

Evaluating Changes In Strontium Chemistry
Of Stream Waters In Response To
Environmental Stress

by

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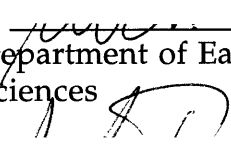
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Abstract

The first measurements of Sr isotopic composition and concentration of archived stream water samples from the Hubbard Brook Experimental Forest in central New Hampshire were collected to evaluate long term trends. The presented data are for two watersheds, one of which was timber harvested in late 1983, and the other is a control watershed. Excess anion deposition, deforestation, and drought are three environmental stresses whose effects are examined in terms of the data set. The relevance of using Sr as a chemical proxy for Ca in environmental studies and the suitability of using Sr isotopic compositions in linear mixing models to characterize and identify the sources of Sr in a complex environment are evaluated using the new Sr isotopic data. Results indicate the need for caution when using Sr as a proxy for Ca in order to create nutrient budgets. The Sr isotopic data are best described in terms of a two-stage mixing model 1) between rain water and the forest canopy and 2) between the resultant mixture (throughfall) and the soil weathering end-member. The similarity in composition between throughfall and stream water makes estimates of the amount of atmospherically derived Sr in the stream waters suspect. Variations in the data presented here are interpreted based on the physical conditions of the system and on the natural and anthropogenic stresses that have been applied to the system over the 27 year history of the archived waters at Hubbard Brook.

Thesis Supervisor: Dr. Samuel A. Bowring

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Chapter 1

Introduction

1.1 Purpose

Natural and anthropogenic changes in an environment are linked to complex chemical and biological systems. Understanding these systems and the ways that changes affect them is a priority for such policy issues as effective land management and emissions control. However, it has proven difficult to characterize environmental systems and human impact adequately. Problems arise when not enough is known about the baseline of an environment or when changes occur over long periods of time. It can also be difficult to evaluate the recovery of an effected system. To this end, the Hubbard Brook Experimental Forest (HBEF) in New Hampshire was established as a facility for the long term study of human impact on and nutrient cycling in small scale ecosystems. Research at Hubbard Brook and at sites around the world demonstrates that stress, applied by such factors as deforestation, acid rain, and drought, is manifested in many different ways (e.g. Åberg *et al.*, 1989, Driscoll *et al.*, 1989, Lawrence *et al.*, 1987, Miller *et al.*, 1993).

The chemistry of a terrestrial ecosystem is at steady state when nutrient outputs from streamflow and harvesting are balanced by inputs from mineral weathering, precipitation, and aerosol deposition (Miller *et al.*, 1993; Figure 1). Mass transport by animals or plants, biological vectors, are likely to have smaller effects, but they can influence both input and output (Likens, 1985). The reservoirs and fluxes of major cations such as calcium, magnesium, sodium, iron, and potassium are influenced by the environmental stresses

applied to the system, and they are among the nutrients necessary for the growth of the biota.

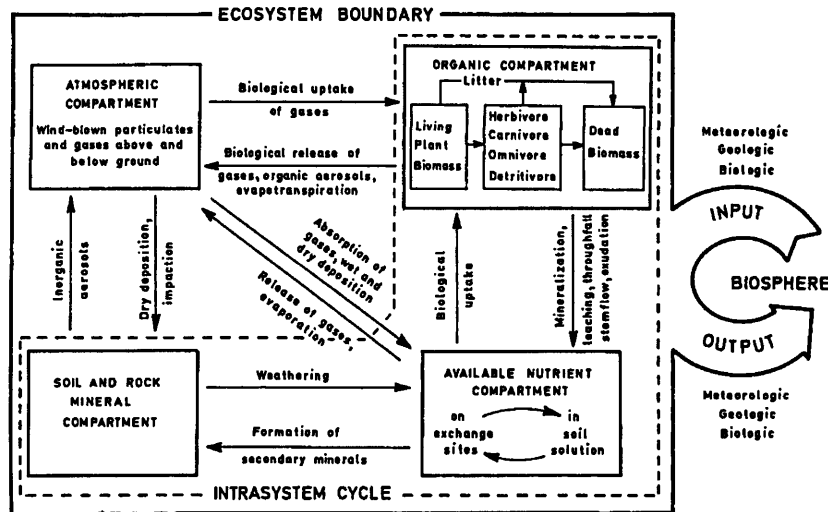


Figure 1: A model of the interrelationships between nutrient pathways and storage compartments within a terrestrial ecosystem. Sources, fluxes, and sites of accumulation are shown (from Likens *et al.*, 1977).

Possible nutrient depletion due to excess anion deposition, or acid rain, is a concern addressed by a number of researchers (e.g. Jacks *et al.*, 1989, Miller *et al.*, 1993). Calcium and its chemical proxy strontium are often used in research as an indicator of the presence of nutrients. The following study examines the long term trends in concentration and composition of Sr, relates the trends to changing environmental stresses, and addresses the validity of studying Sr as a proxy for Ca.

1.2 Hubbard Brook Experimental Forest

1.2.1 History and purpose

In 1955 the U.S. Forest Service set aside a small basin at the southern edge of the White Mountain National Forest in central New Hampshire. The 3,076 ha HBEF was established primarily to study the hydrometeorologic

conditions related to forest land management. By 1963 the research project had grown into the Hubbard Brook Experimental Station (HBES) that was initially concerned with using a small watershed approach to study nutrient cycling and flux (HBES, 1991). Since then, a series of individual watersheds within the basin has been gauged, or instrumented for streamflow measurements, and set aside for whole ecosystem experiments. This study focuses on two watersheds in particular; watershed 5 (W5) is a treated or modified watershed, and watershed 6 (W6) is maintained as a control (Table 1).

Watershed	Area	Established	Treatment
W5	21.9 ha	1962	whole-tree harvest
W6	13.2 ha	1963	none (control)

Table 1: Samples were taken from two watersheds, 5 and 6, whose characteristics are compared above (HBES, 1991).

From October 19, 1983 to May 21, 1984, W5 was harvested by removing the trees with branches and leaves attached. Following a protocol of commercial New England logging companies, all trees greater than ten centimeters in diameter at chest height were removed using skidders after being harvested with a feller-buncher machine in accessible locations and chain saws on inaccessible slopes (HBES, 1991). The recovery of this watershed is being monitored closely.

1.2.2 Site description

The Hubbard Brook Valley is centered at 43° 56'N and 71° 45'W in Grafton County near Woodstock, New Hampshire. USGS 7.5' quadrangle maps for Mt. Kineo and Woodstock cover the area. The basin is eight

kilometers long, five kilometers wide, and is drained west to east by Hubbard Brook, a tributary of the Pemigewasset River. Most of the watersheds that drain into the brook are oriented north-south, and W5 and W6 are adjacent southeast-facing watersheds varying in altitude from 590 m to 853 m above mean sea level and varying in slope from 20 to 30% (Figure 2). The site is 116 km from the Atlantic Ocean and is over 160 km from any large industrial centers (HBES, 1991).

