation. Cependant, la dimension d'intégration des savoirs scientifiques et autochtones demeure hors de la portée de cette thèse. En effet, les travaux touchant aux sciences naturelles se trouvent dans le corps de la thèse et les travaux de collaboration avec les communautés se trouvent en annexe. Naviguer entre les différentes approches des chercheurs et celles des membres des communautés autochtones demeure un défi de taille, bien que des plus passionnants.

Annexe 3 : Comment promouvoir la recherche en collaboration avec les communautés autochtones auprès des chercheurs en début de carrière?

Cette thèse a également fait valoir les approches collaboratives par la création et l'organisation d'ateliers pour les chercheurs en début de carrière visant la promotion de la recherche en collaboration avec les communautés. Les résultats des analyses quantitatives et qualitatives dans ce chapitre soulignent que les ateliers organisés par les pairs sont efficaces dans l'optique de partager des points de vue et de sensibiliser les participants aux cultures, à l'histoire et aux langues autochtones, ainsi que d'offrir une plateforme d'échanges et de réflexion sur ces questions. Ces ateliers sont certes importants, mais ne peuvent suffire à instaurer un changement des pratiques de recherche afin d'y intégrer des approches collaboratives avec les communautés à plus grande échelle dans les sciences naturelles. L'accès à de la formation continue, accessible et reconnue par les universités, qui réunit des participants autochtones et non autochtones, pourrait contribuer à faire évoluer la pratique de la recherche au Canada. Les approches collaboratives pourraient enrichir notre vision de la recherche grâce à l'implication des peuples autochtones ainsi qu'à leur inclusion dans la prise de décisions liées aux priorités en recherche.

Perspectives : Le Nord et la science en perpétuel changement

Tout au long de cette thèse, j'ai cherché à mieux comprendre les tendances écologiques à grande échelle des métaux traces dans les écosystèmes complexes du Nord canadien. L'intérêt de cette question réside dans le fait que le Nord est en évolution rapide, subissant de grands changements environnementaux et socioculturels qui ont d'importantes conséquences sur la santé écosystémique et humaine. Dans ce contexte, il est primordial d'identifier les facteurs environnementaux clés qui ont une incidence sur le transport, la transformation et le transfert trophique des métaux traces. Il importe également d'établir des données de référence et d'utiliser des outils de surveillance environnementale afin de pouvoir détecter les changements importants et d'identifier leurs effets potentiels. Ces informations fourniront des outils nécessaires à l'évaluation de l'impact de ces changements dans le Nord et sur les communautés qui y vivent, et pourraient contribuer à l'élaboration de politiques de mitigation des risques liés à la contamination des écosystèmes nordiques.

Premièrement, nos résultats soulignent le fait qu'il y a de grandes différences dans les variables environnementales qui expliquent la variation de méthylmercure dans les lacs des régions arctiques, en comparaison aux lacs des régions tempérées. Contrairement aux écosystèmes des régions tempérées, nos résultats dans les mares thermokarstiques démontrent de fortes corrélations entre le méthylmercure et les éléments nutritifs (azote, phosphore), ainsi qu'avec les gaz à effet de serre. Dans nos sites d'études du Nord, nous n'avons pas trouvé de corrélations entre les concentrations en méthylmercure et les variables clés qui contrôlent la production de méthylmercure dans les lacs tempérés (ex. température, pH, sulfate). Les résultats du Chapitre 2 démontrent aussi ces différences importantes entre les écosystèmes aquatiques des régions arctiques en comparaison aux régions tempérées. Par exemple, nos résultats suggèrent que la biodilution n'est pas un facteur clé pour l'accumulation de méthylmercure à la base des réseaux trophiques des régions nordiques. Nos résultats soulignent également que, bien que le dégel du pergélisol pourrait jouer un rôle important dans les flux de mercure dans l'Arctique, les effets des changements climatiques risquent d'être variables entre les différentes régions et les différents écosystèmes. Cette thèse met en lumière les conséquences variables et complexes des changements climatiques dans le paysage arctique, et l'importance du dégel du pergélisol, contribuant ainsi à adapter les diverses stratégies de gestion des risques pour le mercure.

