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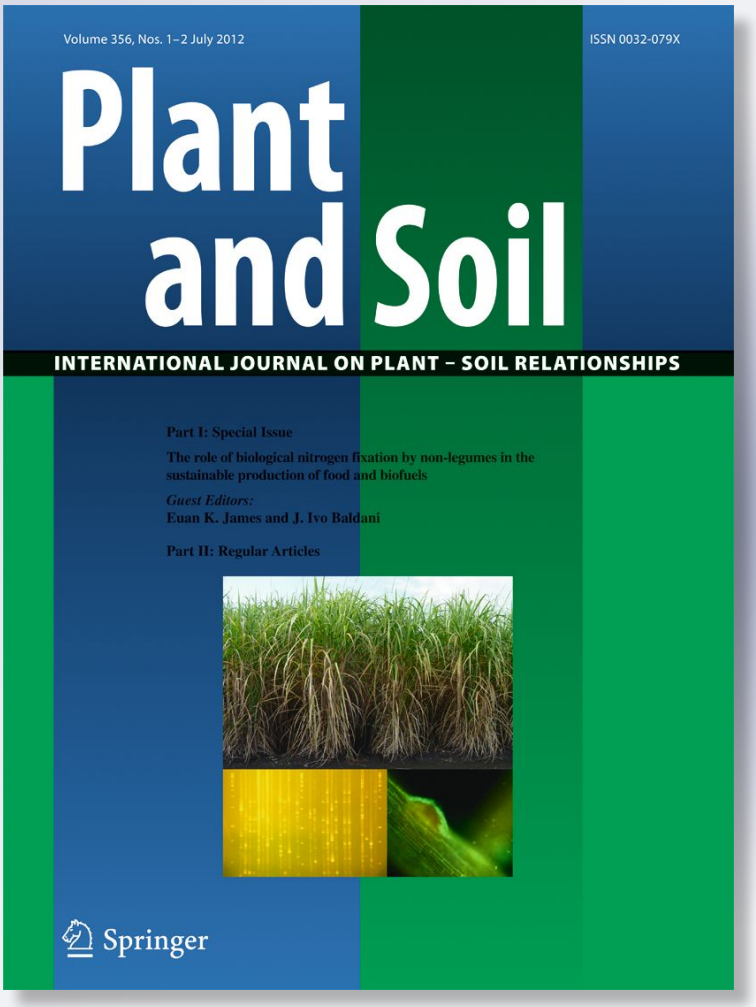


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REGULAR ARTICLE

# Determination of foliar Ca/Sr discrimination factors for six tree species and implications for Ca sources in northern hardwood forests

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**Abstract**
*Background and aims* Discrimination during foliar uptake between the alkaline earth elements Ca and Sr must be understood to fully utilize Ca/Sr and $^{87}Sr/^{86}Sr$ ratios as a monitor of Ca sources to trees. The aim of this study was to determine Ca/Sr discrimination factors [DF = $(Ca/Sr_{plant\ tissue})/(Ca/Sr_{nutrient\ source})$] for six tree species in a northern hardwood forest and use foliar chemistry to consider whether species access measurably different soil reservoirs of Ca and Sr.
*Methods* This was accomplished by measuring the Ca/Sr and $^{87}Sr/^{86}Sr$ ratios of foliage from individual tree species in mixed stands and comparing these ratios to those of soil extracts from soil pits co-located at six sites in the White Mountains, New Hampshire (USA).
*Results* For three species for which DFs have been previously determined, the source of Ca and Sr in foliage can be traced predominantly to recycling of material from organic horizons. Foliar and soil chemistry is consistent with each of the tree species in these six sites deriving Ca and Sr predominantly from the Oie horizon. Thus we can estimate DFs (±1sd) for sugar maple (*Acer saccharum* Marsh.; 1.16±0.13), yellow birch (*Betula alleghaniensis* Britt.; 1.31±0.10), white birch (*Betula papyrifera* Marsh.; 1.30±0.14), pin cherry (*Prunus pensylvanica* L.f.; 1.24±0.09), American beech (*Fagus grandifolia* Ehrh.; 1.78±0.17) and red maple (*Acer rubrum* L.; 1.90±0.15).
*Conclusions* These estimates of discrimination factors allow refinement in the use of Ca/Sr and $^{87}Sr/^{86}Sr$ ratios of foliage to trace Ca sources to plants.

**Keywords** Foliage · Soil · Ca/Sr · $^{87}Sr/^{86}Sr$ · Discrimination factor · Calcium

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## Introduction

Calcium availability can influence a wide range of ecosystem processes (Likens et al. 1998; McLaughlin and Wimmer 1999; Schaberg et al. 2001) including organic matter decomposition (Reich et al. 2005),

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winter frost injury to trees (Hawley et al. 2006), rates of mycorrhizal infection (Juice et al. 2006) and snail abundances (Skeldon et al. 2007). Reports of sugar maple decline in the northern hardwood forest of the northeastern USA (Houston 1999) have been accompanied by observations of Ca deficiency (Mader and Thompson 1969; Kolb and McCormick 1993; Horsley et al. 2000). Depletion of base cations has been inferred to be an impact of acid deposition and forest harvest (Johnson et al. 1992; Federer et al. 1989; Likens et al. 1996), and Ca depletion has been linked to declines in the vigor of some northeastern tree species. Identifying the sources and pathways of Ca cycling in forest ecosystems can advance our understanding of the effects of environmental perturbations and lead to suggestions for methods to mitigate their potential impacts.

