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Calcium inputs and transport in a base-poor forest ecosystem as interpreted by Sr isotopes

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Abstract. Depletion of Ca in forests and its effects on forest health are poorly quantified. Depletion has been difficult to document due to limitations in determining rates at which Ca becomes available for ecosystem processes through weathering, and difficulty in determining changes in ecosystem storage. We coupled a detailed analysis of Sr isotopic composition with a mass balance at Cone Pond Watershed, New Hampshire, in order to further constrain estimates of these processes. Strontium acted as an analog for Ca in most processes except translocation of nutrients within forest vegetation. Variability in mineralogic and Sr isotopic composition of bedrock and soils complicated assessment of the $^{87}Sr/^{86}Sr$ ratio released to solution by weathering reactions. By conducting a mass balance on atmospherically derived Ca, it is possible to distinguish Ca weathering losses from Ca leached from ecosystem pools. The calcium weathering rate estimated by this method was less than half of that determined by mass balance assuming steady state conditions.

Introduction

Acidification of surface waters and decline in forest health may result from depletion of basic cations (Ca, Mg, Na, K) in available pools in forest ecosystems [*Tomlinson*, 1990; *A. H. Johnson et al.*, 1992]. Strong acids in precipitation may facilitate the release of basic cations from forest soils, enhancing leaching losses in drainage waters. In most ecosystems, precipitation supplies only a small fraction of Ca inputs [*Likens et al.*, 1977]. When the supply of basic cations from weathering is insufficient to neutralize acid inputs, acidification of soil and surface waters occurs [*Reuss and Johnson*, 1985]. Calcium depletion may result in declines in forest health, including a decrease in cold hardiness [*DeHayes*, 1992]. Increases in Al to Ca ratios in soil are associated with an inhibition of Ca uptake [*Shortle and Smith*, 1988]. Given increasing nitrogen deposition in many temperate ecosystems, Ca depletion could result in Ca replacing nitrogen as the limiting element for tree growth on sensitive sites.

Large areas in the eastern United States are at risk with respect to the depletion of basic cations [*Galloway and Cowling*, 1978; *Federer et al.*, 1989]. In regions where silicate weathering is dominant, weathering inputs may not be sufficient to replace the accelerated losses of basic cations associated with disturbances such as acidic deposition or intensive forest harvest. However, a complete assessment of the problem, as well as the need to develop air pollution emission control strategies to lessen leaching of Ca, requires a determination of rates at which lost Ca is replaced by weathering. Unfortunately, direct measurement of mineral weathering is problematic [*Drever*, 1982]. Although weathering processes have been generally understood for some time, specific mechanisms and rates in the field remain difficult to determine [*Cronan*, 1985; *Schott and Petit*, 1987]. Furthermore, mass balance studies, typically used to quantify basic cation inputs to, and losses from forested ecosystems [*Likens et al.*, 1977], are limited in their ability to document the sources of leaching losses which may be derived from atmospheric inputs, mineral weathering reactions, or decreases in ecosystem pools, including biomass, forest floor, and the soil cation exchange complex.

Background

To circumvent the difficulties in direct measurement of weathering, we used the Sr isotope method to further define basic cation inputs and transport in a forest ecosystem. Strontium acts as an analog to Ca because both are alkaline earth elements with similar ionic radius and the same valence [*Elias et al.*, 1982; *Jacks et al.*, 1989]. Additionally, geologic sources are reflected in varied isotopic composition of Sr as expressed by the ratio $^{87}Sr/^{86}Sr$. In small watersheds, where the $^{87}Sr/^{86}Sr$ ratios of atmospheric inputs and weathering inputs are distinct and relatively constant over time, this method can be used to trace the transport of Sr through the ecosystem [*Graustein*, 1989].

This technique has been used to identify weathering products in stream water [*Åberg et al.*, 1989] and to determine proportions of canopy leachate and atmospheric deposition in throughfall [*Gosz and Moore*, 1989]. *Miller et al.* [1993] used Sr isotope data to show that soil basic cation pools were stable and that atmospheric deposition supplied the majority of Sr and Ca in biomass and forest floor pools at a relatively Ca-enriched site in the Adirondack Mountains. In the present study we combined the source information gained from Sr isotopic determinations with a detailed annual watershed mass balance to partition the Ca cycle and determine separate mass

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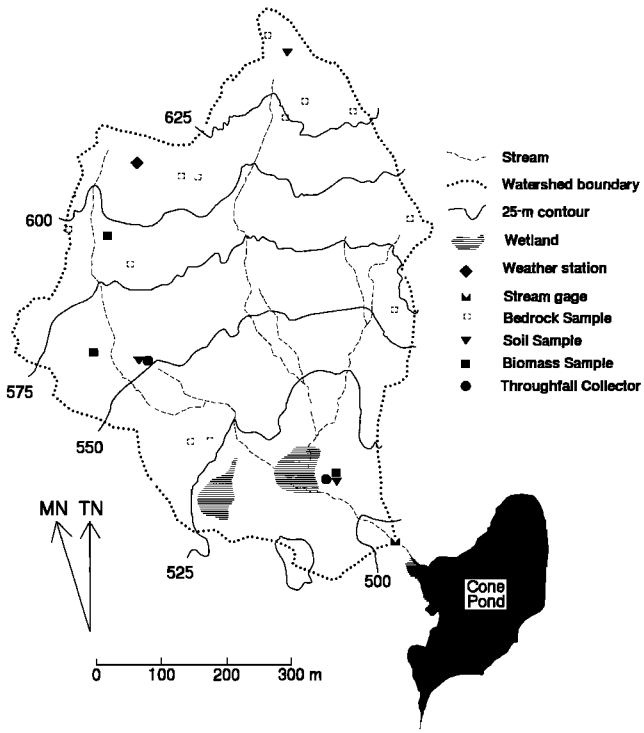

Figure 1. Cone Pond Watershed map and sample site locations.

balances for Ca derived from atmospheric and mineral weathering inputs.

The study site, Cone Pond Watershed (CPW), is located within the White Mountain National Forest, New Hampshire, U.S.A. There may be significant depletion of basic cations in CPW as evidenced by low concentrations of basic cations in drainage waters, depressed pH, and elevated transport of Al [*Bailey et al.*, 1995]. Mineral Sr isotopic composition ($^{87}Sr/^{86}Sr \geq 0.712$) was well separated from atmospheric inputs ($^{87}Sr/^{86}Sr = 0.710$), providing an opportunity to apply the Sr isotope method to a site that is likely susceptible to cation depletion.

Methods

Cone Pond Watershed consists of 53 ha of all-aged (maximum 260 years) forest within the White Mountain National Forest, Thornton, New Hampshire (43°54'N, 71°36'W; Figure 1). The watershed is 80% mixed conifer forest, dominated by red spruce, balsam fir, and eastern hemlock; 15% northern hardwoods, dominated by American beech, yellow birch, and sugar maple; and 5% bedrock outcrop.

The watershed is underlain by sillimanite-grade metapelites of the Silurian Perry Mountain Formation, composed of quartz, muscovite, biotite, and almandine, with accessory sillimanite, Fe-Ti oxides, and retrograde chlorite. Bedrock is exposed along ridges, whereas the remainder of the watershed is mantled by glacial till (<2.5 m thick) derived primarily from local metapelitic and granitic rocks [*Bailey and Hornbeck*, 1992]. Soils include Typic, Lithic and Aquic Haplorthods, with lesser areas of Typic and Terric Borohemists in wetlands associated with the inlet (Figure 1). These soils have developed in a firm, slowly permeable, dense basal till, which limits deep percolation of drainage waters. Hydrologic flow paths are largely confined to upper soil horizons. A seasonal, perched water table develops on top of the C horizon in less well drained sites.

Mass balances were prepared for the water year October 1991 to September 1992 for the 33.4-ha watershed of the inlet to Cone Pond. Comparison of precipitation and streamflow amounts and Ca concentrations between the study year and the two prior and two subsequent years (Figure 2) suggests that the study year is representative of longer-term conditions.

