Evidence for biomagnification of rubidium in freshwater and marine food webs

Linda M. Campbell, Aaron T. Fisk, Xiaowa Wang, Günter Köck, and Derek C.G. Muir

Abstract: Rubidium (Rb), a rarely studied alkali metal, may be an essential ultra-trace element for humans and other organisms. However, very little information exists in regard to the concentrations and distribution of Rb in freshwater and marine food webs. We measured Rb concentrations in freshwater fish from Lake Erie and two Arctic lakes (Lake Hazen and Resolute Lake) and in seabirds, ringed seals, and invertebrates from the marine Northwater Polynya in Baffin Bay. The alkali analogues of Rb, cesium (Cs), and potassium (K) were also analysed in a subset of fish from Lakes Erie and Hazen. Rb and Cs concentrations and Cs:K ratios in the sampled biota are significantly regressed against δ^{15} N values, indicating biomagnification through the food web in diverse ecosystems. However, there is no relationship between K concentrations and δ^{15} N values, indicating a lack of biomagnification and the presence of homeostatistic mechanisms for this essential trace element. Rb must be included with mercury and Cs as metals that consistently biomagnify in diverse food webs and should be considered in multi-element biomagnification studies.

Résumé : Le rubidium (Rb) est un métal alcalin rarement étudié qui peut être un élément en « ultra-trace » essentiel pour les humains et les autres organismes. Il existe, cependant, très peu de données sur ses concentrations et sa répartition dans les chaînes alimentaires aquatiques et marines. Nous avons mesuré les concentrations de Rb dans des poissons d'eau douce du lac Érié et de deux lacs arctiques (Hazen et Resolute), ainsi que dans des oiseaux marins, des phoques annelés et des invertébrés dans la polynie des eaux du nord de la baie de Baffin. Nous avons aussi analysé les analogues alcalins du rubidium, le césium (Cs) et le potassium (K), dans un sous-ensemble de poissons des lacs Érié et Hazen. Il y a une relation significative entre les concentrations de Rb et de Cs et le rapport Cs:K dans les organismes échantillonnés, d'une part, et δ^{15} N, d'autre part, ce qui indique qu'il se produit une biomagnification dans le réseau alimentaire des divers écosystèmes. Il n'y a pas, cependant, de relation entre les valeurs de K et de δ^{15} N, ce qui indique l'absence de biomagnification pour cet élément en trace essentiel et la présence de mécanismes homéostatiques. Il faut ajouter le Rb à Hg et Cs dans la liste des métaux qui subissent systématiquement une biomagnification dans les réseaux alimentaires et en tenir compte dans les études de biomagnification qui considèrent plusieurs éléments chimiques.

[Traduit par la Rédaction]

Introduction

Trophic transfer of metals in food webs has been a cause for concern for decades, especially as mercury (Hg), methylmercury, and cesium (Cs) have been demonstrated to exhibit biomagnification potential in freshwater and marine ecosystems worldwide and can provoke toxicity responses (Rowan and Rasmussen 1994; Mason et al. 1995). Very few elements, such as selenium and even zinc (Zn), are also known to biomagnify in certain ecosystems (i.e., Quinn et al. 2003), but many elements, such as copper (Cu) or iron (Fe), do not biomagnify in food webs, owing to either homeostatistic mechanisms or biochemical aspects that prevent trophic accumulation (Wang 2002). However, many other elements in the periodic table, including rubidium (Rb), have not yet been assessed for biomagnification potential in food webs.

Rb is a rarely studied but abundant alkali metal located between potassium (K) and Cs in the periodic table. Rb is associated with K and Cs minerals worldwide, including mica and alkali-feldspar minerals in soils (Jones 1992) and illite clays (Perel'man 1965), granite (Heier and Billings 1970), and granitic pegmatites, especially pollucite and lepidolite ores (Cerny et al. 2003). Like Cs, Rb is a K⁺ analogue and can compete with K⁺ for enzymatic sites in fish and other organisms (Peters et al. 1999; Tipsmark and Madsen 2001). The importance of Rb as an ultra trace essential element to humans and other biota has been the subject of conjecture, based on a study that demonstrated poor health

Received 24 February 2004. Accepted 22 October 2004. Published on the NRC Research Press Web site at http://cjfas.nrc.ca on 31 May 2005.

J18004

L.M. Campbell,^{1,2} X. Wang, and D.C.G. Muir. National Water Research Institute, Environment Canada, 867 Lakeshore Road, Burlington, ON L7R 4A6, Canada.

A.T. Fisk. Warnell School of Forest Resources, University of Georgia, Athens, GA 30602-2152, USA.

G. Köck. Austrian Academy of Sciences, Dr. Ignaz Seipel-Platz 2, A-1010 Vienna, Austria.

¹Corresponding author (e-mail: campbelm@biology.queensu.ca).