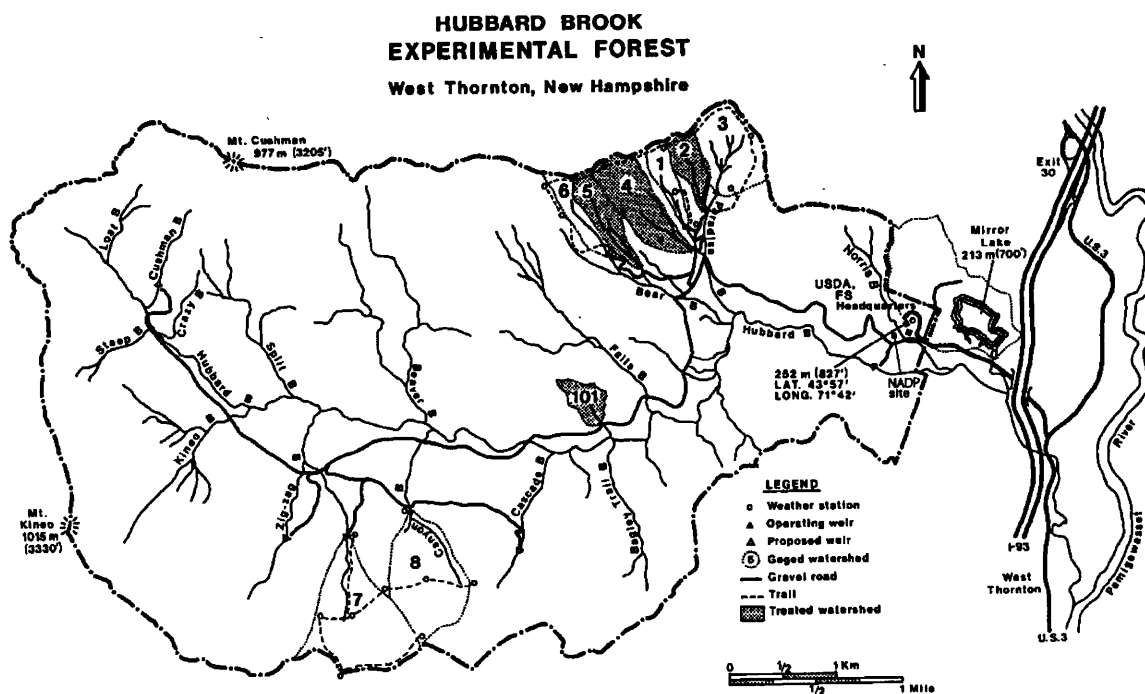


Figure 2: The Hubbard Brook Experimental Forest, showing the drainage streams and gauged watersheds (from Likens *et al.*, 1977).

The bedrock of W5 and W6 in the eastern portion of the basin is primarily the Silurian Rangeley Formation. These rocks are meta-pelites and quartzites, medium to coarse grained, consisting of feldspar, quartz, biotite, muscovite, and sillimanite; the schists have calc-silicate pods, are locally sulfidic, and contain garnet (Barton, 1993 and HBES, 1991). They were

originally mapped as the Devonian Littleton Formation which is separated from the Rangeley schists by a thrust fault near the southern boundary of the basin. The Rangeley Formation underwent three stages of deformation and is locally intruded by pegmatites, basaltic dikes, and plutons including the Late Devonian Concord Granite. In the western part of the basin the Devonian Kinsman Quartz Monzonite, a foliated pluton with megacrysts of alkali-feldspar, crops out (HBES, 1991).

The soils and surficial features of the basin all developed subsequent to the final retreat of the glaciers approximately 14,000 years ago. Today, the thickness of the till varies from zero to nine meters, with an average of two meters (Likens, 1985). The recognizable composition of the till corresponds to a mix of the lithologies from both nearby and from a wedge-shaped area extending several miles to the northwest, from the direction of the glacial advance (Bailey and Hornbeck, 1992). The soils are generally Spodosols, sandy loam in texture, very rocky, and well-drained with little clay. They are derived from the till but not from the bedrock, which appears virtually unweathered (Figure 3). The pH of the soils is ≤ 4.5 , and they are relatively infertile (HBES, 1991).

An organic-rich forest floor layer 20 to 200 mm in thickness overlies an eluvial horizon (E), from which organic and inorganic materials are dissolved and removed by infiltrating water. These salts, organic compounds, and oxides of iron and aluminum accumulate below in the illuvial horizon (B). The C horizon corresponds to the till, or the little-altered unconsolidated material, and the R horizon corresponds to bedrock (FitzPatrick, 1980). When trees are uprooted, the organic-rich soils are mixed or inversely layered with the mineral, or less organic-rich, soils, affecting the nutrient cycles and weathering. Locally, the top of the C horizon may be an impermeable pan or

fragipan that restricts both the growth of root systems and the infiltration of water, and the average depth to the C horizon at Hubbard Brook is 0.6 m (HBES, 1991).

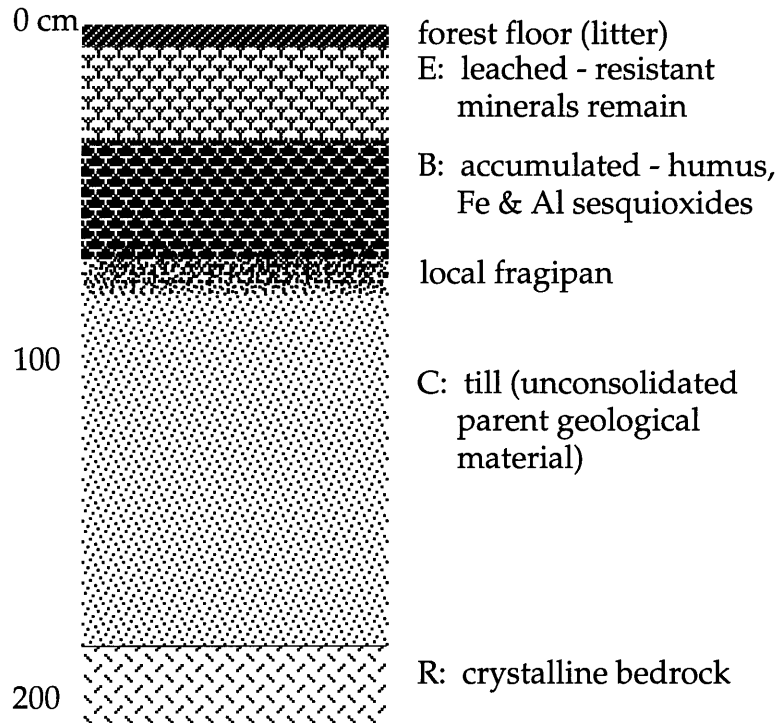


Figure 3: Scaled outline of prominent soil and mineral horizons at HBEF.