Atmospheric precipitation was measured with standard and recording rain gauges at the pond shore and at an open ledge in the upper watershed (Figure 1). Bulk precipitation for chemical analysis was collected weekly via a polyethylene funnel at the upper weather station. Throughfall samples were collected weekly at two plots representing coniferous and deciduous forest cover types. At each plot, throughfall from 10 randomly located collectors was composited into a single sample. Collectors consisted of polyethylene funnels with cleaned polyester wool filters to minimize particulate inputs during the warmer months, and open polyethylene bags stretched over a cylindrical polyvinyl chloride (PVC) frame during the snow season.

Soil water samples were collected with zero-tension pan lysimeters at the base of the Oa horizon and within the Bs horizon at each of three sites which span the range of soil and forest cover types present. Stream water outputs from the watershed were measured continuously at a V notch weir. Grab samples for chemical analysis of stream water were collected at the weir at a maximum of weekly intervals, for a total of 61 samples.

In order to obtain basic cation concentration and Sr isotopic composition data that could be coupled to an annual watershed mass balance with a reasonable analytical effort, monthly volume-adjusted samples of bulk precipitation, throughfall from coniferous and deciduous stands, and streamwater were prepared from weekly collections. Resulting composites were representative of the overall time period covered; however, any information from event-based variability or with changes in hydrologic conditions was lost. Soil water samples, taken at

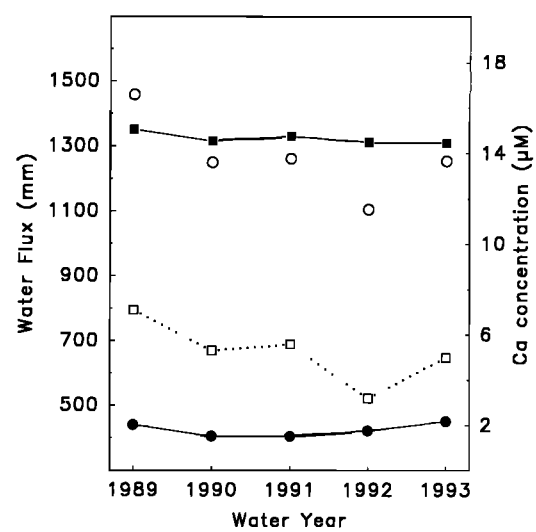

Figure 2. Precipitation (millimeters; open circles), streamflow (millimeters; open squares), and calcium concentrations (μM) in bulk precipitation (solid circles) and stream water (solid squares) for 5 years at the Cone Pond Watershed. Detailed Ca and Sr mass balances were prepared for the 1991 water year.

longer time intervals, were not composited. All water samples were preserved at pH 2 with Teflon-distilled HNO_3, filtered with a 0.45-μm cellulose nitrate filter, evaporated, and taken up and stored in either 2 N HCl or 3 N HNO_3. All laboratory work was done with distilled reagents in class 100 filter units.

Annual ion uptake by trees was calculated by multiplying ion content times annual mass production of individual tree components (boles, branches, leaves, and roots) [*Waring and Schlesinger*, 1985]. Samples of foliage, branches, bark, wood, and roots were taken from two trees each of red spruce, balsam fir, eastern hemlock, American beech, yellow birch, and sugar maple for chemical analysis. Litter fall (leaves and small branches) was sampled with plastic traps at 45 locations. Return to the forest floor via fallen boles, branches, and dead roots was not determined.

Samples of wood, foliage, and roots for isotopic analysis were obtained from a red spruce removed from the forest adjacent to the coniferous throughfall site. In order to examine interspecific variability in biomass chemistry, wood samples were also analyzed from American beech and sugar maple. All biomass samples were oven dried, ground with a Wiley mill, and dissolved in a hot nitric-perchloric acid mixture.

Biomass storage was determined by measuring all trees on a stratified random sample of nine 0.04-ha plots in 1991 and again in 1994. A paired differences test for independent samples ($p = 0.05$) showed no significant difference between the two data sets, suggesting that ion storage in vegetation changes little from year to year in the "old-growth" forest at Cone Pond.

Bedrock samples were collected with a portable saw at 12 sites chosen randomly from all exposures in the watershed. Whole rock samples were crushed in a shatter box. Mineral separates were hand picked for almandine, biotite, muscovite, and chlorite from a disk-milled composite of the 12 bedrock samples and plagioclase and hornblende from one C horizon soil sample. Whole rock and mineral separates were dissolved in hot hydrofluoric and perchloric acid for 24 hours in a Teflon capsule. Soil samples from each horizon in three profiles were air-dried, crushed in a shatter box and dissolved using the same method.

Calcium was measured by flame atomic absorption spectrophotometry [*Slavin*, 1968]. Strontium was separated by ion exchange chromatography using Dowex 50WX-8 or Eichrom Sr-spec resin. Samples loaded onto Dowex columns were dissolved in 2 N HCl, then loaded onto columns that were previously calibrated using radioisotopes of Rb, Ca and Sr. Ultrapure 2 N HCl was washed through the column, and Rb and Sr were collected after specific volumes of acid had passed though (Rb was collected at 6.5 to 8.0 mL; Sr was collected at 14 to 18 mL). Sr-spect columns were also utilized following the method of *Horwitz et al.* [1991]. This involved cleaning the column with 4 free column volumes of H_2O; conditioning the column with 4 free column volumes of 3 N HNO_3; loading the sample; rinsing with 30 free column volumes of 3 N HNO_3 to strip Ca, Rb, and other cations; and collecting Sr with 10 free column volumes of H_2O. Strontium and Rb were measured by isotope dilution with thermal ionization mass spectrometry with both single and multiple collector machines. Each mass spectrometer run consisted of at least 100 individual measurements of $^{87}Sr/^{86}Sr$. Measurements were normalized to $^{86}Sr/^{88}Sr = 0.1194$. NBS-987 was periodically measured to check accuracy; 28 analyses yielded a mean $^{87}Sr/^{86}Sr = 0.71036 \pm 0.00048$ on the single collector machine and 0.71026 ± 0.00001 on the multiple collector machine (compared to an accepted value of 0.71025). The blank Sr was less than 1 ng, generally much less than 1% of the Sr isolated from each sample.

Proportions of Sr from atmospheric and mineral weathering end-members in watershed pools and fluxes were calculated with a linear mixing model [*Graustein*, 1989]:

$$\text{Ratio}_{atm}(X) + \text{Ratio}_{min}(1 - X) = \text{Ratio}_{mix}$$
$$\text{Ratio} = {}^{87}Sr/({}^{87}Sr + {}^{86}Sr) \quad (1)$$

where X is the proportion of Sr from the atmosphere, mix indicates the watershed flux or pool to be modeled, atm indicates the atmospheric end-member, and min indicates the mineral weathering end-member.

Using Sr isotopic compositions and assuming that Sr behaves as a proxy for Ca, the Ca mass balance was partitioned into atmospheric and mineral weathering components. The atmospheric end-member was taken as the mean Sr isotopic composition of bulk precipitation. Uncertainty in the Sr isotope composition released to solution by weathering reactions results from heterogeneity in mineral Sr isotopic composition in soils and bedrock. Thus a range of mineral weathering end-members were considered, with the implications for each on modeled mixtures discussed.

Results and Discussion

Isotopic Composition

Rock and soil. Bedrock was the most radiogenic and isotopically variable component of the ecosystem with a mean $^{87}Sr/^{86}Sr$ ratio of 0.760 for the 12 whole rock samples (Figure 3; all isotopic data are listed in Table 1). The variability of Sr isotopic composition within the Perry Mountain Formation illustrates both the power and the challenge of applying the Sr isotope method to ecosystem studies. The isochron plot (Figure 3) demonstrates the rationale of Sr isotope systematics. When the rock originally crystallized, $^{87}Sr/^{86}Sr$ was homogeneous throughout the formation. Over time, as ^{87}Rb decayed to ^{87}Sr ($\lambda = 1.42 \times 10^{-11}$/yr), minerals with a higher Rb/Sr ratio became increasingly enriched in radiogenic ^{87}Sr. Individual samples with a greater proportion of Rb-rich minerals thus have higher present-day $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios (Figure 3).