Given the importance of Ca to forest ecosystems, refinement of tools that track the sources, pathways and bioavailability of Ca are needed. The trace element Sr, which like Ca is an alkaline earth element, is taken up by plants in similar ways to Ca and can be used to aid in distinguishing among various sources of Ca through the use of Ca/Sr and/or $^{87}Sr/^{86}Sr$ ratios (e.g. Graustein and Armstrong 1983; Gosz and Moore 1989; Åberg et al. 1989; Miller et al. 1993; Bailey et al. 1996; Bélanger and Holmden 2010). Whereas Ca has important physiological functions, Sr is not known to have any function and is believed to be passively taken-up and substituted for Ca (Elias et al. 1982). In some ecosystem processes, such as ion exchange on clays, Ca and Sr behave almost identically (Appelo and Postma 1993) due to their divalent charge and similar hydrated radius ($r_{Ca}$=0.272 nm vs. $r_{Sr}$=0.274 nm; Marcus and Kertes 1968). In other processes, such as ion exchange on soil organic matter, Ca may be retained preferentially over Sr to a small degree (Baes and Bloom 1988; Blum et al. 2008). The $^{87}Sr/^{86}Sr$ ratio varies in different geologically and atmospherically derived materials due to the radioactive decay of $^{87}Rb$ to $^{87}Sr$ over geological timescales. Strontium isotopes do not fractionate significantly upon biological uptake or during ion exchange, and what little fractionation may occur is normalized from the data along with instrumental mass fractionation during analysis (e.g. Blum et al. 2000). Therefore, the $^{87}Sr/^{86}Sr$ ratio provides an unambiguous signal and can be a useful tool for distinguishing among Sr sources, but to make the link between Sr sources and Ca sources requires a detailed knowledge of the behavior of Ca compared to Sr in ecosystem processes.

Many previous studies have explored the use of Ca/Sr and $^{87}Sr/^{86}Sr$ ratios of foliage in forest biogeochemistry. Until recently most studies assumed that the Ca/Sr ratio did not change appreciably upon plant uptake (≤a factor of 1.4) based on studies of nutrient uptake from solution in agricultural plants (Runia 1987), but recent studies have showed more widely variable Ca/Sr ratios within various tree components (Poszwa et al. 2000; Watmough and Dillon 2003; Bullen and Bailey 2005; Beauregard and Côté 2008; Drouet and Herbauts 2008). Studies in a wide range of locations have used $^{87}Sr/^{86}Sr$ ratios to determine Sr sources to foliage and to then infer Ca sources based on the assumption that Ca/Sr discrimination is not large (Dambrine et al. 1997; Poszwa et al. 2002, 2004; Kennedy et al. 2002; Blum et al. 2002; Dijkstra et al. 2003; Drouet et al. 2005; Berger et al. 2006). If Ca/Sr discrimination occurs in plants, then mixing models that determine endmember contributions from Ca/Sr and $^{87}Sr/^{86}Sr$ ratios are inaccurate because the assumption of Ca and Sr mass balance does not hold. In some studies, $^{87}Sr/^{86}Sr$ ratios in soils and trees have been used to constrain sources of Sr from atmospheric deposition and weathering, but were not used to infer Ca sources due to the lack of knowledge of Ca/Sr discrimination (Porder et al. 2005; Bullen and Bailey 2005).

Accurately determining Ca/Sr discrimination in uptake by trees has proven to be challenging because of the wide range of Ca/Sr ratios among soil extracts and soil depths and because of uncertainty as to which sources are accessed by trees and how Ca and Sr are redistributed among various tissues within trees. In a recent paper Drouet and Herbauts (2008) evaluated the discrimination of Ca compared to Sr in 23 stands of European beech (*Fagus sylvatica* L.) and 10 stands of pedunculate oak (*Quercus robur* L.) located throughout Belgium. They found that Ca/Sr discrimination between the exchange fraction of soil organic horizons and bole wood was relatively small, and that most discrimination in trees occurred between the bole and the foliage. They concluded that Ca and Sr behaved similarly in all tree compartments and that there were characteristic discrimination factors for each tree species that did not change appreciably across sites with differing soil Ca status.

Dasch et al. (2006) utilized a whole-watershed $CaSiO_3$ addition experiment to circumvent some of the previously mentioned problems inherent in measuring discrimination factors. Using $CaSiO_3$ as a Ca source (with Ca/Sr and $^{87}Sr/^{86}Sr$ ratio very different from the

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natural nutrient sources to the ecosystem) allowed Dasch et al. (2006) to show that various plant species take up Ca and Sr into foliage in a constant proportion relative to their nutrient source. They determined discrimination factors [DF = $(Ca/Sr_{plant\ tissue})/(Ca/Sr_{nutrient\ source})$] for foliage of sugar maple, yellow birch and American beech, which were found to discriminate for Ca over Sr in foliage (DF=1.14±0.12, 1.16±0.09 and DF=1.9±1.2, respectively. In contrast, Dasch et al. (2006) found that roots of sugar maple, yellow birch and American beech had discrimination factors of less than 1 (DF= 0.60±0.07, 0.70±0.55 and 0.66±0.06, respectively suggesting that there may be little or no net Ca/Sr discrimination between soil Ca and Sr sources and trees as a whole. Indeed wood and roots of many species have been observed to have lower Ca/Sr ratios than foliage (Watmough and Dillon 2003; Drouet and Herbauts 2008).

Dasch et al. (2006) suggested that once the foliar discrimination factor is empirically determined for a species using a tracer application, Ca/Sr ratios could be used in conjunction with $^{87}Sr/^{86}Sr$ ratios to determine the sources of Ca found in that species. However, that experiment included only three tree species, and only two of them took up Ca rapidly enough to allow determination of the DF with sufficient precision to be useful in the time-frame of that study. Estimating the discrimination between Ca and Sr during plant uptake for a larger number of species is needed to facilitate the wider application of Ca/Sr and $^{87}Sr/^{86}Sr$ ratios as ecosystem tracers to aid in the understanding of Ca biogeochemistry (Dasch et al. 2006; Drouet and Herbauts 2008).

