Fate and trophic transfer of rare earth elements in temperate lake food webs

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Lanthanides, food webs, aquatic systems, bioaccumulation, biogeochemistry, trophic dilution, stable isotopes, depuration.

ABSTRACT

Many mining projects targeting rare earth elements (REE) are in development in North America, but the background concentrations and trophic transfer of these elements in natural environments have not been well characterized. We sampled abiotic and food web components in 14 Canadian temperate lakes unaffected by mines, to assess the natural ecosystem fate of REE. Individual REE and total REE concentrations (sum of individual element concentrations, ΣREE) were strongly related with each other throughout different components of lake food webs. Dissolved organic carbon and dissolved oxygen in the water column, as well as ΣREE in sediments, were identified as potential drivers of aqueous ΣREE. Log_{10} of median bioaccumulation factors ranged from 1.3, 3.7, 4.0 and 4.4 L/kg (wet weight) for fish muscle, zooplankton, predatory invertebrates and non-predatory invertebrates, respectively. [ΣREE] in fish, benthic macroinvertebrates and zooplankton declined as a function of their trophic position, as determined by functional feeding groups and isotopic signatures of nitrogen ($\delta^{15}N$), indicating that REE were subject to trophic dilution. Low concentrations of REE in freshwater fish muscle compared to their potential invertebrate prey suggest that fish fillet consumption is unlikely to be a significant source of REE to humans in areas unperturbed by mining activities. However, other fish predators (e.g., piscivorous birds and mammals) may accumulate REE from whole fish as they are more concentrated than muscle. Overall, this study provides key information on the baseline concentrations and trophic patterns for REE in freshwater temperate lakes in Quebec, Canada.

INTRODUCTION

The demand for rare earth elements (REE, which include lanthanide metals, Sc and Y) is expected to grow significantly over the next 25 years[1], and many new mining projects are being developed across North America. In Canada alone, a country that has the fourth largest rare earth oxide resources in the world after China, Australia and Russia[2], there are currently more than 200 exploration projects under development. While the general local impacts of REE mining are expected to be similar to those of other hardrock minerals, the environmental impacts of the increased prevalence of REE in global surface waters are unknown [3]. Moreover, certain REE applications, such as their use in agricultural fertilizers [4], have the potential to contaminate relatively large areas of aquatic and terrestrial environments. While overall REE profiles from atmospheric deposition have changed since the onset of industrialization [5], there is also evidence that the modern use of REE is associated with increases in levels of total REE in aquatic environments [3, 6, 7]. Although REE are indeed toxic under certain conditions to a variety of organisms [8, 9], further research is needed to determine whether there are patterns of toxicity that apply to the whole group of elements.

In addition to their toxicity, and unlike well-studied trace metals (e.g. Hg, Cd and Pb), it is unclear to what extent REE accumulate or biomagnify in aquatic food webs, and whether accumulation patterns differ from one element to another. A field study conducted by Mayfield and Fairbrother[10] reported negative relationships between age or body size and REE concentrations for some fish species and elements, and inferred that REE had limited potential for biomagnification based on qualitative trophic position assessments of these fish. Weltje et al. [11]

showed that the ratios of REE concentrations in snails to those in their presumptive feed (*Potamogeton pectinatus* pond weed) ranged usually between 1 and 5, indicating that the extent of biomagnification in this food chain was low. To our knowledge, very few studies have quantitatively related REE bioaccumulation with trophic position through natural aquatic food webs. This has become a major field of research for other contaminants, whereby stable isotopes of nitrogen and carbon ($\delta^{15}N$ and $\delta^{13}C$) are commonly used to quantify the degree of trophic transfer and potential sources of energy (carbon) and contaminants to food webs[12, 13]. This technique has allowed researchers to compare trophic transfer of contaminants among disparate aquatic food webs and relate potential differences to ecosystem characteristics [14, 15].

In areas unimpacted by mining activities, natural geological sources and atmospheric deposition are likely the main sources of REE to aquatic ecosystems. The concentration of REE in freshwater systems will depend on weathering, pH, redox (Eh) conditions, adsorption on iron and manganese oxides[16] and clay minerals, as well as complexation with inorganic and organic ligands (e.g. CO_3^{-2}, PO_4^{-3}, humic and fulvic acids)[17]. Some REE, such as Eu and Ce, have different oxidation states that lead to geochemical anomalies under certain pH and Eh conditions.

In order to better characterize the fate of REE in aquatic ecosystems unaffected by mining activities in North America, we studied 14 temperate lake ecosystems in southern Québec (Canada) and determined: 1) whether individual REE elements behave similarly, i.e. as a group, with respect to their concentrations in water and sediments and bioaccumulation patterns in aquatic organisms; 2) whether potential environmental drivers controlling REE levels in water and animals could be identified; 3) whether REE concentrations were a function of trophic position of organisms through food webs, and whether REE are biomagnified or undergo trophic dilution in lakes. This study on ecosystems unaffected by mining provides important baseline information on the trophic patterns of REE in natural aquatic systems.

MATERIAL AND METHODS

Study sites

Our study sites included 14 lakes in southern Quebec (Canada) located in two geological provinces (three lakes in the Appalachian province and eleven lakes in the Grenville province) and along a significant water quality gradient, with values of dissolved organic carbon ranging from 2.6 to 8.5 mg/L and calcium levels ranging from 47 to 379 µM in surface waters (Fig. S1; Table S1). These lakes are relatively small (surface: 0.1 to 4.7 km^2) and shallow (maximum depth: 7.6 to 25 m; Dr. Richard Carignan, unpublished data.). Nine of 14 lakes developed hypoxic hypolimnia with dissolved oxygen levels below 1 ppm. These lakes are representative of many North American temperate lakes not affected by mining activities. To our knowledge, the results of this study represent the largest data set on background REE levels in temperate lake ecosystems. These lakes are not located in an area known for rare earth mineral deposits and should therefore not be affected by local geological point sources. According to interactive provincial mineral deposit maps (http://sigeom.mines.gouv.qc.ca), some lakes in the Grenville province are located in the vicinity of deposits of iron (Croche – St.-Hippolyte, Pin Rouge), nickel (Goulet, Héroux), titanium (Pin

Rouge), and uranium (Méduse, Second Roberge), whereas lakes from the Appalachian provinces are near deposits of copper (Argent, Choinière, Orford) and gold (Argent, Orford).

Field sampling

In each lake, sediments, water, zooplankton, and benthic invertebrates were sampled within a period of two consecutive days, in late July or August of 2011 (lakes Chicot, Croche – Mauricie, Croche – St.-Hippolyte, Goulet, Héroux, Méduse, Perchaude, Pin Rouge, Second Roberge, Trottier) or 2012 (lakes Argent, Choinière, Morency, Orford). Fish were collected in early September of the same sampling year (2011 or 2012) within each lake. Unfiltered water was sampled in the epilimnion (0.5 m below the surface) and the hypolimnion (1 m above the sediments) of each lake at its deepest point, after having assessed the position of the thermocline by depth profiles with a YSI600QS multiparameter probe. A peristaltic pump with Teflon and Norprene tubing was used to collect unfiltered water in triplicate in amber glass bottles; samples were double-bagged, preserved with a final HCl concentration of 0.2% (Omnitrace Ultra, EMD) and kept at 4 °C. Glassware was acid-washed (45% HNO_3; 5% HCl) as were plastic ware and tubing (10% HCl) for 12 h, then rinsed three times with milliQ water (18.2 MΩ•cm). A protocol of "clean hands, dirty hands" appropriate for ultra-trace metal sampling[18] was used to sample water.

Integrated zooplankton samples from the first 6 m of the water column were collected during daylight with a plankton net (200 µm mesh size), rinsed with milliQ water and frozen (-20 °C). Sediments were sampled at the deepest point with an Ekman grab (15 x 15 x 15 cm) and samples of the top 10 cm of sediments were frozen (-20 °C).

Benthic invertebrates were either sampled with a benthic kick net in the littoral zone or with a sediment grab sampler at deeper locations. Samples were sieved, sorted and identified to the lowest practical taxonomic level[19] with the help of a dissecting scope. Taxa collected included Amphipoda (Gammaridae), Bivalvia, *Chaoborus* species, Chironomidae, Ephemeroptera (Caenidae, Heptageniidae, Leptophlebiidae), Gastropoda, Hydracarina, Isopoda, Megaloptera (Sialidae), and Odonata (Aeshnidae, Coenagrionidae, Gomphidae, Libellulidae). After sorting, benthic invertebrates were rinsed with Milli-Q water before freezing, without a depuration step.

A side experiment was conducted to assess the impact of depuration on REE levels measured in benthic invertebrates. Chironomids were collected in Lake Triton, a small Precambrian Shield Lake located at the Station de biologie des Laurentides (Université de Montréal). After sampling, half of the chironomids were immediately placed in vials and frozen (7 vials containing 4 chironomids each). The other half were placed in another series of 7 vials and left to depurate for 50 h before being frozen.

Beach seine (1 m x 20 m) and minnow traps were used to collect fish which were euthanized with a clove oil solution. Captured species included brown bullhead (*Ameiurus nebulosus*), creek chub (*Semotilus atromaculatus*), pumpkinseed sunfish (*Lepomis gibbosus*), smallmouth bass (*Micropterus dolomieu*), white sucker (*Catostomus commersonii*) and yellow perch (*Perca flavescens*). Fish samples were kept at -20 °C in re-sealable plastic bags until processing in the lab, where they were measured for length and weight. A dorsal muscle sample was taken from each fish with acid-cleaned forceps and scalpel, and stored at -20 °C in plastic bags. For one sample lake, Lake Croche (St.-Hippolyte), carcasses were also kept to compare the difference in REE concentrations between carcasses and muscles. Note that carcasses contained all tissues except the tissue sample taken from the dorsal muscle.

Chemical analysis

REE measured in this study include Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. Sc was excluded due to known analytical interference with ICP-MS analysis [21]. All biota and sediment samples were freeze-dried and homogenized prior to chemical analysis. For benthic invertebrates, whole bodies were pooled within taxa in each lake for stable isotope and REE analyses. For fish, samples of dorsal muscle for each individual fish were analyzed for isotopes and REE. All REE concentrations in sediments and biota are reported in nmol/g on a dry weight basis (d.w.). REE analysis in lake water was conducted on unfiltered samples and all water REE concentrations are reported in nmol/mL or in nM. For convenience, we also included summary data in units of nmol/g and ng/g in Table S8.

All REE analyses were conducted at the Université de Montréal by inductively-coupled plasma mass spectrometry (ICP-MS, Perkin-Elmer NexION 300x). Details on detection limits are reported in Table S2. Filtered water samples were preserved with HNO_3 (2%) before analysis. For sediments and biota, 2 to 100 mg of dried sample were digested in clean Teflon tubes (HNO_3 45%, HCl 5%) 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 mL of ACS grade hydrogen peroxide (30% H_20_2) before each cycle. Samples were diluted with ultra-pure water into trace metal clean falcon tubes before analysis. Quality assurance procedures for REE analysis included the analysis of blanks and intra-lab standards (TORT-2; lobster hepatopancreas, NRC) for REE concentrations which were compared against concentrations determined by the Centre d'expertise en analyse environnementale (CEAEQ, Government of Québec) using the same extraction methods. On average, water samples varied by 17% compared to CEAEQ (Table S3), sediment by 7% (Table S4) and TORT-2 results by 13% (Table S5). Note that for sediments, we were below certified values as we did not use a full extraction method with hydrofluoric acid (HF), but a partial extraction more representative of the labile fraction which is available to organisms.

Stable isotope analyses were conducted at the G.G. Hatch Stable Isotope Laboratory (University of Ottawa). Approximately 1 mg of each biological sample (fish, benthic invertebrate or zooplankton) was weighed into tin capsules and analysed for nitrogen stable isotopes ($\delta^{15}N$) using an elemental analyzer (Elementar Isotope Cube) interfaced to an isotope ratio mass spectrometer (Thermo Conflo III and Thermo Delta Advantage). Nitrogen isotope values in all samples were standardized to atmospheric nitrogen (N_2). Quality assurance samples included triplicate analyses of an intra-lab standard with each batch, as well as duplicate analyses of approximately 10% of samples (summary in Table S6).

Water chemistry analyses

All lakes were sampled for water chemistry, including dissolved organic carbon (DOC; IO Aurora 1030 carbon analyzer), anions (ion chromatography, Waters), and cations (atomic, absorption spectrophotometer, Agilent). Quality assurance was performed using certified materials, namely Perade-09 for DOC (Environment and Climate Change Canada, ECCC) and RN-10 for anions and cations (ECCC). In addition, the physico-chemical properties of the water column, including temperature, pH, conductivity, and dissolved oxygen, were measured using a YSI 600QS meter (YSI Incorporated). The probe was calibrated for quality assurance using standard pH solutions (pH of 4, 7 and 10, Hanna Instruments) and a standard solution of 100 μS/cm (Anachemia) for conductivity. Analytical details can be found in MacMillan et al.[20] Morphometric data on the study lakes was obtained using ArcGIS software.