With the exception of the manipulated watersheds, the forest has been undisturbed since 1910-1919 when it was logged commercially. The vegetation is 80 to 90% hardwood and 10 to 20% conifer, typical of a developing, second-growth, northern hardwood forest. Species include white birch, balsam fir, and red spruce at higher altitudes and on rocky or north-facing slopes. White ash, yellow birch, American beech, and sugar maple dominate the other areas. For the first ten years after a forest disturbance, the pin cherry is the predominant species in re-colonizing the forest (HBES, 1991).

The climate at Hubbard Brook is classified as humid continental (Likens *et al.*, 1977). Although the summers are short and cool and an average of 1.5 m of snowpack accumulates every winter, the soil remains unfrozen year-round. The weather changes rapidly, and temperature extremes are highly variable both daily and annually. Air masses typically move from the continent over the basin; the winter season is characterized by northwesterlies and the summer by southwesterlies. The movement of the polar air during the fall and winter can create cyclonic disturbances that move up the east coast, introducing some maritime air to the HBEF (Likens *et al.*, 1977).

Although the precipitation in the HBEF averages 110 mm per month throughout the year, streamflow is variable with four important seasonal flow regimes. A period of maximum flow due to the snowmelt occurs during the months of March, April, and May. Summer, particularly July, August and September, is the baseflow season during which most water in the system is lost through evapotranspiration. Smaller watersheds in the HBEF may have no streamflow for extended periods during dry summers, and the streamflow for all the watersheds is highly variable. The months of October, November and December correspond to the recharge period during which evapotranspiration stops and the soil water deficits are eliminated, allowing conditions of steady streamflow (Likens *et al.*, 1977). Finally, January and February have diminished flow because the precipitation is stored as snowpack, and 25-33% of the annual precipitation occurs as snow (Figure 4).

For the research presented here, the HBEF has four prominent advantages; 1) the contribution of deep groundwater from the fractured bedrock to the watershed output is small relative to the lateral flow in the till contributed by precipitation (Figure 5), 2) evapotranspiration, streamflow, and

precipitation control most of the flux of water into and out of the watershed, simplifying mass balances, and the watersheds are relatively similar in most of their physical characteristics, making inter-watershed comparisons possible, 3) New Hampshire is 87% forested, making Hubbard Brook's isolation from major population areas a benefit for geochemical research (HBES, 1991), and 4) the HBES database of chemical and hydrometeorological information, as well as selected archived stream water samples from as early as 1967, allow the presentation of a long-term study of changing chemical trends within the basin.

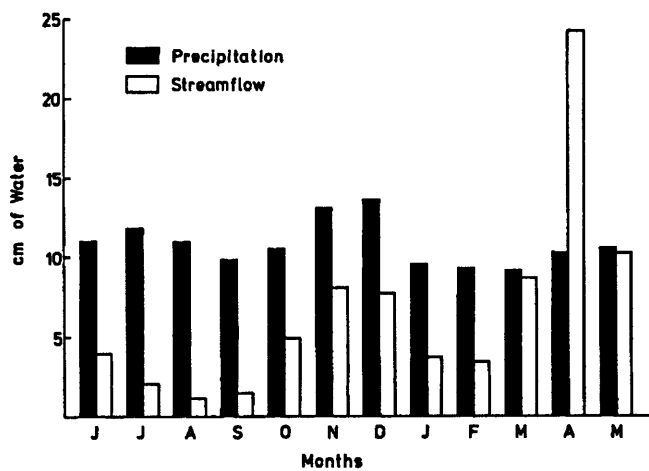


Figure 4: Averages from 1956 to 1974 for the streamflow and precipitation in the HBEF (from Likens *et al.*, 1977).

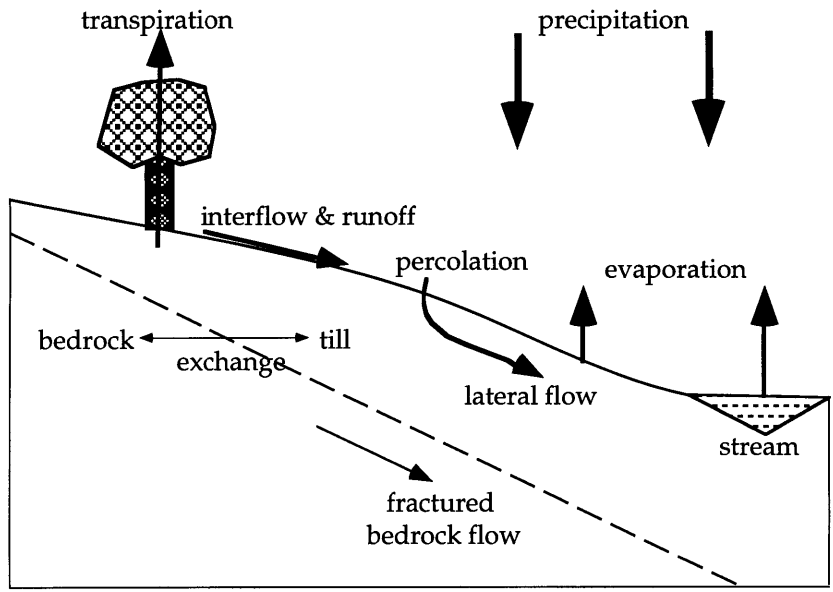


Figure 5: Schematic diagram showing fluxes of water into and out of the watersheds. Arrows indicate relative magnitudes of each contribution.

Chapter 2

Methods

2.1 Chemistry

Naturally occurring Sr, element 38, has four isotopes, ^{88}Sr , ^{87}Sr , ^{86}Sr , and ^{84}Sr , comprising approximately 82.53, 7.04, 9.87, and 0.56 mole percent of the natural abundance, respectively. When these isotopes are incorporated into solutions or biological or crystalline materials, they are not fractionated relative to one another because of their relatively high masses and similar ionic radii. Therefore, the accepted constant ratios of $^{86}\text{Sr}/^{88}\text{Sr}$ and $^{84}\text{Sr}/^{86}\text{Sr}$ are 0.1194 and 0.056584. All of the natural Sr isotopes are stable, but ^{87}Sr is derived from the emission of a β^- particle from ^{87}Rb . The reaction has a decay constant $\lambda = 1.42 \times 10^{-11} \text{ y}^{-1}$, so the relative abundance of ^{87}Sr in any given sample is variable and depends on the age of the sample and the initial Rb/Sr ratio (Faure, 1986). In other words, a high initial abundance of rubidium in an old rock means a high fraction of ^{87}Sr in the total Sr content today. The time integrated Rb/Sr ratio is significant because the radiogenic Sr can be used as an isotopic tracer. Whether the Sr in the system comes from the atmosphere or any of the soil, till, or bedrock types, each source has its own isotopic composition that will contribute to the overall composition of the stream water.