In a recent study we (Blum et al. 2008) utilized the sugar maple DF determined by Dasch et al. (2006) to explore which soil cation reservoirs contributed Ca and Sr to sugar maple foliage in six forest stands in the White Mountains of New Hampshire (USA). At each of the sites, on the time-scale of annual uptake, we found the dominant source of Ca and Sr to sugar maple foliage to be the decomposition and recycling of Ca from organic horizons. The Ca/Sr and $^{87}Sr/^{86}Sr$ ratios of sugar maple foliage could be explained with the Oie horizon as the dominant source for this annual uptake, with the possibility that lesser amounts of Ca were contributed by the Oa horizon. The comparison of $^{87}Sr/^{86}Sr$ ratios of sugar maple foliage with a variety of soil extracts and atmospheric deposition showed that on the longer timescale of forest Ca-pool development (thousands of years), $^{87}Sr/^{86}Sr$ in foliage and the Oie horizon was always intermediate between mineral soil-weathering and atmospheric values, confirming that these are the two important sources of Sr to the foliage and in turn to the Oie horizon, which is largely derived from foliage litter. Comparison of soil extract and foliar Ca/Sr and $^{87}Sr/^{86}Sr$ also showed that the variation in foliar Ca/Sr and $^{87}Sr/^{86}Sr$ across the sites was controlled largely by differences in soil parent material Ca/Sr and $^{87}Sr/^{86}Sr$.

In another study conducted in the White Mountains of New Hampshire (USA), Fahey and Blum (2011) utilized a forest floor transplant experiment to show the importance of the Oie horizon in the nutrition of sugar maple seedlings. The sites investigated by Fahey and Blum (2011) and Blum et al (2008) have thick organic horizons (5–15 cm) due to slow decomposition in the cool climate and to a lack of earthworms (Schaller et al. 2010). Under these conditions the organic horizons represent a large pool of Ca through which the majority of Ca taken up by trees is recycled (Likens et al 1998).

In the study reported here we provide analyses of $^{87}Sr/^{86}Sr$ in foliage collected in 2003, and Ca/Sr in foliage collected in both 2003 and 2004, for six tree species at the same six sites studied by Blum et al. (2008). We compare foliar chemistry with previously published data for soil exchangeable cation chemistry (Blum et al. 2008; for soil samples collected in 2003) to gain insight into the sources of Sr and Ca for these species. Using DFs determined for sugar maple, yellow birch and American beech from a fertilization experiment (Dasch et al. 2006), we evaluate the soil sources of Ca and Sr to these species. We then revise our estimates of DFs for these three species and for the first time provide estimates of DF values for three additional species; white birch, pin cherry and red maple. The values we have determined for DFs will be beneficial for future studies of Ca acquisition in forests where any of the six tree species studied are present and provides a means for relating Ca/Sr and $^{87}Sr/^{86}Sr$ in potential soil reservoirs to foliar values.

## Materials and methods

### Study sites

This study was conducted at six northern hardwood stands in the White Mountains National Forest, New Hampshire (USA). Three of the six stands (H1, H4, and H6) are located within 2 km of each other in the

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Bartlett Experimental Forest, and the remaining three stands are located 20 km north (M5), 14 km southwest (M6), and 11 km north-northeast (T30) of the Bartlett Experimental Forest (see Blum et al. 2008 for map of study sites). The six stands range in age (the time between cutting and sample collection) from 13 to 66 years and are under study to investigate nutrient cycling as a function of stand age following forest harvest (Hamburg et al. 2003; Yanai et al. 2000, 2006). Due to differences in successional status, species composition varies among the stands (Yanai et al. 2000), but each stand includes sugar maple (*Acer saccharum* Marsh.; SM), American beech (*Fagus grandifolia* Ehrh.; BE), yellow birch (*Betula alleghaniensis* Britt.; YB), white birch (*Betula papyrifera* Marsh.; WB), and red maple (*Acer rubrum* L.; RM). Younger stands also include pin cherry (*Prunus pensylvanica* L.f.; PC), an early-successional species.

The climate is humid-continental with a mean annual temperature of 5°C and annual precipitation of ~1,400 mm (Bailey et al. 2003). Soils are coarse-loamy, mixed, frigid, Typic Haplorthods (Spodosol) developed on glacial till derived from local igneous and metamorphic bedrock (Nezat et al. 2004, 2007; Schaller et al. 2010). The Oie horizon was distinguished as undecomposed or moderately decomposed organic matter and ranged from 1 to 12 cm in thickness. The Oa horizon was distinguished by decomposed (sapric) organic matter and ranged from 1 to 15 cm in thickness. Combined organic soil horizons (Oie and Oa) were 5–15 cm in thickness in these six sites and overlie mineral soils that are 48–82 cm in thickness (Yanai et al. 2006; Schaller et al. 2010). The slopes at the study sites range between 3% and 20% and elevations range from 320 to 550 m. No earthworms were observed in any of the soil pits excavated (Schaller et al 2010) and this may help explain the absence of short-term mixing of soils in the region (Kaste et al. 2007).

### Foliage collection and processing

In October 2003 and November 2004, recently fallen leaves were collected before they contacted the forest floor either in plastic litter baskets (2003) or onto plastic tarps (2004) spaced along 5 transects at each site. Leaves were separated by species to form a single composite sample for each species at each site, oven dried at 60°C and then finely ground to increase sample homogeneity and facilitate digestion. Approximately 0.5 g of each foliage sample was digested in ultra-pure distilled $HNO_3$ and HCl using high-pressure microwave digestion in reinforced XP-1500 Teflon vessels (MARS 5, CEM Corporation, Matthews, NC), evaporated to dryness, and re-dissolved in ultra-pure 5% $HNO_3$ acid for analysis. Data from Blum et al. (2008) that are used in this study include analyses of Oie horizons digested following the same procedure as for foliage, and the soil exchange fraction was extracted from 0.5 g soil samples in 5 ml of 1 M $NH_4Cl$ for 20 h.

### Chemical analyses

Elemental concentrations were measured using an inductively coupled plasma optical emission spectrometer (ICP-OES; PE-3300DV, Perkin Elmer, Norwalk, CT). Five- to eight-point linear calibration curves had $R^2$ values greater than 0.9999. One in-house standard and two High-Purity® solutions (Trace Metals in Drinking Water and CRM Soil Solution A) were analyzed for quality control before and after each 10-sample sequence. Analyses agreed with certified values to within ±5%.