²Present address: School of Environmental Studies, Queen's University, Kingston, ON K7L 3N6, Canada.

1161

of goats fed low-Rb (<0.28 mg·kg⁻¹·day⁻¹) diets relative to those fed high-Rb diets (>1 mg·kg⁻¹·day⁻¹) (Nielsen 1998). Some cyanobacterial species can grow in Rb media in absence of K⁺, albeit more slowly than those grown in K⁺sufficient media (Richie 1997). "Safe" concentrations are not known, although experimental toxic responses linked with elevated Rb have been observed in mammals fed low-K high-Rb diets, which are linked to physiological interference with K⁺ and sodium (Na⁺) (Kosla et al. 2002). Toxic responses have also been described in cultured oysters (*Crassostera gigas*), with elevated Rb concentrations linked to ionic modification and tissue disorganization (Salaün and Truchet 1996)

Transfer of Rb between predator and prey has been documented (Johnson and Reeves 1995; Nyholm and Tyler 2000) and Rb has been used as a tracer in insect dispersal studies, since emerging insects will retain the Rb signature from preemergent exposure (Johnson and Reeves 1995; Payne and Dunley 2002). Hypothetically, biomagnification involves the co-uptake of Rb and Cs, which have smaller cation radii than K⁺, via active transport H⁺ and K⁺ membrane channels in primary producers and the subsequent transfer and accumulation of Rb and Cs up the food chain (Rowan and Rasmussen 1994). Even so, consistent biomagnification of Rb across food webs has not yet been demonstrated. Stable nitrogen (N) isotopes have been used as a trophic-position indicator and to estimate the biomagnification potential of contaminants and metals in diverse ecosystems (e.g., Kidd 1998). The ratio of ¹⁵N to ¹⁴N (in biological tissues relative to air), which is expressed as delta-¹⁵N (δ^{15} N), in tissue typically increases consistently by 3.4%-3.6% with each trophic transfer because ¹⁵N is retained from the food resource relative to ¹⁴N. Since concentrations of biomagnifying contaminants and metals also increase with trophic position, there will be a significant relationship between the biomagnifying compound with increasing $\delta^{15}N$ values in biota, therefore linear-regression slopes can be used to predict metal and contaminant behaviour within food webs.

The objective of this study was to compare Rb concentrations and biomagnification in freshwater and marine food webs spanning over 30° latitude. The littoral northeastern Lake Erie ecosystem in Long Point Bay (42°47'N, 80°11'W) includes a number of fish species, including smallmouth bass, Micropterus dolomieu, and the round goby, Neogobius melanostomus, a Ponto-Caspian invader. Lake Hazen, the largest lake above the Arctic Circle (Quttinirpaaq National Park, Ellesmere Island, 81°40'N, 73°0'W), and Resolute Lake (Quasuittuq, Cornwallis Island, 74°43'N, 94°58'W) both contain non-anadromous Arctic char, Salvelinus alpinus, which span a wide trophic gradient from omnivory to piscivory. The Northwater (NOW) Polynya in Baffin Bay (77°N, 75°W, 50 000 km²) is a large permanent opening in the sea ice that supports large numbers of Arctic cod, Boreogadus saida, marine birds, mammals, and invertebrates. This study represents the first time that comparative evidence for biomagnification of Rb and Cs (based on stable N isotopes) in freshwater and marine food webs has been presented.

Methods

Arctic char were collected from Lake Hazen in 2003 and Resolute Lake in 2001 using gill nets (Köck et al. 2004). Various littoral fish species were collected from Lake Erie in 2002 using overnight gill-netting. Physiochemical parameters of these freshwater lakes are listed in Table 1. From the marine NOW Polynya in 1998, seal samples were obtained from Inuit hunters and birds were collected by shotgun, zooplankton with vertical tows of 1 m diameter 250 µm mesh net, and Arctic cod by hand-held nets (Fisk et al. 2001).

All analyses of Rb and other elements were conducted using inductively coupled plasma-sector field mass spectrometry at low resolution (NLET Method 02-2704/5) at the National Water Research Institute, Burlington, Ontario (National Laboratory for Environmental Testing 2003). To ascertain relationships with Cs and K, subsamples from Lakes Erie and Hazen were processed using the same method but including standards for determining Cs and K concentrations. The dried Lake Erie fish samples were converted to wet weight, assuming 80% water content, which is a standard assumption in the literature. The Arctic samples were not dried. Approximately 25%-30% of an analytical run was dedicated to various quality control samples, including certified reference materials from the National Research Council of Canada (DORM-2, DOLT-2 and TORT-2) and duplicates. No certified values were available for Rb; however, values for 11 elements in DORM-2 (dogfish muscle) averaged within 12.7% of certified values.