Data handling and analysis

REE concentrations

Total REE concentrations were calculated as the sum of the concentrations of each individual element (ΣREE; Sc was excluded [21]) in nmol/g of dry weight (biota and sediments) or nmol/mL (water). For each element, REE concentrations in blanks were subtracted from samples where the REE blank concentrations were higher than the detection limit (DL). When the concentration of a given element in a sample was below the DL (to the nearest ± 0.001 ng/L), we used half the DL in the calculations. The frequency of detection of each element, sorted by sample type, is shown in Table S7. In the text, we also refer to heavy and light REE. Heavy REE include Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu[17]; Y is technically not heavy but is usually pooled with heavy REE because of its chemical behavior. Light REE include La, Ce, Pr, Nd, Pm, Sm, Eu [17], although the specific elements in each group vary between studies.

Taxonomic grouping of invertebrates

The taxonomic groups of captured benthic invertebrates (as well as the level of identification that was possible for different samples) varied across the 14 study lakes (Table S8). This is a common feature of studies that include lacustrine invertebrates and is compounded by issues such as the differences in maturity of individuals among systems (since many freshwater invertebrate taxa are short-lived). Therefore, functional feeding groups were assigned to all benthic invertebrate samples based on Merritt et al. [22] and Barbour et al. [23] (Table S8). The presence of these feeding groups varied across lakes, so invertebrates were further grouped into either non-predatory (filter-collectors, gatherer-collectors, scrapers and shredders) or predatory groups within each lake. All Ephemeroptera were assumed to be non-predatory, given that the families collected were primarily gatherer-collectors[22] (Table S8). The predatory Tanypodinae sub-family of Chironomidae were excluded from statistical analysis, and all other Chironomidae were assumed to be non-predatory given that the other two major sub-families, the Chironominae and Orthocladiinae, can be classified as such[22, 23]. Although benthic invertebrate samples were collected both in the littoral zone and at depth, only samples from the epilimnion (littoral samples and depth samples above the thermocline) were used in comparisons of REE concentrations between predatory and non-predatory invertebrates. All statistical analyses herein are based on these predatory and non-predatory invertebrate groupings.

Baseline $\delta^{15}N$ adjustments

Within each lake, the $\delta^{15}N$ composition of the lowest non-predatory invertebrate was used to adjust the $\delta^{15}N$ values ($\delta^{15}N_{adj}$) of all other organisms within that system. This adjustment makes it possible to compare $\delta^{15}N$ of food web organisms while considering potential variation in baseline $\delta^{15}N$ values among different ecosystems [24, 25]. Data from a large group of Canadian lakes, including from some of the same systems as in the current study, indicated that overall, predatory invertebrates had $\delta^{15}N$ values approximately 2.12 ‰ higher than non-predatory invertebrates [26]. Therefore, in the two current study lakes (Argent and Morency) where no $\delta^{15}N$ data were available for a non-predatory group, this value of 2.12 ‰ was subtracted from the lowest individual $\delta^{15}N$ value of all predatory invertebrates within those two systems. This result was then used as an estimate of the non-predatory $\delta^{15}N$ value, which was used to obtain $\delta^{15}N_{adj}$ for all other organisms in those lakes. This approach allowed us to maximize the number of systems that were included in our analysis of REE trophic transfer through lake food webs.

Statistical analyses

Prior to analysis, all data were examined for normality and homogeneity of variance using Kolmogorov-Smirnov and Levene's tests, respectively ($\alpha = 0.05$ for both tests). When necessary, data were normalized by $\log_{10}$-transformation to reduce skewness; this included all individual element and ΣREE concentrations, as well as fish length and weight (Table S9; and see specific details of analyses that follow). Comparisons of $\log_{10}$-ΣREE concentrations among different groups of organisms across lakes were conducted using Welch's analysis of variance (ANOVA) and Games-Howell comparisons ($\alpha = 0.05$). This approach allowed us to avoid assuming equality of variance between groups of organisms with different sample sizes.[27]

Pearson correlation analyses were used to explore relationships between mean lake physico-chemical characteristics (see Table S1) and ΣREE in biota. For these analyses, all variables were normalized by $\log_{10}$-transformation except calcium (square-root transformed) and pH (not transformed) prior to analyses. The significance of correlations was assessed with and without Holm correction [28]. Ordinary least-squares regression analyses and non-linear regression analyses were used to assess the relationship between $\log_{10}$-ΣREE concentrations and $\delta^{15}N_{adj}$ using all available data.

Data on pH and REE sediments concentrations were not available for all lakes (n = 10 lakes with sediment REE data and n = 13 lakes with pH data; Table S1). For this reason, two sets of principal component analyses (PCAs) were conducted with available lake water and sediment chemistry data. The first set of PCAs included the 10 lakes for which sediment REE concentration and pH data were available (Table S1). For these 10 lakes, separate PCAs were conducted using either lake water chemistry variables from the epilimnion and hypolimnion, in addition to sediment characteristics. The second set of PCAs included all 14 study lakes; again, two separate PCAs were conducted using either epilimnetic or hypolimnetic lake water chemistry variables. Sediment variables (ΣREE concentration and organic matter content) and pH were not included in the second set of PCAs in order to maximize the number of systems included in the analyses. For all PCAs, all lake characteristics were normalized by $\log_{10}$-transformation except calcium (square-root transformed) and pH (not transformed) and standardized (mean of 0, standard deviation of 1).

RESULTS AND DISCUSSION

Relationships between different REE

Individual rare earth elements and ΣREE were strongly related with each other through all components of the lake food webs, including biotic and abiotic matrices. Relationships between selected light and heavy elements as well as ΣREE are shown in Fig. S2. Regression coefficients were all statistically significant and ranged from 0.94 to 0.99. Although Ce, Eu and Gd have been shown to exhibit anomalous concentration patterns relative to the other REE[11, 16, 29], their relationships were consistent with bioaccumulation patterns of the other elements. Relationships among individual elements and ΣREE were more variable within fish muscle data (Fig. S2); this may be a function of the generally low concentrations of all REE in fish muscle compared to other biota and sediments (Table S8). It is already well established that REE behave as a homogeneous group of elements in abiotic matrices, however these strong correlations between REE in biological matrices have not been well studied. As individual REE were all strongly related with each other, we focused on ΣREE in the following sections.

REE concentrations in water and sediments

ΣREE concentrations averaged 0.53 ± 0.39 nM (mean ± standard deviation) in epilimnetic lake water and 1.62 ± 2.35 nM in the hypolimnetic waters (Fig. 1). When comparing paired data for ΣREE in surface vs. bottom waters, bottom waters were on average 2.5 times more concentrated. Sediments averaged 1.15 ± 0.50 mmol ΣREE/kg (Fig. 1). Even though samples came from two geological provinces (Fig. S1; Table S1), ΣREE concentrations varied by less than two orders of magnitude across lakes, with maximum / minimum value ratios (max:min; Table S1) of 3.7 for sediments, 12.5 for epilimnetic waters and 50.4 for hypolimnetic waters.

Principal component analysis (Fig. 2, S3) of the physico-chemical characteristics of the lakes revealed that ΣREE levels in surface waters and bottom waters were both positively correlated with DOC and with ΣREE in sediments. Although the number of lakes considered is small, lakes from the Appalachian geological province tended to form a distinct group from those located in the Grenville region (Fig. S3). When ΣREE in sediments was removed from the analysis (Fig. 2), dissolved oxygen concentration emerged as an important variable inversely related to ΣREE in water.

These findings are in general agreement with results from Weltje et al. [11] who reported REE concentrations in the nM range in surface waters and in the sub-mmol/kg range in sediments of several highly industrialized sites of The Netherlands near Rotterdam. However, they are approximately up to three orders of magnitude lower than those reported in rivers affected by REE mining in China[30]. Moreover, our results indicate that ΣREE in sediments, and surface and bottom waters were positively correlated with each other, and with DOC. The correlation with DOC may be related to the high binding capacity of organic matter such as humic acids for dissolved metals [31] and could be related to cotransport of REE with DOC from the drainage basin. Higher concentrations were also found in oxygen-poor waters, which could potentially be explained by REE desorption from Fe oxides[31] and phosphates[32] under reductive conditions in anoxic or hypoxic waters. Weltje et al. [11] similarly reported higher REE levels in pore waters compared to surface waters.

Concentrations of REE in aquatic organisms

When considering trophic transfer, REE concentrations in fish may be of interest for assessing transfer to humans (in which case fish muscle should be considered), or transfer to other predators (in which case whole fish may be more relevant). ΣREE were 32, 40 and 275 times higher in whole body than in muscles for brown bullhead, creek chub and white sucker, respectively (Fig. 1). ΣREE concentrations in benthic invertebrates were approximately 1000 times higher than those in fish muscle (median of 20 nmol/g versus 0.02 nmol/g, respectively). Non-predatory benthic invertebrates (mean ± SD; 60 ± 69 nmol/g) had significantly higher ΣREE than predatory benthic invertebrates (16 ± 14 nmol/g) and zooplankton (13 ± 12 nmol/g) (Welch's ANOVA, $F = 9.00$, $p = 0.001$; Fig. 1).

To our knowledge, this is one of the first datasets on REE accumulation in natural aquatic food webs. Comparison of this data with published data is therefore difficult, particularly for zooplankton and benthic invertebrates. For fish, mean ΣREE concentrations in whole bodies ranged from 0.11 ± 0.13 (brown bullhead; size range: 125-157 mm) to 0.45 ± 0.44 mg/kg (white sucker; size range: 123-162 mm; Table S9) (using units of mg/kg dry weight for comparison with published data),. These concentrations lie within the range described for larger size classes (when available) of nine freshwater fish species collected from a North American reservoir (State of Washington, USA) unaffected by mining. In this study, the mean size range for whole fish was from 330 mm for Kokanee to 527 mm for largescale sucker, and the REE concentration range was from 0.021 mg/kg for walleye to 0.47 mg/kg for longnose sucker[10]. When comparing with smaller size classes reported by Mayfield and Fairbrother[10] (<300 mm) (where sample sizes are low and REE values are more variable) our results still lie within the corresponding range of values (0.05 to 1.98 mg/kg). This latter study also reported much lower concentrations in fish fillets compare to whole bodies. In contrast, a recent report on common freshwater species collected in markets from seventeen cities in Shandong (China) found ΣREE levels of around 0.175 mg/kg in muscles when converted to dry weight for comparison (assuming 80% moisture for the conversion)[33]. These results from China are approximately 30 times higher for fish muscle tissues than in this study (our range: 0.003 for white sucker to 0.010 mg/kg for creek chub), and suggest that geographical variations in REE levels that should be further investigated.

We determined the variation in REE levels in biota across all lakes through correlation analyses and bivariate regressions (Table S10; Fig. 3). Mean ΣREE levels in zooplankton were higher in lakes with higher ΣREE in both epilimnetic and hypolimnetic lake water and sediments. No significant correlation was found for any other biotic groups, when Holm correction was applied (Table S10). With respect to zooplankton, this taxonomic group has been shown to react rapidly to changes in aqueous metal concentrations[34], and it may therefore be a good short-term integrator of REE in the aquatic environment. It is however surprising that ΣREE levels in benthic organisms were not correlated with levels in sediments. This lack of relationship may be partly due to the pooling of organisms in broad categories; this pooling was needed to maximize the amount of biomass available for analysis. A more in-depth analysis at higher taxonomic resolution would be warranted to better understand the relationship between sediment contamination and bioaccumulation by benthic organisms.

Bioaccumulation factors of REE

We calculated the bioaccumulation factor (BAF), defined as the ratio of a chemical concentration in an organism to the concentration in water using field data; in this context, chemical concentration in the aquatic organism results from all possible routes of exposure (e.g., diet and respiratory surfaces)[35]. Concentrations in animals were converted to their wet weight equivalent (assuming 80% moisture), for literature comparison. Median log-BAF values spanned more than three orders of magnitude, ranging from 1.3, 3.7, 4.0 and 4.4 L/kg for fish muscle, zooplankton, predatory invertebrates and non-predatory invertebrates, respectively (Table S11).

For fish muscle (log BAF: 1.3 L/kg on a wet weight basis), these results are slightly lower than BAFs calculated by Mayfield and Fairbrother[10] for La, Ce and Y with reported log of geometric means of 1.7, 2.4 and 1.9 L/kg, respectively. This indicates that, in general, fish muscle, the main tissue consumed by humans, have a low bioaccumulation potential for REE. In contrast, organisms lower in the food webs have higher BAFs, with maximum values found for non-predatory invertebrates.

