



Changes in Sr/Ca, Ba/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between trophic levels in two forest ecosystems in the northeastern U.S.A.

JOEL D. BLUM^{1,2}, E. HANK TALIAFERRO³, MARIE T. WEISSE³ & RICHARD T. HOLMES³

¹*The University of Michigan, Department of Geological Sciences, Ann Arbor, MI 48109, U.S.A.*; ²*Dartmouth College, Department of Earth Sciences, Hanover, NH 03755, U.S.A.*;

³*Dartmouth College, Department of Biological Sciences, Hanover, NH 03755, U.S.A.*

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Abstract. The variability and biological fractionation of Sr/Ca, Ba/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were studied in a soil–plant–invertebrate–bird food chain in two forested ecosystems with contrasting calcium availability in the northeastern U.S.A. Chemical measurements were made of the soil exchange pool, leaves, caterpillars, snails, and both the femurs and eggshells of breeding insectivorous migratory songbirds. $^{87}\text{Sr}/^{86}\text{Sr}$ values were transferred up the food chain from the soil exchange pool to leaves, caterpillars, snails and eggshells without modification. Adult birds were the one exception; their $^{87}\text{Sr}/^{86}\text{Sr}$ values generally reflected those of lower trophic levels at each site, but were lower and more variable, probably because their strontium was derived in part from foods in tropical winter habitats where lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are likely to predominate. Sr/Ca and Ba/Ca ratios decreased at each successive trophic level, supporting previous suggestions that Sr/Ca and Ba/Ca ratios can be used to identify the trophic level at which an organism is primarily feeding. The changes in Sr/Ca and Ba/Ca ratios we measured for vegetation and insects were comparable to similar measurements made previously (but based on single samples of each organism) in an alpine ecosystem. Changes in Sr/Ca and Ba/Ca ratios between birds and their food have not previously been measured, but the values we obtained were similar to those for herbivorous and carnivorous mammals at similar trophic levels. Our results provide evidence that supports the use of Sr/Ca ratios in the determination of human paleodiets and suggests that Sr/Ca ratios may also provide a useful tool in studies of modern food webs. Furthermore, our findings suggest that ^{90}Sr from nuclear fallout will not bioaccumulate in forests and that changes in Sr/Ca ratios between trophic levels will need to be considered in some cases when using $^{87}\text{Sr}/^{86}\text{Sr}$ as a tracer of calcium biogeochemistry.

Introduction

Calcium is one of the more abundant elements in the Earth's crust and plays a vital role in many different biological and biogeochemical processes. Calcium belongs to the alkaline earth metals (Group 2A on the periodic table) which also include beryllium, magnesium, strontium, barium, and the radioactive element radium. Strontium and barium are non-nutrient trace elements that tend to substitute for calcium as trace constituents during nutrient uptake, internal distribution, and excretion within organisms (Elias et al. 1982; Sillen 1992; Gierth et al. 1998; Graustein 1989) and can thus be used as tracers of various inputs of calcium to ecosystems and food webs. Organisms, however, are able to differentiate somewhat between calcium, strontium and barium during nutrient uptake from food sources, and in this process strontium and barium are excluded relative to calcium resulting in lower Sr/Ca and Ba/Ca ratios at higher trophic levels (Elias et al. 1982; Sillen 1992).

In most forest biogeochemical studies it has been assumed that calcium and strontium display nearly identical behavior, and therefore that $^{87}\text{Sr}/^{86}\text{Sr}$ ratios provide accurate tracers of calcium sources and cycling in forest ecosystems (Gosz et al. 1983; Graustein & Armstrong 1983; Åberg et al. 1989; Miller et al. 1993; Bailey et al. 1996; Blum & Erel 1997; Kennedy et al. 1998). However, in archeological applications it is the differences in Sr/Ca ratios between plants and animals that have been widely used to ascertain the paleodiets of ancient humans (e.g., Sillen & Kavanagh 1982; Sillen 1992). Finally, in radioecological applications, changes in Sr/Ca ratios between soil nutrients and pasture grasses have been used to make predictions about the fate of ^{90}Sr from nuclear fallout in human food sources (e.g., Veresoglou et al. 1995).