Stable-isotope values were analysed using continuous-flow isotope-ratio mass spectrometer technology (L.M. Campbell and D.C.G. Muir). The ratios of stable N isotopes were measured against N₂ in ambient air, and delta notation (δ) is used to indicate the parts per thousand ($%_c$) differences in the isotopic ratio of the sample from the reference standard. Standard deviations for the analytical standards and replicate samples inserted in every run were $\pm 0.3\%_c$ for $\delta^{15}N$.

Relationships of Rb, Cs, and K with $\delta^{15}N$ and with each other were determined by simple linear regressions in SYSTAT[®] version 10 (Systat Software Inc. 2000). Prior to regressing, metals were log¹⁰-transformed to ensure normality of distribution. Plots of residuals versus predicted values were examined to ensure homoscedasticity. To compare Rb concentrations in Arctic char from Lakes Hazen and Resolute, an independent-samples t test was utilized, with normality and homogeneity of variances assessed first (i.e., Shapiro–Wilk test).

Results

Fish from Lake Erie, especially higher trophic level omnivores and piscivores such as freshwater drum (*Aplodinotus grunniens*) and smallmouth bass, usually had higher mean Rb concentrations relative to other fishes and biota from the Arctic (Fig. 1; Table 2). Arctic char from Lake Hazen have significantly higher Rb concentrations than those from Resolute Lake (Table 2; *t* test, *t* = 3.467, df = 35, $p \le 0.001$). Significant regressions of log[Rb] with δ^{15} N values are observed in all systems sampled (Fig. 1), with slopes ranging from 0.064 to 0.081 (Table 3). Log[Cs] is also significantly regressed with δ^{15} N values in Lakes Erie and Hazen, with slopes of 0.112 and 0.140, respectively (Table 3). Log[K] did not show significant relationships with δ^{15} N values in Lake Erie or Lake Hazen (Table 3).

Å

I I I

I

(

	Lake Hazen (1990–1998) ^a	Resolute Lake (1997–2002)	Lake Erie (Aug. 2001) ^b
Area (km ²)	541.8	1192	25 655
θH	8.40±0.01	8.28 ± 0.18^{c}	8.23±0.1
Conductivity (µS·cm ⁻¹)	149±10	252.7 ± 32.6^{c}	271.7±0.6
Alkalinity (µequiv.·L ⁻¹)	1085±487		9367±577
Chlorophyll $a \ (\mu g L^{-1})$		< 0.1 ^d	1.0 ± 0.0
$SO_4 (mg \cdot L^{-1})$	7.2±4.4	20.3^{d}	22±0.0
fotal dissolved N (µg·L ⁻¹)	102±76	0.09^{d}	267±23
fotal dissolved P (µg·L ⁻¹)	2.9±3.2	0.012^{d}	4.0±0.0
Dissolved inorganic C (µg·L ⁻¹)	1380±163		21.7±0.2
Dissolved organic C (μ g·L ⁻¹)	69±51		1.8 ± 0.0
Na (mg·L ^{-1})	0.61±0.06	10.9 ± 1.5^{c}	9.46 ± 0.04
$K (mg \cdot L^{-1})$	0.51±0.06	0.9 ± 0.1^{c}	1.44 ± 0.04
$Mg (mg \cdot L^{-1})$	2.9±0.3	5.9 ± 0.9^{c}	8.45±0.02
$\operatorname{Ca}(\operatorname{mg} \cdot \mathrm{L}^{-1})$	25.2±2.5	26.8 ± 3.8^{c}	32.5±0.87
$Zn (mg \cdot L^{-1})$	0.005 ± 0.003	0.01 ± 0.01^{c}	1.2±0.4
$Cu (mg \cdot L^{-1})$	0.007±0.003	0.03 ± 0.04^{c}	1.8 ± 0.06
$Vi (mg \cdot L^{-1})$	0.013±0.007		0.6 ± 0.1
Fe (mg·L ^{-1})	0.040 ± 0.076	0.02 ± 0.02^{c}	7.3±0.56
$Ba (\mu g \cdot L^{-1})$	14.17±1.17		22.3±0.6
Sr ($\mu g \cdot L^{-1}$)	128±13		157.0±3.5
$Cd (\mu g \cdot L^{-1})$		0.025 ± 0.019^{c}	nd ^e
Pb $(\mu g \cdot L^{-1})$		0.022 ± 0.003^{c}	$nd^{e} - 0.01$

Table 1. Physiochemical parameters (average \pm standard deviation) of the sampled freshwater lakes.

^aFrom Babaluk et al. (1999).

^{*b*}Integrated photic-zone samples (n = 3) collected near Peacock Point (42°46′30′′, 79°58′57′). Unpublished data from T. Howell, Ontario Ministry of Environment and Energy, 125 Resources Road, Etobicoke, ON M9P 3V6, Canada.

^cFrom Köck et al. (2004).