Strontium is the fourth Group IIA alkaline earth element, and Ca is the third. Each has a +2 valence state as an ion, but Sr has an ionic radius of 1.13 Å, and Ca has a radius of 0.99 Å. This similarity allows the less abundant Sr to behave in a chemically similar manner but prevents it from replacing Ca in all conditions. Ca^{+2} can fit into six and eight-fold coordinated lattice sites, whereas Sr^{+2} prefers the more spacious eight-fold sites in a crystal.

Major minerals with ideal sites for replacement include plagioclase, apatite, and aragonite. The potassium in K-feldspars can also be replaced when the Sr^{+2} is accompanied by the replacement of Si^{+4} by Al^{+3} (Faure, 1986). Thus the presence of Sr is not always analogous to that of Ca, but its occurrence is similar.

Sr/Ca concentration ratios taken for most waters, plants, and many rocks in the environment fall between 10×10^{-3} and 20×10^{-3} . Åberg *et al.* (1989) observe a small decrease in the Sr/Ca ratio due to a degree of biological preference for the uptake of Ca over Sr in species such as spruce and pine, and Bailey *et al.* (1994) measure much lower ratios for HBEF specimens of red spruce than the local environmental average. Another variation from the constant Sr/Ca ratio occurs when calcium-rich waters have their Ca concentration buffered by the atmospheric partial pressure of CO_2 (P_{CO_2}) at equilibrium with dissolved calcite (Wadleigh *et al.*, 1985), but the low Ca concentrations at this locale ($\ll 19$ ppm) rule out this effect. As a first approximation, this research assumes that the sources and fluxes of Ca and Sr are analogous, however the validity of this assumption is subsequently evaluated. If Sr is a relatively reliable proxy for Ca, a major nutrient and buffering cation, then information about the source as well as the concentration of Ca is available.

Rubidium generally follows K through the geochemical cycle, and they are the fourth and third Group IA alkali metals with ionic radii of 1.48 Å and 1.33 Å, respectively. Rb^{+1} substitutes for K^{+1} in such major mineral groups as micas, K-spars, and some clays and evaporites, and the ^{87}Rb then decays to ^{87}Sr with time (Faure, 1986). Some researchers report evidence for the preferential weathering of ^{87}Sr over ^{86}Sr , but they debate its cause and effect. All the authors agree, however, that any environmental system has multiple

sources of Sr with different isotopic ratios, and that the output composition of that system depends on the mixing of the component end-members (e.g. Åberg, 1990, Brass, 1975, Edmond 1992).

2.2 Techniques

2.2.1 Sample selection and collection

Strontium concentration and isotopic composition data were acquired by thermal ionization mass spectrometry for a suite of stream water samples spanning the archived history of W5 and W6. It was first necessary to determine which samples would be most suitable for analysis. As this was a survey study, one or two samples from a given year would suffice, but the varying seasonal streamflow regimes described above mean that various reservoirs of Sr could influence the sample chemistry depending on the sample date. For instance, summer baseflow samples are more likely to reflect soil and bedrock composition, except after storm events, whereas fall recharge samples might reflect mixing information from all the reservoirs. Figure 5 shows the relative contributions of the water fluxes, but seasonal variations are significant. After the growing season, reduced evapotranspiration results in more water-saturated soil and increased lateral flow velocities of the soil water, whereas the limited lateral flow during the summer is strongly influenced by storms. A suite of mid-summer samples from W5 were analyzed and compared with a matching suite of late fall samples. All subsequent samples were from fall collection dates because of fewer perceived extremes in isotopic composition and limited periods of low streamflow.

To remain consistent with the collection technique of the archived samples, modern samples from 1993 and 1994 were collected in new high density polyethylene bottles washed four times with the stream water before

being filled for collection in the fifth wash. Subsamples of the archived waters were taken in new bottles rinsed only once because of the limited quantities of sample. It is common protocol to acidify water samples before analysis in order to dissolve any Sr that might have precipitated or been adsorbed onto the plastic walls of the bottle. Since the archived waters had never been acidified, the modern samples were left unacidified to maintain consistency. Weirs located at the mouths of each of the watersheds provided a consistent sample collecting location.

Seven other samples were analyzed in addition to the 30 W5 stream water and the 20 W6 stream water samples. A lysimeter sample from the spring snowmelt of 1994, probably the lowest pH time of the year, was taken for the lower portion of each watershed from the B_{s2} soil horizon, where "s" denotes deposition of sesquioxides of Fe and Al, and "2" denotes the subdivision of the illuvial horizon. Two groundwater samples were pumped from a bedrock fracture 33.5 m below the ground surface through a well located next to the USDA Forest Service Headquarters building. They were taken in the fall of 1994 after 15 and 30 minutes of pumping in order to ensure the well was purged of stagnant water that had been in contact with the iron casing of the well for extended periods of time. Additionally, mineral separates of a Cone Pond Watershed plagioclase and hornblende and a Rangeley schist plagioclase were analyzed to see how their compositions might affect the final composition of the watershed output.

2.2.2 Strontium isolation procedure and sample preparation

Mass spectrometry requires the separation of the element of interest from the rest of the sample in order to eliminate isobaric interference caused by other ion species having a similar mass to charge ratio and to prevent the inhibition of ionization of the element of interest by other cations. Following

the outline of the method described by Pin and Bassin (1992), the Sr in the HBEF samples is prepared in a clean lab. A small volume of cation-specific, pH-sensitive, ion exchange medium (~50 μL Sr Spec resin from Eichrom Industries) is loaded into a clean column in ultra-pure water, and the columns are then washed twice with water and once with distilled 3.5 N HNO_3 . The water samples are dried in Teflon beakers and re-dissolved overnight in 500 μl of 3.5 N HNO_3 . They are centrifuged for 30 minutes to separate any remaining solids, and then the liquid portions are loaded onto the columns – the liquid is allowed to drip through completely in each step. Four subsequent washes with 300 μl of 3.5 N HNO_3 eliminate Al, Ca, Fe, Mg, Mn, and Ti from the column, then Ba and K. The Sr is then eluted with two washes of 500 μl of water. Two μl of distilled H_3PO_4 are added to the strontium-water mixture, and the water is driven off, leaving the Sr in a gel of H_3PO_4 . Total procedural blanks for this technique were less than four picograms total Sr during the course of this investigation.