Of the four mineral separates analyzed, biotite was the most radiogenic, with a $^{87}Sr/^{86}Sr$ ratio of 2.59, reflecting a crystal structure that does not readily accept divalent alkaline earths. In contrast, chlorite had the lowest ratio, 0.737. Minerals lacking monovalent alkali sites in the lattice but rich in Ca, such as plagioclase or apatite, would be expected to have a $^{87}Sr/^{86}Sr$ similar to the initial ratio of the rock, given by the ordinate intercept of the isochron [*Faure*, 1986], calculated at 0.727 by York regression [*York*, 1969]. While this variability complicates the simple assessment of the overall isotopic composition of Sr released from weathering reactions, it provides the opportunity to trace the products from weathering of individual minerals if mineral compositions and abundance are well known.

Soil C horizons, representing relatively unweathered till (the soil parent material), had relatively constant $^{87}Sr/^{86}Sr$ at 0.722–0.724 (Figure 4). The degree of weathering can be expected to decrease in mineral soil from the highly altered E horizon, just below the organic surface horizons, to the parent till in the C horizon. This is consistent with the pattern of increasing concentration of Ca and Sr with depth (Figure 4). Variation of $^{87}Sr/^{86}Sr$ within soil profiles was inconsistent between sample

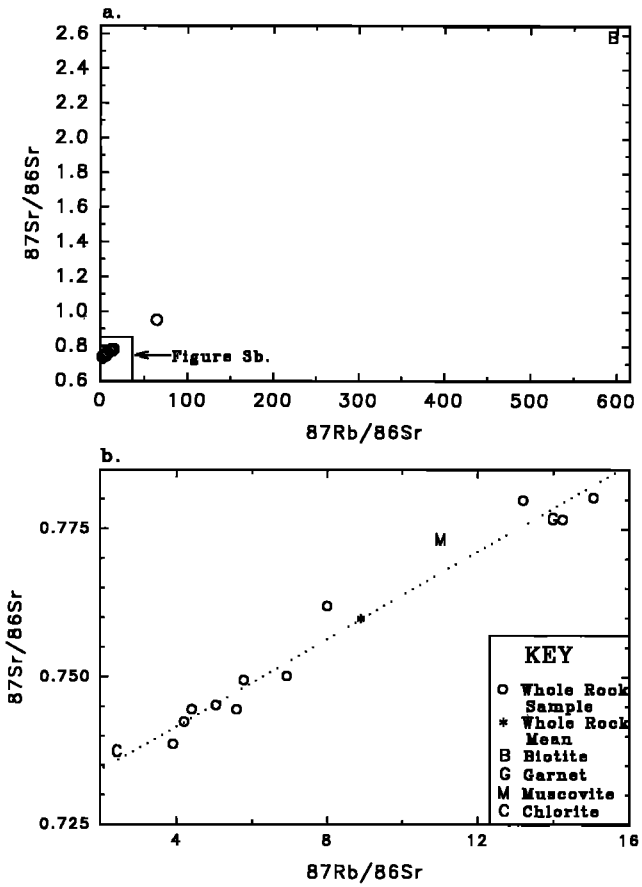

Figure 3. Perry Mountain Formation isochron plot with regression line for (a) all bedrock data and (b) samples excluding the biotite separate and the most radiogenic whole rock sample.

locations. The expected pattern of an increase in $^{87}Sr/^{86}Sr$ in weathered compared to unweathered materials, due to more rapid weathering of Ca/Sr-rich minerals compared to K/Rb-rich minerals [*Bottino and Fullagar*, 1968; *Dasch*, 1969] was not always evident at CPW. This discrepancy may be due to spatial variations in soil mineralogy [*Hyman*, 1993], the influence of Sr associated with organic matter, the prevalence of lateral rather than vertical hydrologic flow paths, or soil mixing due to tree throw by wind, which is extensive in White Mountain soils [*Pilgrim and Harter*, 1977]. Soil profiles at two locations (Figures 4a and 4c) showed an increase in $^{87}Sr/^{86}Sr$ from the C to the Bs horizon, whereas a third site (Figure 4b) showed a slight decrease. Upper soil profiles showed the most variability, reflecting variations in organic matter content and probably also in mineralogy.

While the till is partially derived from the underlying bedrock, there are also contributions from other local bedrock units, especially other Silurian metasedimentary units and the Devonian Kinsman Quartz Monzonite [*Bailey and Hornbeck*, 1992]. One might expect all of these units to be uniform with respect to Sr isotope systematics (i.e., to lie along the same isochron), as all were subject to Acadian regional metamorphism. However, the till samples (C horizon, Figure 4) would plot well below the bedrock isochron (Figure 3). Either the till has been influenced by contributions from rock units with lower initial $^{87}Sr/^{86}Sr$, or radiogenic Sr has been preferentially weathered from the soil, including the relatively unweathered C horizon.

Plagioclase and hornblende samples were separated from the C horizon sample at profile b in order to assess the potential contribution of these two soil minerals. Neither mineral is common in the bedrock, however both are among the most Ca-rich of the soil minerals found in the watershed [*Hyman*, 1993]. The Sr isotopic composition of plagioclase was 0.7122, lower than any $^{87}Sr/^{86}Sr$ ratio measured in this study with the exception of bulk precipitation, while hornblende had a $^{87}Sr/^{86}Sr$ ratio of 0.7225, close to the value for bulk soil in this sample (Figure 4). These relatively low values indicate the contribution from rock units with a lower isochron *Y* intercept than the underlying bedrock.

Waters. The average ratio in precipitation ($^{87}Sr/^{86}Sr$ = 0.710) was slightly higher than ocean water ($^{87}Sr/^{86}Sr$ = 0.7092 [*Hess et al.*, 1986]). This pattern is consistent with other studies which have found an isotopic composition of rainwater slightly greater or less than ocean water, depending on the influence of dust derived from local geologic sources [*Graustein and Armstrong*, 1983; *Åberg et al.*, 1989; *Andersson et al.*, 1990; *Miller et al.*, 1993]. In addition, it might be expected that minor amounts of biologic materials (pollen, leaf particles, insects) contribute to the $^{87}Sr/^{86}Sr$ signature of bulk precipitation. As the samples were filtered and mineral dust contaminants are relatively insoluble, the deviation from seawater values might be expected to reflect influence of the more soluble biologic contributions. To the extent that biologic materials reflect the Sr composition of the local geologic substrate, either possibility would have a similar influence on the $^{87}Sr/^{86}Sr$ ratio of bulk precipitation.

Throughfall showed little temporal variation in $^{87}Sr/^{86}Sr$, suggesting that the compositing technique masked interstorm or weekly variability in canopy-atmosphere interactions. The consistent deviation from bulk precipitation indicates that canopy-atmosphere interactions were active year-round, despite a lack of a deciduous canopy from November through April (Figure 5). Deciduous throughfall had an isotopic composition almost identical to that of biomass (see below), suggesting that the increase in Sr concentration between bulk precipitation and throughfall under the deciduous canopy was due to leaching of cations from the canopy biomass. Coniferous throughfall was intermediate in isotopic composition between biomass and bulk precipitation, indicating a greater influence of atmospheric Sr in coniferous throughfall. This pattern is consistent with other studies which have found greater dry deposition in coniferous versus deciduous canopies. *Gosz and Moore* [1989] found little evidence of canopy leaching in throughfall from an Engelmann spruce canopy in New Mexico in contrast to a mixture of atmospheric and canopy Sr in throughfall under a nearby aspen canopy. The data from CPW imply a pattern of greater canopy leaching than noted in the New Mexico study, possibly due to elevated inputs of acidic deposition at CPW.

Soil water Sr composition was similar to, or had a lower $^{87}Sr/^{86}Sr$ ratio than bulk soil at each site (Figure 4), consistent with the model of Sr in soil water derived from a mixture of atmospheric inputs and soil mineral weathering. The unadjusted mean soil water $^{87}Sr/^{86}Sr$ of 0.722 was intermediate between bulk soil and stream water values (below).