^dUnpublished data from D.C.G. Muir and X. Wang, National Water Research Institute, Environment Canada, 867 Lakeshore Road, Burlington, ON L7R-4A6, Canada.

^eNot detected.

Arctic char from Lake Hazen tend to have higher K and Cs concentrations than most fish species from Lake Erie, which is the opposite of the trend for Rb (Table 2). Rb concentrations in fish from both lakes are significantly regressed with Cs and K concentrations (Table 3). However, relationships for Cs and K concentrations are dissimilar, showing significance for fish from Lake Erie but not for those from Lake Hazen (Table 3). Although K concentration was not significantly regressed with δ^{15} N values for fish in Lake Erie, there may be a slight trophic-level-related increase in K concentration, based on significant relationships of K with Cs and Rb concentrations for fish in Lake Erie.

Discussion

Most biological Rb and Cs kinetics studies make use of radionuclides (Richie 1997; Peters et al. 1999). For example, ⁸⁶Rb, ¹³⁷Cs, and ¹³⁴Cs are frequently used as proxy tracers of K-linked transport (Tipsmark and Madsen 2001; Leggett et al. 2003). While different isotopes of an element can have varying biochemical properties (as handily illustrated by the use of δ^{15} N in this study), total Rb and Cs kinetics, including both stable (¹³³Cs, ⁸⁵Rb) and radioactive isotopes, can be approximated by those radionuclide studies. Based on those studies and our results, important factors likely affecting Rb bioavailability and concentration in freshwater and marine ecosystems are (*i*) sources and ambient concentrations of Rb

in water and sediment, (*ii*) ambient K^+ concentrations, (*iii*) ambient pH and temperature, and (*iv*) trophic position.

Possible anthropogenic sources of Rb and Cs include coal-burning. Rb in coals and fly ash is related with Cs and K and can be a significant source in local environments (Ward et al. 1999; Seredin 2003). The large coal-fired Nanticoke Generating Station on Lake Erie is near Long Point Bay and may partially explain the elevated Rb concentrations in the Lake Erie fish (although not the low Cs concentrations relative to Lake Hazen Arctic char). However, a trace-element study in western Lake Erie in 1984 did not show elevated Rb concentrations in adult yellow perch, Perca flavescens (mean $3 \ \mu g \cdot g^{-1}$ wet weight) caught near an Ohio power plant in comparison with those from a reference site several kilometres away (Hatcher et al. 1992). Rb concentrations in the Ohio yellow perch are similar to those found for the same species in this study, suggesting consistent Rb uptake by fish over time and space in Lake Erie. The most likely sources of Rb in lakes include Rb-rich geological features (Heier and Billings 1970) and Rb minerals in soil (Jones 1992). For example, drinking water derived from areas with increased Rb mineralization will have correspondingly high aqueous Rb concentrations (Anke and Angelow 1995). The type of mineralization and the proportions of Cs, Rb, and K found in lake catchments are probably important factors determining baseline aquatic alkali concentrations and elemental ratios in freshwater ecosystems.

Fig. 1. Regressions of Rb concentrations in biota versus their δ^{15} N values for freshwater (*a*) and marine (*b*) sites. To simplify the plots, data points for various species sampled from Lake Erie (broken line) and the North Water Polynya are shown as the mean ± standard deviation, while data for Arctic char from Resolute Lake (dotted line) and Lake Hazen (solid line) are shown individually. Regression lines for all sites are based on individual data, not the mean values.



Even so, studies have shown that Rb concentrations in terrestrial plants are only weakly related to Rb concentrations in surrounding soil because the pH, K⁺ content, and even Na⁺ content of soil have a more significant impact on Rb and Cs bioavailability to plants and subsequently to animals (Drobner and Tyler 1998; Nyholm and Tyler 2000). Furthermore, increasing K⁺ concentrations in ambient water and sediment are linked to reduced ¹³⁷Cs bioaccumulation in fish and invertebrates (Rowan and Rasmussen 1994). As a result, marine fish tend to have lower Cs concentrations relative to fish from soft-water lakes (Rowan and Rasmussen 1994). This trend is reflected in marine Arctic cod, which had lower Rb concentrations (0.3–0.5 $\mu g \cdot g^{-1}$) relative to all the freshwater fish (0.7–4.5 $\mu g \cdot g^{-1}$). Even the piscivorous seabirds and seals from the marine NOW Polynya had Rb concentrations (0.2–1.7 $\mu g \cdot g^{-1}$) lower than or similar to those of omnivorous fish from Lake Erie (1.7–4.5 $\mu g \cdot g^{-1}$). In addition, comparing individuals of the same species from two different lakes can provide additional insights into Rb biogeochemistry. For example, Arctic char from Lake Hazen had significantly higher Rb concentrations and a higher log[Rb]: δ^{15} N slope than those from Resolute Lake. Lake Hazen has

lower ionic water concentrations (K = 0.5 mg·L⁻¹, Na = 0.6 mg·L⁻¹, and conductivity = 149 μ S·mm⁻¹) than Resolute Lake (0.9 mg·L⁻¹, 10.9 mg·L⁻¹, and 253 μ S·mm⁻¹, respectively). Increased uptake and biomagnification of Rb by Arctic char may result when ambient K and other ionic concentrations are low (Peters et al. 1999), suggesting that Rb concentration in fish is dependent not only upon the amount of ambient Rb but also upon the ratios of Rb to other alkali metals in the environment.