Although preliminary studies have been carried out (e.g., Elias et al. 1982), the degree to which Sr/Ca and Ba/Ca ratios change between trophic levels in forest ecosystems, and the variability of these ratios within trophic levels in forests, had not been investigated in detail prior to this study. Herein we report on the patterns and variability in Sr/Ca, Ba/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the soil-plant-invertebrate-bird food chain in two forest ecosystems in the northeastern U.S.A., which were chosen for their contrasting levels of calcium availability. We measured the calcium, strontium and barium concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of approximately 100 samples, which included the soil cation exchange pool, leaves, caterpillars, snails, and the bones and eggshells of insectivorous female songbirds.

Study areas and methods

Samples were collected in mid to late June of 1996 and 1997 from two study sites: the Hubbard Brook Experimental Forest in West Thornton, New Hampshire and the Charles Downer State Forest in Sharon, Vermont. Hubbard Brook is the site of long-term biogeochemical investigations (e.g., Likens & Bormann 1995) and ecological studies of migratory songbirds (e.g., Holmes et al. 1996) and it is at this site where we did the most extensive sampling. The second site (Downer Forest) was chosen because of the naturally-higher calcium content and contrasting $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of its soils. Hubbard Brook is underlain by calcium-poor crystalline silicate rocks of the Upper Rangeley Formation (Lyons et al. 1997), whereas Downer Forest is underlain by calcium-rich carbonate and silicate rocks of the Waits River Formation (Doll et al. 1961). Soils at both sites are typical of those found in New England and are young ($\sim 13,000$ years) podzols developed on glacial tills derived mostly from local bedrock (e.g., Bailey & Hornbeck 1992). Forests at both sites consist primarily of northern hardwoods; mostly sugar maple (*Acer saccharum*), American beech (*Fagus grandifolia*), yellow birch (*Betula alleghaniensis*) and striped maple (*A. pensylvanicum*).

At each of the two sites all sample types were collected within a circular sampling area with a diameter of ~ 400 m. Female Black-throated Blue Warblers (*Dendroica caerulescens*: Parulidae hereafter BTBW) were followed at each site until their nests were found. BTBWs arrive at the sites after migration from their wintering sites in the Caribbean region in mid to late May and immediately begin nest building. They generally lay clutches of 4 to 5 eggs (one per day) within two weeks of arrival at the breeding sites (Holmes 1994). After they had completed their clutches, the adult females and all of their eggs were collected under permit from federal and state agencies and with procedures approved by the Institutional Animal Care and Use Committee of Dartmouth College. Caterpillars (Families Geometridae and Notodontidae) were collected from nine locations within the 400 m diameter sampling area at each site. Six snails were also collected at Hubbard Brook and one at Downer Forest. Leaf samples were collected at nine locations in each 400 m diameter sampling area and included samples from three sugar maple, three American beech and three striped maple trees. Each leaf sample included 15–20 leaves from a single tree. Four soil samples were collected in the Hubbard Brook sampling area and three soil samples were collected at the Downer Forest sampling area. Samples were taken from the upper-most 10 cm of soil (the forest floor plus the first few cm of the mineral soil). Concentrations of exchangeable cations are much higher in the upper-most 10 cm of soil than in the deeper mineral soils (Johnson et al. 1991) and thus it

is the upper-most 10 cm that is most representative of the soil cation exchange pool.

Adult female warblers were dissected and their femurs were removed and cleaned. Eggs were stored frozen and then broken open allowing easy separation of egg contents from shells. Although egg shells were analyzed separately, measured values for multiple shells from a single clutch were averaged to yield a single value for each clutch. Caterpillars were frozen prior to analysis, and snail shells were separated from other tissues prior to analysis. All samples were weighed in the fresh frozen state, then dried overnight at 105 °C and weighed to determine “dry weight.” Caterpillars and leaves were ashed overnight in acid-washed silica crucibles at 500 °C. One gram of each soil sample was gently shaken overnight with 10 ml of 1 M ammonium acetate (buffered at pH 7) to extract samples of the soil cation exchange pool, and the solution was then separated by centrifugation and evaporated to dryness. All samples were digested in ultra-pure nitric and hydrochloric acids, evaporated to dryness, and then redissolved in ultra-pure 5% nitric acid for analysis. Solutions were diluted to appropriate concentration ranges, spiked with a yttrium internal standard, and analyzed for the concentrations of calcium, strontium and barium using a Finnigan ELEMENT magnetic sector inductively coupled plasma mass spectrometer with an analytical uncertainty of ~5%. A second aliquot of each solution containing 100 to 1000 ng of strontium was eluted through ion-specific cation exchange columns using Sr-Spec resin. Approximately 75 ng of each pure strontium fraction was loaded onto a tungsten filament with Ta₂O₅ powder. Total procedural blanks including all reagents were <40 pg strontium and thus negligible. Isotope ratios were measured with a Finnigan MAT 262 thermal ionization mass spectrometer. ⁸⁷Sr/⁸⁶Sr ratios were normalized to a ⁸⁶Sr/⁸⁸Sr ratio of 0.119400 and over 100 isotope ratios were measured for each sample, yielding a mean ⁸⁷Sr/⁸⁶Sr ratio for each sample with an analytical uncertainty of less than ±0.000020 (2 S.D.). The mean ⁸⁷Sr/⁸⁶Sr value obtained for 32 replicate analyses of interlaboratory calibration standard NIST-987 was 0.710262 ±0.000026 (2 S.D.).