When expressed as a function of ΣREE in water, BAFs displayed a significant inverse relationship with every taxonomic group except zooplankton (Fig. S3). This inverse relationship between BAF and aqueous ΣREE levels is consistent with trends reported for other metals by DeForest et al.[35] who attributed this phenomenon to multiple factors including, for instance, active regulation and saturable uptake kinetics at high concentrations. However, additional controlled studies are needed to determine whether this inverse relationship for REE is driven by real biochemical processes, or whether it is more a function of the mathematical coupling of BAF to aqueous contaminant concentrations [36].

Note that in this study, we did not depurate benthic invertebrates to remove gut contents, since our main goal was to understand trophic transfer, and predators consume non-depurated prey. However, we performed a depuration experiment in parallel to this study on chironomids from Lake Triton, located in the Grenville geological province. Results indicated that depuration is needed for all REE considered (La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb, Y), with an average ratio of REE in undepurated vs depurated animals of 1.75 ± 0.05 (Fig. 4). The BAFs reported here for benthic invertebrates should therefore be considered upper limits, and could be corrected using the ratio of undepurated to depurated levels. Note however that BAFs are often calculated using undepurated organisms, as is the case in the meta-analysis of metal BAFs by DeForest et al.[35] In our depuration experiments, light REE (e.g. La, Ce, Nd, and also Y) tended to have higher concentrations than heavier REE. This general trend was also seen in all matrices from all lakes, namely water, sediments and biota (see detection frequencies, Table S7) and is consistent with results from other studies [17].

Trophic transfer of REE

ΣREE concentrations tended to decrease with increasing trophic level. This can be seen by the logarithmic decrease in ΣREE from non-predatory to predatory benthic invertebrates and zooplankton, and subsequently to fish muscle and whole fish (Fig. 2). A more quantitative analysis is given using stable isotopic signature ($\delta^{15}N_{adj}$) to better trace trophic position (Fig. 5). Approximately 73% of the variance in ΣREE levels in aquatic organisms was explained by $\delta^{15}N_{ad}$, with generally the same sequence of organisms found along the regression line (non-predatory benthos > predatory benthos > zooplankton > fish muscle) as was found using the functional feeding group approach. The trends reported here are for all 14 lakes combined because data sets from some lakes were incomplete for some trophic levels. However similar trends were apparent for individual lakes (see Fig. S4).

These trends are consistent with the concept of trophic dilution[37] , according to which there is a decrease in contaminant concentration as trophic level increases. This decrease arises from the balance of ingestion and elimination processes, favouring a net loss of contaminant from prey to predator. We quantified the trophic magnification slope (TMS) [13] commonly calculated for other contaminants (slope = -0.59, Fig. 5). This approach showed the marked contrast between REE bioaccumulation and trophic transfer patterns in lake food webs compared to contaminants such as mercury (Lavoie et al. [14]and references therein) and organic pollutants[38], but is consistent with the relatively low trophic transfer factors found for most metals[35, 39]. For instance, in the meta-analysis of 205 aquatic food webs worldwide reported by Lavoie et al. [14], TMS values for methylmercury ranged from +0.08 to +0.53. In contrast, in the study of Cui et al.[40] on metal(loid) transfer in the Yellow River Delta in China, negative slopes were reported for As, Cr, Cu, Mn, Ni, and Pb, although these slopes were not significant.

Overall, these findings are encouraging from a human toxicological perspective, since fish muscle is the main fish tissue consumed by human populations and is found to be consistently low in REE in the study area. However, from an ecotoxicological perspective, our results indicate that whole fish is more concentrated than fish muscle. Fish predators (e.g., piscivorous birds and mammals) are therefore likely to be exposed to greater REE concentrations from whole fish as compared to only fish muscle.

This study provides a baseline for REE levels currently encountered in natural aquatic ecosystems at temperate latitudes in Canada, in the absence of mining activities related to REE extraction. REE behave as a relatively homogeneous group of elements and it appears that they tend to undergo trophic dilution along food webs. Future work should consider other types of North American ecosystems (marine and terrestrial) at different latitudes where mining projects are likely (e.g., northern latitudes in Canada). More in-depth analysis of specific elements and specific taxa is likely to uncover stronger environmental relationships. Finally, organ-specific and subcellular bioaccumulation[41] could provide insight into REE handling strategies by aquatic organisms.

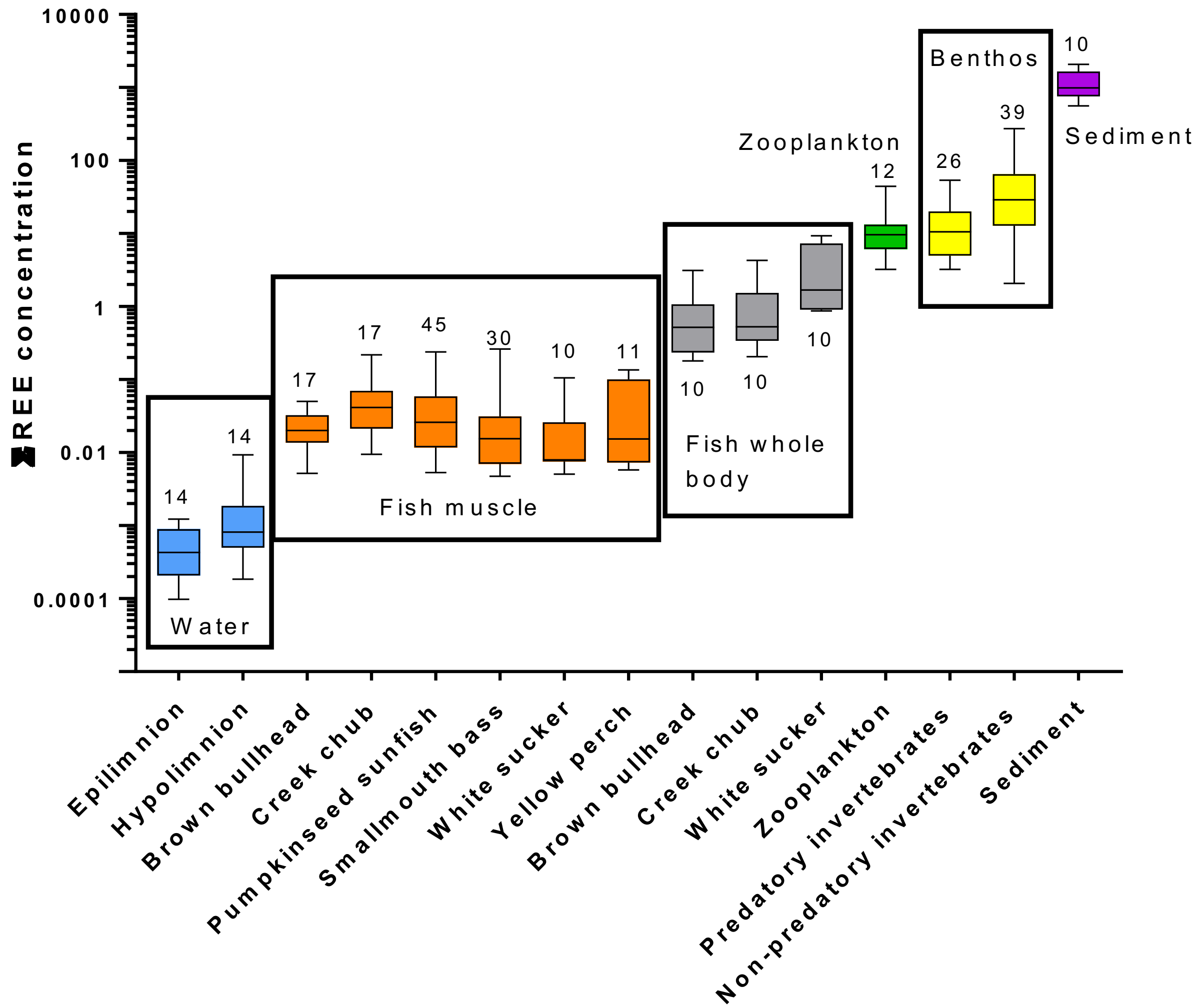

Figure 1. Concentrations of rare earth elements [ΣREE] in different components of lake ecosystems. Data are from 14 lakes in southern Québec, Canada. [ΣREE] in water are given in nmol/mL, whereas those for biota and sediments are given in nmol/g of dry weight. Sample sizes

are shown next to each box. Lower and upper margins of boxes show 25th and 75th percentiles, respectively; whiskers delimit minimum and maximum values.

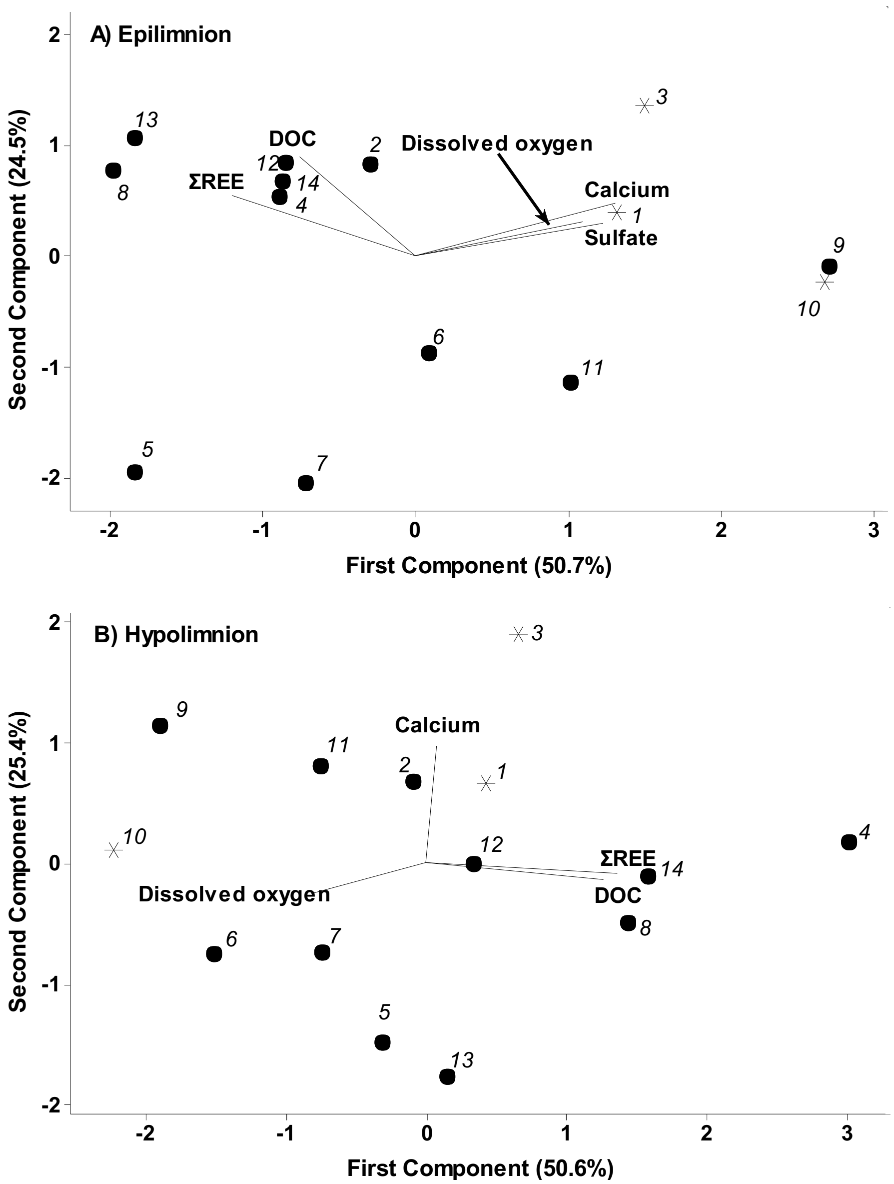

Figure 2: Correlation bi-plots showing the results of Principal Component Analysis (PCA) of chemical characteristics of 14 lakes in southern Québec, Canada. Separate PCAs were conducted using A) epilimnetic and B) hypolimnetic lake chemistry variables. The percentage of total

variance explained by each component is shown in parentheses. Solid and open circles represent lakes located in the Grenville and Appalachian geological provinces, respectively. Data points are numbered according to the corresponding lake: 1) Argent, 2) Chicot, 3) Choinière, 4) Croche (Mauricie), 5) Croche (St.-Hippolyte), 6) Goulet, 7) Héroux, 8) Méduse, 9) Morency, 10) Orford, 11) Perchaude, 12) Pin Rouge, 13) Second Roberge, 14) Trottier. Note that hypolimnetic sulfate data were unavailable for Second Roberge, so this variable was not included in the PCA shown in panel B). See Methods for further details of data handling and analysis.