Another important factor is temperature, as ¹³⁷Cs and ⁸⁶Rb uptake in fish is temperature-dependent, and more rapid depuration of these radionuclides will occur with increase in temperature (Peters et al. 1999). Lake Erie is the warmest site in this study, and Long Point Bay water has higher K (1.4 mg·L⁻¹) and Na (9.5 mg·L⁻¹) concentrations and conductivity (272 μ S·mm⁻¹) relative to the northern lakes. This would seem to suggest that both Rb and Cs concentrations should be lowest in fish from Lake Erie, while K concentrations should be higher. However, the Lake Erie fish tend to contain higher Rb and lower Cs and K concentrations than other freshwater fish. These contrary results, the opposite of what one would expect from the literature on plants and Cs,

Table 2. Sampling sites and sp	secies sampled, with the nu	mber of samples analysed (N),	δ ¹⁵ N (%	60), and mean F	th and Cs (µg	$\cdot g^{-1}$ wet weight) and k	✓ (mg·g ⁻	1 wet weight) conc	entrations.
Site	Common name	Scientific name	Ν	δ ¹⁵ N	Rb	Total length (cm)	N^{a}	Cs	К
Long Point Bay, Lake Erie	Alewife	Alosa pseudoharengus	4	12.0 ± 0.7	2.1 ± 0.6	14.4 ± 0.6		I	
	Common carp	Cyprinus carpio	1	14.1	1.7		1	0.006	2.9
	Freshwater drum	Aplodinotus grunniens	5	15.5 ± 1.1	4.5 ± 0.4	38.0 ± 4.4	5	0.016 ± 0.003	3.6 ± 0.2
	Gizzard shad	Dorosoma cepedianum	٢	11.6 ± 0.4	1.7 ± 0.2	24.4 ± 11.5	1	0.004 ± 0.002	3.1 ± 01.8
	Pumpkinseed	Lepomis gibbosus	1	12.5	2.2				
	Rock bass	Ambloplites rupestris	9	15.5 ± 0.9	2.8 ± 0.5	187.2±47.3	4	0.006 ± 0.003	3.3 ± 0.2
	Round goby	Neogobius melanostomus	9	13.6 ± 0.5	1.7 ± 0.2	12.1 ± 4.1			
	Smallmouth bass	Micropterus dolomieu	15	16.0 ± 0.5	3.3 ± 0.3	319.5 ± 86.8	5	0.014 ± 0.0004	4.1 ± 0.2
	White bass	Morone chrysops	4	15.9 ± 0.2	2.3 ± 0.2	177.3 ± 11.9	4	0.007 ± 0.001	3.4 ± 0.5
	White perch	Morone americana	0	14.8 - 15.2	2.3 - 2.4	228–237	0	0.006 - 0.007	3.3 - 3.6
	White sucker	Catostomus commersoni	С	14.2 ± 0.5	1.8 ± 0.3	30.3 ± 3.4	ю	0.006 ± 0.002	3.9 ± 0.5
	Yellow perch	Perca flavescens	11	15.4±0.8	3.3±0.7	213.5±46.9	L	0.008 ± 0.004	$3.4{\pm}0.2$
Lake Hazen	Arctic char	Salvelinus alpinus	20	11.3 ± 1.8	1.0 ± 0.4	44.7 ± 11.1	20	0.21 ± 0.16	4.3 ± 0.4
Resolute Lake	Arctic char	Salvelinus alpinus	17	11.8 ± 1.2	0.7 ± 0.2	39.3±2.9			
NOW Polynya	Ice algae		3	5.1 ± 0.1	0.2 ± 0.02				
•	Calanid copepod	Calanus hyperboreus	ю	7.8 ± 0.01	0.3 ± 0.1				
	Mixed zooplankton		4	8.5 ± 0.1	0.2 ± 0.1				
	Ice amphipod	Themisto libellula	С	9.7 ± 0.1	0.7 ± 0.1				
	Mysid	Mysis oculata	С	10.4 ± 0.1	0.5 ± 0.1				
	Arctic cod	Boreogadus saida	б	14.1 ± 0.2	0.4 ± 0.1				
	Dovekie	Alle alle	10	10.9 ± 0.4	1.7 ± 0.2				
	Blacklegged kittiwake	Rissa tridactyla	10	13.3 ± 0.4	1.4 ± 0.1				
	Black guillemot	Ceppus grylle	10	13.7 ± 0.1	1.7 ± 0.2				
	Thick-billed murre	Uria lomva	10	13.5 ± 0.6	1.7 ± 0.2				
	Ivory gull	Pagophilia eburnea	S	14.1 ± 0.6	2.0 ± 0.3				
	Northern fulmar	Fulmarus glacialis	10	14.2 ± 0.5	2.2 ± 0.4				
	Glacuous gull	Larus hyperboreus	10	16.5 ± 0.7	2.2 ± 0.4				
	Thayer's gull	Larus thayeri	1	17.2	1.7				
	Ringed seal	Pusa hispida	6	17.4 ± 0.3	1.7 ± 0.3				
Note: Values are given as the "Because subsets of Lake Erie :	mean ± standard deviation. and Lake Hazen samples were	analysed for Cs and K, the numbe	rs analys	sed are different	from the origina	ıl totals analysed for $\delta^{15}N$	f and Rb,	hence the second N	column.