Strontium isotope ratios were determined on aliquots of Sr separated from each of the 2003 samples using cation exchange chromatography, with a thermal ionization mass spectrometer (TIMS, MAT-262, Finnigan, Bremen, Germany). Methods of chemical separation and isotope ratio measurement of Sr were described in detail by Dasch et al. (2006). Between 100 and 200 isotope ratios were measured for each sample, yielding a mean $^{87}Sr/^{86}Sr$ ratio with an analytical uncertainty of less than ±0.000030 (±2σ). Repeated measurements of NBS-987 during the period of analysis resulted in a mean $^{87}Sr/^{86}Sr$ value of 0.710237±0.000025 (±2σ, $n$=138).

## Results

### $^{87}Sr/^{86}Sr$ ratios in foliage

The $^{87}Sr/^{86}Sr$ ratio of 2003 foliage for all species across the six stands ranged from 0.7135 to 0.7215 (Table 1, Fig. 1). There was generally a narrower range in $^{87}Sr/^{86}Sr$ ratios among species at each site compared to the differences across sites for each

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species. There was no consistent trend across sites of higher or lower $^{87}Sr/^{86}Sr$ for particular tree species. Some sites displayed very little range in $^{87}Sr/^{86}Sr$ among species (<0.00025; T30, M5) compared to higher variation among species at other sites (>0.00055; H1, H4, H6, M6). The order of sites by increasing average foliar $^{87}Sr/^{86}Sr$ was H4, H6, T30, M5, H1, M6 and does not correlate with stand age (Table 1, Fig. 1).

### Ca and Sr concentrations and Ca/Sr ratios in foliage

The Ca concentration in foliage across the six stands and two years of observation ranged from 7.27 to 17.0 mg/g and the Sr concentrations ranged from 14.8 to 145 μg/g (Table 1). In order to reduce some of the variability associated with spatial heterogeneity and year to year climate differences we averaged the concentrations for each tree species within each site for the years 2003 and 2004, resulting in Ca concentrations of 7.50–16.1 mg/g and Sr concentrations of 15.4–130 μg/g. The average Ca concentrations in foliage for each species across the six sites was: SM (11.0±2.2 mg/g, 1sd); YB (12.8±1.6 mg/g, 1sd); WB (10.2±1.2 mg/g, 1sd); PC (12.8±2.1 mg/g, 1sd); BE (8.60±1.0 mg/g, 1sd); and RM (12.8±1.5 mg/g, 1sd). The average Sr concentrations in foliage for each species across the six sites was: SM (59.2±41.6 μg/g, 1sd); YB (58.7±36.6 μg/g, 1sd); WB (47.5±30.9 μg/g, 1sd); PC (59.1±39.1 μg/g, 1sd); BE (29.7±19.3 μg/g, 1sd); RM (37.4±25.2 μg/g, 1sd). The percent standard deviation relative to the mean Ca concentration varied by species from 12.1% (WB) to 19.9% (SM) and for Sr concentrations from 62.3% (YB) to 70.2% (SM).

The Ca/Sr molar ratio of averaged 2003 and 2004 foliage across the six stands ranged from 241 to 1227 (Table 1; Fig. 2). Based on the summary of Ca and Sr concentrations given above it is clear that variation in Sr concentrations dominates over variation in Ca in controlling Ca/Sr ratios of foliage. This is consistent with trees requiring a somewhat fixed amount of Ca in foliage to fulfill physiological functions, and control mechanisms to avoid excess Ca accumulation. In contrast, Sr has no known physiological role and exhibits much wider variations in concentration. In general, within sites SM had the lowest Ca/Sr, YB, WB and PC were intermediate, and BE and RM were highest (Fig. 2). The order of sites with increasing Ca/Sr in SM foliage and the Oie horizon is T30, M5, H6, H4, H1, M6. Ca/Sr ratios at the various sites do not correlate with stand age (Table 1).

## Discussion

### $^{87}Sr/^{86}Sr$ ratios in foliage and soils

The $^{87}Sr/^{86}Sr$ ratios of the Oie digest and soil cation exchange fractions for the same sites from which we report foliage values were published by Blum et al. (2008) and are plotted on Fig. 1 for comparison with foliage values. There is a strong correlation between the average $^{87}Sr/^{86}Sr$ ratios of the soil exchange fractions and the site average for foliage from trees at the same sites ($R^2=0.98$; $p<0.01$). At the two sites that had the least variability in foliar $^{87}Sr/^{86}Sr$ (T30 and M5) we also observe the least variability in $^{87}Sr/^{86}Sr$ with depth in soils (Fig. 1), suggesting a lesser degree of spatial heterogeneity in soil $^{87}Sr/^{86}Sr$ at these sites. At sites H6 and H1 foliage from some species have lower $^{87}Sr/^{86}Sr$ than any of the soil pools (Fig. 1). This is likely the result of spatial heterogeneity in the forest which results in differences in the $^{87}Sr/^{86}Sr$ of the rooting environment of the trees that contributed leaf samples, compared to the three locations at which soil pits were located. There are also a few anomalous foliage values that we also attribute to heterogeneity within sites, such as the BE sampled at site H6, which has lower $^{87}Sr/^{86}Sr$ than the soils and other tree species sampled at site H6 (Fig. 1). Sr isotopes do not allow distinction among Oie, Oa and mineral soil horizon exchange pools as Sr sources for the trees at these sites. Mineral soil acid extracts at each of these sites have $^{87}Sr/^{86}Sr$ ratios much higher than the soil exchange complex and the soil organic horizons (>0.01 higher), suggesting that the exchange pool and organic horizon $^{87}Sr/^{86}Sr$ values are explained by a mixture of mineral derived Sr (higher $^{87}Sr/^{86}Sr$) with atmospherically derived Sr (lower $^{87}Sr/^{86}Sr$) (Blum et al. 2008).