Little temporal variation in stream water $^{87}Sr/^{86}Sr$ was observed (Figure 5), again likely due to compositing of samples. These results suggest that on a monthly basis there was a consistent mixture of source areas for stream water. Individual stream water samples collected during a pilot sampling pro-

Table 1a. Rock and Soil Isotopic Data

Sample	Strontium			Rubidium		
	$^{87}Sr/^{86}Sr$	Mean Deviation, $\times 10^{-5}$	Sr, ppm	$^{85}Rb/^{87}Rb$	Mean Deviation, $\times 10^{-5}$	Rb, ppm
Perry Mountain Formation, Whole Rock Samples						
Sp3	0.74522	4.7	105.10	1.15231	30.7	182.01
Sp12	0.77990	15.7	30.90	0.80678	12.4	139.90
Sp13	0.74942	5.2	95.68	0.98293	44.8	190.11
Sp22	0.76197	7.5	101.00	1.24786	14.0	277.60
Sp27	0.74454	5.3	97.66	0.77600	41.3	147.82
Sp30	0.74447	4.1	104.53	1.17726	15.3	200.87
Sp31	0.74245	6.2	117.27	0.86920	176.2	169.52
Sp34	0.77661	2.1	132.05	1.71731	3.3	645.44
Sp39	0.78037	8.6	110.40	1.78535	136.5	570.40
Sp45	0.73867	1.3	166.54	1.0468	33.3	224.05
Sp50	0.94995	13.8	34.90	1.85753	29.2	764.05
Sp52	0.75017	5.0	76.80	0.90475	31.6	182.79
Perry Mountain Formation, Mineral Separates						
Muscovite	0.77311	7.7	79.36	1.98533	106.6	300.25
Biotite	2.58553	78.9	9.89	2.42977	46.3	1719.26
Chlorite	0.73734	15.5	32.43	0.52033	12.9	27.15
Garnet	0.77666	5.5	1.61	0.50944	1.9	7.74
Soil Samples						
1-Oa	0.72214	1.2	38.95	0.42059	29.8	35.56
1-E	0.72264	1.4	80.23	0.60892	12.0	57.55
1-Bh	0.72312	0.7	81.15	0.77915	15.8	73.46
1-Bs	0.72372	1.1	86.17	0.94084	3.1	82.37
1-Cd	0.72159	0.6	116.26	0.97458	25.1	102.27
5-Oa	0.72309	7.9	33.64	0.35641	3.0	29.30
5-A	0.72472	8.7	54.64	0.37898	4.5	47.75
5-Bs	0.72328	5.5	61.60	0.54302	30.9	53.51
5-C	0.72413	8.0	96.50	0.88360	32.0	91.40
8-Oa	0.72576	15.9	29.90	0.19088	8.2	28.23
8-E	0.72790	8.3	81.85	0.93833	23.9	93.60
8-Bhs2	0.72621	11.2	98.86	0.93339	22.3	105.60
8-BC	0.72226	8.7	122.66	0.95601	11.5	102.85
Soil Mineral Separates						
Plagioclase	0.71221	1.0	440.7			
Hornblende	0.72250	1.0	13.95			

gram showed great variation in $^{87}Sr/^{86}Sr$ with varying hydrologic conditions. A grab sample collected during extreme base flow conditions contained $^{87}Sr/^{86}Sr$ of 0.7442, reflecting inputs from much more radiogenic sources, probably bedrock weathering. Therefore while the compositing technique may ensure that the data are quantitatively representative of the Sr composition lost from the watershed in stream water on a monthly basis, any process level information on variation in source areas or hydrologic flow paths has been lost.

Biomass. Isotopic composition of Sr was least variable in biomass of all materials analyzed, with the lowest ratio for sugar maple wood within 0.1% of the highest ratio for American beech wood (Table 2). Wood, foliage, and root samples collected from a single red spruce were essentially identical in $^{87}Sr/^{86}Sr$. Biomass $^{87}Sr/^{86}Sr$ was in the same range but less variable than shallow soil water $^{87}Sr/^{86}Sr$ (Figure 4), which ranged from 0.7198 to 0.7217. Short-term temporal variation in soil water might be expected due to changing flow paths with varying hydrologic conditions. The vegetation appears to attenuate variations in Sr isotopic composition as assimilation occurs over a number of growing seasons.

Sr as an Analog to Ca

Within each type of sample analyzed there was a consistent Sr/Ca ratio, suggesting parallel sources and behavior of these elements. Monthly fluxes of these two elements revealed similar patterns in precipitation, throughfall, and stream water (Figure 6). Molar Sr/Ca ratios ranged from an average of 1.3×10^{-3} in coniferous throughfall to 3.3×10^{-2} in bulk soil. This variability is greater than that found by *Åberg et al.* [1989], who reported Sr/Ca ratios of 1×10^{-2} to 2×10^{-2} in rain, throughfall, runoff, soil exchangeable cations, soil minerals, and vegetation in a coniferous watershed in Sweden.

In contrast to the relative isotopic homogeneity of biomass samples, the Sr/Ca ratio was much more variable in biomass than in other ecosystem components. This resulted from a rather constant Sr concentration in biomass, with a factor of 4 between the lowest and highest concentrations, compared to Ca, which varied by a factor of 20. Wood samples for the three species analyzed were relatively uniform, with a molar Sr/Ca ratio of about 3.3×10^{-3}, similar to that of soil water. Red spruce roots and foliage had much lower ratios (Table 2),

Table 1b. Water Isotopic Data

Sample	$^{87}Sr/^{86}Sr$	Mean Deviation $\times 10^{-5}$	Sr
	Bulk Precipitation		
Oct.	0.71025	9.8	0.28
Nov.	0.71197	1.1	0.13
Jan.	0.71122	0.7	0.14
March	0.70999	0.8	0.49
May	0.71035	0.9	0.41
July	0.70994	0.9	0.18
Sept.	0.71053	0.9	0.15
	Coniferous Throughfall		
Oct.	0.71842	2.5	0.88
Nov.	0.71838	11.3	2.05
Dec.	0.71802	2.9	2.04
Jan.	0.71830	1.6	1.69
Feb.	0.72113	11.3	2.11
March	0.71850	12.0	2.28
April	0.71858	11.1	1.56
May	0.71833	9.9	2.54
June	0.71921	10.2	1.35
Aug.	0.71858	0.9	1.83
	Deciduous Throughfall		
Oct.	0.71951	2.7	1.39
Nov.	0.72065	43.7	0.53
Dec.	0.71834	3.1	0.60
Jan.	0.71988	46.2	0.57
June	0.71893	0.9	1.47
July	0.72042	17.3	0.90
Aug.	0.72188	14.8	1.16
Sept.	0.72101	11.7	0.77
	Inlet		
Oct.	0.71930	17.5	7.63
Nov.	0.71942	10.6	7.26
Dec.	0.71918	20.7	11.13
Jan.	0.72089	13.4	6.55
Feb.	0.71929	1.8	7.53
March	0.71902	0.9	6.55
April	0.72117	2.1	6.30
May	0.71918	1.6	7.22
June	0.72098	16.8	8.05
July	0.72040	17.4	8.00
Aug.	0.72024	5.2	8.14
Sept.	0.71959	7.9	7.46
Grab 1*	0.7211		8.3
Grab 2†	0.7442		22.4
	Soil Water Samples: July 1992		
1 Oa	0.72173	2.2	5.76
1 Bs	0.72251	2.1	4.50
4 Oa	0.72558	13.2	6.10
4 Bs	0.71675	9.8	9.29
5 Oa	0.72095	14.7	6.33
5 Bs	0.72309	24.0	6.51
8 Oa	0.71982	0.7	3.86
8 Bs	0.72023	0.7	5.87
5 Bs‡	0.72326	11.9	5.39
	Biomass		
Spruce wood	0.72030	0.8	2.50
Spruce needle	0.72027	1.3	4.46
Spruce needle	0.72018	1.4	4.36
Spruce needle	0.72055	11.6	NA
Spruce needle	0.72079	11.3	4.67
Spruce root	0.72024	1.	8.57
Beech wood	0.72083	0.6	5.65
Maple wood	0.72004	4.0	9.05

Biomass Sr concentrations are in parts per million; all others are in parts per billion.
*May 12, 1989.
†Sept. 12, 1989.
‡March 1993.

possibly indicating discrimination by trees in the assimilation of Ca and Sr in these tissues. This finding contrasts with the findings of *Åberg et al.* [1989], which show no discrimination between these elements by vegetation.