Campbell et al.

Regression	Site	N^a	Slope	Intercept	$R_{\rm adj}^2$	р
Log[Rb] vs. δ ¹⁵ N	Erie	65	0.067	-0.575	0.470	< 0.001
	Resolute	17	0.064	-0.920	0.603	< 0.001
	Hazen	20	0.081	-0.926	0.655	< 0.001
	NOW	94	0.073	-0.851	0.501	< 0.001
Log[Cs] vs. δ^{15} N	Erie	32	0.112	-3.796	0.283	0.001
	Hazen	20	0.140	-2.367	0.660	< 0.001
Log[K] vs. δ^{15} N	Erie	32	0.012	3.366	0.051	0.113
	Hazen	20	0.009	3.531	0.093	0.103
$Log([Cs]:[K])$ vs. $\delta^{15}N$	Erie	32	0.100	-4.162	0.261	0.002
	Hazen	20	0.131	-2.897	0.554	< 0.001
Log[Rb] vs. log[Cs]	Erie	32	0.457	1.385	0.597	< 0.001
	Hazen	20	0.320	0.238	0.266	0.012
Log[Rb] vs. log[K]	Erie	32	1.015	-3.175	0.115	0.044
	Hazen	20	2.428	-8.831	0.306	0.007
Log[Cs] vs. log[K]	Erie	32	2.233	-10.021	0.212	0.003
	Hazen	20	-0.260	0.156	0.000	0.980

Table 3. Linear-regression equations for relationships between Rb, Cs, and K concentrations and δ^{15} N for biota from Lake Erie, Lake Hazen, Resolute Lake, and the NOW Polynya.

^aThe number of samples included in each regression.

indicate that the biogeochemistry and bioavailability of alkali metals in aquatic environments require more research.

Peters et al. (1999) pointed out that the biological halflives of ⁸⁶Rb (9-181 days) are shorter than those of K and Cs radionuclides (37-600 days) in various fish species. This explains the lower biomagnification potential of Rb, as indicated by its lower $\log[Rb]:\delta^{15}N$ slope relative to Cs, because Rb is more rapidly depurated than Cs from freshwater biota. Within fish species, no correlations or weakly significant correlations were found for Rb with size (p = 0.069 - 0.888), suggesting that biomagnification of Rb is significant within a food-web context, but not necessarily within species. More exploration is needed to determine whether fish species that experience large dietary shifts with size show a corresponding significant relationship of Rb concentration with size. For example, a radiocesium food-web study showed that while Cs will biomagnify through various food webs, there were still variable patterns in Cs biomagnification within fish species, which were attributed to consumption rates (Rowan et al. 1998). Furthermore, the slope values for log[Rb] and log[Cs] are lower than those seen for log[Hg] versus δ^{15} N regressions (0.2–0.3) for aquatic food webs worldwide, as summarized in Campbell et al. (2003). In other words, Rb and Cs do not biomagnify as rapidly as ubiquitous methylmercury, which forms stable protein complexes. However, the consistent biomagnification of Rb and Cs in food webs indicates that these alkali metals should be considered along with Hg and organic contaminants when studying biomagnifying compounds in food webs.

Prior to the widespread use of cost-effective $\delta^{15}N$ measurements as a trophic-level indicator in the early 1990s, Cs:K ratios were used as a numerical surrogate for trophic position in food-web studies (Mearns et al. 1981), and were even successfully applied to biomagnification research in California marine ecosystems (Young et al. 1980). The increase in Cs:K ratio with trophic level has been estimated to be 2.4–2.5 (Mearns et al. 1981), while the increase in $\delta^{15}N$ value of biota with trophic level has been traditionally assumed to be 3.4%-3.6% (Minagawa and Wada 1984). Based on these hypothetical trophic values, the slope of the log([Cs]:[K]) versus δ^{15} N regression should be 0.106–0.117. The slopes for this regression for Lakes Erie and Hazen are 0.100 and 0.131, respectively, and interestingly, the mean value of these two slopes is 0.116, quite close to the maximum hypothetical slope. Although unknown variability will influence trophic-level-related changes in Cs:K ratios and δ^{15} N values, further investigation of alkali-metal trophodynamics and biogeochemistry may provide an additional tool for food-web analyses.