Results

⁸⁷Sr/⁸⁶Sr ratios of two forest food chains

⁸⁷Sr/⁸⁶Sr ratios within each trophic level at both Hubbard Brook and Downer Forest display a range of variation that is far in excess of the analytical reproducibility of the individual measurements. The mean ⁸⁷Sr/⁸⁶Sr ratios of soil exchange samples in each of the two sites were distinct (Figure 1),

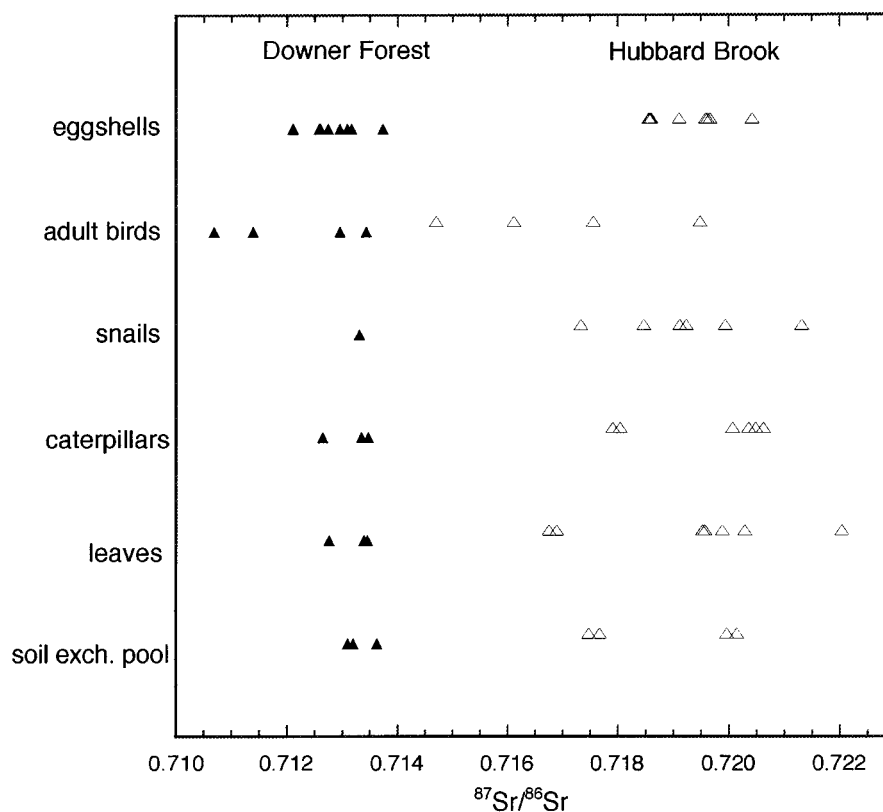


Figure 1. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the soil cation exchange pool, leaves of deciduous trees, caterpillars, snails and the bones and eggshells of Black-throated Blue Warblers analyzed from Hubbard Brook (open symbols) and Downer Forest (closed symbols). The analytical uncertainty of each individual analysis is smaller than the symbol size.

with Hubbard Brook displaying higher and more variable ratios (0.71880 ± 0.00144 , 1 S.D.) than Downer Forest (0.71330 ± 0.00028 , 1 S.D.). This difference primarily reflects the differing compositions and ages of the geological substrate on which soils at each location have developed, modified some by atmospheric deposition of strontium with $^{87}\text{Sr}/^{86}\text{Sr}$ equal to ~ 0.7100 (Bailey et al. 1996; JD Blum unpub. data). The range of $^{87}\text{Sr}/^{86}\text{Sr}$ values at Hubbard Brook and Downer Forest is consistent with weathering of different minerals within the soil parent material (till) as well as the addition of atmospheric deposition to the forest (e.g., Miller et al. 1993; Bailey et al. 1996). As expected, we found the mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of leaves, caterpillars and snails from within each site similar to that of the soil exchange pool at each site (Table 1, Figure 1).