### Ca and Sr concentrations and Ca/Sr ratios in foliage and soils

The Ca/Sr ratios of the soil cation exchange fractions for these sites sampled in 2003 (Blum et al. 2008) are plotted on Fig. 2 for comparison with averaged 2003

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**Table 1** $^{87}Sr/^{86}Sr$ ratios, Ca and Sr concentrations, and Ca/Sr ratios for tree foliage, Oie horizon soil digests and soil exchange fractions of the Oa, 0–10 cm mineral soil and 10–20 cm mineral soil horizons (exch). Abbreviations for tree species are given in the text. Soil data and 2003 SM foliar data was previously published in Blum et al. (2008)

| Year | | 2003 | 2003 | 2003 | 2003 | 2004 | 2004 | 2004 |
|---|---|---|---|---|---|---|---|---|
| Sample Type | Site (age in years) | $^{87}Sr/^{86}Sr$ | Ca mg/g | Sr μg/g | Ca/Sr mol/mol | Ca mg/g | Sr μg/g | Ca/Sr mol/mol |
| | H6 (16 year) | | | | | | | |
| Foliage | | | | | | | | |
| SM | | 0.714385 | 12.1 | 51.2 | 517 | 13.1 | 56.9 | 503 |
| YB | | 0.714420 | 12.2 | 42.4 | 629 | 13.5 | 45.3 | 651 |
| WB | | 0.714596 | 9.86 | 32.8 | 657 | 9.95 | 40.2 | 541 |
| PC | | 0.714259 | 12.6 | 45.3 | 608 | 12.2 | 44.2 | 603 |
| BE | | 0.713511 | 8.63 | 18.7 | 1010 | 8.78 | 27.2 | 706 |
| RM | | 0.715109 | 12.2 | 28.8 | 927 | 11.3 | 26.5 | 932 |
| Soil | | | | | | | | |
| Oie digest | | 0.714985 | 10.2 | 46.6 | 478 | | | |
| Oa exch | | 0.714738 | 1.86 | 11.7 | 348 | | | |
| 0–10 cm exch | | 0.715089 | 0.228 | 1.81 | 275 | | | |
| 10–20 cm exch | | 0.714707 | 0.095 | 0.82 | 253 | | | |
| | M6 (21 year) | | | | | | | |
| Foliage | | | | | | | | |
| SM | | 0.720023 | 9.46 | 24.2 | 856 | 8.32 | 17.8 | 1017 |
| YB | | 0.720248 | 10.3 | 24.4 | 924 | 14.4 | 33.4 | 937 |
| WB | | 0.720155 | 8.98 | 18.8 | 1046 | 10.3 | 20.9 | 1073 |
| PC | | 0.720154 | 9.82 | 25.6 | 837 | 12.2 | 32.7 | 816 |
| BE | | 0.720414 | 8.10 | 14.8 | 1199 | 8.39 | 16.3 | 1119 |
| RM | | 0.720580 | 12.2 | 21.5 | 1239 | 12.5 | 22.5 | 1213 |
| Soil | | | | | | | | |
| Oie digest | | 0.720765 | 8.7 | 28.5 | 667 | | | |
| Oa exch | | 0.720086 | 1.45 | 6.25 | 507 | | | |
| 0–10 cm exch | | 0.720541 | 0.11 | 0.52 | 460 | | | |
| 10–20 cm exch | | 0.721403 | 0.084 | 0.45 | 411 | | | |
| | MS (24 year) | | | | | | | |
| Foliage | | | | | | | | |
| SM | | 0.717713 | 13.3 | 102.4 | 284 | 9.84 | 69.3 | 310 |
| YB | | 0.717568 | 16.2 | 112.8 | 314 | 15.9 | 108 | 322 |
| WB | | 0.717661 | 10.5 | 69.8 | 329 | 13.2 | 86.8 | 332 |
| PC | | 0.717812 | 13.1 | 91.5 | 313 | 17.0 | 115 | 323 |
| BE | | 0.717722 | 9.55 | 46.2 | 452 | 10.4 | 51.6 | 441 |
| RM | | 0.717803 | 13.8 | 62.1 | 486 | 11.9 | 49.9 | 521 |
| Soil | | | | | | | | |
| Oie digest | | 0.717907 | 12.9 | 111.9 | 252 | | | |
| Oa exch | | 0.717630 | 1.40 | 16.0 | 191 | | | |
| 0–10 cm exch | | 0.717686 | 0.26 | 2.91 | 198 | | | |
| 10–20 cm exch | | 0.717718 | 0.11 | 1.23 | 195 | | | |
| | T30 (53 year) | | | | | | | |
| Foliage | | | | | | | | |
| SM | | 0.715588 | 15.4 | 144.5 | 233 | 13.2 | 115 | 251 |
| YB | | 0.715518 | 10.9 | 89.6 | 266 | 13.6 | 111 | 268 |
| WB | | 0.715578 | 10.9 | 89.9 | 265 | 12.2 | 98.5 | 271 |

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**Table 1** (continued)