Par l'entremise de cette thèse, j'ai également étudié de façon détaillée le comportement, la bioaccumulation, et les dynamiques trophiques des éléments de terres rares dans l'environnement. Ces résultats pourraient contribuer à l'élaboration des politiques intégrant le suivi environnemental de ces contaminants d'intérêt émergeant, en ciblant les groupes d'organismes qui démontrent un bon potentiel de biomonitorage, tels que le zooplancton, les organismes benthiques et les lichens. Dans ces régions nordiques non contaminées en terres rares, les niveaux faibles de ces éléments dans la chair des vertébrés indiquent que la consommation des tissus n'est probablement pas une route d'exposition importante pour les habitants du Nord. Les évaluations d'impact environnemental de l'exploitation minière devront donc intégrer l'utilisation des biomoniteurs de terres rares et devront également évaluer les autres impacts majeurs des mines de terres rares, tels que la pollution atmosphérique, le rejet d'eaux usées acides et les résidus radioactifs.

Bien qu'une approche collaborative n'ait pas été la principale méthodologie utilisée pour les recherches écotoxicologiques de cette thèse, mes travaux s'inscrivent dans un changement de paradigme de recherche grâce à ma participation aux activités de recherche et d'éducation collaboratives. Ces activités ont contribué à renforcer les capacités scientifiques des communautés nordiques, à l'engagement des communautés dans la prise de décisions liées aux priorités de recherche, et à soutenir la création des programmes de suivi environnemental mené par et pour les communautés. Avoir participé aux projets collaboratifs a également amélioré la qualité et l'impact de cette thèse, en plus d'avoir grandement contribué à mon développement en tant que chercheur nordique. En effet, la collecte des données de nombreux chapitres de cette thèse n'aura pas été réalisable sans les conseils, la collaboration, et le soutien de nos collaborateurs dans les communautés du nord. Le transfert de connaissances de cette thèse a compris des rencontres communautaires fréquentes, la production des rapports et dépliants en langage courant, la création d'une bande dessinée, et la participation à des camps scientifiques. Ces activités ont grandement amélioré l'accessibilité de nos résultats pour les acteurs locaux. Traduire la science dans un langage accessible est essentiel afin de construire des ponts entre la science et le domaine politique de manière à pallier les défis complexes émergeant de la société moderne.

Afin de répondre aux défis complexes émergents, la science prend actuellement une tangente multidisciplinaire dans l'optique d'intégrer des connaissances provenant d'autres disciplines et d'autres écoles de pensée. Dans ce contexte, j'ai espoir que cette thèse puisse contribuer à l'avancement du savoir scientifique sur le mercure et sur les éléments de terres rares dans les écosystèmes arctiques, en plus de favoriser la collaboration mutuellement bénéfique et l'échange de connaissances entre les chercheurs et les communautés autochtones.

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ANNEXE 1: Destin et transfert trophique des terres rares dans les réseaux trophiques aquatiques des lacs tempérées

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Contributions en tant que 3e auteure: analyse et compilation de données, contrôle de qualité des données, analyses statistiques, interprétation des données, révision du manuscrit.

ANNEXE 2: IMALIRIJIIT: un programme de suivi environnemental communautaire dans le bassin versant de la rivière George, Nunavik

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Contributions en tant que 3e auteure: collecte de données, analyses des données en laboratoire, interprétation de données, rédaction et révision du manuscrit.

ANNEXE 3: Former les chercheurs en début de carrière à la recherche en contexte autochtone : le potentiel des ateliers par les pairs

Article soumis : MacMillan, G. A.*, Falardeau, M.*, Girard, C., Dufour-Beauséjour, S., Lacombe-Bergeron, J., Menzies, A. K., & Henri, D. (2018). **Highlighting the potential of peer-led workshops in training early career researchers for conducting research with Indigenous communities**. Preprint : SocArXiv, 8 Nov. 2018. DOI:10.31235/osf.io/vxust

* Co- premières-auteurs

Soumis le 7 novembre 2018 à *Facets*.