Table 1. Mean and standard deviation (S.D.) of Ca (mg/g), Sr ($\mu\text{g/g}$) and Ba ($\mu\text{g/g}$) concentrations, Sr/Ca and Ba/Ca ratios (mg/g), and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios within each sample type. The number of samples analyzed (n) is also given for concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

	n	Ca		Sr		Ba		Sr/Ca		Ba/Ca		$^{87}\text{Sr}/^{86}\text{Sr}$		
		Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	n	Mean	S.D.
HUBBARD BROOK														
Soil cation exch.	4	0.12	0.08	0.73	0.55	2.74	2.15	5.26	1.87	27.0	21.0	4	0.71880	0.00144
Leaves	9	7.93	2.54	32.4	17.8	33.2	23.8	3.96	1.43	4.21	2.56	9	0.71919	0.00191
Caterpillars	9	1.33	0.20	2.62	1.53	2.91	1.21	1.91	0.93	2.18	0.73	6	0.71957	0.00126
Snails	6	221	77	360	110	111	54	1.67	0.27	0.56	0.27	6	0.71923	0.00134
Warbler bones	4	66.3	14.3	23.0	5.3	22.4	5.8	0.35	0.08	0.34	0.05	4	0.71696	0.00205
Eggshells	4	220	42	265	45	62.4	30.1	1.24	0.36	0.28	0.13	4	0.71926	0.00088
DOWNER FOREST														
Soil cation exch.	3	0.52	0.38	2.65	1.65	9.28	0.41	5.29	1.02	26.0	18.7	3	0.71330	0.00028
Leaves	9	6.99	4.15	26.0	19.1	10.6	4.4	3.28	1.34	2.41	2.16	3	0.71318	0.00037
Caterpillars	9	2.01	0.85	4.98	2.60	13.5	9.4	2.48	0.71	8.02	8.12	3	0.71315	0.00045
Snails	1	350	—	841	—	45.6	—	2.40	—	0.13	—	1	0.71330	—
Warbler bones	4	66.6	2.3	36.1	24.0	20.7	14.9	0.54	0.03	0.31	0.21	4	0.71211	0.00129
Eggshells	4	253	24	389	73	129	45	1.51	0.53	0.49	0.30	4	0.71283	0.00069

The mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of eggshells were also very close to the values of the soil exchange pool, leaves and insects at both Hubbard Brook and Downer Forest (Table 1, Figure 1). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of adult birds from each of the two sites were distinct, with Hubbard Brook displaying higher and more variable ratios (0.71696 ± 0.00205 , 1 S.D.) than Downer Forest (0.71211 ± 0.00129 , 1 S.D.). At both sites $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of adult birds were more variable and tended toward lower $^{87}\text{Sr}/^{86}\text{Sr}$ values than vegetation, insects or eggs (Table 1, Figure 1).

Sr/Ca and Ba/Ca ratios of two forest food chains

Sr/Ca and Ba/Ca ratios within each trophic level at both Hubbard Brook and Downer Forest display a range of variation that is far in excess of the analytical reproducibility of the individual measurements (Table 1). To present this range of natural variability graphically we plot the Sr/Ca and Ba/Ca ratios on a logarithmic scale (Figures 2 and 3). At both Hubbard Brook and Downer Forest, respectively, the mean values of the Sr/Ca ratio (in mg/g) decrease systematically up the food web from 5.26 and 5.29 in the soil exchange pool to 0.35 and 0.54 in the adult birds (Table 1). Similarly, at both Hubbard Brook and Downer Forest, respectively, the mean values of the Ba/Ca ratio (in mg/g) decrease (although not as systematically as Sr/Ca) up the food web from 27 and 26 in the soil exchange pool to 0.34 and 0.31 in the adult birds (Table 1).