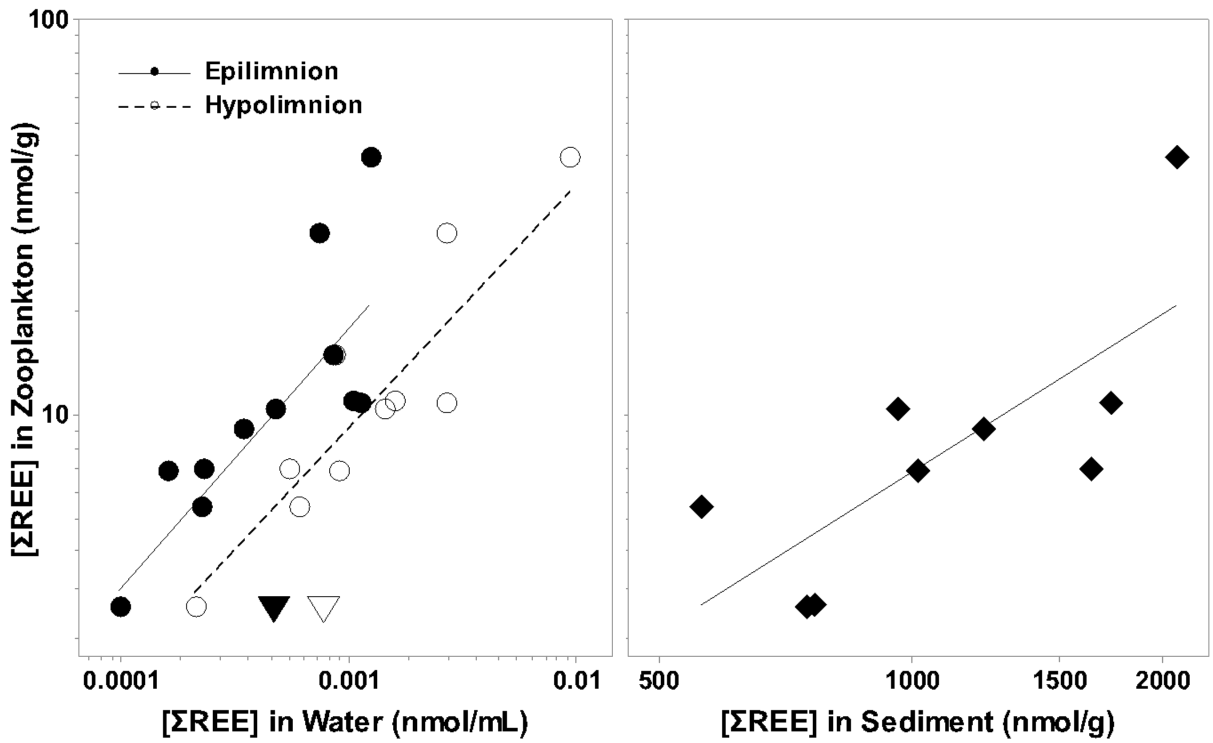

Figure 3. Relationships between mean [ΣREE] in bulk zooplankton, lake water (left panel) and surface sediments (right panel) in up to 12 lakes in southern Québec, Canada. The linear regression relationship for hypolimnetic water was stronger (R^2 = 0.679, p = 0.001, n = 12) than for epilimnetic water (R^2 = 0.509, p = 0.009, n = 12) and sediment (R^2 = 0.570, p = 0.019, n = 10)

across lakes. The triangles (bottom of the left panel) represent lake Pin Rouge (closed symbol for epilimnion, open symbol for hypolimnion), which had studentized residuals of -2.54 and -2.44 for epilimnetic and hypolimnetic water, respectively; when this lake was excluded from regression analyses, both relationships were stronger (epilimnion $R^2 = 0.646$, $p = 0.003$, $n = 11$; and hypolimnion $R^2 = 0.761$, $p < 0.001$, $n = 11$).

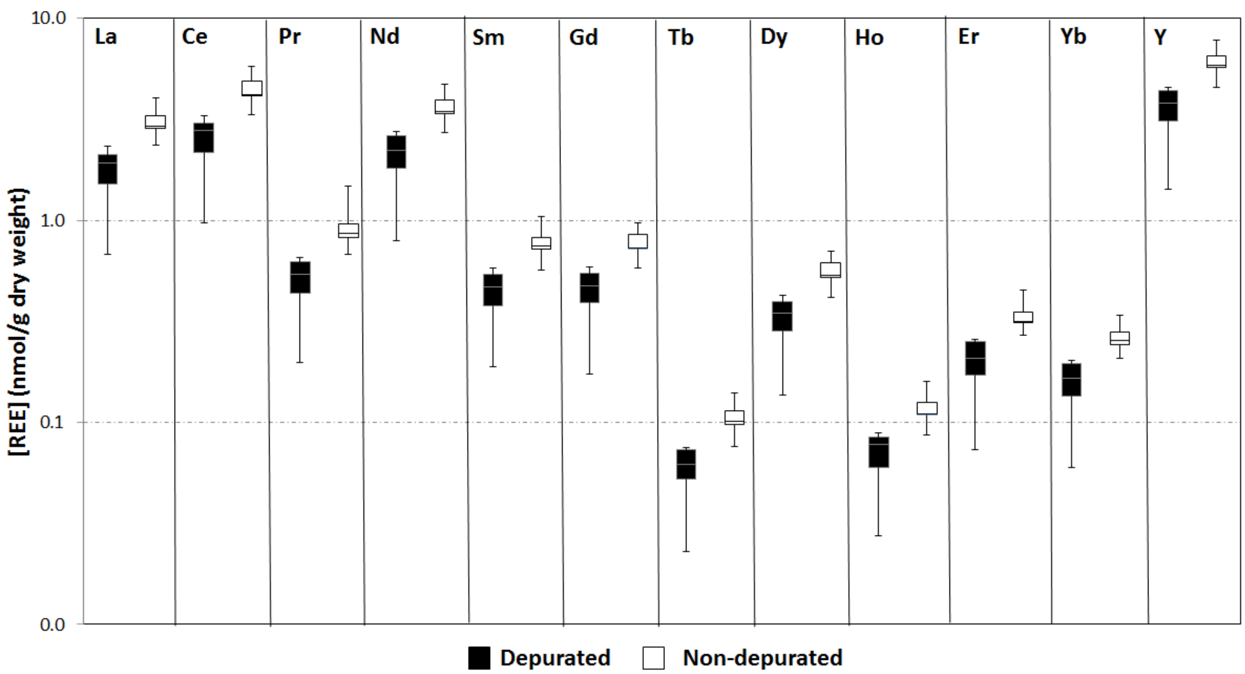

Figure 4. Concentrations of different REEs (on a log scale) in chironomids that were either depurated or not depurated. Samples were taken from Lake Triton, southern Quebec.

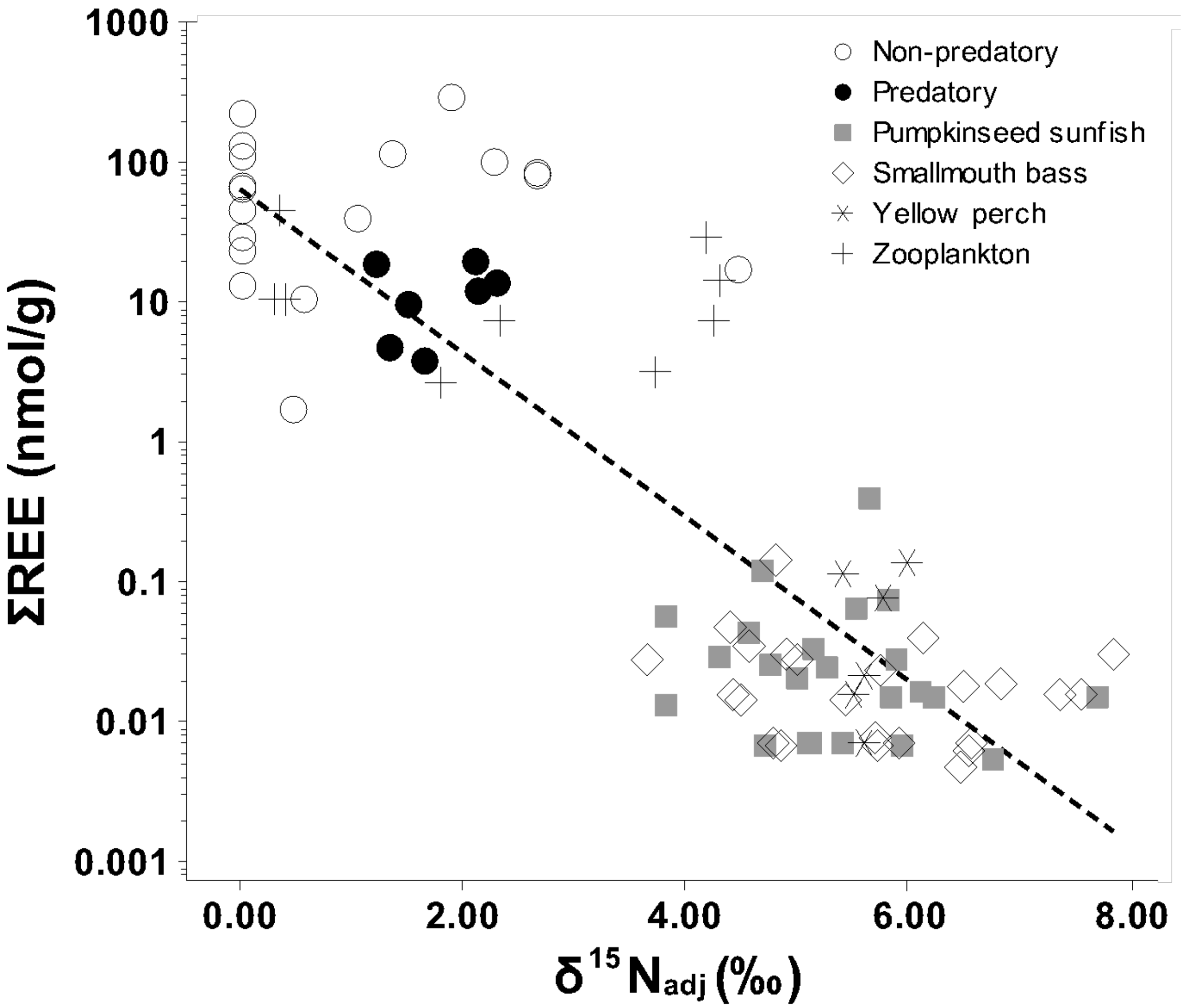

Figure 5. Decline in total rare earth element concentrations in predatory and non-predatory benthic invertebrates (whole bodies), bulk zooplankton and fish muscle with trophic position ($\delta^{15}N_{adj}$) from 11 lake food webs in southern Québec, Canada. Data from lakes Choinière, Croche (St.-Hippolyte), and Héroux were not included because it was not possible to adjust $\delta^{15}N$ for these food webs (see Methods section for details). The linear regression for $\log_{10}$-[ΣREE] versus $\delta^{15}N_{adj}$ is shown as an estimate of the trophic magnification slope commonly calculated for other

contaminants ($\log_{10}$-[ΣREE] = 1.817 - 0.585* $\delta^{15}N_{adj}$, $R^2 = 0.728$, $p < 0.001$, n = 87; Lavoie et al. 2013[14]). Quadratic and cubic regression relationships had similar strength ($R^2 = 0.730$, $p < 0.001$; and $R^2 = 0.774$, $p < 0.001$, respectively).

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was prepared using contributions from all authors. All authors have given approval to the final version of the manuscript. TP and MA designed the study. TP and AAG collected data. Data was analyzed by MGC, TP, GAM and MA. Table and figures were prepared by MGC and AAG. MGC, MA and GAM prepared the manuscript.

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Notes

The authors declare no competing financial interest.