| Year | | 2003 | 2003 | 2003 | 2003 | 2004 | 2004 | 2004 |
|---|---|---|---|---|---|---|---|---|
| Sample Type | Site (age in years) | $^{87}Sr/^{86}Sr$ | Ca mg/g | Sr μg/g | Ca/Sr mol/mol | Ca mg/g | Sr μg/g | Ca/Sr mol/mol |
| BE | | 0.715559 | 9.16 | 56.2 | 356 | 10.4 | 62.1 | 366 |
| RM | | 0.715423 | 12.3 | 74.3 | 362 | 14.5 | 86.0 | 369 |
| Soil | | | | | | | | |
| Oie digest | | 0.715606 | 9.8 | 95.2 | 225 | | | |
| Oa exch | | 0.715595 | 1.43 | 16.0 | 195 | | | |
| 0–10 cm exch | | 0.715569 | 0.18 | 2.76 | 144 | | | |
| 10–20 cm exch | | 0.715678 | 0.065 | 0.95 | 149 | | | |
| | H1 (62 year) | | | | | | | |
| Foliage | | | | | | | | |
| SM | | 0.717422 | 10.9 | 39.6 | 601 | 8.08 | 26.8 | 659 |
| YB | | 0.717723 | 10.1 | 29.4 | 752 | 13.7 | 39.0 | 768 |
| WB | | 0.718028 | 8.29 | 23.9 | 757 | 9.37 | 26.7 | 767 |
| BE | | 0.717863 | 7.74 | 15.8 | 1068 | 7.56 | 14.9 | 1109 |
| RM | | 0.718158 | 9.80 | 19.2 | 1116 | 8.72 | 17.3 | 1102 |
| Soil | | | | | | | | |
| Oie digest | | 0.719075 | 10.4 | 39.9 | 570 | | | |
| Oa exch | | 0.718365 | 1.42 | 7.25 | 428 | | | |
| 0–10 cm exch | | 0.718958 | 0.100 | 0.58 | 374 | | | |
| 10–20 cm exch | | 0.719372 | 0.372 | 3.85 | 211 | | | |
| | H4 (66 year) | | | | | | | |
| Foliage | | | | | | | | |
| SM | | 0.714186 | 9.91 | 34.0 | 637 | 8.33 | 28.3 | 643 |
| YB | | 0.714482 | 10.1 | 30.5 | 725 | 12.9 | 38.7 | 729 |
| WB | | 0.713994 | 8.99 | 30.7 | 641 | 9.66 | 31.4 | 673 |
| BE | | 0.714456 | 7.75 | 17.8 | 952 | 7.27 | 15.2 | 1046 |
| RM | | 0.714873 | 12.0 | 22.6 | 1160 | 9.36 | 17.5 | 1169 |
| Soil | | | | | | | | |
| Oie digest | | 0.714380 | 10.6 | 42.9 | 540 | | | |
| Oa exch | | 0.714475 | 1.75 | 7.94 | 482 | | | |
| 0–10 cm exch | | 0.714198 | 0.128 | 0.74 | 376 | | | |
| 10–20 cm exch | | 0.715126 | 0.463 | 3.08 | 329 | | | |

and 2004 foliage values. The Ca/Sr ratio of the exchange complex decreases with depth at each site and this is likely due to preferential retention of Ca on the organic horizon exchange sites (Blum et al. 2008). As the soil Oie horizon Ca/Sr ratio increases from one site to the next, the Ca/Sr ratio of the foliage of each species increases and the difference in Ca/Sr between species also increases.

The ratio of the Ca/Sr ratios between the SM and Oie (the discrimination factor; DF) remains nearly constant across sites ($n$=6) with an average value of 1.16±0.13 (1sd), which is within the uncertainty of the DF for SM of 1.14±0.12 (1sd) measured by Dasch et al. (2006). The ratio of the Ca/Sr ratios between the SM and Oa also remains constant across the sites, but if the Oa is assumed to be the sole source of Ca and Sr to SM foliage the DF that results is 1.50±0.20 (1sd), which is considerably higher than the DF for SM of 1.14±0.12 (1sd) measured by Dasch et al. (2006). Blum et al. (2008) used the agreement in the DF value calculated between SM and Oie with the Dasch et al. (2006) value to argue that the Oie was the dominant source of Ca and Sr to SM foliage on the timescale of annual uptake. There is likely an additional contribution to plant uptake of Ca from

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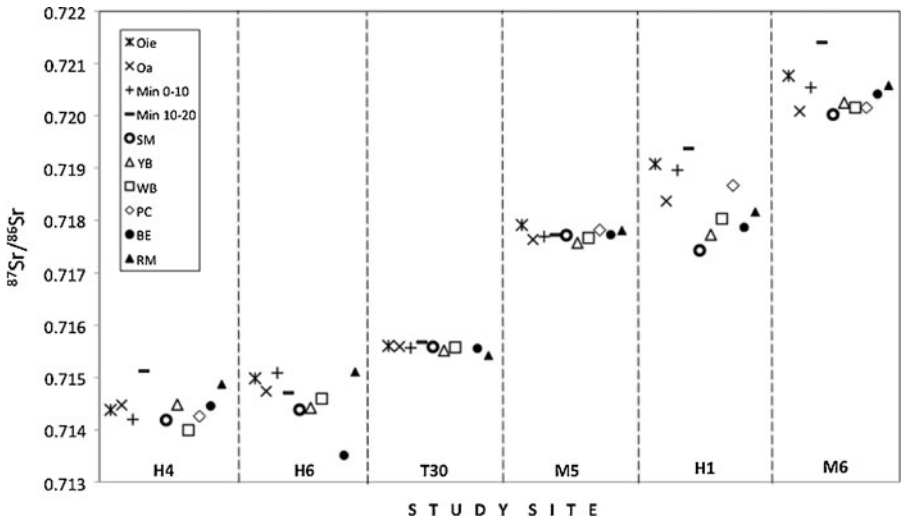


**Fig. 1** The $^{87}Sr/^{86}Sr$ ratio of Oie total digest, the exchange fraction of the Oa, mineral soil 0–10 cm and mineral soil 10–20 cm, and foliage (collected in 2003) from six tree species are plotted for each of six northern hardwood forest study sites in order of increasing site $^{87}Sr/^{86}Sr$. The $^{87}Sr/^{86}Sr$ ratio of the soil Oie and exchange pool is generally reflected in the $^{87}Sr/^{86}Sr$ ratio of vegetation at each site

other horizons, but based on the Ca/Sr ratio this is inferred to be small (Fig. 3), and certainly less that 50% (Blum et al. 2008). A study of rooting depths at the same sites investigated in this study (Yanai et al. 2006) showed that rooting density decreased with depth and that the combined Oie and Oa horizons contained 31% of total root biomass and 34% of fine-root (<2 mm) biomass. Whereas deeper roots may be more important for water acquisition, shallow roots appear to be more important for Ca and Sr acquisition.