Elias et al. [1982] found a constant Sr/Ca ratio in analyses of humus, soil water, and sedge in a grassland ecosystem. In woody plants, differences in Sr/Ca ratio between soil moisture and roots were not substantive. However, reduction did appear to occur during xylem transport from stem to leaf. The data from CPW are more consistent with the conclusions of *Elias et al.* [1982] in that soil water and wood had similar Sr/Ca ratios whereas a much lower Sr/Ca ratio was evident in the foliage sample. Furthermore, the low ratios in throughfall compared to bulk precipitation suggest that throughfall is influenced by canopy leaching of biomass with a relatively low Sr content.

Cation Source Modeling: Identification of End-Members

Ecosystem pools and fluxes were modeled as mixtures of atmospheric and mineral weathering end-members on the basis of Sr isotopic composition (Figure 7). Precision in measurement of $^{87}Sr/^{86}Sr$ ratios leads to an uncertainty of 3% in modeled mixtures.

The atmospheric end-member was taken as the volume-adjusted mean of the bulk precipitation samples. Several studies, including this one, have found $^{87}Sr/^{86}Sr$ in atmospheric precipitation to be close to the seawater composition, varying above or below this value depending on the composition of $^{87}Sr/^{86}Sr$ in local geologic materials. As biomass is also influenced by the Sr composition of its substrate, particles of biomass in atmospheric precipitation would have the same effect on $^{87}Sr/^{86}Sr$ as would particles of mineral dust. In a silicate terrain such as the White Mountains, dust composed of plant material is likely to be much more soluble than mineral dusts and thus have a greater influence on Sr concentrations and isotopic composition of atmospheric precipitation.

The influence by local materials on bulk precipitation can be considered as material recycled from within the watershed rather than as an atmospheric input. If bulk precipitation is modeled via equation (1) as a mixture of biomass contamination and atmospheric input with a composition of ocean water, then 3% of Sr in bulk precipitation would be derived from biomass inputs. This value represents a conservative overestimate of the atmospheric input due to the potential impact of dusts derived from within the watershed.

Given the range in isotopic composition of various minerals, the validity of a single end-member to describe the weathering contribution needs to be qualified. The isotopic composition of Sr released by weathering reactions is the composite of the isotopic compositions of each weathering reactant. Thus given a suite of minerals, each with its own weathering rate and isotopic composition, there is a unique isotopic composition of Sr released to solution. The constraint on defining such a system with a single end-member is that the end-member may only be valid for the area and time period specified. As mineralogic composition of the weathering substrate varies spatially, an end-member which describes the watershed is not necessarily the same as an end-member for any subset of the watershed, be it a subwatershed or a specific soil profile.

Furthermore, if the weathering rate of any mineral varies over time, then the end-member could change. For example, over a long time period (e.g., thousands of years of soil development), easily weathered minerals might become depleted in the soil profile relative to more resistant minerals. This could

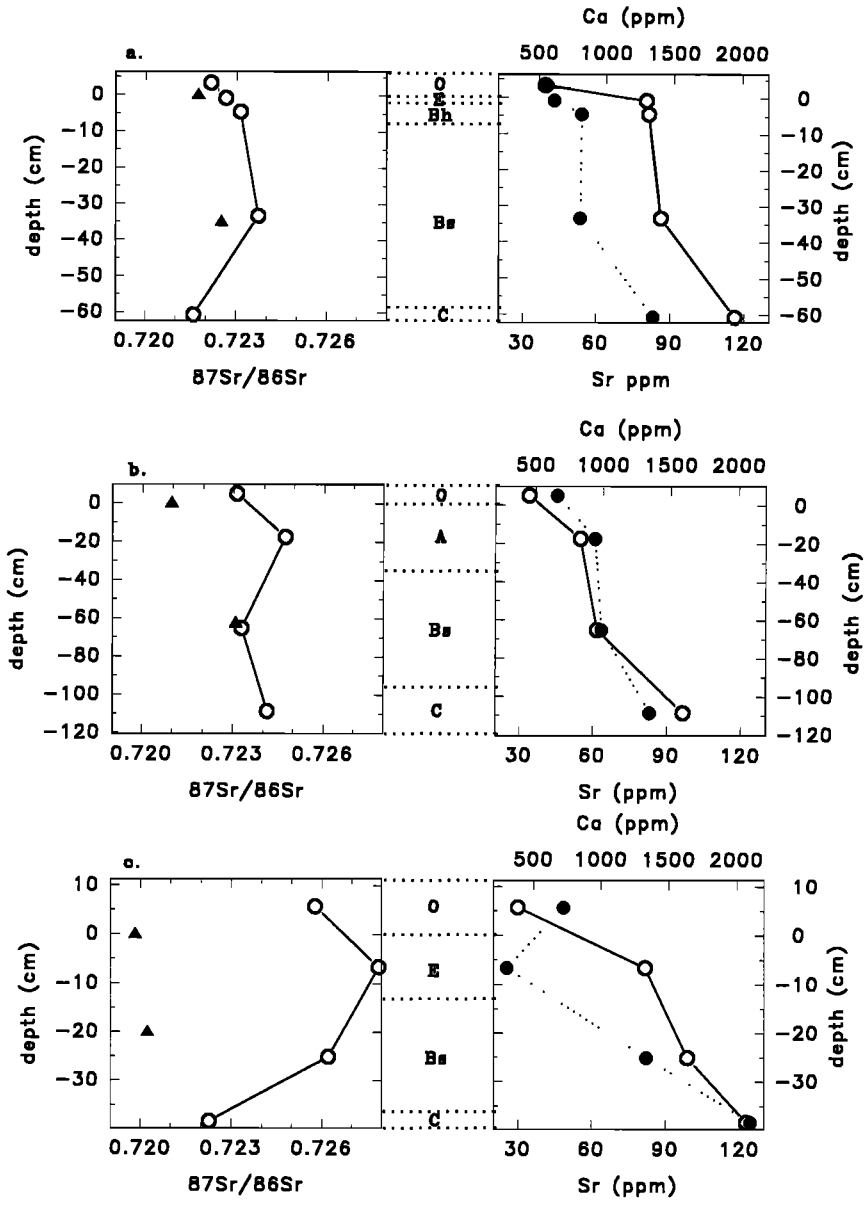

Figure 4. Soil Sr and Ca chemistry at three profiles (a, b, and c). The left column shows $^{87}Sr/^{86}Sr$ with depth for bulk soil (circles) and soil water (triangles) samples. The right column shows Ca (solid circles) and Sr (open circles) concentration for the same three profiles. The central column indicates horizons at each site.

result in a change in the isotopic composition of Sr released to solution. Within shorter time periods (e.g., hundreds of years) one would not expect variation in the relative weathering contributions of individual minerals due to depletion.

Although heterogeneity in soil mineral and bedrock $^{87}Sr/^{86}Sr$ ratios prevents assignment of an exact mineral weathering end-member without further data on mineralogic composition and depletion in weathering zones, there are constraints that can be made on the range of possibilities. Overall, minerals ranged in $^{87}Sr/^{86}Sr$ ratio from 0.7122 for soil plagioclase to 2.59 in bedrock biotite. Within this range, a minimum possible value for the weathering end-member of 0.720 is predicated by the composition of biomass and stream water at this value. If biomass and stream water represent mixtures of atmospheric and weathering Sr, then the weathering end-member must have a higher $^{87}Sr/^{86}Sr$ ratio. Soil water $^{87}Sr/^{86}Sr$ ratios as high as 0.7256 and a grab stream water sample at 0.7442 indicate contributions more radiogenic than the bulk soil, possibly from biotite or garnet in the soil or bedrock.

If the end-member were as low as 0.720 then this would indicate that biomass Sr is exclusively derived from weathering. The spruce- and fir-dominated forest at CPW is characterized as having essentially all of its active feeder roots within the forest floor. This would suggest that atmospheric deposition should be an important source of base cations for vegetation uptake. Sr isotope studies in New Mexico [*Gosz and Moore*, 1989] and New York [*Miller et al.*, 1993] have found a high percentage of atmospheric Sr in spruce biomass.