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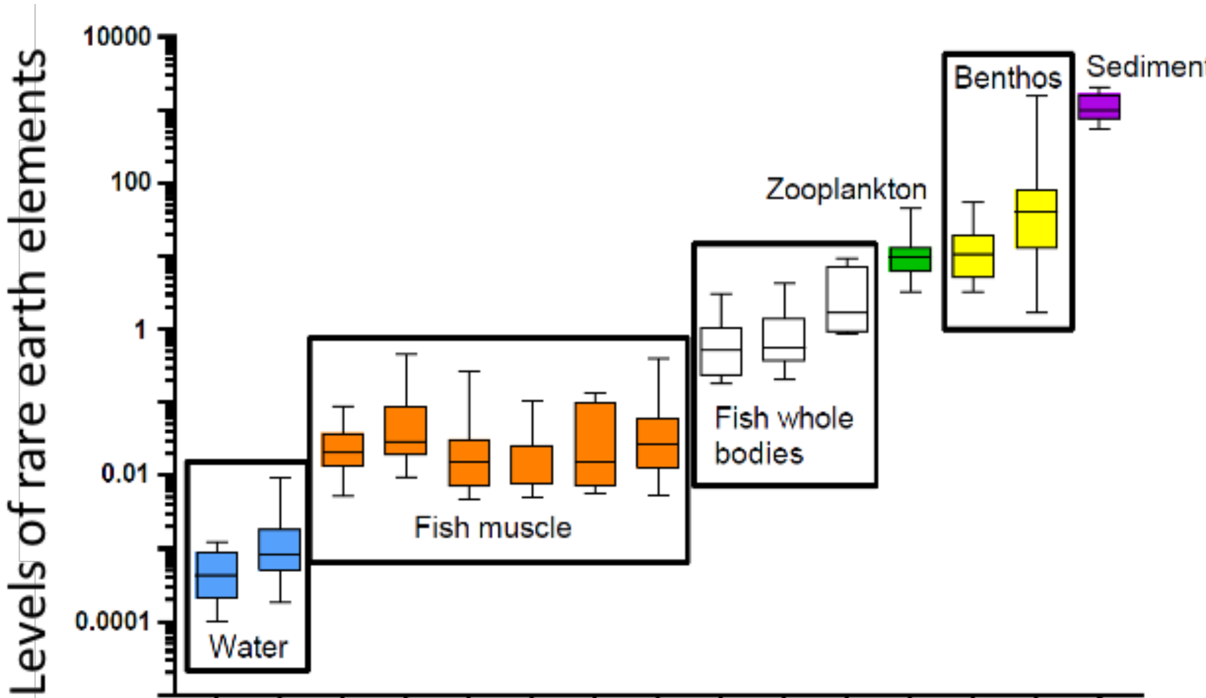
TOC/ABSTRACT ART



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SUPPORTING INFORMATION

Fate and trophic transfer of rare earth elements in temperate lake food webs

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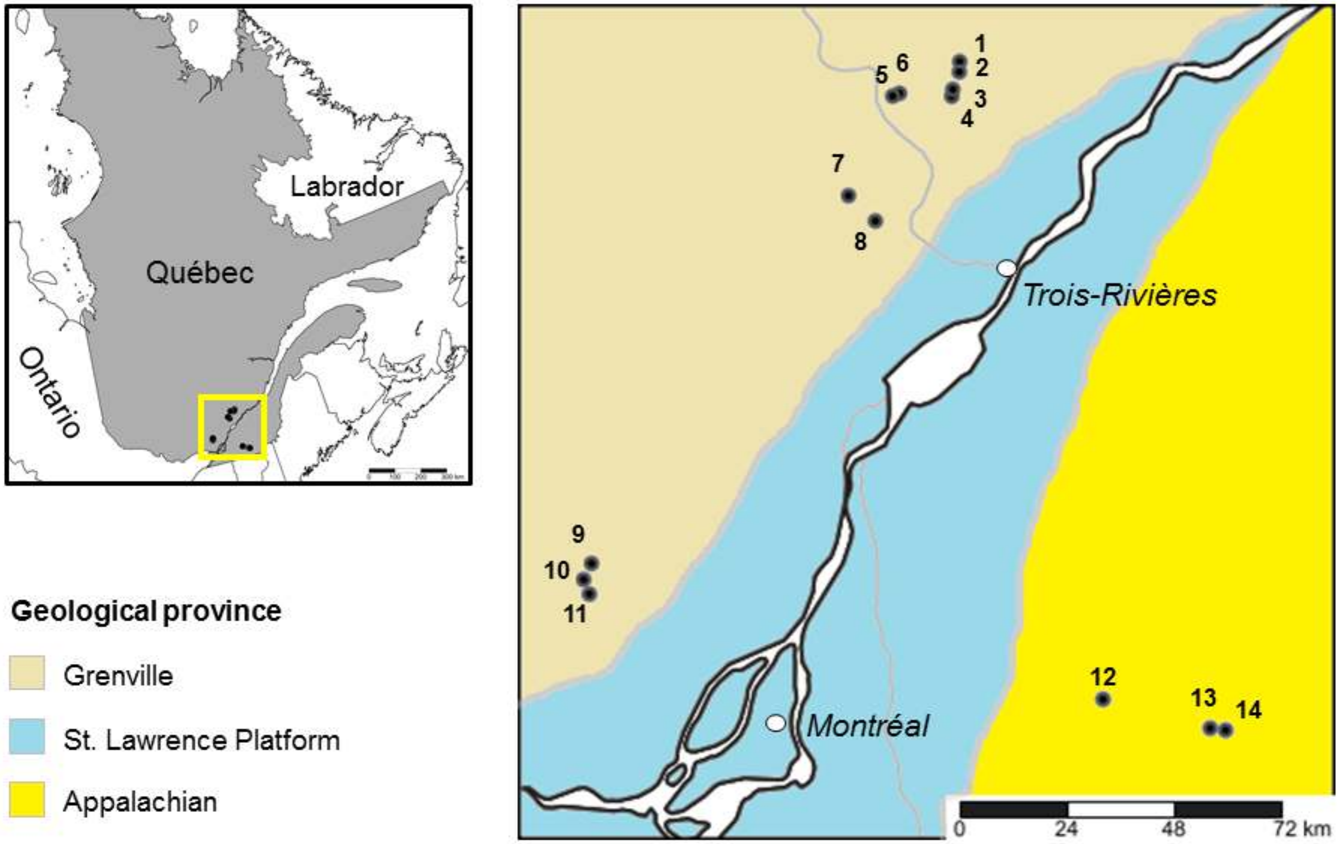

Figure S1: Map of the study area in southern Québec, Canada (yellow square in left panel) and enlarged view (right panel) showing the locations o the 14 lakes sampled and their geological province (Ministère de l'énergie et des ressources naturelles du Québec https://www.mern.gouv.qc.ca/english/mines/geology/geology-overview.jsp), July-September of 2011 or 2012 (right panel). 1. Croche (Mauricie); 2 Chicot; 3. Second Roberge; 4. Méduse; 5. Trottier; 6. Perchaude; 7. Goulet; 8. Héroux; 9. Croche (St.-Hippolyte); 10. Pin Rouge; 11. Morency; 12 Choinière; 13. Argent; 14. Orford.

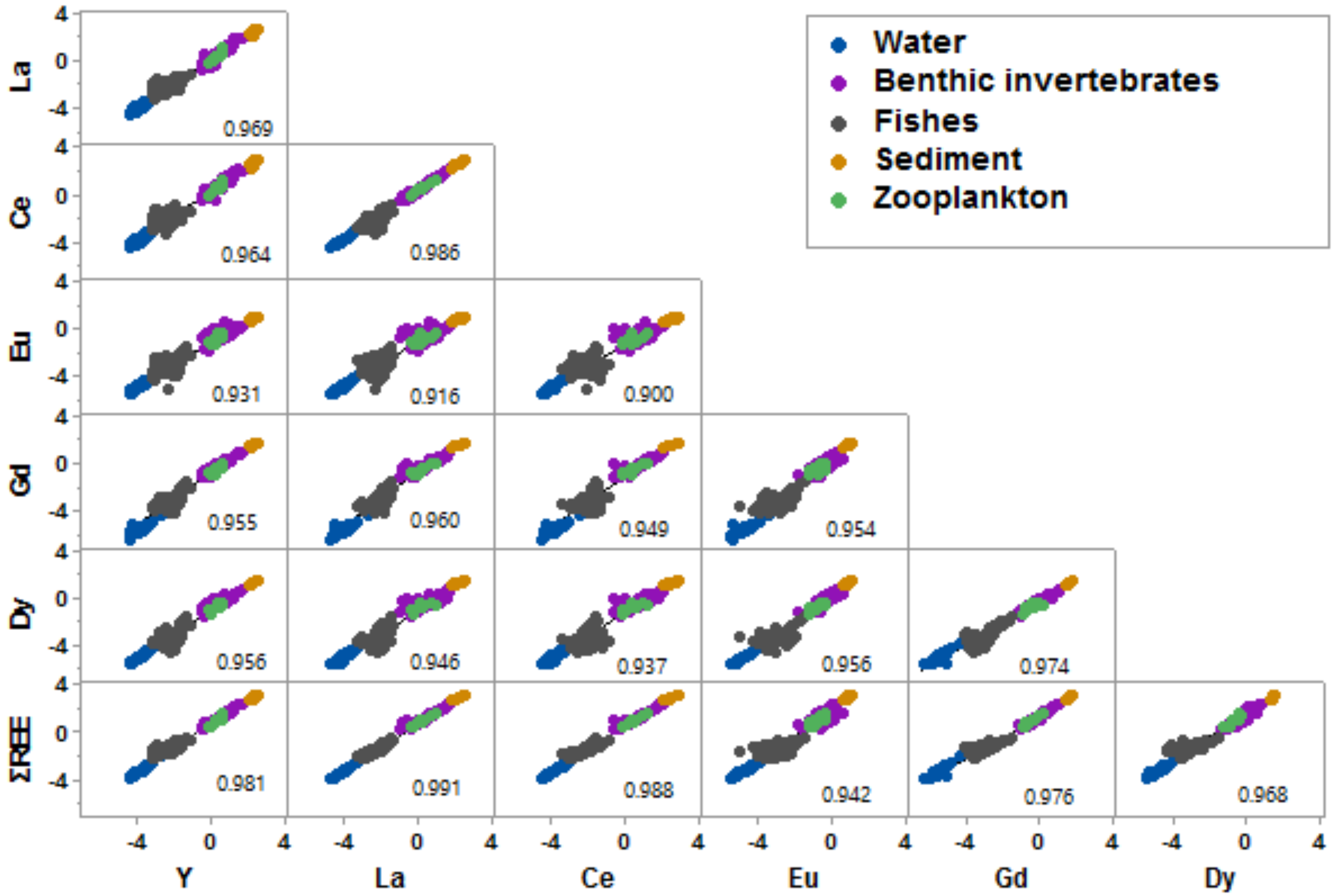

Figure S2: Relationships between concentrations of selected and total rare earth elements (ΣREE) through different sample matrices from 14 lake ecosystems in southern Québec, Canada. All concentrations are log_{10}-transformed (nmol/g in sediments and biota; nmol/mL in water). Regression coefficients (R^2) are shown for each relationship; all were highly significant ($p < 0.001$). Fishes refer to fish muscles, and not whole bodies. Scandium was excluded from the analysis. A related correlation matrix can be found in Table 7.