Changes between trophic levels can be summarized as biopurification factors (BPF) following Elias et al. (1982):

$$x\text{-BPF} = \frac{x/\text{Ca (of trophic level } \tau)}{x/\text{Ca (of trophic level } \tau + 1)}$$

where Ca is calcium concentration and x is either strontium or barium concentration. Before we present BPFs we discuss whether the mean Sr/Ca or Ba/Ca ratios are significantly different between adjacent trophic levels. To test this statistically we performed an analysis of variance (ANOVA) following standard methods (e.g., Miller & Miller 1993). The *P*, *F* and *df* values from the ANOVA comparing mean values of Sr/Ca and Ba/Ca between adjacent trophic levels are given along with the calculated BPFs in Table 2. All 18 BPFs given in Table 2 are significant at the *P* = 0.20 level, 13 of 18 are significant at the *P* = 0.10 level, and 11 of 18 are significant at the *P* = 0.05 level. Each calculated BPF is significant at the *P* = 0.05 level in at least one of the two field sites.

Sr-BPF values at Hubbard Brook and Downer Forest, respectively, were 1.3 and 1.6 between soil and leaves, 2.1 and 1.3 between leaves and caterpillars, and 5.5 and 4.6 between caterpillars and adult birds. Ba-BPF values at

Table 2. Biopurification factors (BPF) based on Sr/Ca and Ba/Ca ratios and results of ANOVA analysis testing the significance of differences in mean Sr/Ca and Ba/Ca ratios between trophic levels (*P*, *F*, *df*).

	Sr/Ca ratio				Ba/Ca ratio			
	BPF	<i>P</i>	<i>F</i>	<i>df</i>	BPF	<i>P</i>	<i>F</i>	<i>df</i>
HUBBARD BROOK								
Soil/								
Leaves	1.33	0.194	1.90	12	6.41	0.006	11.4	12
Leaves/								
Caterpillars	2.07	0.002	13.0	17	1.93	0.042	4.9	17
Caterpillars/								
Warbler bones	5.46	0.007	10.7	12	6.41	<0.001	24.1	12
Snails/								
Warbler bones	4.77	<0.001	85.0	9	1.65	0.151	2.5	9
Snails/								
Eggshells	1.35	0.014	7.20	21	2.00	0.003	11.0	21
DOWNER FOREST								
Soil/								
Leaves	1.61	0.040	5.50	11	10.8	0.002	17.1	11
Leaves/								
Caterpillars	1.32	0.129	2.60	17	0.30	0.063	4.0	17
Caterpillars/								
Warbler bones	4.59	<0.001	26.1	12	25.9	0.091	3.4	12

Hubbard Brook and Downer Forest, respectively, were 6.4 and 10.8 between soil and leaves, 1.9 and 0.3 between leaves and caterpillars, and 6.4 and 26 between caterpillars and adult birds. Eggshells are produced during periods of rapid calcium ingestion by adult birds during egg-laying, apparently due to their ingestion of snail shells (Graveland & van der Wal 1996; Taliaferro et al. 1999). Thus, we have also calculated BPF values for snails relative to adult birds and snails relative to eggshells. At Hubbard Brook Sr-BPF and Ba-BPF values were 4.7 and 1.7 for snails relative to birds, and 1.4 and 2.0 for snails relative to eggshells. Values related to snails are not calculated for Downer Forest because only one snail was analyzed.

Discussion

Variability of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios

$^{87}\text{Sr}/^{86}\text{Sr}$ values were transferred up the food chain from the soil exchange pool to leaves, caterpillars, snails and eggshells without modification. Adult birds were the one exception; their $^{87}\text{Sr}/^{86}\text{Sr}$ values generally reflected those of lower trophic levels at each site, but were lower and more variable, probably because their strontium was derived in part from foods in tropical winter habitats where lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are likely to predominate. This is a good demonstration of the difference between strontium isotopes as tracers compared to the light stable isotopes (i.e., those of hydrogen, carbon, nitrogen and oxygen) that are more commonly used in biological applications. Variation in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is produced only by radioactive decay in rocks over geological timescales. Once an isotope ratio is locked into a biogeochemical reservoir it is unaffected by the mass-dependent isotope fractionation that results in variations in the light stable isotope ratios (and Sr/Ca ratios) between trophic levels (e.g., Graustein 1989; Koch et al. 1994). Therefore, we can confidently conclude that the variability of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios within each study site represent mixing of at least two different strontium sources (or endmembers). It is interesting that inputs from these contrasting endmembers have not been homogenized within the forest ecosystem, even at the higher trophic levels. These endmembers are likely to represent the weathering of different minerals within the soil parent material (till) as well as the addition of atmospheric deposition to the forest.