Contributions en tant que co-1e auteure: plan de recherche, création et planification de l'atelier, collecte et analyses des données, interprétation de données, rédaction et révision du manuscrit.

ANNEXE 4: Autres Contributions

Articles publiés (et évalués par des pairs) :

1) Vonk, J. E., Tank, S. E., Bowden, W. B., Laurion, I., Vincent, W. F., Alekseychik, P., Amyot, M., Billet, M. F., Canário, J., Cory, R. M., Deshpande, B. N., Helbig, M., Jammet, M., Karlsson, J., Larouche, J., MacMillan, G., Rautio, M., Walter Anthony, K. M., and Wickland, K. P. (2015). **Reviews and syntheses: Effects of permafrost thaw on Arctic aquatic ecosystems,** *Biogeosciences*, 12, 7129–7167.

2) Chételat, J., Richardson, M. C., MacMillan, G. A., Amyot, M., & Poulain, A. J. (2017). **Ratio of Methylmercury to Dissolved Organic Carbon in Water Explains Methylmercury Bioaccumulation Across a Latitudinal Gradient from North-Temperate to Arctic Lakes**. *Environmental Science & Technology,* 52(1), 79-88.

Articles de vulgarisation scientifique :

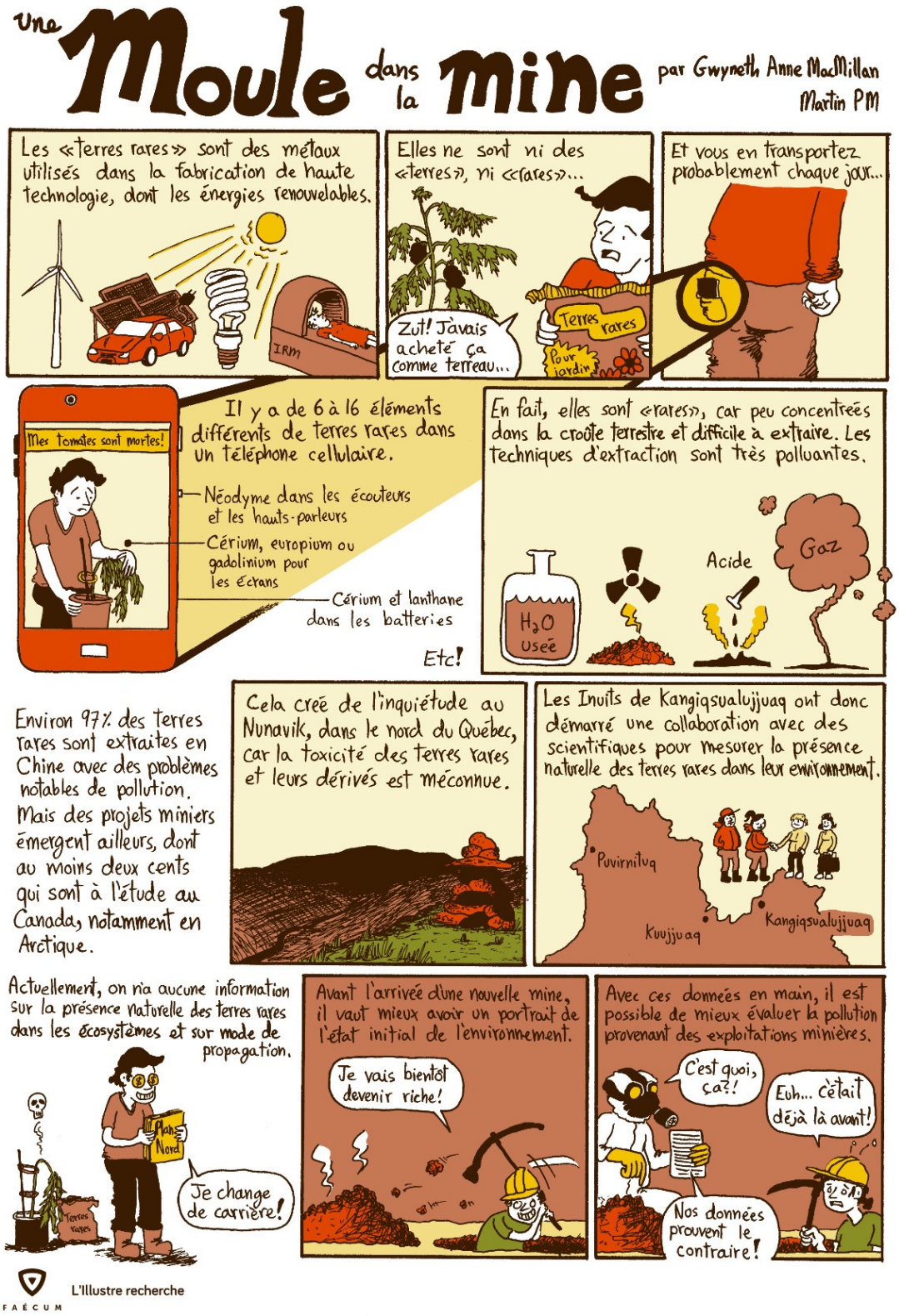
1) MacMillan, G. (2018). Blog post: Canadian STEM Femmes. *19. To the fearless female pioneers of science, and to my grandmother Eluned*. Disponible en ligne : https://www.ic.gc.ca/eic/site/063.nsf/eng/97564.html