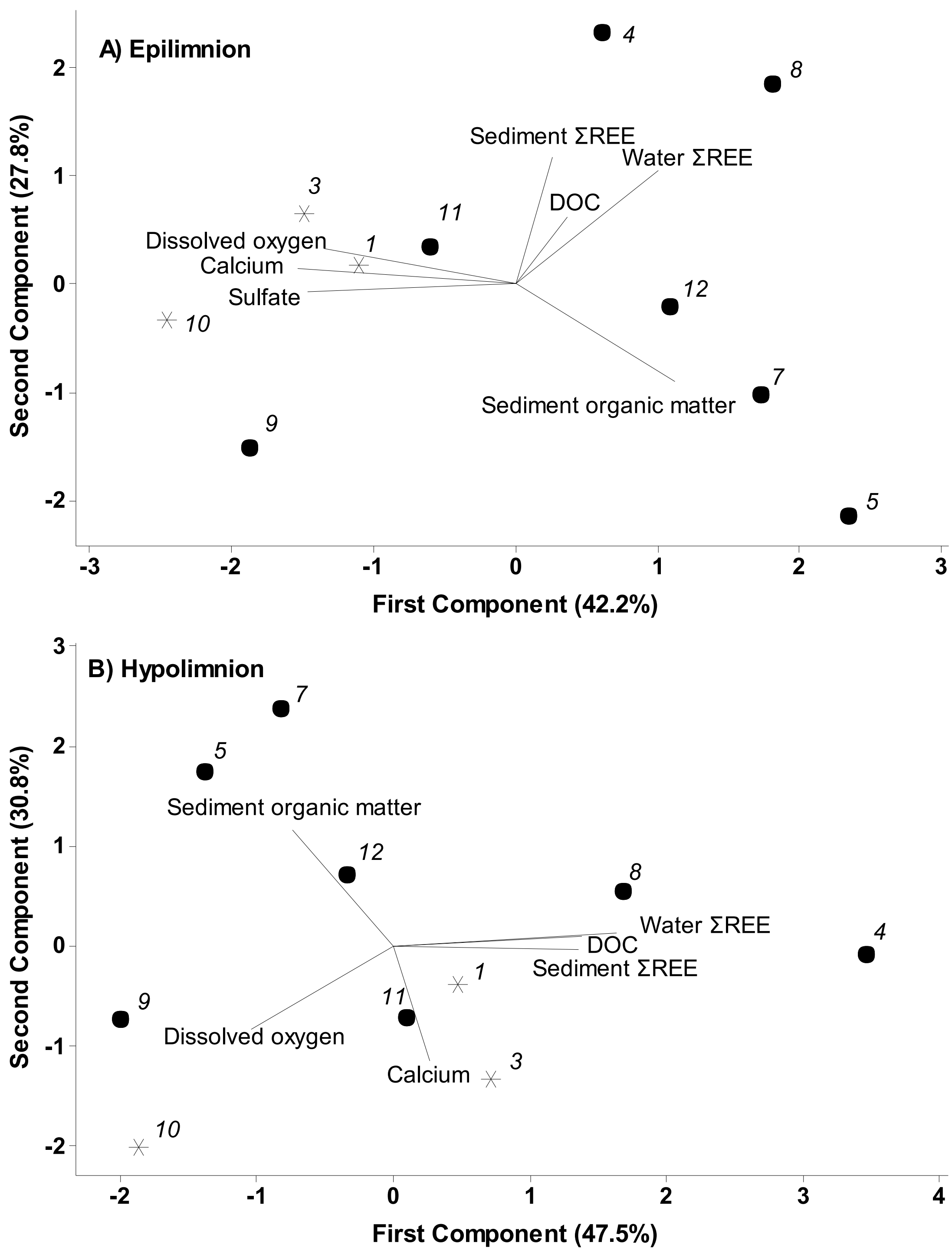

Figure S3. Correlaton bi-plots showing the results of Principal Component Analysis (PCA) of chemical characteristics of 10 lakes in southern Québec, Canada for which sediment ΣREE concentration data were available. Separate PCAs were conducted using A) epilimnetic and B) hypolimnetic lake chemistry variables. The percentage of total variance explained by each component is shown in parentheses. Solid circles and asterisks represent lakes located in the Grenville and Appalachian geological regions, respectively. Data points are numbered according to the corresponding lake as in Figure 2 of the main text: 1) Argent, 3) Choinière, 4) Croche (Mauricie), 5) Croche (St.-Hippolyte), 7) Héroux, 8) Méduse, 9) Morency, 10) Orford, 11) Perchaude, 12) Pin Rouge. See Methods for further details of data handling and analysis.

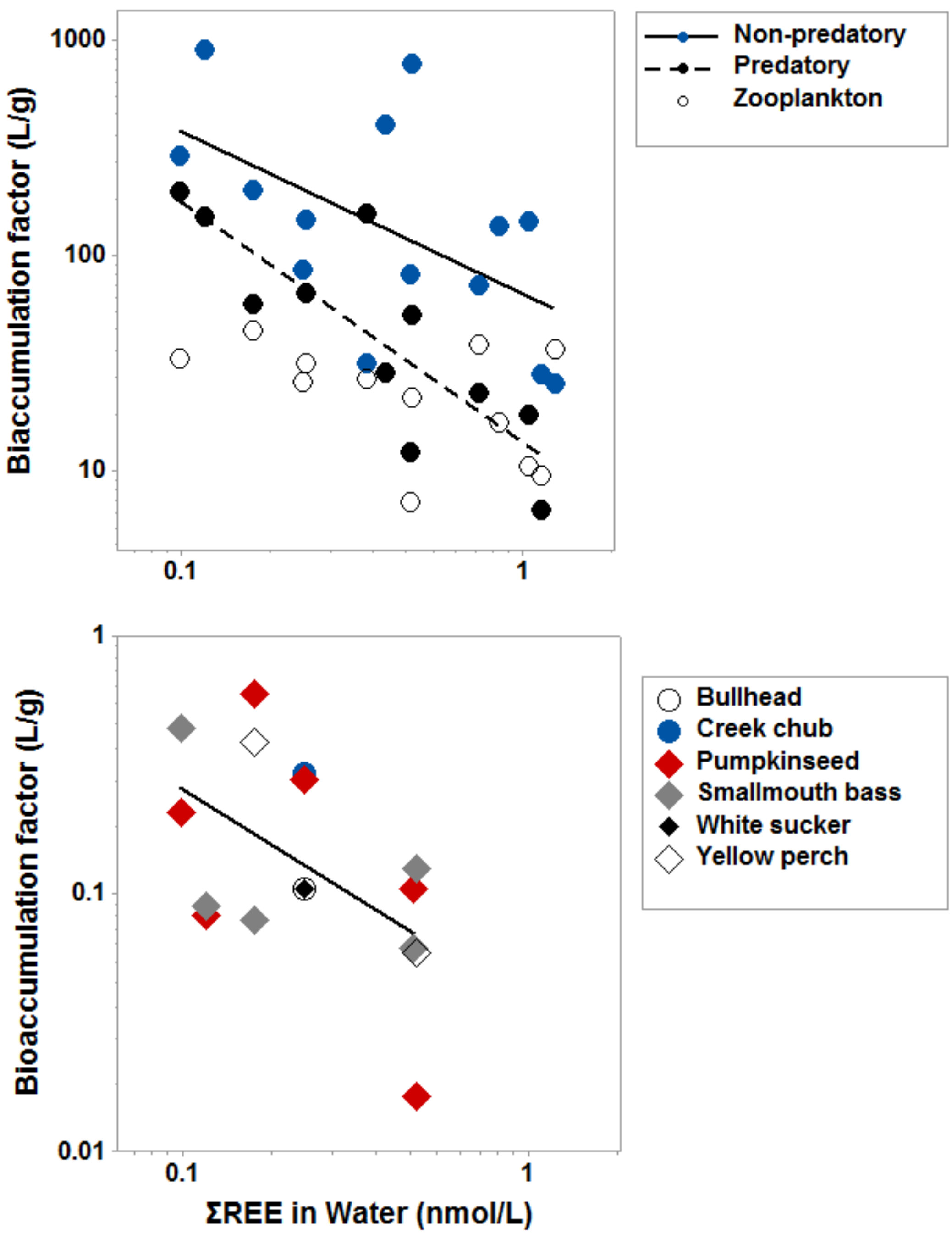

Figure S3: Bioaccumulation factors (BAFs) for total rare earth element concentrations (ΣREE) in predatory and non-predatory benthic invertebrates and zooplankton (top panel) and fish muscle (bottom panel) in relation to ΣREE in lake surface water. BAFs were calculated as the ratio of mean ΣREE in each biotic group (nmol/g) per lake to ΣREE in lake surface water (nmol/L; Deforest et al. 2007). Linear regressions were significant for non-predatory ($R^2 = 0.313$, $p = 0.038$) and predatory invertebrates (0.698, $p = 0.001$), but not significant for zooplankton ($R^2 = 0.252$, $p = 0.127$). Regression was also significant for fish muscle (all species combined, $R^2 = 0.289$, $p = 0.032$).

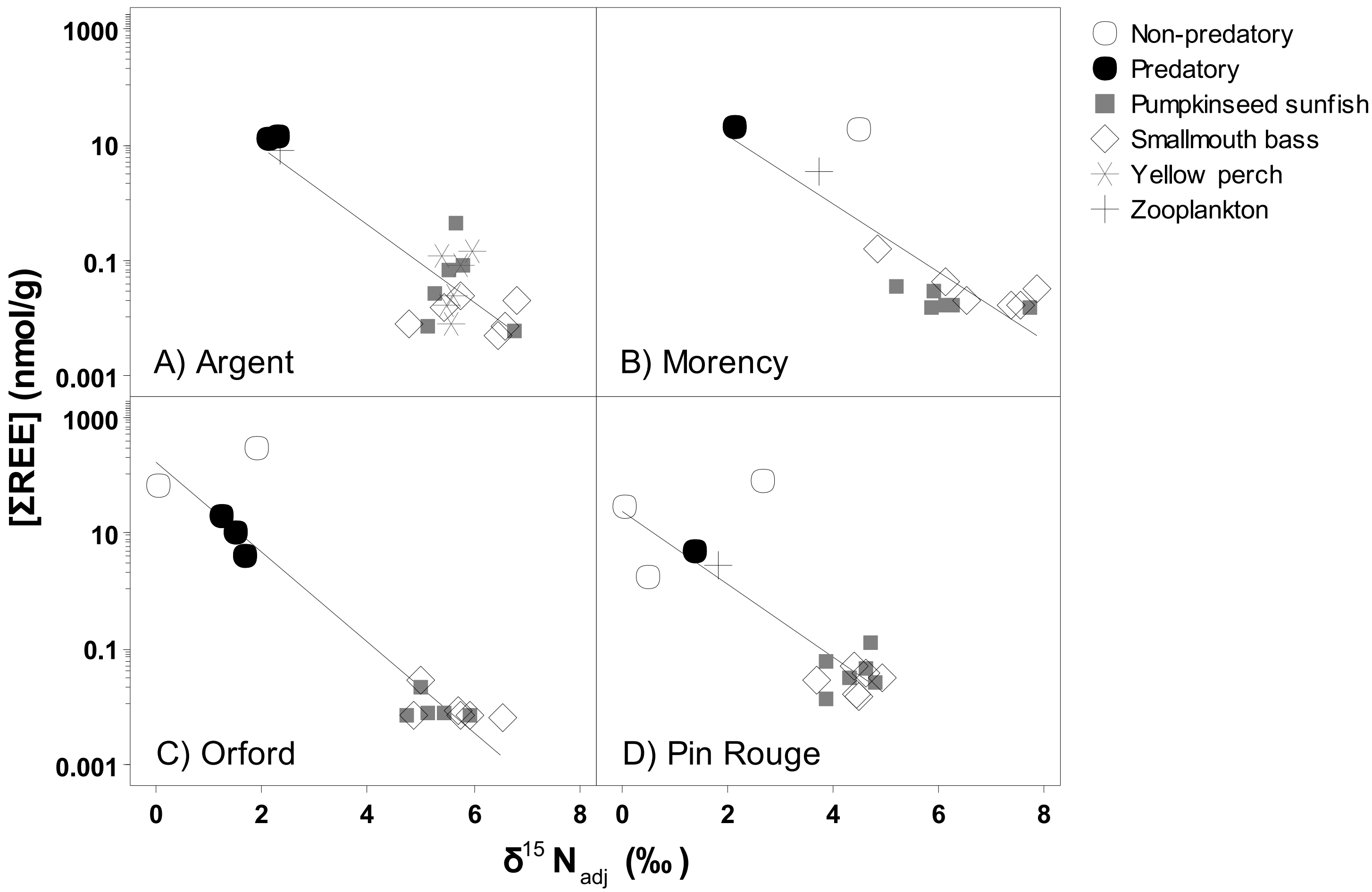

Figure S4: Linear regression relationships between ΣREE concentrations (nmol/g of dry weight) versus trophic position inferred from $\delta^{15}N_{adj}$ (see Methods section of the main text for details of $\delta^{15}N$ adjustment) in four selected lake food webs in southern Québec, Canada. All regression relationships were significant ($p < 0.001$) and regression coefficients were as follows: A) $R^2 = 0.706$, n = 21; B) $R^2 = 0.699$, n = 15; C) $R^2 = 0.891$, n = 16; D) $R^2 = 0.679$, n = 17.