Two aliquots for each sample are analyzed, one for isotopic composition (IC) and one spiked with a known quantity of ^{84}Sr spike (~0.01 g MIT ^{84}Sr spike #4) for concentration analysis, or isotope dilution (ID). Approximately 1.5 ml of stream water is run for each ID and 5 ml for each IC (~50-100 ng of Sr are analyzed for the IC's). The Sr concentration of the spike is 1.458 ppm, which is about three orders of magnitude greater than that of the water samples. Therefore, the minor portions of ^{86}Sr , ^{87}Sr , and ^{88}Sr present in the spike are great enough to distort the natural isotopic ratios. This is why a separate aliquot must be run to find the true composition of the Sr.

The mineral separates have high enough concentrations of Sr that the isotope composition can be determined and the Sr concentration can be

calculated from the same spiked aliquot. The grains are digested in a heated mixture of 300 μl of 7 N HNO_3 and 1 ml HF. The first volume is allowed to evaporate rapidly, and a second volume of acid is added, sealed, and heated at 150°C for four days. The mixture is then dried down, and the residue is dissolved in 5 ml of 6 N HCl, sealed and heated over night. This mixture is allowed to evaporate, and the final residue is dissolved in 600 μl of 3.5 N HNO_3 over night and then loaded onto the ion-exchange columns.

2.2.3 Mass spectrometry

The summer samples from W5 were analyzed at the University of Kansas, Lawrence facility after the Sr extraction chemistry was completed at the MIT clean lab with the assistance of Mark L. Huang, a summer intern student. All other samples were run on the MIT EAPS VG Sector 54 thermal ionization mass spectrometer. The samples were loaded in a clean environment onto single ribbon rhenium filaments in a solution of TaCl and H_3PO_4 , and the volatiles were driven off. In the machine, the samples were ionized, and a magnetic sector was used to disperse the isotopes by mass. Analyses were performed using the dynamic-multicollector mode with $^{88}\text{Sr} = 1\text{V}$ for the water samples and $^{88}\text{Sr} = 3\text{V}$ for the mineral separates. Techniques used at the University of Kansas were adopted from those used at MIT and are essentially identical.

Chapter 3

Data

3.1 Watershed 5 data table

	Sample Date	[Sr] ppb	[Ca] ppm	$^{87}\text{Sr}/^{86}\text{Sr}$	Streamflow (mm)
1	Jul/5/1971	10.7	1.37	0.7209470	2.770
2	Nov/1/1971	10.4	1.44	0.7209926	8.887
3	Nov/7/1973	10.4	1.64	0.7209425	29.999
4	Jul/8/1975	10.2	1.39	0.7222960	0.235
5	Nov/14/1975	9.4	1.39	0.7209121	45.526
6	Nov/8/1977	8.8	1.39	0.7209532	9.138
7	Jul/2/1979	8.3	1.10	0.7208550	4.012
8	Oct/8/1979	8.8	1.23	0.7209562	41.483
9	Jul/5/1982	7.6	1.09	0.7209599	10.631
10	Oct/4/1982	7.4	1.05	0.7212554	1.325
11	Jul/10/1983	11.1	1.46	0.7221870	0.744
12	Oct/30/1983	8.3	1.16	0.7214950	1.756
13	Jul/1/1984	9.5	1.33	0.7208233	66.748
14	Nov/4/1984	24.5	3.26	0.7209534	7.018
15	Jul/7/1985	24.3	3.17	0.7209270	6.765
16	Oct/27/1985	20.6	2.85	0.7210214	11.072
17	Jul/13/1986	8.9	1.29	0.7210077	2.558
18	Oct/26/1986	10.9	1.60	0.7210764	5.051
19	Jul/12/1987	9.2	1.32	0.7212560	5.602
20	Oct/25/1987	8.9	1.31	0.7210712	10.225
21	Jul/3/1988	8.7	1.39	0.7215190	1.384
22	Oct/31/1988	9.4	1.47	0.7211817	5.149
23	Jul/3/1989	9.6	1.30	0.7212380	4.285
24	Oct/18/1989	9.8	1.44	0.7210273	21.543
25	Oct/29/1990	8.8	1.41	0.7210668	47.668
26	Nov/5/1991	8.6	1.35	0.7210718	7.314
27	Oct/20/1992	8.1	1.36	0.7211469	12.644
28	Jul/5/1993	10.7	1.44	0.7218730	0.642
29	Oct/4/1993	8.9	1.65	0.7210870	14.842
30	Jul/15/1994	12.8		0.7218200	

Table 2: Collection dates, strontium & calcium concentrations, Sr isotopic compositions, and cumulative streamflows for the week preceding sample collection for treated W5.

3.2 Watershed 6 data table

	Sample Date	[Sr] ppb	[Ca] ppm	$^{87}\text{Sr}/^{86}\text{Sr}$	Streamflow (mm)
1	Dec/19/1967	10.2	1.35	0.7205305	27.013
2	Nov/14/1968	7.0	1.04	0.7206209	2.608
3	Nov/3/1969	8.5	1.35	0.7204479	5.128
4	Nov/1/1971	10.1	1.36	0.7206177	10.435
5	Oct/24/1972	7.8	1.14	0.7205457	4.895
6	Nov/7/1973	9.4	1.50	0.7205287	32.571
7	Oct/22/1975	9.0	1.31	0.7204963	67.871
8	Oct/31/1977	8.0	1.14	0.7210620	7.609
9	Oct/31/1978	6.4	0.98	0.7205788	2.060
10	Nov/8/1979	7.7	1.05	0.7205576	21.371
11	Oct/19/1981	6.8	1.00	0.7205440	27.000
12	Oct/27/1983	6.1	0.93	0.7206769	2.379
13	Nov/4/1984	5.2	0.76	0.7207638	1.812
14	Oct/27/1985	6.1	0.91	0.7206475	11.565
15	Nov/1/1987	6.0	0.89	0.7208279	24.059
16	Oct/31/1988	6.2	0.95	0.7205946	5.503
17	Oct/30/1989	6.8	0.99	0.7205547	14.353
18	Oct/29/1991	5.8	0.89	0.7205965	8.813
19	Nov/6/1993	5.7	0.86	0.7209792	24.465
20	Nov/3/1994	5.8		0.7205996	

Table 3: Collection dates, strontium & calcium concentrations, isotopic compositions, and cumulative streamflows for the week preceding sample collection for reference W6.

3.3 Groundwater, soil water, and mineral data

	Sample Name	Sample Date	[Sr] ppb	$^{87}\text{Sr}/^{86}\text{Sr}$
1	soil water WS-6 Bs2	May/11/1994	6.4	0.7197850
2	soil water WS-5 Bs2	May/11/1994	5.9	0.7219612
3	well FSE-5 pump 15m	Nov/3/1994	177.9	0.7165909
4	well FSE-5 pump 30m	Nov/3/1994	191.9	0.7164532
5	CPW 5C plagioclase		444700.0	0.7122110
6	SRL plagioclase		837480.0	0.7204890
7	CPW 5C hornblende		13950.0	0.7225010

Table 4: Sample dates, strontium concentrations, and isotopic compositions for well water, lysimeter, and mineral separate samples.