A provisional assignment of the mineral weathering Sr end-member at $^{87}Sr/^{86}Sr = 0.7251$, or close to that of bulk soil (Figure 7) was made by mass balance comparisons of adjacent soil horizons within the weathering profile. This number was calculated by comparing Sr concentration and composition between adjacent soil horizons. This method relies on the

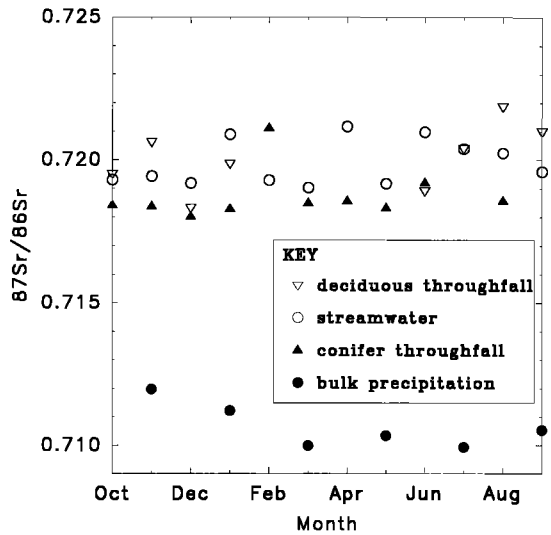

Figure 5. Temporal variation in $^{87}Sr/^{86}Sr$ for monthly composite water samples.

questionable condition that weathering has resulted in a negligible loss of mass. Additionally, the influence of organic matter deposition in mineral horizons is not accounted for. Given these limitations, the value calculated is slightly higher than that of the bulk soil mean, consistent with a weathering input dominated by soil weathering, with a small additional input derived from bedrock. With this end-member, equation (1) gives 32% of biomass Sr derived from atmospheric sources, a value that indicates that the provisional end-member may be conservatively low as a greater influence of atmospheric sources on biomass Sr is expected.

Although plagioclase had by far the highest concentration of Sr of all minerals analyzed, its extremely low $^{87}Sr/^{86}Sr$ ratio compared to the possible range for the mineral weathering end-member indicates that it is relatively unimportant as a weathering reactant. Plagioclase was not found in an electron microprobe scan of Perry Mountain Formation thin sections taken from CPW bedrock samples. In addition, plagioclase in soil samples appears to have fresh surfaces, in contrast to the highly pitted, sponge-like appearance of hornblende grains. Pitted rinds of bedrock samples reveal active dissolution of biotite and garnet on outcrop surfaces. Both these physical indicators, as well as the likely range of strontium isotopic composition released by weathering, argue for a combination of hornblende, garnet, and biotite as the dominant weathering reactants. More detailed studies of mineral depletion in soil horizons and bedrock weathering rinds as well as further $^{87}Sr/^{86}Sr$ analyses of mineral materials are needed to further constrain the weathering end-member isotopic composition and to determine relative weathering contributions of dominant reactants.

Mass Balance Partition

Given the atmospheric and mineral weathering proportions of measured watershed fluxes and pools (Figure 7), the Ca cycle was partitioned into separate mass balances for each of the atmospheric and weathering sources (Figure 8). A method to estimate the proportion of watershed losses due to weathering was devised based on a mass balance for Ca derived from the atmosphere (A detailed example calculation illustrating this method is given in the appendix). The model was calculated for the provisional weathering end-member as well as a range of possible end-members to illustrate the effect of end-member choice on calculated weathering and ecosystem depletion rates.

In order to assess additional atmospheric inputs beyond those measured in bulk precipitation, throughfall was modeled as a mixture of cations leached from the canopy and cations deposited from the atmosphere. A pair of simultaneous equations were solved assuming that Sr leached from the canopy had the same isotopic composition as the canopy and that additional atmospheric deposition had the same isotopic composition as bulk precipitation. This method yielded an estimate of 3 mol/(ha yr) for additional deposition of Ca to the canopy, compared to 17 mol/(ha yr) for bulk deposition (Figure 8). These results are consistent with the findings of *Baker* [1990], who found that artificial collectors are relatively efficient collectors of dry deposition of chemicals, such as Ca, which are associated with coarse particle sizes. Thus little additional dry deposition of Ca to the canopy would be expected, beyond that caught in a bulk precipitation collector.

The total input of Ca from the atmosphere of 20 mol/(ha yr) was about one half of the loss of atmospherically derived Ca in stream water (37 mol/(ha yr)). This pattern suggests that an ecosystem pool of Ca was being depleted (i.e., a net loss of storage within the forest). Net depletion of stored Ca could be derived from the biomass pool, mineralization of organic matter in the forest floor, or loss of exchangeable cations. At the nearby Hubbard Brook Experimental Forest (HBEF) there is evidence of declining Ca content in the forest floor over the last 20 years [*Yanai et al.*, 1993]. For each of these pools at CPW, the Sr isotopic composition was similar to that of biomass, suggesting that depleted material was approximately 32% atmospheric and 68% mineral in origin. Therefore depletion of one of these pools by 17 mol/(ha yr) of atmospheric Ca was accompanied by depletion of 36 mol/(ha yr) of Ca derived from weathering reactions (Figure 8).

Figure 9 illustrates the effect of weathering end-member choice on modeled Ca fluxes. At end-members less than $^{87}Sr/^{86}Sr = 0.722$, there is a net retention of atmospheric Ca in the ecosystem, and the weathering rate is equal to the watershed loss of 103 mol Ca/(ha yr). For end-members greater than $^{87}Sr/^{86}Sr = 0.722$, the model predicts lesser weathering rates with consequently greater depletion rates, with a minimum weathering rate of about 10 mol Ca/(ha yr) for end-members in the vicinity of the mean bedrock Sr isotope composition. Within this range the most likely composition of the weather-

Table 2. Biomass Sr and Ca Chemistry at Cone Pond Watershed

Sample	$^{87}Sr/^{86}Sr$	Sr, ppm	Ca, ppm	Sr/Ca*
		Red Spruce		
Wood	0.72030	2.5	320	3.6×10^{-3}
Foliage	0.72045	4.5	5270	1.4×10^{-6}
Roots	0.72024	8.6	6840	5.8×10^{-4}
		American Beech		
Wood	0.72083	5.6	790	3.2×10^{-3}
		Sugar Maple		
Wood	0.72004	9.0	1350	3.0×10^{-3}

*Sr/Ca expressed as a molar ratio.

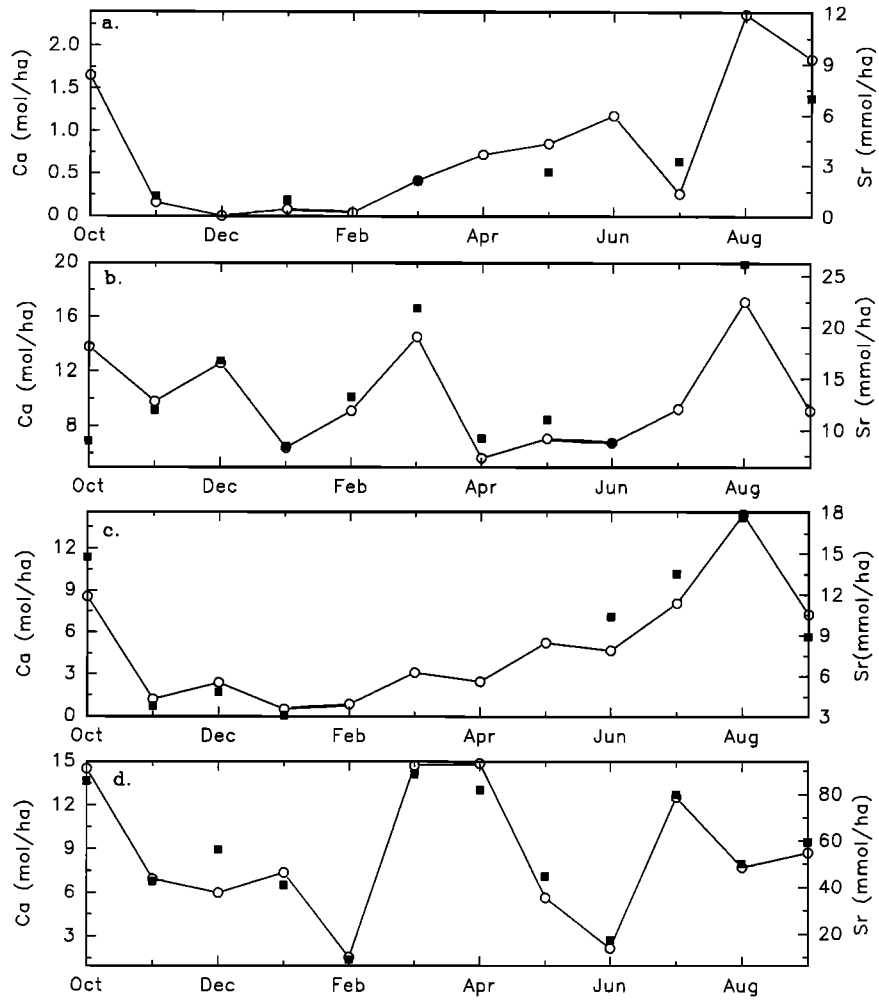

Figure 6. Temporal variation in Ca (open circles) and Sr (solid squares) fluxes for (a) bulk precipitation, (b) coniferous throughfall, (c) deciduous throughfall, and (d) stream water.