Table S1: Physico-chemical characteristics of fourteen study lakes in southern Québec, Canada.*

Lake	ΣREE (nmol/L)		Ca^{2+} (µmol/L)		Conductivity (µS/cm)		DO (mg/L)		DOC (mg/L)		pH		SO_4^{2-} (µmol/L)	
	Epi	**Hypo**	**Epi**	**Hypo**	**Epi**	**Hypo**	**Epi**	**Hypo**	**Epi**	**Hypo**	**Epi**	**Hypo**	**Epi**	**Hypo**
Argent	0.160	0.908	248.6	223.7	84	83	10.23	0.91	5.44	5.20	7.54	6.92	34.05	31.50
Chicot	0.848	0.862	166.0	192.0	71	99	9.51	0.48	5.54	3.17	8.01	7.11	39.00	53.74
Choinière	0.470	1.427	378.7	378.7	110	115	9.24	0.96	5.25	4.94	7.96	7.03	59.93	37.96
Croche (Mauricie)	1.228	9.320	114.0	194.0	43	125	9.23	0.48	5.06	9.25	6.76	6.32	40.20	20.21
Croche (St.-Hippolyte)	0.224	0.604	47.4	56.3	14	22	7.93	1.49	4.21	4.59	7.11	6.29	27.30	23.50
Goulet	0.393	0.646	86.0	98.0	32	42	9.61	2.76	3.37	2.31	6.99	6.78	39.60	42.12
Héroux	0.345	0.346	76.0	66.9	40	110	9.00	0.35	2.58	2.89	6.70	6.23	26.30	-
Méduse	1.122	2.676	91.0	132.0	49	95	9.08	0.97	7.49	6.81	6.92	6.18	27.40	22.87
Morency	0.098	0.211	263.9	272.3	103	104	9.46	2.74	3.91	2.74	8.11	7.54	79.70	85.38
Orford	0.116	0.185	214.6	203.8	129	124	10.94	10.30	3.48	3.44	8.22	8.14	50.47	48.33
Perchaude	0.229	0.547	149.0	223.0	57	98	9.40	1.11	2.84	3.09	7.49	7.10	45.30	23.66
Pins Rouges	0.463	0.766	126.0	169.2	38	57	9.28	1.31	7.99	5.95	7.24	6.28	33.71	51.02
Second Roberge	1.032	1.594	84.0	70.8	28	33	9.26	6.47	8.50	6.21	-	-	29.80	32.30
Trottier	0.736	2.637	84.0	160.0	29	51	8.89	0.75	6.63	6.95	7.14	6.93	52.20	56.94
Max:Min	12.53	50.38	7.99	6.73	9.21	5.68	1.38	29.43	3.29	4.00	1.23	1.32	3.03	4.22

**Water chemistry variables in each lake were measured at the surface (epilimnion; epi) and below the thermocline (hypolimnion; hypo); n = 1 for all chemica variables. Dashes are shown to indicate instances where data were unavailable for a given parameter. Water sampling was conducted in July and August of 201 (lakes Chicot, Croche-Mauricie, Croche – St.-Hippolyte, Goulet, Héroux, Méduse, Perchaude, Pin Rouge, Second Roberge, Trottier) and 2012 (lakes Argent Choinière, Morency, Orford). See Methods section of the main text for details. Lake depth data were provided by Dr. Richard Carignan (unpublished data) an other morphometric characteristics were determined using ArcGIS.*

Table S1 (continued)

Lake	Sediment ΣREE (nmol/g)	Sediment % organic matter	Surface area (km^2)	Maximum depth (m)	Thermocline depth (m)	Watershed area (km^2)	Geological region
Argent	1018	20	1.1	16	5.0	56.5	Appalachian
Chicot	-	-	0.9	21	3.5	15.7	Grenville
Choinière	959	18	4.7	10	5.5	127.8	Appalachian
Croche (Mauricie)	2076	15	1.0	11	4.5	12.4	Grenville
Croche (St.-Hippolyte)	560	47	0.2	11	4.3	0.8	Grenville
Goulet	-	-	0.4	22.5	3.5	6.2	Grenville
Héroux	1215	54	0.3	23	3.5	2.3	Grenville
Méduse	1732	25	0.3	7.6	3.5	5.7	Grenville
Morency	746	32	0.3	20	5.0	2.2	Grenville
Orford	792	13	1.4	15	6.0	7.5	Appalachian
Perchaude	1637	18	0.2	12	4.5	0.8	Grenville
Pin Rouge	763	41	0.2	14	2.5	7.4	Grenville
Second Roberge	-	-	0.6	20	5.0	8.7	Grenville
Trottier	-	-	0.1	25	5.0	0.2	Grenville

Table S2. Mean limits of detection (ng/L) of rare earth element concentration analyses in biotic tissues, water and sediment. Samples were analyzed in four separate batches: fishes, benthic invertebrates and zooplankton, water, and sediments.

	Sediment	Fishes	Invertebrates & Zooplankton	Water
Y	1.96	0.13	4.29	0.06
La	2.39	0.35	5.24	0.03
Ce	4.06	0.40	4.69	0.05
Pr	1.09	0.12	3.90	0.04
Nd	2.47	0.10	4.82	0.16
Sm	1.19	0.07	4.00	0.18
Eu	1.16	0.08	4.70	0.02
Gd	1.22	0.13	3.90	0.07
Tb	1.11	0.08	4.70	0.02
Dy	1.09	0.10	4.70	0.05
Ho	1.08	0.05	3.90	0.05
Er	1.27	0.08	3.90	0.05
Tm	1.11	0.09	3.90	0.06
Yb	1.12	0.09	3.90	0.12
Lu	1.11	0.12	3.90	0.05

TABLE S3: Intercalibration for four natural unfiltered water samples for the CEAEQ (Centre d'expertise en analyse environnementale du Québec) and the laboratory at Université de Montréal.

	KJ4		KJ2		KJ8		KJ10	
Element	CEAEQ	UdeM	CEAEQ	UdeM	CEAEQ	UdeM	CEAEQ	UdeM
Y	0.083	0.083	0.176	0.16	0.042	0.04	0.256	0.24
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	0.21	0.222	0.444	0.412
Pr	0.063	0.065	0.111	0.11	0.029	0.032	0.135	0.13
Nd	0.208	0.204	0.373	0.344	0.093	0.092	0.459	0.424
Sm	0.026	0.03	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	0.02	0.016
Lu	0.001	0.001	0.002	0.002	0.001	0	0.003	0.003

TABLE S4: Comparison of measured REE concentration in certified sediment reference materials (STSD-1, nmolg-1 d.w) for this study (UdeM, Université de Montréal) and an interlaboratory calibration (CEAEQ, Centre d'expertise en analyse environnementale du Québec, CEAEQ). Note: recovered concentrations are lower than certified values due to differences in extraction methods (total multi-acid dissolution versus partial extraction methods to estimate the labile fraction). There are no certified values for Pr, Gd, Ho, Er, Tm.

Standard	STSD-1	STSD-1	STSD-1
Type	Sediment	Sediment	Sediment
Lab	Certified	CEAEQ	UdeM
Replicas	N = 6 - 11	N = 2	N = 9
Y	472	315	271 (22)
La	216	173	170 (9.5)
Ce	364	293	282 (19)
Pr	-	50	46 (3.4)
Nd	194	194	191 (13)
Sm	40	39	37 (2.7)
Eu	11	8.6	7.6 (0.6)
Gd	-	36	37 (2.4)
Tb	8	4.5	4.8 (0.3)
Dy	34	29	25 (1.7)
Ho	-	5.0	4.8 (0.3)
Er	-	16	14 (1.0)
Tm	-	2.0	1.8 (0.1)
Yb	23	16	12 (0.9)
Lu	5	1.9	1.9 (0.1)

TABLE S5: Intercalibration for REE concentrations (ngg^{-1}) measured in TORT-2 reference material (National Research Council Canada) for the laboratory at the CEAEQ (Centre d'expertise en analyse environnementale du Québec) and this study (UdeM, Université de Montréal, n=3).

	CEAEQ			**UdeM**		
Element	Mean		SD	Mean		SD
Y				510	±	46
La	1700	±	na	1492	±	137
Ce	1900	±	na	1337	±	122
Pr	260	±	na	183	±	16
Nd	940	±	na	731	±	64
Sm	160	±	na	97	±	6
Eu	18	±	na	19	±	2
Gd	140	±	na	132	±	8
Tb	16	±	na	13,5	±	1
Dy	76	±	na	62	±	4
Ho	14	±	na	12,6	±	1
Er	34	±	na	34	±	2
Tm	4.0	±	na	3,4	±	0.4
Yb	17	±	na	16	±	1.1
Lu	2.0	±	na	2,2	±	0.3

Table S6: Quality assurance results for duplicates and an intra-lab standard analyzed with each batch of samples (fish, invertebrates and zooplankton) for carbon and nitrogen stable isotopes.

Sample batch		$\delta^{15}N$ (mean ± SD)	n
Mean difference between duplicates			
Fish		0.18 ± 0.17 ‰	16
Invertebrates & zooplankton		0.52 ± 0.61 ‰	6
Intra-lab standard results			
	Established value	-3.90 ‰	n/a
Fish	Measured value	-3.87 ± 0.03 ‰	3
Invertebrates	Measured value	-3.89 ± 0.07 ‰	3

Table S7. Frequencies of detection of rare earth elements (REE) in biotic and abiotic samples from 14 lakes in southern Québec.*

Element	Non-predatory invertebrates (n = 49)	Predatory invertebrates (n = 26)	Zooplankton (n = 17)	Water (n = 48)	Sediment (n = 12)
Y	0.96	0.65	1	1	1
La	1	0.96	1	1	1
Ce	1	0.92	1	1	1
Pr	0.86	0.50	0.92	1	1
Nd	0.98	0.77	1	1	1
Sm	0.76	0.35	0.83	1	1
Eu	0.37	0.12	0.08	1	1
Gd	0.84	0.35	0.83	1	1
Tb	0.27	0.12	0.08	1	1
Dy	0.61	0.31	0.50	1	1
Ho	0.29	0.12	0.08	0.98	1
Er	0.51	0.23	0.17	1	1
Tm	0.12	0.00	0.00	0.83	1
Yb	0.49	0.19	0.08	1	1
Lu	0.10	0.00	0.00	0.93	1

** Frequency of detection was calculated as the number of samples for which the concentration of a given REE was above the detection limit as a fraction of the total number of samples of a given type (fish, benthos, zooplankton, water, sediment).*

Table S7 (continued)

Element	Fish								
	Brown bullhead		Creek chub		Pumpkinseed	Smallmouth bass	White sucker		Yellow perch
	Muscle (n = 17)	Whole (n = 10)	Muscle (n = 17)	Whole (n = 10)	Muscle (n = 45)	Muscle (n = 30)	Muscle (n = 10)	Whole (n = 10)	Muscle (n = 11)
Y	0.76	1.00	0.88	1.00	0.73	0.50	0.40	1.00	0.55
La	0.88	1.00	0.94	1.00	0.69	0.60	0.70	1.00	0.64
Ce	0.82	1.00	0.88	1.00	0.78	0.57	0.60	1.00	0.55
Pr	0.65	1.00	0.76	1.00	0.53	0.40	0.40	1.00	0.36
Nd	0.88	1.00	0.94	1.00	0.78	0.60	0.60	1.00	0.82
Sm	0.65	0.70	0.71	0.83	0.51	0.30	0.20	1.00	0.18
Eu	0.71	1.00	1.00	1.00	0.16	0.13	0.20	1.00	0.27
Gd	0.41	1.00	0.76	1.00	0.40	0.17	0.20	1.00	0.36
Tb	0.00	0.50	0.18	0.58	0.11	0.07	0.00	1.00	0.09
Dy	0.47	1.00	0.47	1.00	0.36	0.13	0.10	1.00	0.36
Ho	0.00	0.70	0.18	0.83	0.09	0.07	0.00	1.00	0.09
Er	0.06	1.00	0.24	1.00	0.20	0.03	0.00	1.00	0.09
Tm	0.00	0.30	0.12	0.50	0.09	0.03	0.00	1.00	0.09
Yb	0.06	1.00	0.24	1.00	0.13	0.03	0.00	1.00	0.09
Lu	0.06	0.30	0.12	0.33	0.11	0.07	0.00	1.00	0.09

Table S8. Summary of total rare earth elements concentrations [ΣREE] and stable nitrogen isotope values ($\delta^{15}N$ and adjusted $\delta^{15}N$ or $\delta^{15}N_{adj}$*) in biota from 14 lakes in southern Québec, Canada.

	[ΣREE] (ng/g)				[ΣREE] (nmol/g)					$\delta^{15}N$ (‰)					$\delta^{15}N_{adj}$ (‰)		
Taxonomic group and lake	**Mean**	**SD****	**Min**	**Max**	**Mean**	**SD**	**Min**	**Max**	**n**	**Mean**	**SD**	**Min**	**Max**	**n**	**Mean**	**SD**	**n**
NON-PREDATORY INVERTEBRATES																	
Amphipoda (Gammaridae): Gatherer-Collectors																	
Argent	5566				41.0				1								
Morency	2223				16.9				1	11.04				1	4.46		1
Bivalvia (freshwater mussels): Filter-Collectors																	
Héroux	276				2.1				1								
Méduse	1469				10.8				1								
Perchaude	644				4.8				1								
Chironomidae (excluding Tanypodinae																	
Argent	6909				51.1		51.1	51.1	1								
Chicot	13770				101.7		101.7	101.7	1	7.41				1	2.285		1
Choinière	1686				12.42		12.42	12.42	1								
Croche (Mauricie)	5276				38.91		38.91	38.91	1	7.935				1	1.055		1
Croche (Saint-Hippolyte)	1365	690	862	2150.9	10.2	5.3	6.6	16.2	3								
Méduse	1167		965	1368.8	8.617	2.3	7.0	10.2	2	4.09				1	0.57		1
Morency	3710				28.18		28.18	28.18	1								
Perchaude†	6439		1731.3	11147	47.89	49.61	12.81	82.97	2	2.86		1.53	4.18	2	1.33		2
Pin rouge	10730				81.07		81.07	81.07	1	7.74				1	2.65		1
Second Roberge†	14804				110.3		110.3	110.3	1	5.12				1	0		1
Trottier†	8920				65.24		65.24	65.24	1	1.05				1	0		1
Decapoda																	
Pins Rouges										1.53				1	0		1
Ephemeroptera (Caenidae, Heptageniidae, Leptophlebiidae): Gatherer-Collectors																	
Argent	2634		1214	4055	18.6	14.6	8.3	28.9	2								
Croche (Saint-Hippolyte)	4216		2693	5738	32.4	17.4	20.1	44.7	2								
Pin rouge	3889				29.1				1	5.09		5.09	5.09	1	0		1