3.4 Error analysis

The measured $^{87}\text{Sr}/^{86}\text{Sr}$ composition data is normalized exponentially for fractionation to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$, and the $^{84}\text{Sr}/^{86}\text{Sr}$ data used to calculate the concentration is linearly normalized. On the basis of multiple analyses of the isotopic composition of the standard NBS-987, the external reproducibility of these samples is 15 ppm for the mineral separates run at 3V ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710250 \pm 0.000011$) and 51 ppm for the water samples run at 1V ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710250 \pm 0.000036$).

The regression of data for spiked water samples follows the equation outlined in Faure (1986). Data for the mineral separates is reduced with a program that iteratively strips the spike composition from the data. The reliability of the concentration values is conservatively quoted to within 5% for the water samples and 0.1% for the mineral separates. However, relative to the natural variations of the composition and concentration in the system, the error bars for both are almost imperceptible when plotted at appropriate scales. Therefore, they are excluded from the subsequent plots. A possible exception to this case might be October 31, 1977 from W6 which is likely to have larger than normal error associated with it. Only twenty ratios were measured, as opposed to the usual protocol of one hundred, and they had a relatively high error associated with them.

The HBES database contains major element analyses, including Ca, for each of the archived waters. The Ca analyses are made by atomic adsorption soon after sample collection. Until ten years ago, the samples were analyzed at Cornell University. Currently the samples are analyzed on a Perkin Elmer Atomic Adsorption Spectrophotometer at the Institute of Ecosystem Studies, Millbrook, New York. Lanthanum is added to prevent interference, and reproducibility is conservatively quoted to within 0.1 ppm concentration.

The Ca information included here is from the ongoing Hubbard Brook ecosystem database (Buso, in preparation).

Chapter 4

Discussion

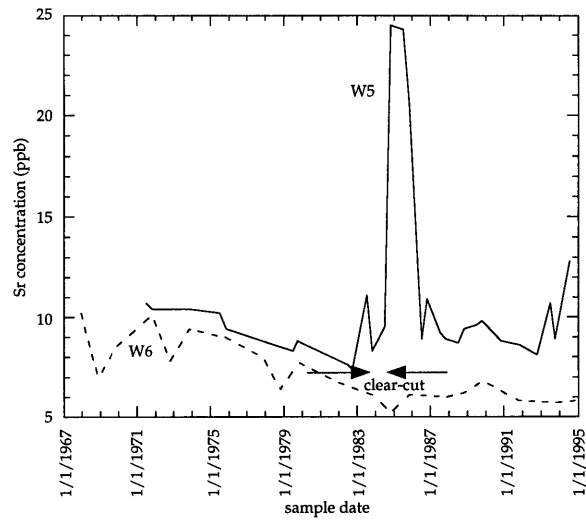
4.1 Deforestation recovery

4.1.1 Recovery of a harvested watershed

Examination of the stream water data for both watersheds shows that the concentration of Sr in the waters is generally less than 11 parts per billion, and the values tend to decrease over time; Ca data also show this decreasing trend. The most striking feature in the entire concentration data set, however, is the peak in Sr and Ca concentration in W5 soon after the deforestation. The peak is not apparent in the control watershed data set (W6), and it lasts from the fall of 1984 until the end of 1985. Interestingly, the clear-cutting ended in May, 1984 with tree removal extending into the summer (Figures 6a & b). This chemical pattern has been observed previously in studies of the major cations in other vegetation elimination experiments (Likens *et al.*, 1969) and in other cations in the W5 whole-tree harvest experiment (Lawrence *et al.*, 1987).

Commercial clear-cutting impacts an environment by reducing evapotranspiration, disrupting normal soil drainage patterns with roads and truck tracks, forcing the development of a different forest community profile, exporting the biomass nutrient reservoir, and physically mixing the soil horizons. These physical changes must lead to the chemical changes observed in this data set and by other researchers. Lawrence *et al.* (1987) observe the spatial and temporal changes in Al concentration and speciation for the period bracketing the harvesting experiment in W5. Aluminum is of interest because its solubility increases at lower pH, and the species in which it is found at low pH interact more readily than others with biological systems.

a)



b)

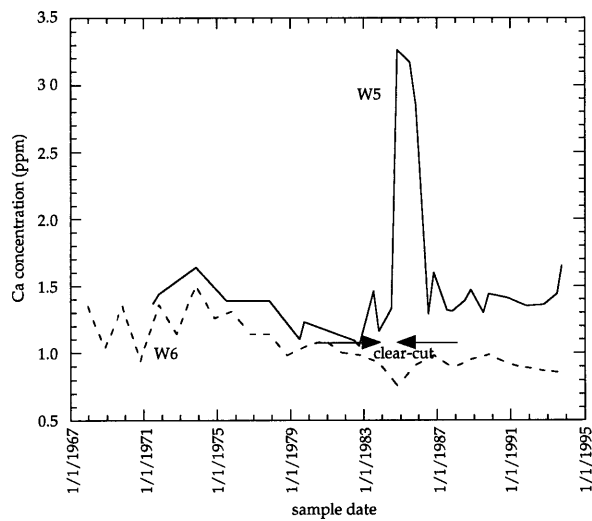


Figure 6: a) Strontium concentration trends over the histories of the treated W5 (solid line) and the reference W6 (broken line).
b) Calcium concentration trends.

Elevated concentrations of Al can be toxic to fish, stunt plant growth (Driscoll and Schecher, 1988), and may inhibit Ca uptake, resulting in Ca nutrient deficiencies (Bailey *et al.*, 1994). Lawrence *et al.* (1987) also report pH trends and anion concentrations over the same period. They observe a

dramatic increase in NO_3^- concentration at the start of the growing season of 1984, a concurrent increase in the total concentration of base cations, and a decrease in SO_4^{2-} . Two to four months later, the pH decreased and the Al concentration increased. This is unusual because an increase in acidity would be expected to coincide with the measured increase in nitrate ion.

The trends in total base cations observed by Lawrence *et al.* (1987) are similar to those apparent in this Sr and Ca data set even though this survey is divided into annual and semi-annual increments, while theirs is divided into monthly increments. Ordinarily, low summer streamflow coincides with the elevated evapotranspiration associated with the growing season (Figure 4), but vegetation loss elevates the contribution of lateral flow and interflow of shallow surface waters to the streamflow volume (Figure 7). Also the disruption of the normal soil drainage paths may limit the volume of water which can reach the deep till. As a result, more water moves as interflow, passing through the soil organic layer and the forest floor. This water increases the mineralization and resulting nitrification of the organic layer. Consequently the NO_3^- concentration rises early in the experiment. Lawrence *et al.* (1987) note that the delay of a few months between the NO_3^- elevation and the decrease in pH indicates that the system is able to buffer the acid input with an increase in base cation flux, the appearance of which is noted both in their data set and in the set presented in this research. Additionally, Al dissolution increases at lower pH, and they observe an increase in Al, as expected.