ing end-member is at $^{87}Sr/^{86}Sr = 0.723–0.727$. In this range the ratio of atmospheric to weathering input rates is reasonably reflected in the modeled biomass composition (Figures 7 and 8).

The Ca weathering rate of 30 mol/(ha yr) estimated by this method is about 5% of recent estimates from nearby HBEF [*Johnson et al.*, 1994]. If ecosystem pools are assumed to be at steady state, then the weathering rate estimate at CPW would be 84 mol Ca/(ha yr), still about 20% of the HBEF estimate. Despite similarity in geologic substrate between these two sites, weathering rates may be different due to local variation in abundance of primary minerals or thickness of soils [*Bailey and Hornbeck*, 1992]. Comparison of these two approaches suggests that determination of weathering by mass balance approach, assuming steady state ecosystem storage, substantially overestimates weathering inputs and may ignore ecologically significant losses of basic cations from available pools.

In this study, net biologic uptake was assumed to be zero. This forest has never been harvested and, based on biomass plot inventory appears to be at steady state conditions. If, on the other hand, the forest were agrading, net biologic uptake would constitute an additional sink for atmospherically derived Ca. Higher weathering and/or soil depletion rates would be required to complete the mass balance in this case.

Stocks of Ca in the soil exchange pool were only one third of the amount of Ca stored in the biomass pool, whereas reserves of Ca in <2-mm mineral soil were 6 times larger than the amount of Ca stored in the biomass pool. This is in contrast to HBEF, where the exchangeable Ca pool is 39 times larger than the biomass pool [*C. E. Johnson et al.*, 1992]. This pattern suggests that the ecosystem at CPW would be very sensitive to disturbance and might not be able to recover from long term depletion of Ca in soil pools. Continuation of the input, output, and depletion rates as determined for the year of study could result in the depletion of Ca comparable to the size of the forest floor Ca pool in less than 60 years, suggesting the potential for a major change in ecosystem function.

It is unknown how long the forest could endure chronic depletion of Ca pools without substantial reduction in vigor or changes in composition. *Shortle and Smith* [1988] showed that a molar Al/Ca ratio of ≥1 in the fine root environment is typical of sites exhibiting spruce decline. Soil water samples from CPW typically have Al/Ca ratios of 5 to 6, suggesting the potential for aluminum-induced calcium deficiency syndrome at this site.

This site has no unusual characteristics that would suggest it does not represent large areas of eastern North America with thin soils and slowly weathering silicate mineralogy. Given the

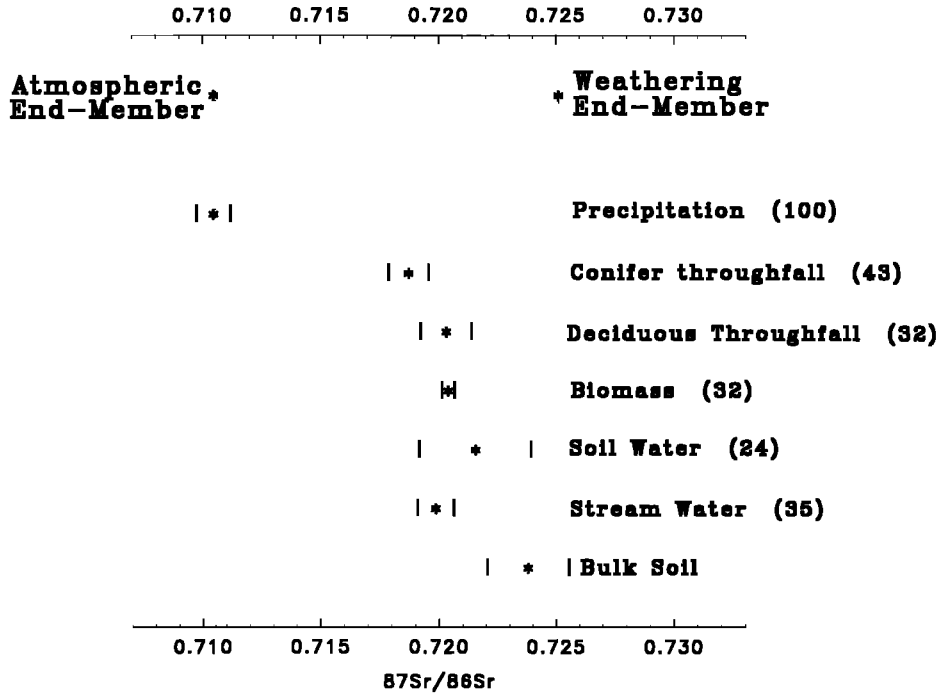

Figure 7. Mean ecosystem $^{87}Sr/^{86}Sr$ ratios. The bars indicate ±1 standard deviation. The modeled percentage of atmospheric Sr in each mixture as calculated by equation (1) is indicated in parentheses.

low base saturation of the soil exchange complex, the small size of this pool in relation to other ecosystem pools, and the low rate of basic cation inputs from the atmosphere or mineral weathering, recovery of this site from surface water acidification would proceed very slowly, even if Ca losses are moderated by reductions in sulfur and nitrogen emissions.

Conclusions

1. Ratios of Sr/Ca suggest little discrimination between these elements for ecosystem processes except transport of cations from bole to foliage within trees.
2. Isotope end-member modeling as well as low Sr/Ca ra-

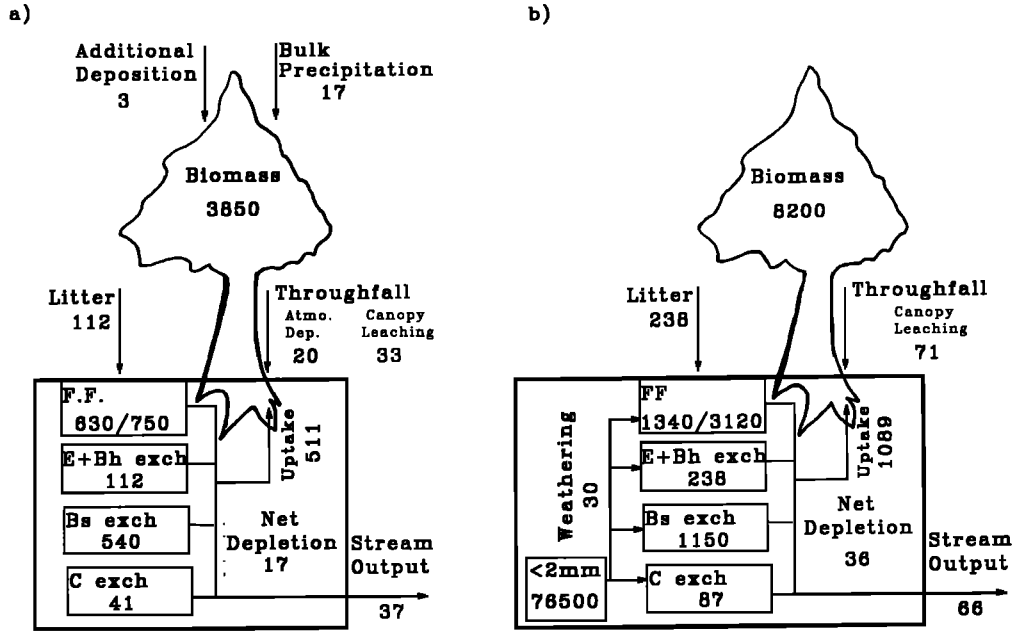

Figure 8. Mass balance of Ca derived from (a) atmospheric and (b) mineral weathering sources. Units are moles per hectare for ecosystem pools and moles per hectare per year for fluxes.