Comparison with previous measurements of Sr and Ba biopurification factors

The only previous study of strontium and barium in complex natural food chains determined BPFs for several trophic levels in an alpine meadow in the Sierra Nevada Mountains, California (Elias et al. 1982). These investigators studied a food chain that is significantly different from the one we studied (rock-sedge-vole-marten), and in most cases used single samples from each trophic level, precluding the assessment of Sr/Ca and Ba/Ca variability within trophic levels. Nevertheless, there are several BPFs that are interesting to compare between the two studies. Elias et al. (1982) did not analyze the soil exchange pool, but instead reported BPFs for strontium and barium between soil parent material (rock) and sedge leaves of 2.6 and 16, respectively. These values are similar to BPF values we measured for strontium and barium between the soil exchange pool and leaves (Hubbard Brook: 1.3 and 6.4; Downer Forest: 1.6 and 11). Elias et al. (1982) reported BPFs for strontium

and barium between sedge leaves and insects of 3.0 and 2.5, which differ considerably from our values between leaves and caterpillars (Hubbard Brook: 2.1 and 1.9; Downer Forest: 1.3 and 0.3), but have the similar feature that this is the only case of a feeding relationship in either study where the BPF for strontium was larger than the BPF for barium. Elias et al. (1982) also measured BPFs for strontium and barium between sedge leaves and voles of 4.1 and 7.7, and between voles and martens of 5.8 and 7.3, which are similar to our values calculated between caterpillars and birds (Hubbard Brook: 5.5 and 6.4; Downer Forest: 4.6 and 26). Thus, we find that herbivorous and carnivorous mammals display BPF values for strontium and barium very similar to those of insectivorous songbirds.

There are several additional studies that have investigated changes in Sr/Ca (but not Ba/Ca) across trophic levels motivated by two main applications: (1) investigation of the behavior of strontium relative to calcium in modern human food chains in order to determine possible human exposures to radioactive ^{90}Sr from nuclear fallout and (2) the archaeological use of Sr/Ca as a paleodiet indicator in fossil human bones (i.e., determination of the degree of herbivory of a population). Investigators in these disciplines have used the terms “observed ratio” and “distribution ratio” to describe changes in Ca/Sr across trophic levels – these values are simply the reciprocal of the BPF. Because the motivation for this previous research has been on the human food chain, most work on plants has been directed towards human food sources (Runia 1987) or pasture plant species (Veresoglou et al. 1996). We know of no previous measurements of BPFs involving leaves of deciduous trees, but Sr-BPFs for leaves and shoots of alfalfa, barley and tomato range from 1.1 to 1.4, compared to the values we measured of 1.3 and 1.6. The only other Sr-BPFs for which there are previous measurements are for adult herbivorous mammals, which range from 2.9 in mice to 6.2 in wild kangaroo rats (see references in Sillen & Kavanagh 1982). These values compare favorably with our Sr-BPF values for songbirds of 5.5 and 4.6 and Elias et al.’s (1982) values of 4.1 and 5.8 for voles and martens.

Sillen and Kavanagh (1982) pointed out that young mammals tend to have much lower Sr-BPFs than adults (1 to 2 rather than 3 to 6 in adults) perhaps due to the extremely high calcium demands during the rapid growth in infants. Although this is quite speculative, we suggest that this may be somewhat analogous to the high calcium demands on birds experienced during egg laying. We observed a similarly low Sr-BPF value of 1.4 at Hubbard Brook; calculated based on the Sr/Ca ratios of the food source for songbirds during egg-laying (snails) with the eggshells that they produce.