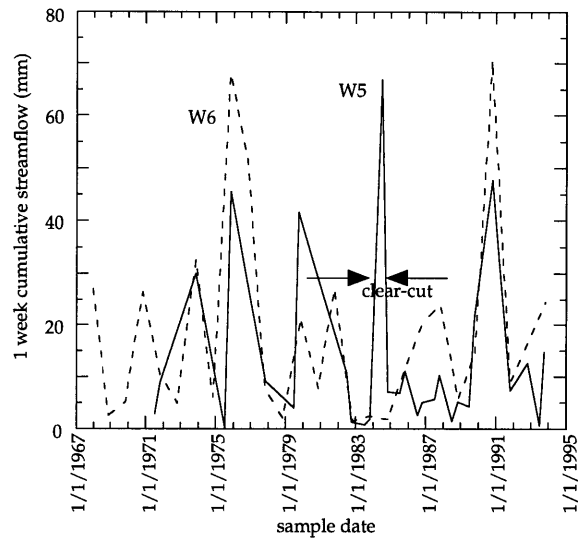


Figure 7: The streamflow summed for the seven days prior to sample collection is recorded here as cumulative streamflow associated with each sample date. Highs and lows are concurrent for W5 (solid line) & W6 (broken line) except for the period of reduced evapotranspiration associated with the growing season following the treatment of W5. Streamflow integrated over time is a volumetric term which is then normalized over the area of the watershed to get a dimension of length (mm).

The other notable feature of Figure 6 is the high degree of variability in cation concentration following the clear-cutting of W5. In contrast to W6, this seems to indicate that any presumed recovery of the watershed ten years later does not correspond to stable chemical conditions in the soil. Also, there is a higher concentration of cations in W5 stream waters compared to those in W6 relative to the concentration differences between W5 and W6 before the deforestation. Perhaps the different vegetative community that developed, the mixing of soil horizons, or the rapidly aggrading nature of the forest causes elevated cation loss. In particular, the surfaces of clay particles, humus, and some oxides are negatively charged, resulting in a high capacity to attract positively charged ions. These soil-exchangeable sites are filled with cations

such as Ca and Sr. Disturbing the soil with machinery may expose these components to greater weathering by the organic and strong acids, such as humic, sulfuric, and nitric, that dominate the system. Whatever the mechanism, the changing cation fluxes indicate that the weathering rates are still elevated and variable in the treated watershed.

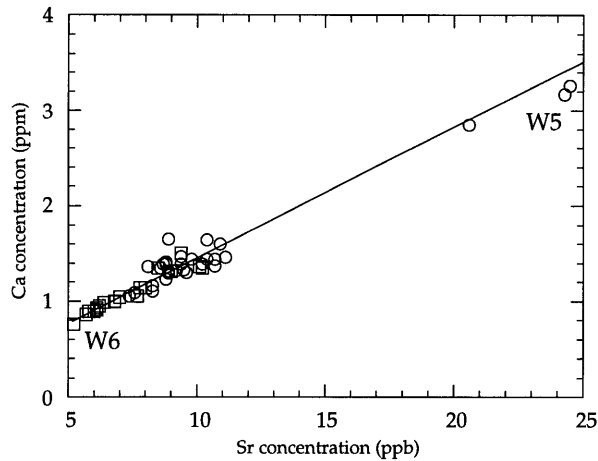
An adequate explanation for the distinctive small peaks in concentration around the time of deforestation on the shoulders of the large peak is elusive. The second one may be part of the general post-treatment variability, but the timing of the first peak precedes the harvesting. Very low streamflow can be associated with higher cation concentrations, and the week prior to the sample date of July 10, 1983 corresponds to very low streamflow conditions. NO_3^- is taken up by trees during transpiration, but the small amount of slow-moving soil water interacts with the mineral soil, increasing its base cation concentration (Driscoll and Schecher, 1988). Since the watersheds encompass only the smallest tributaries in the system, soil water can interact with the minerals on its way from the ridge to the weir, and most water enters the stream before arriving at the weir. Assuming the contributions from the bedrock are relatively small, these small watersheds have precipitation-dependent residence times for the soil water, and the composition of the associated water is entirely dependent on the interactions it has with the materials through which it passes.

4.1.2 Release of strontium relative to calcium: impact of deforestation

Using Sr as a proxy for Ca in the geochemical cycle is a technique frequently used when examining environmental systems (e.g. Åberg *et al.*, 1989, Bailey *et al.*, 1994, Jacks *et al.*, 1989, Miller *et al.*, 1993). In the concentration data presented in the current data set, the Sr and Ca concentrations generally vary linearly, indicating apparent concurrence of the

elements in this system (Figure 8a). Plotting the ratios of the concentrations over time, however, is more illustrative (Figure 8b). The W6 data fluctuates around a constant baseline, whereas the W5 data reveals that samples collected immediately after deforestation have higher Sr/Ca ratios, plotting somewhat below the line in Figure 8a. These initially high Sr/Ca ratios are followed by a notable decrease in the Sr/Ca ratios.

a)



b)

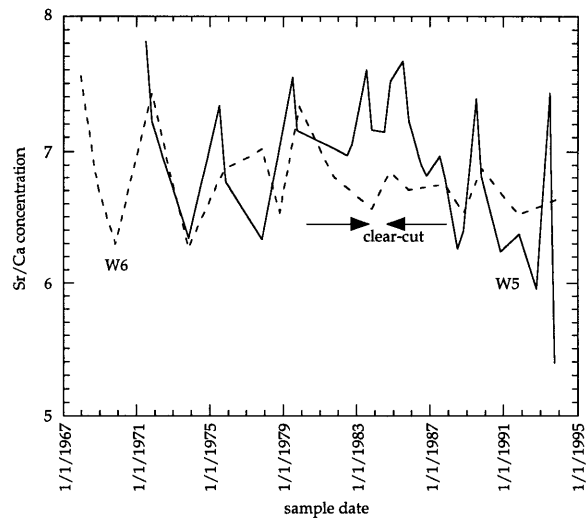


Figure 8: a) Strontium versus calcium plots linearly. b) The Sr/Ca ratio versus time demonstrates that strontium and calcium are not strictly analogous. Sr/Ca values are $\times 10^{-3}$.