Second Roberge	36729				274.2				1								
Trottier	5695				41.7				1								
Gastropoda (freshwater snails): Scrapers																	
Chicot	15065				111.8				1	6.49				1	1.37		1
Héroux	2638				19.4				1								
Isopoda: Gatherer-Collectors																	
Goulet	8827				64.87				1								
Méduse†	8708		6200.2	11216	64.44	26.27	45.87	83.02	2	3.52				1	0		1
Morency	4248	4230.2	1691.5	9131.1	32.09	31.76	12.81	68.75	3								
Orford†	7805		6546.5	9062.7	57.63	13.13	48.35	66.91	2	2.735				1	0		1
Oligochaeta: Gatherer-Collectors																	
Chicot†										5.13				1	0		1
Choinière	2860				20.8				1								
Croche (Mauricie)†	3180				23.3				1	6.88				1	0		1
Simuliidae: Filter-Collectors																	
Goulet†										3.92				1	0		1
PREDATORY INVERTEBRATES																	
***Chaoborus* spp.**																	
Argent	919		724	1115	6.2	1.9	4.9	7.5	2	10.36		10.10	10.62	2	6.24		2
Choinière	720				4.9				1								
Hydracarina (freshwater mites)																	
Méduse	470				3.2				1								
Perchaude	2083				15.2				1								
Second Roberge	744				5.0				1								
Megaloptera (Sialidae)																	
Argent	1299				9.0				1								
Goulet	2009				13.4				1								
Orford	1556		565	2547	11.4	10.6	3.8	18.9	2	4.17		3.95	4.38	2	1.43		2
Odonata (Aeshnidae, Coenagrionidae, Gomphidae, Libellulidae)																	
Argent†	1829		1793	1866	12.8	1.0	12.1	13.5	2	6.33		6.24	6.42	2	2.21		2
Choinière	4736		3105	6367	34.8	16.9	22.9	46.7	2								

Goulet	1205				8.8				1								
Héroux	7100				53.6				1								
Méduse	1567				11.4				1								
Morency†	2536				19.2				1	8.68				1	2.1		1
Orford	3210		1298	5122	23.4	19.3	9.8	37.0	2	4.23				1	1.50		1
Pin rouge	784		619	949	5.6	1.3	4.6	6.5	2	6.42				1	1.33		1
Second Roberge	4352				32.4				1								
Trottier	2327	2560	566	5263	16.9	18.8	4.1	38.5	3								
ZOOPLANKTON	1723	1641	419	6100	12.8	11.9	3.2	44.4	12	6.78	2.40	3.71	11.23	12	2.40	1.76	9
Argent	944				7.2				1	6.44				1	2.32		1
Chicot	1822				14.1				1	9.42				1	4.30		1
Choinière	1383				10.2				1	11.23				1			
Croche (Mauricie)	6100				44.4				1	7.23				1	0.35		1
Croche (Saint-Hippolyte)	764				5.8				1	3.71				1			
Héroux	1198				9.1				1	5.87				1			
Méduse	1370				10.6				1	3.82				1	0.3		1
Morency	419				3.2				1	10.30				1	3.72		1
Perchaude	960				7.2				1	5.77				1	4.24		1
Pin rouge	437				3.3				1	6.88				1	1.79		1
Second Roberge	1458				10.7				1	5.52				1	0.4		1
Trottier	3820				28.4				1	5.22				1	4.17		1
FISHES																	
Brown bullhead (*Ameiurus nebulosus*)																	
Croche (Saint-Hippolyte)	3.11	1.81	0.75	6.51	0.023	0.014	0.005	0.050	17	7.34	0.78	5.79	8.49	17			
Creek chub (*Semotilus acromaculatus*)																	
Croche (Saint-Hippolyte)	8.72	9.05	1.38	30.15	0.065	0.068	0.009	0.218	17	7.20	0.91	5.71	8.56	11			
Pumpkinseed sunfish (*Lepomis gibbosus*)																	
Argent	4.76	4.31	0.77	9.95	0.035	0.032	0.005	0.074	5	9.81	0.65	9.23	10.87	5	5.69	0.65	5
Choinière	1.09	0.21	0.97	1.46	0.008	0.002	0.007	0.010	5	13.89	0.39	13.50	14.52	5			
Croche (Saint-Hippolyte)	8.39	7.67	2.64	35.03	0.061	0.052	0.020	0.238	18	6.92	0.46	6.10	7.58	18			

Morency	2.70	1.03	1.95	4.19	0.020	0.008	0.015	0.032	6	12.73	0.84	11.73	14.27	6	6.15	0.84	6
Orford	1.35	0.82	0.95	2.81	0.009	0.006	0.007	0.020	5	7.97	0.47	7.44	8.67	5	5.23	0.47	5
Pin rouge	6.48	5.55	1.72	17.11	0.048	0.039	0.013	0.121	6	9.41	0.42	8.91	9.85	6	4.32	0.42	6
Smallmouth bass (*Micropterus dolomieu*)																	
Argent	1.78	1.06	0.68	3.31	0.013	0.008	0.005	0.023	6	10.09	0.79	8.89	10.94	6	5.97	0.79	6
Choinière	8.40	14.84	1.00	38.49	0.058	0.101	0.007	0.263	6	15.20	0.79	14.14	16.13	6			
Morency	5.88	6.76	1.94	19.43	0.043	0.048	0.015	0.140	6	13.28	1.13	11.39	14.43	6	6.70	1.13	6
Orford	1.43	1.10	0.88	3.67	0.010	0.008	0.006	0.027	6	8.36	0.62	7.59	9.28	6	5.62	0.62	6
Pin rouge	3.90	1.76	1.91	6.56	0.028	0.012	0.014	0.047	6	9.49	0.41	8.73	9.98	6	4.40	0.41	6
White sucker (*Catostomus commersonii*)																	
Croche (Saint-Hippolyte)	3.28	3.47	0.73	9.39	0.023	0.025	0.005	0.067	10	5.71	0.67	5.03	7.31	10			
Yellow perch (*Perca flavescens*)																	
Argent	8.64	7.89	1.02	19.59	0.062	0.055	0.007	0.135	6	9.76	0.20	9.53	10.10	6	5.64	0.20	6
Choinière	3.80	5.60	0.83	13.79	0.027	0.041	0.006	0.101	5	13.95	0.66	13.26	15.00	5			

*See "Methods" for an explanation of δ^{15}N adjustment.

**SD = standard deviation; SD is shown only for results where n ≥ 3.

† Denotes taxonomic group in a given lake which was used to adjust δ^{15}N (see "*Baseline δ^{15}N adjustments*" in the Methods section of the main text)

Table S9: Summary of fish length and weight data by species and lake (SD = standard deviation)

		Length (mm)				Weight (g)			
Species and lake	**n**	**Mean**	**SD**	**Min**	**Max**	**Mean**	**SD**	**Min**	**Max**
Brown bullhead									
Croche (Saint-Hippolyte)	17	169	19	145	206	75.01	39.14	36.45	157.50
Creek chub									
Croche (Saint-Hippolyte)	17	130	32	84	179	28.22	18.60	6.52	60.70
Pumpkinseed sunfish									
Argent	5	125	58	51	198	52.184	53.584	1.99	130.96
Choinière	5	134	30	90	165	44.380	25.320	11.44	70.38
Croche (Saint-Hippolyte)	18	76	21	46	108	9.653	8.020	1.48	26.03
Morency	6	108	32	67	147	24.617	19.971	4.16	54.07
Orford	5	131	12	114	144	44.152	14.351	26.34	61.39
Pin rouge	6	123	19	86	140	33.708	12.140	10.52	42.34
Smallmouth bass									
Argent	6	124	61	61	217	38.69	49.02	2.42	126.80
Choinière	6	99	31	57	145	13.38	11.57	2.01	33.48
Morency	6	107	51	44	193	22.08	28.34	1.32	77.60
Orford	6	116	35	64	154	22.03	15.15	3.21	42.98
Pin rouge	6	77	7	69	87	5.78	1.61	4.23	8.04
White sucker									
Croche (Saint-Hippolyte)	10	183	47	107	244	69.38	41.19	13.93	129.56
Yellow perch									
Argent	6	115	39	66	162	16.70	14.02	2.33	38.23
Choinière	5	156	54	90	213	42.91	32.34	6.32	74.14

Table S10. Summary of correlation matrices (Pearson correlation analyses, r*) between physical and chemical characteristics of lake water (epilmnetic and hypolimnetic) and surface sediments (top 10 cm) and total rare earth element concentrations [ΣREE] in benthic invertebrates, pumpkinseed sunfish and bulk zooplankton from up to 14 lake food webs (n = number of lakes for each correlation) in southern Québec.

	Non-predatory invertebrates			Predatory invertebrates			Pumpkinseed			Bulk zooplankton		
Variable	**r**	**p**	**n**	**r**	**p**	**n**	**r**	**p**	**n**	**r**	**p**	**n**
Lake physical characteristics												
Lake surface area	**0.603**	**0.022**	14	0.167	0.624	11	-0.614	0.195	6	0.187	0.561	12
Maxiumum depth	0.064	0.829	14	0.401	0.221	11	0.167	0.752	6	0.024	0.940	12
Thermocline**	0.106	0.717	14	-0.094	0.783	11	-0.512	0.299	6	0.126	0.696	12
Watershed area	0.499	0.069	14	-0.131	0.700	11	-0.252	0.631	6	-0.013	0.967	12
Epilimnetic water chemistry												
[ΣREE]	0.212	0.467	14	-0.159	0.64	11	-0.001	0.999	6	**0.714**	**0.009**	11
Ca^{2+}	0.427	0.128	14	0.072	0.833	11	-0.590	0.218	6	-0.226	0.481	12
Dissolved oxygen	0.352	0.217	14	-0.156	0.646	11	-0.318	0.539	6	-0.041	0.899	12
DOC	0.263	0.364	14	-0.552	0.079	11	0.407	0.424	6	0.153	0.636	12
pH	0.520	0.069	13	0.073	0.841	10	-0.803	0.054	6	-0.381	0.248	11
Sulfate	0.369	0.195	14	0.167	0.624	11	-0.746	0.089	6	-0.034	0.917	12
Hypolimnetic water chemistry												
[ΣREE]	0.100	0.734	14	-0.324	0.33	11	0.263	0.615	6	***0.824***	***0.001***	12
Ca^{2+}	0.361	0.205	14	-0.082	0.81	11	-0.610	0.199	6	-0.025	0.939	12
Dissolved oxygen	0.402	0.154	14	-0.149	0.663	11	-0.497	0.316	6	-0.455	0.137	12
DOC	-0.051	0.862	14	-0.400	0.222	11	0.448	0.373	6	0.550	0.064	12
pH	0.470	0.105	13	0.203	0.575	10	-0.665	0.150	6	-0.163	0.633	11
Sulfate	0.260	0.391	13	0.248	0.490	10	-0.413	0.416	6	-0.329	0.323	11
Sediment physico-chemical characteristics												
[ΣREE]	-0.113	0.756	10	-0.005	0.991	8	-0.194	0.713	6	**0.755**	**0.019**	8
% organic matter	-0.630	0.051	10	0.162	0.702	8	0.587	0.221	6	-0.572	0.107	8

* Significant correlations are shown in bold, and those that remain significant after Holm correction are shown in italics (Holm 1979).

** Thermocline was expressed as the ratio of the depth of the thermocline to the maximum depth of each lake.

Table S11: Bioaccumulation factors (L/kg, $\log_{10}$-transformed) of total rare earth elements (ΣREE) in lake food web organisms relative to epilimnetic lake water.

	Benthic invertebrates			Fish muscle					
Lake	Non-predatory	Predatory	Zooplankton	Bullhead	Creek chub	Pumpkinseed	Smallmouth bass	White sucker	Yellow perch
	n = 36	n = 18	n = 12	n = 17	n = 17	n = 45	n = 30	n = 10	n = 11
Argent	5.30	4.77	4.65			2.77	1.89		2.59
Chicot	5.13		4.22						
Choinière	5.89	4.72	4.34			1.21	2.09		1.77
Croche (Mauricie)	4.40		4.56						
Croche (Saint-Hippolyte)	4.93		4.41	2.02	2.46	2.44		2.02	
Goulet	5.61	4.45							
Héroux	4.49	5.19	4.42						
Méduse	4.45	3.81	3.98						
Morency	5.46	5.29	4.52			2.31	2.64		
Orford	5.96	5.18				1.91	1.95		
Perchaude	5.16	4.82	4.50						
Pin rouge	4.91	4.08	3.85			2.02	1.79		
Second Roberge	5.15	4.26	4.01						
Trottier	4.86	4.36	4.59						