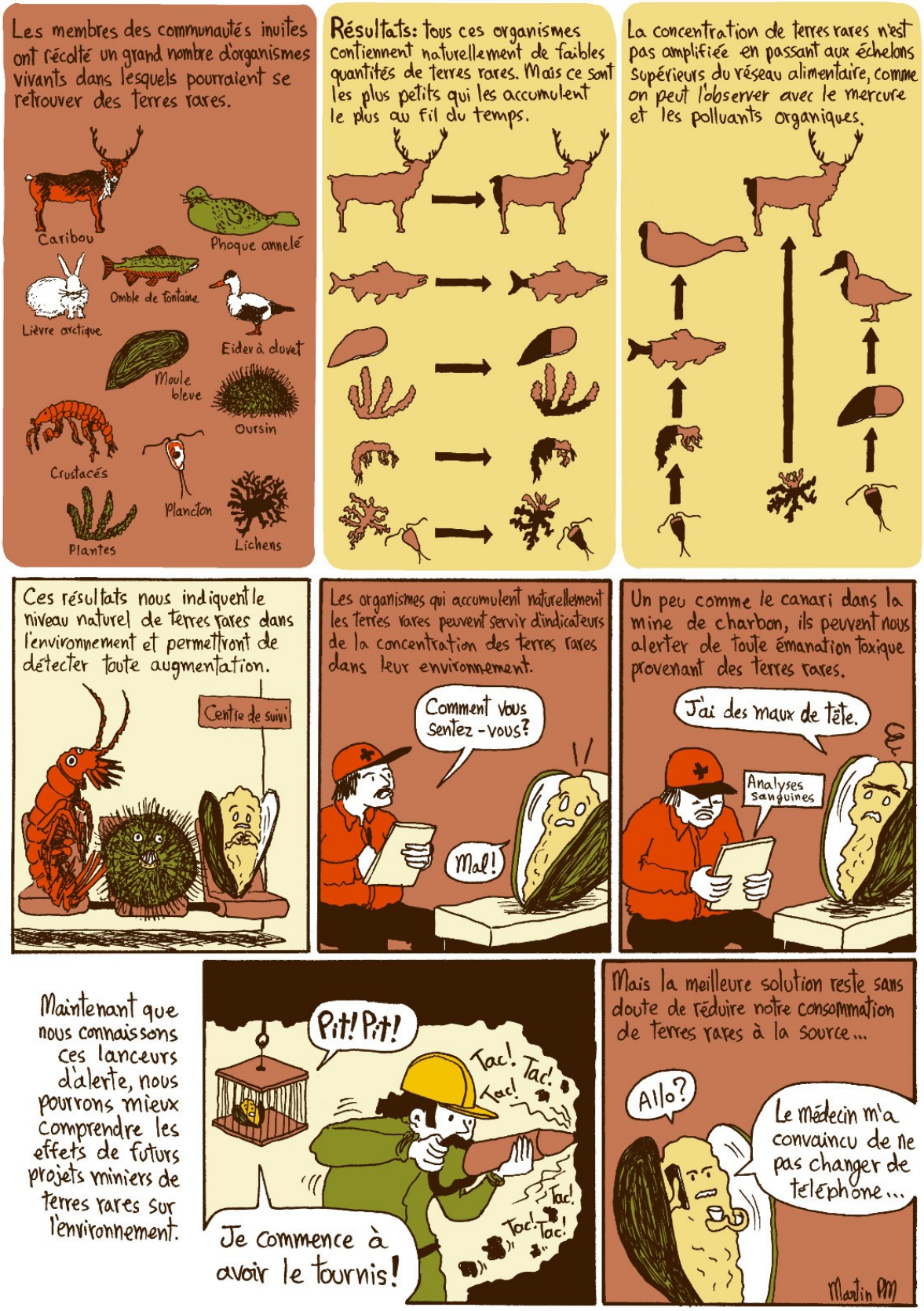
2) MacMillan, G. (2017). Three blog posts for Espaces Autochtones, Radio Canada. a) « *Le défi d'une scientifique Qallunnaat* » b) « *Aimez-vous faire du camping avec les Qallunaat ?* » c) « *Quelques astuces pour partager ses résultats de recherche avec les communautés autochtones nordiques* ». Disponible en ligne :: https://ici.radio-canada.ca/nouvelle/