Acknowledgements

Staff at the Canadian National Laboratories for Environmental Testing at the National Water Research Institute prepared and analysed the biotic samples. The Lake Erie fish samples were obtained and processed for a separate study in collaboration with Dr. Robert E. Hecky and Reagan Johnston, Department of Biology, University of Waterloo, and Dixie Greenwood, Lake Erie Management Unit, Ontario Ministry of Natural Resources, Port Dover. Arctic sampling was undertaken with the assistance of National Water Research Institute Research Support Services, Parks Canada, at Quttinirpaaq National Park, the Polar Continental Shelf Project at Resolute Lake (Nunavut), and the captains and crew of the Coast Guard vessel Pierre Radisson. The Lake Resolute sampling was carried out within the framework of the International Geosphere-Biosphere Programme (Austrian Academy of Sciences). Dr. Todd Howell, Ontario Ministry of Environment, Toronto, provided the physiochemical data for Lake Erie in Table 1. Funding included, in part, a Postdoctoral Fellows Award from the Natural Sciences and Engineering Research Council of Canada to Linda Campbell, Northern Ecosystem Initiative funds to Aaron Fisk, Austrian Academy of Sciences (IGBP Research Program) funding to Günter Köck, and Environment Canada Great Lakes 20/20 and Northern Contaminants Program (Indian and Northern Affairs Canada) funding to Derek Muir.

References

- Anke, M., and Angelow, L. 1995. Rubidium in the food chain. Frescenius' J. Anal. Chem. 352: 236–239.
- Babaluk, J.A., Heuring, L.G., Reist, J.D., and Billeck, B.N. 1999. Selected chemical analyses of water from lakes in Ellesmere Island National Park Reserve, Northwest Territories. Can. Data Rep. Fish. Aquat. Sci. No. 1050.
- Campbell, L.M., Hecky, R.E., Nyaundi, J., Muggide, R., and Dixon, D.G. 2003. Distribution and food-web transfer of mercury in Napoleon and Winam Gulfs, Lake Victoria, East Africa. J. Gt. Lakes Res. 29(Suppl. 2): 267–282.
- Cerny, P., Chapman, R., Teertstra, D.K., and Novák, M. 2003. Rubidium- and cesium-dominant micas in granitic pegmatites. Am. Minerol. **88**: 1832–1835.
- Drobner, U., and Tyler, G. 1998. Conditions controlling relative uptake of potassium and rubidium by plants from soils. Plant Soil, **201**: 285–293.
- Fisk, A.T., Hobson, K.A., and Norstrom, R.J. 2001. Influence of chemical and biological factors on trophic transfer of persistent organic pollutants in the Northwater Polynya marine food web. Environ. Sci. Technol. 35: 732–738.
- Hatcher, C.O., Ogawa, R.E., Poe, T.P., and French, J.R.P. 1992. Trace elements in lake sediment, macrozoobenthos, and fish near a coal ash disposal basin. Freshw. Ecol. **7**: 257–269.
- Heier, K.S., and Billings, G.K. 1970. Rubidium. *In* Handbook of geochemistry. *Edited by* K.H. Wedepohl. Springer-Verlag, Berlin and Heidelberg. pp. 37-C-1 to 37-N-1.
- Johnson, P.C., and Reeves, R.M. 1995. Incorportion of the biological marker rubidium in gypsy moth (Lepidoptera: Lymantriidae) and its transfer to the predator *Carabus nemoralis* (Coleoptera: Carabidae). Environ. Entomol. 24: 46–51.
- Jones, R.L. 1992. Extractable rubidium in surface horizons of Illinois soils. Soil Sci. Soc. Am. J. 56: 1453–1454.
- Kidd, K.A. 1998. Use of stable isotope ratios in freshwater and marine biomagnification studies. *In* Environmental toxicology. *Edited by J.* Rose. Gordon and Breach Science Publishers, Amsterdam. pp. 357–376.
- Köck, G., Babaluk, J., Berger, B., Bright, D., Doblander, C., Flannigan, M., et al. 2004. Fish from sensitive ecosystems as bioindicators of global climate change — High-Arctic 1997– 2003. *Edited by* G. Köck. Veroeff. Univ. Innsbruck No. 245 (ISBN-3-901249-68-0).
- Kosla, T., Skibniewska, E., Debski, B., and Urbanska-Slomka, G. 2002. Rubidium in the trophic chain soil–plants–animals. Trace Elem. Electrolytes, 4: 171–176.
- Leggett, R.W., Williams, L.R., Melo, D.R., and Lipsztein, J.L. 2003. A physiologically based biokinetic model for cesium in the human body. Sci. Total Environ. **317**: 235–255.
- Mason, R.P., Reinfelder, J.R., and Morel, F.M.M. 1995. Bioaccumulation of mercury and methylmercury. Water Air Soil Pollut. **80**: 915–921.
- Mearns, A.J., Olson, R.J., Young, D.R., and Schafer, H.A. 1981. Trophic structure and the cesium–potassium ratio in pelagic ecosystems. Calif. Coop. Ocean. Fish. Investig. Rep. No. 22.