Similarly to SM, the ratio of the Ca/Sr ratio of each of the other five tree species to the Ca/Sr ratio of the Oie also remains nearly constant across a wide range of Oie Ca/Sr values, but with different values for each of the different species. The relationship between the ratio of Ca/Sr in foliage of each species and Ca/Sr in the Oie is illustrated graphically by plotting the Ca/Sr ratio of the 2003 and 2004 averaged foliage versus the Ca/Sr ratio of the Oie at each site (Fig. 3). Foliage from each of the six species during each year of

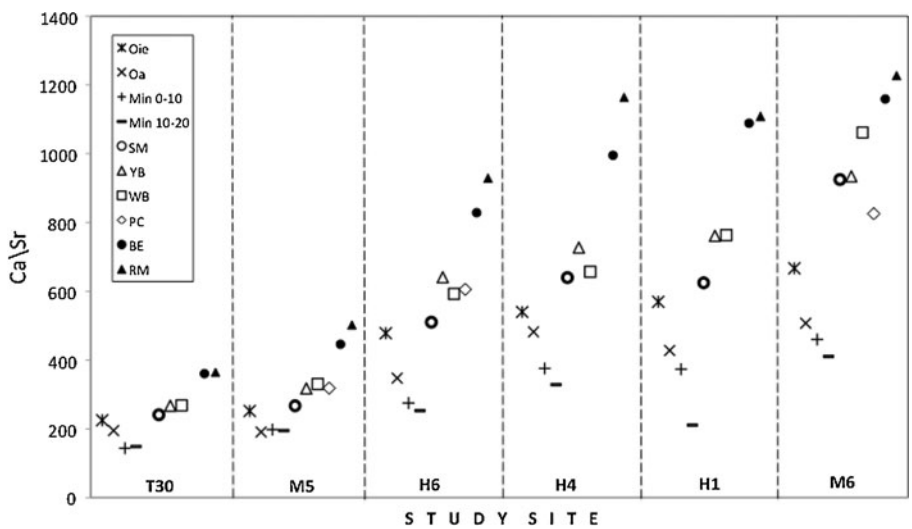


**Fig. 2** The molar Ca/Sr ratio of Oie total digest, the exchange fraction of the Oa, mineral soil 0–10 cm and mineral soil 10–20 cm, and foliage (the average for collected in 2003 and 2004) from six tree species are plotted for each of the six study sites in order of increasing site Ca/Sr. The Ca/Sr ratio of the soil Oie and exchange pool is generally reflected in the Ca/Sr ratio of vegetation at each site. The order of the Ca/Sr ratio among sample types at each site remains nearly constant, but the range of Ca/Sr ratios between sample types increases with increasing Oie Ca/Sr from site to site

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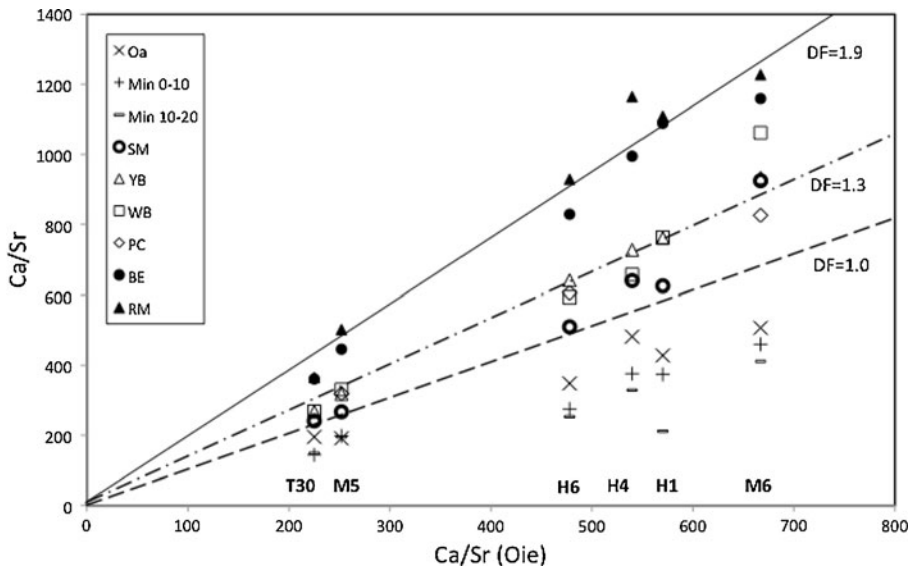


**Fig. 3** The molar Ca/Sr ratio of Oie total digest at each site plotted against the Ca/Sr ratio of the exchange fraction of the Oa, mineral soil 0–10 cm and mineral soil 10–20 cm, and foliage (average of 2003 and 2004) from six tree species. Also plotted is a dashed line with a slope of 1.0, a dash-dot line with a slope of 1.3 and a solid line with a slope of 1.9 for reference. If the Oie represents the nutrient source for foliage (as argued in the text) then the slopes for each tree species plotted versus the Oie will be equivalent to discrimination factors

collection defines a linear array when plotted against the Ca/Sr of the Oie (Fig. 3). If one assumes that the Oie is the dominant source of Ca and Sr to foliage on an annual basis, then these slopes are equivalent to DFs for each species. Lines with slopes corresponding to DF values of 1.0, 1.3 and 1.9 are, therefore, plotted on Fig. 3 as reference values for comparison with foliage. The mean and standard deviation of the DFs calculated at each site for each year and for the 2 years combined are shown on Table 2. Dasch et al. (2006) determined DFs (±1sd) for three of these species using a tracer experiment that yielded values of 1.14±0.12 for SM, 1.16±0.06 for YB, and 1.9±1.2 for BE. The DF values of Dasch et al. (2006) can be compared to those derived from this study (for 2003, 2004 and the 2 years combined), which are based on the assumption that the Oie as the sole nutrient source for the three tree species that are in common between the studies (Table 1). The DFs for SM and BE are in close agreement between the two studies as indicated by unpaired t-tests ($p$=0.72 and $p$=0.18, respectively), yet YB values are distinct ($p$=0.03). Contribution of Ca and Sr from deeper soil cation exchange pools does not provide an explanation for the somewhat differing YB foliar DF value because deeper soil pools have lower, rather than higher, Ca/Sr. One possible explanation for the discrepancy in the DF for YB is that the determination of DFs by Dasch et al. (2006) used overstory leaves sampled from the canopy and the determination in this study used freshly fallen leaves that had not contacted the forest floor. In Blum et al. (2008) we addressed this issue by comparing the Ca/Sr ratios of