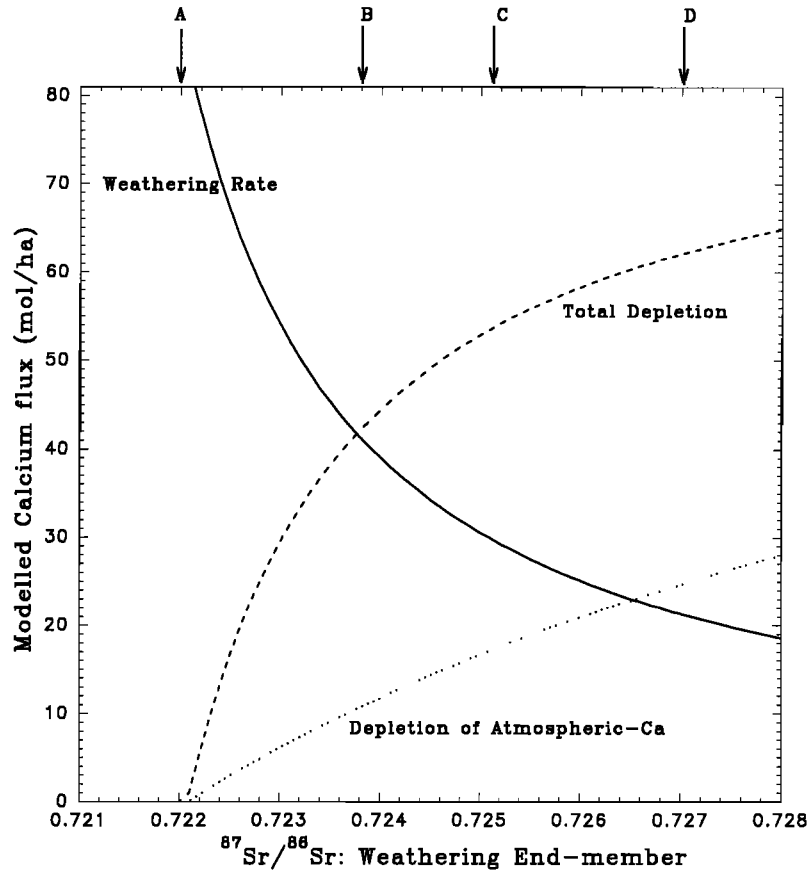

Figure 9. Effect of choice of weathering end-member $^{87}Sr/^{86}Sr$ on variation in modeled annual depletion and weathering rates. Reference points with respect to the weathering end-member are as follows: A, 0.7220, value at which there is no ecosystem depletion; B, 0.7238, mean bulk soil composition; C, 0.7251, provisional end-member; and D, 0.727, bedrock isochron intercept.

tios in throughfall indicate that most of the Sr and Ca in throughfall is derived from canopy leaching rather than from wash-off of dry deposition.

3. Variability in mineral Sr isotopic composition complicates assessment of $^{87}Sr/^{86}Sr$ ratio of Sr released by weathering reactions. Results of the present study as well as those of *Bain and Bacon* [1994] demonstrate the importance of a thorough knowledge of site mineralogy and mineral Sr systematics in order to properly interpret ecosystem Sr isotope studies. The effects of weathering, spatial variability in parent material, and organic matter deposition need to be taken into account when assessing patterns in $^{87}Sr/^{86}Sr$ within the soil weathering profile. Although transported soil parent material in this glaciated region complicates assessment of mineral weathering, even in regions with residual soils, mineral isotope heterogeneity is to be expected due to variations in Sr/Rb ratio in individual mineral species.

4. Watershed Ca losses may be partitioned into losses due to weathering versus losses due to depletion of ecosystem pools by conducting a mass balance on atmospherically derived Ca. This approach requires an estimate of total atmospheric deposition as well as an indication of the origins of Ca in ecosystem pools subject to depletion.

5. Coupling of isotopic end-member modeling with a mass balance showed that depletion of basic cation pools may be an important contributor to stream water losses from this watershed. This depletion is probably due to a reduction in basic cation storage in the forest floor or from the cation exchange complex. Given low inputs via weathering and atmospheric deposition compared to the depletion rate, as well as the relatively large rate of depletion compared to storage in available soil pools, continuation of basic cation depletion could be expected to have a major impact on the function of this ecosystem.

6. The striking difference in base status and estimated weathering rates between CPW and HBEF, two similar sites which lie in close proximity to each other, underscores the need to better understand spatial variation in site specific parameters such as soil mineralogy and disturbance history, in order to develop regional models from study of specific sites.

Appendix: Mass Balance Partition Calculations

1. Calculate the watershed throughfall flux by multiplying the flux at each site by the area of each cover type; sum for the total.

Coniferous	144.3 × 0.78 =	112.5 mol Ca/ha
Deciduous	59.6 × 0.19 =	11.3 mol Ca/ha
Open	17.3 × 0.03 =	0.5 mol Ca/ha
Total		124.4 mol Ca/ha

2. Calculate the proportion of each end-member in the watershed throughfall flux by multiplying the flux at each site

by its atmospheric proportion (Figure 7) and by its area; sum for the total.

Atmospheric	
Coniferous	$144.3 \times 0.78 \times 0.44 = 49.5$ mol Ca/ha
Deciduous	$59.6 \times 0.19 \times 0.33 = 3.7$ mol Ca/ha
Open	$17.3 \times 0.03 \times 1.0 = 0.5$ mol Ca/ha
Total	53.0 mol Ca/ha
Weathering	
Coniferous	$144.3 \times 0.78 \times 0.56 = 63.0$ mol Ca/ha
Deciduous	$59.6 \times 0.19 \times 0.67 = 7.6$ mol Ca/ha
Total	71.4 mol Ca/ha

3. Partition throughfall into atmospheric deposition and canopy leachate. This was done by assuming that atmospheric deposition caught by the canopy in excess of bulk deposition had the same isotopic composition as bulk deposition, whereas canopy leachate had the same isotopic composition as biomass.

	Atmospheric Source	Weathering Source
Atmospheric deposition	x	0
Canopy leachate	y	z

Constraints are $y/(y + z) = 0.32$ (atmospheric portion of biomass), $x + y = 53.0$ (step 2), and $z = 71.4$ (step 2). Solve for y (33.5 mol Ca/ha) and x (19.6 mol Ca/ha).

4. Calculate the loss of atmospheric Ca from the watershed by multiplying the stream water flux by the proportion of stream water derived from atmospheric deposition.

$$103.0 \text{ mol Ca/ha} \times 0.36 = 36.6 \text{ mol Ca/ha}$$

Calculate the depletion of Ca of atmospheric origin by subtracting the total atmospheric deposition rate of 19.6 mol Ca/ha (step 3) from the loss of atmospheric Ca in stream water.

$$36.6 \text{ mol Ca/ha} - 19.6 \text{ mol Ca/ha} = 17.1 \text{ mol Ca/ha}$$

5. Calculate the depletion of Ca of weathering origin by assuming that the depleted pool has the isotopic composition of biomass.

$$x/(17.1 \text{ mol Ca/ha} + x) = 0.32 \qquad x = 36.4 \text{ mol Ca/ha}$$

The total depletion rate is then 36.4 + 17.1 = 53.5 mol Ca/ha

6. Calculate the weathering rate by subtracting the depletion of Ca of mineral origin from the watershed loss of Ca of mineral origin.

$$103.0 \text{ mol Ca/ha} \times 0.64 = 65.9 \text{ mol Ca/ha}$$

$$65.9 \text{ mol Ca/ha} - 36.4 \text{ mol Ca/ha} = 29.9 \text{ mol Ca/ha}.$$

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