3) MacMillan, G. (2012). '*La contamination des cours d'eau par un mélange de produits pharmaceutiques*.' Revue DIRE : revue des cycles supérieurs de l'Université de Montréal, 21(3): 28-32. En ligne : http://www.fondationtrudeau.ca/sites/default/files/u5/vol21no3.pdf

4) MacMillan, G. (2014). '*L'Arctique, un puits toxique'*. Revue DIRE : revue des cycles supérieurs de l'Université de Montréal, 23(1). En ligne : https://www.ficsum.com/dire-archives/volume-23-numero-1-hiver-2014/sciences-lArctique-un-puits-toxique-5/

ANNEXE 5: BD « Une Moule dans la Mine »




Les membres des communautés inuites ont récolté un grand nombre d'organismes vivants dans lesquels pourraient se retrouver des terres rares.
Caribou
Phoque annelé
Omble de fontaine
Lièvre arctique
Eider à duvet
Moule bleue
Oursin
Crustacés
Plancton
Plantes
Lichens
Résultats: tous ces organismes contiennent naturellement de faibles quantités de terres rares. Mais ce sont les plus petits qui les accumulent le plus au fil du temps.
La concentration de terres rares n'est pas amplifiée en passant aux échelons supérieurs du réseau alimentaire, comme on peut l'observer avec le mercure et les polluants organiques.
Ces résultats nous indiquent le niveau naturel de terres rares dans l'environnement et permettront de détecter toute augmentation.
Centre de suivi
Les organismes qui accumulent naturellement les terres rares peuvent servir d'indicateurs de la concentration des terres rares dans leur environnement.
Comment vous sentez-vous?
Mal!
Un peu comme le canari dans la mine de charbon, ils peuvent nous alerter de toute émanation toxique provenant des terres rares.
J'ai des maux de tête.
Analyses sanguines
Maintenant que nous connaissons ces lanceurs d'alerte, nous pourrons mieux comprendre les effets de futurs projets miniers de terres rares sur l'environnement.
Pit! Pit!
Tac! Tac! Tac!
Tac! Tac!
Tac! Tac!
Je commence à avoir le tournis!
Mais la meilleure solution reste sans doute de réduire notre consommation de terres rares à la source...
Allo?
Le médecin m'a convaincu de ne pas changer de téléphone...
Martin PM