**Table 2** Mean and standard deviation (in parentheses) of Ca/Sr discrimination factors (DF) for foliage of six species (abbreviations given in text) collected in 2003, 2004 and averaged for 2003 and 2004, from six northern hardwood forest sites in the White Mountains of NH. These values are based on the assumption that the Oie horizon is the sole Ca source to trees. Values based on the average foliar values for 2003 and 2004 ($n$=6 stands) are given in bold and are the recommended values. DF estimates from the tracer experiment of Dasch et al. (2006) are given for comparison. These values do not rely on any assumptions concerning the soil source of Ca

| Species | DF 2003 | DF 2004 | DF '03+ '04 | DF (Dasch et al) |
|---|---|---|---|---|
| SM | 1.13 (0.09) | 1.19 (0.19) | **1.16 (0.13)** | 1.14 (0.12) |
| YB | 1.33 (0.13) | 1.29 (0.08) | **1.31 (0.10)** | 1.16 (0.06) |
| WB | 1.32 (0.14) | 1.28 (0.18) | **1.30 (0.14)** | |
| PC | 1.26 (0.02) | 1.21 (0.03) | **1.24 (0.09)** | |
| BE | 1.82 (0.17) | 1.73 (0.39) | **1.78 (0.17)** | 1.9 (1.2) |
| RM | 1.91 (0.18) | 1.89 (0.20) | **1.90 (0.15)** | |

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overstory YB leaves and fresh litterfall at a single site near the H1, H4 and H6 sites studied in this investigation. Based on an average of six overstory and eight fresh litter samples we found that YB overstory had a mean Ca/Sr ratio that was 8% lower than fresh litter. Although we do not have enough data to know if this result is generally applicable, it would have the effect of shifting the YB DF value determined by Dasch et al. (2006) from 1.16±0.06 (1sd) to a value of 1.25±0.06 (1sd), which decreases by half the difference between the Dasch et al. (2006) value and the value of 1.31±0.10 (1sd) determined here. Other possible explanations are that DFs differ somewhat between sites for YB for reasons we have not yet identified, or that either our methodology, or that of Dasch et al. (2006), somewhat underestimated uncertainties in the DF values.

Based on general agreement in DFs from Dasch et al. (2006) and this study we conclude that for SM, YB and BE, the dominant source of Ca and Sr to foliage on the timescale of annual uptake at each study site is the Oie horizon. If we assume that the other tree species have the same soil source, then we can calculate DFs for the additional species WB, PC and RM at each of the six sites. As there are not yet any determinations of DF for these species using tracer experiments, the estimates made here should be verified with tracer experiments, but they are currently the best available for WB, PC and RM. We point out that the ratio of the Ca/Sr of WB, PC and RM litter to the Ca/Sr of the Oie horizon during both 2003 and 2004 is nearly constant at each site (±~10% relative sd), and this observation strengthens further the argument that the Oie is indeed the dominant source of Ca to WB, PC and RM. The average and standard deviation for the DFs calculated based on this assumption and the combined 2003 and 2004 foliar data are recommended as DF values for these species (Table 2).

The mechanism for Ca/Sr discrimination in trees is not known in detail but Drouet and Herbauts (2008) and Gierth et al. (1998) argued that discrimination occurs in the passage of Ca and Sr through the endodermis that separates conducting vessels from the leaf mesophyll. Discrimination between Ca and Sr may also occur by ion exchange processes during ascent in the xylem (Clarkson 1984) or by preferential binding of Ca in Ca-oxalate precipitated in bark or other tree tissues (Gulpin et al. 1995). Whatever the Ca/Sr discrimination mechanism(s) is, it is notable that it is more prominent in American beech and red maple compared to the other species that we have studied and suggests there are physiological differences in these species that lead to greater Ca/Sr discrimination.

## Conclusions and implications

This study is a follow-up to a study of the Ca/Sr and $^{87}Sr/^{86}Sr$ ratios of soils and sugar maple foliage at the same six study sites discussed herein (Blum et al. 2008). In that paper it was concluded that the dominant source of Ca on an annual basis to sugar maple foliage was recycling from the Oie horizon, which is composed largely of foliar litterfall and lesser amounts of root turnover and inputs of coarse woody debris. The present study extends the previous finding for sugar maple to yellow birch and American beech and suggests that the finding is also applicable to white birch, pin cherry and red maple, because all six species have consistent ratios of Ca/Sr in leaves compared to the Oie horizon. It is important to keep in mind, however, that on the longer timescale of the development of soil Ca pools (thousands of years), the primary source of Ca and Sr in the organic soil horizons and mineral soil exchange pool is a combination of weathering derived and atmospherically derived Ca and Sr (Blum et al. 2008).

The most significant new finding of this work is the first determination of foliar Ca/Sr discrimination factors for white birch, pin cherry and red maple, and confirmation of DFs for sugar maple, yellow birch and American beech by an independent method. We have also demonstrated that sugar maple, yellow birch and American beech growing on Spodosols, which retain large stores of Ca in organic soil horizons, do not derive a large proportion of new Ca from mineral soil horizons on an annual basis, consistent with our previous mass balance calculation (Blum et al. 2008). However, this is not the case for trees growing on many other soil types (Drouet et al. 2005, 2007; Dambrine et al. 1997; Poszwa et al. 2004) and better knowledge of DFs for a wide range of tree species should allow better estimates of the depth of Ca acquisition from soils using Ca/Sr and $^{87}Sr/^{86}Sr$ ratios of foliage. Of particular interest would be comparisons of the depth of Ca acquisition for tree species reported here from sites with and without a well-developed O horizon (eg, Lucash et al. in press). Such comparisons may help

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us to understand the implications of shifts in soil nutrient distribution resulting from factors such as changing land-use, introduction of earthworms, agricultural practices, loses of tree species due to pests, and changing soil pH as a result of acid deposition.

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