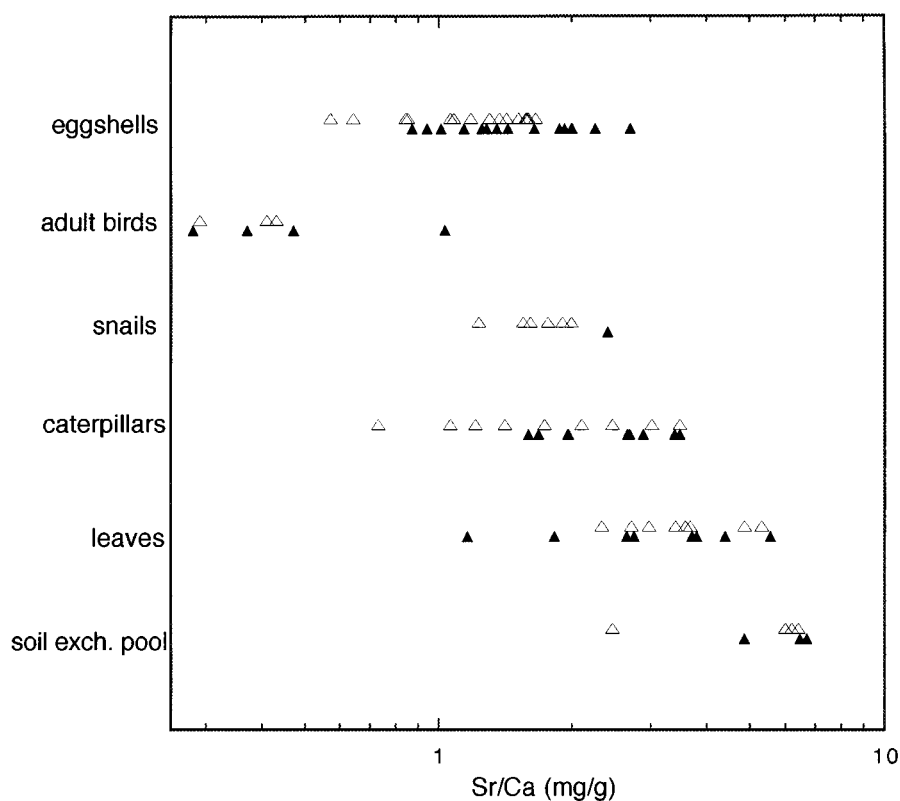


Figure 2. Sr/Ca ratios (in mg/g) of the soil cation exchange pool, leaves of deciduous trees, caterpillars, snails and the bones and eggshells of Black-throated Blue Warblers analyzed from Hubbard Brook (open symbols) and Downer Forest (closed symbols). The analytical uncertainty of each individual analysis is smaller than the symbol size.

Implications and potential applications

Our study of the biological purification of calcium relative to strontium and barium in two forest food chains sheds new light on the biogeochemistry of alkaline earth metals in forest ecosystems. In two small northern hardwood forest plots we found a systematic trend toward lower Sr/Ca ratios at each stage up the soil–plant–invertebrate–bird food chain. We have also documented the level of variability of Sr/Ca ratios within each trophic level in these small forest plots and find that although the differences between trophic levels are in most cases statistically significant, the variability within each trophic level is quite high (Table 1, Figures 2 and 3). We caution that multiple samples from each trophic level are necessary to make meaningful comparisons between trophic levels. Barium BPFs display the same general