pp. 99–110 (also available at http://calcofi.org [accessed 16/05/2005]).

- Minagawa, M., and Wada, E. 1984. Stepwise enrichment of ${}^{15}N$ along food chains: further evidence and the relation between $\delta^{15}N$ and animal age. Geochim. Cosmochim. Acta, **48**: 1135–1140.
- National Laboratory for Environmental Testing. 2003. NLET schedule of services. National Water Research Institute, Environment Canada, Burlington, Ont.
- Nielsen, F.H. 1998. Ultratrace elements in nutrition: current knowledge and speculation. J. Trace Elem. Exp. Med. 11: 251–274.
- Nyholm, N.E.I., and Tyler, G. 2000. Rubidium content of plants, fungi and animals closely reflects potassium and acidity conditions of forest soils. For. Ecol. Manag. 134: 89–96.
- Payne, J.C., and Dunley, J.E. 2002. Use of an elemental marker, rubidium, to study dispersal of aquatic insects. J. North Am. Benthol. Soc. 21: 715–727.
- Perel'man, F.M. 1965. Rubidium and caesium. [Translated from Russian by R.G.P. Towndrow.] The Macmillan Co., New York.
- Peters, E.L., Schultz, I.R., and Newman, M.C. 1999. Rubidium and cesium kinetics and tissue distributions in channel catfish (*Ictalurus punctatus*). Ecotoxicology, 8: 287–300.
- Quinn, M.R., Feng, X., Folt, C.L., and Chamberlain, C.P. 2003. Analyzing trophic transfer of metals in stream food webs using nitrogen isotopes. Sci. Total Environ. 317: 73–89.
- Richie, R.J. 1997. Rubidium transport in the cyanobacterium Synechococcus R-2 (Anacystis nidulans, S. leopoliensis) PCC 7942. Plant Cell Environ. 20: 907–918.
- Rowan, D.J., and Rasmussen, J.B. 1994. Bioaccumulation of radiocesium by fish: the influence of physicochemical factors and trophic structure. Can. J. Fish. Aquat. Sci. 51: 2388–2410.
- Rowan, D.J., Chant, L.A., and Rasmussen, J.B. 1998. The fate of radiocesium in freshwater communities — Why is biomagnification variable both within and between species? J. Environ. Radioact. 40: 15–36.
- Salaün, M.-L., and Truchet, M. 1996. Étude, par émission ionique secondaire, de l'accumulation du rubidium dans les tissus mous de l'huître *Crassostrea gigas* (Mollusque, Lamellibranche). Cah. Biol. Mar. **37**: 329–340.
- Seredin, V.V. 2003. Anomalous concentrations of trace elements in the spetsugli germanium deposit (Pavlovka Brown coal deposit, southern Primorye): Communication 2. Rubidium and cesium. Lithol. Miner. Resour. 38: 233–241.
- Systat Software Inc. 2000. SYSTAT[®]. Version 10 [computer program]. Systat Software Inc., Point Richmond, Calif.
- Tipsmark, C.K., and Madsen, S.S. 2001. Rapid modulation of Na⁺/K⁺-ATPase activity in osmoregulatory tissues of a salmonid fish. J. Exp. Biol. **204**: 701–709.
- Wang, W.-X. 2002. Interactions of trace metals and different marine food chains. Mar. Ecol. Prog. Ser. 243: 295–309.
- Ward, C.R., Spears, D.A., Booth, C.A., Staton, I., and Gurba, L.W. 1999. Mineral matter and trace elements in coals of the Gunnedah Basin, New South Wales, Australia. Int. J. Coal Geol. 40: 281–308.
- Younge, D.R., Mearns, A.J., Jan, T.-K., Heesen, T.C., Moore, M.D., Eganhouse, R.P., et al. 1980. Trophic structure and pollutant concentrations in marine ecosystems of southern California. Calif. Coop. Ocean. Fish. Investig. Rep. No. 21. pp. 197–206 (also found at http:// www.calcofi.org [accessed 16/05/2005]).