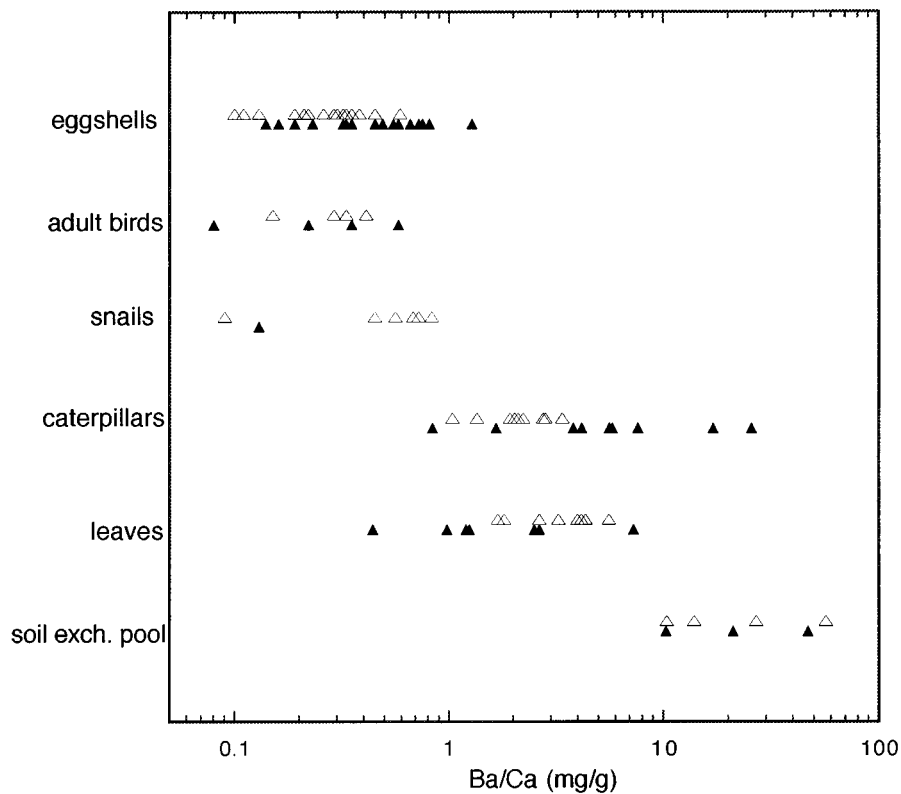


Figure 3. Ba/Ca ratios (in mg/g) of the soil cation exchange pool, leaves of deciduous trees, caterpillars, snails and the bones and eggshells of Black-throated Blue Warblers analyzed from Hubbard Brook (open symbols) and Downer Forest (closed symbols). The analytical uncertainty of each individual analysis is smaller than the symbol size.

patterns as for strontium and in most instances are equal to or higher than Sr-BPFs. However, strontium displays more systematic behavior than barium and, therefore, strontium appears to be more useful in trophic level studies for distinguishing between food sources of organisms.

Our results demonstrate that biological fractionation of the Sr/Ca ratio can be useful within the context of forest biogeochemical processes. Previous studies have not had sufficiently large data sets to resolve the magnitude of this fractionation across trophic levels (Elias et al. 1982; Åberg et al. 1989; Miller et al. 1993; Bailey et al. 1996). In our study we find that differences in the Sr/Ca ratios between trophic levels are large enough that they may have to be considered in some cases when using the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as a tracer of calcium in ecosystem compartments. For example, because of the importance of canopy leaching in determining throughfall calcium concentration (Bailey

et al. 1996; Likens et al. 1998) we expect that throughfall will have an average Sr/Ca ratio similar to foliage and thus ~50% lower than the soil exchange pool. If a difference in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio between throughfall and soil water were then used to calculate the contribution of strontium from each source to streamflow during a rainfall event, this value calculated for strontium would not be equal to the correct value for calcium. The contribution of calcium from throughfall would be underestimated due to its lower Sr/Ca ratio. By measuring both the Sr/Ca ratio and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of all samples in an ecosystem study the correct contribution of calcium from two endmembers can, however, be calculated.

There has been considerable interest within the field of radioecology in understanding processes related to the introduction of the radionuclide ^{90}Sr (from nuclear fallout) into food webs (e.g., Veresoglou et al. 1995). Extensive studies have been carried out on pasture grasses and grains, which are important pathways for human exposure, but not on forest ecosystems. Based on our results we suggest that ^{90}Sr would not be expected to become concentrated in northern hardwood forest vegetation, insects or animals, because $^{90}\text{Sr}/\text{Ca}$ ratios will behave identically to the Sr/Ca ratios we have measured, and thus will decrease at each successive trophic level. In fact, the 10 to 15-fold biopurification of strontium from calcium that we observed between the soil exchange pool and birds demonstrates a natural mechanism preventing forest animals from accumulating ^{90}Sr .

The high degree of similarity in the biogeochemical behavior of strontium relative to calcium that we observed between Hubbard Brook and Downer Forest, in spite of major differences in soil parent material and soil exchange pool calcium concentration (Table 1), suggests that Sr/Ca ratios may provide a useful tool in studies of modern food webs. For example, it seems likely that Sr/Ca ratios can be used to determine the proportions of an omnivorous animal's diet that is derived from vegetation versus animal sources. Although further work is needed, we also predict that insectivorous insects will also have higher Sr/Ca than herbivorous insects. These types of differences in Sr/Ca ratios may be useful in determining the mix of food types making up the diet of birds and other organisms (e.g., Novoa et al. 1996; Polis & Strong 1996).

Differences in the Sr/Ca ratios of different trophic levels has been used extensively in archeology to determine the degree of herbivory of human paleodiets (e.g., Sillen & Kavanagh 1982; Price et al. 1985; Runia 1987; Sillen 1992). Our study provides information that is relevant to several of the underlying assumptions of these archeological studies. Firstly, a general assumption is often made that biopurification factors for leaves versus soils are close to 1 and display a maximum range from 1 to 1.4 (Runia 1987). We

find that leaves in deciduous northern forests have BPFs between 1.3 and 1.6, slightly higher than the range of values previously reported. Secondly, our measurement of Sr-BPFs between caterpillars and songbirds of 5.5 and 4.6 are consistent with the range of 3 to 6 reported for mammals, and suggests that the dietary consumption of birds will be indistinguishable from consumption of mammals in human paleodietary studies.

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