Apparently the HBEF environment gets its Sr and Ca from different sources when stressed. The decrease in forest canopy during the deforestation and the change in vegetation species distribution following the deforestation influence the chemistry of the throughfall, or bulk precipitation that interacts with the forest canopy. Other cation reservoirs may also be influenced, such as the soil-exchangeable pool which is physically mixed by the heavy logging machinery. Strontium does not follow Ca strictly through the geochemical cycle, and the dissolution of the ions shows some visible differences indicated here by the non-linear behavior in the Sr/Ca systematics. This data does not invalidate the proxy assumption, but it does indicate the need for caution, especially in disturbed watersheds.

The Sr and Ca concentration data also alleviate some of the concern about the fact that the samples were left unacidified before analysis. The W6 data is constant in the long term, indicating no loss of Sr relative to Ca in the older samples. The Ca analyses were made soon after the samples were collected, and some of the Sr analyses were made 27 years later. The effects of ion adsorption and precipitation during storage appear minimal.

4.2 Anion deposition

4.2.1 History of regional acid rain

The increased acidity of precipitation is due largely to anthropogenic emissions of SO₂ and NO_x which are hydrolyzed to strong acids in the presence of water vapor in the atmosphere (Driscoll *et al.*, 1989). These anions may also fall as dry deposition aerosols that mix with water on the ground or in the vegetation canopy to form acids. Measurements are sparse and somewhat controversial, but the pH of the precipitation in the eastern United States began falling as early as the 1950's. At Hubbard Brook, the lowest pH levels were recorded in 1971, and the pH has been increasing ever

since (Driscoll *et al.*, 1989). This trend coincides with a decrease in SO₂ emissions from the combustion of fossil fuels and a decrease in the concentration of SO₄²⁻ in the bulk precipitation. Sulfuric acid dominates the input of acid equivalents, but the proportion of equivalents provided by nitric acid has more than doubled in the last 30 years (Likens, 1985). Like the increase in NO₃⁻ following the harvest of W5, this trend may influence the flux of base cations in the system.

4.2.2 The acid signal in the stream water data

Driscoll *et al.* (1989) do not measure a coincident drop in stream water pH matching that of the precipitation. Instead, the long term trend of pH in W6 waters has been constant around 4.9 since 1964 with a notable drop below 4.8 from 1969 to 1975. Driscoll *et al.* (1989) feel that an observed decline in the sum of base cations matching the drop in SO₄²⁻ prevents pH from increasing, and propose two explanations for the drop in buffering cations: atmospheric deposition of cations is decreasing relative to washout in the stream water and the release from cation pools is diminishing relative to washout. Both of these factors would lead to reduced concentrations.

Figure 9 shows fluctuations for both ions until 1974 when a trend of decreasing Sr and Ca concentrations characterizes the rest of the history of W6, a trend that is also apparent in Driscoll *et al.*'s base cation plots (1989). In W5 information presented in Figures 6a and b, the trend lasts until clear-cutting in 1983. Numerous authors conclude that wet and dry atmospheric inputs to an ecosystem account for a surprising amount of various cations available to the system (e.g. Åberg *et al.*, 1988, Driscoll *et al.*, 1989, Graustein and Armstrong, 1983). Their estimates vary as do the ecosystems they studied, but they feel that the impact of deposition on the available cation pools is significant. Driscoll *et al.* (1989) estimate that the percent of base

cations made available to W6 by wet and dry precipitation has dropped from 20% in 1965 to less than 5% today. They also feel that the bulk of the decrease in stream water base cation concentration is derived from the observed decreasing trend in precipitation concentration.

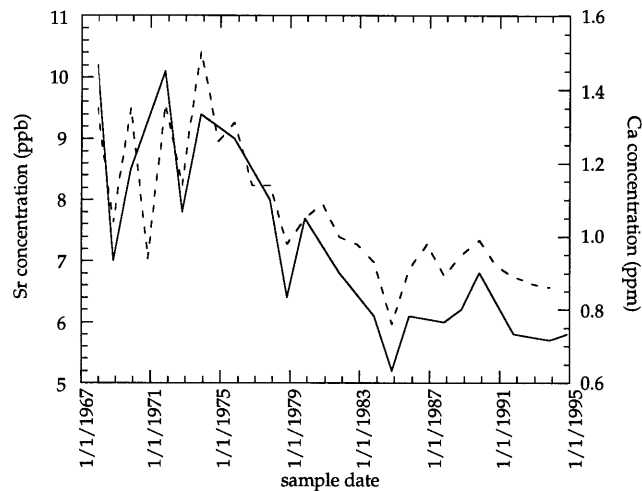


Figure 9: Plot of strontium (solid line) and calcium (broken line) data over the history of W6.

Changing emissions standards have reduced the inputs of anions over the last few decades. Driscoll *et al.* (1989) note that the quandary of acidification may lie in its control if the atmospheric inputs of cations control the degree of acidification in this environment. If the source of cations is the same as that of the anions or if their depositions are linked by an atmospheric process regardless of their source, then their trends will move in step such that anion deposition will not deplete the buffers. If the deposition of atmospheric anions and cations is unrelated, then continuing inputs of anions in excess of the cations will result in acidification. Unfortunately, little is currently known about the atmospheric sources and dispersal of anions and cations, and various methods of estimating the fraction of cations

available to the environment that are derived from the atmosphere yield very different results.

More difficult to evaluate are the contributions of the biomass pools and the soil-exchangeable cation sites to the decreasing trends in Ca and Sr concentration. It appears that fewer base cations are leached from the soils concomitant with a decrease in strong acid input. However, the variable nature of the soils and the uncertainties in evaluating the weathering of tills makes this a difficult hypothesis to approach. If the exchangeable sites have a strong affinity for Ca and Sr, they will be a lasting buffer pool, whereas lower affinities will correspond to rapid cation depletion. Also, the till is not deeply weathered, so it is uncertain to what degree it serves as a cation pool.

Interestingly, the clear-cutting experiment also led to the acidification of soils and waters. High acid flux corresponds to increased cation loss in the timber harvesting experiment and in the history of regional acid rain. Whereas there may be evidence to indicate that diminished atmospheric deposition may have a strong influence on the decreasing concentration of cations in the case of acid rain, it is unlikely that atmospheric deposition influences the cation concentrations in the harvesting experiment. Driscoll *et al.* (1989) question the magnitude of the contribution of the mineral and soil pools to the buffering of the acid deposition. During the harvesting experiment, however, the cation pools that are internal to the ecosystem must be capable of buffering the rise in acidity because there is no concomitant rise in atmospheric cation deposition during the mid-1980's. Thus, here is strong evidence that an ecosystem need not be dependent on atmospheric input to buffer excess anions. This is pertinent to many previous studies that assume atmospheric inputs of cations contribute significantly to the supply of acid buffers in the ecosystem.

4.3 Impact of relative drought seasons

4.3.1 Composition and streamflow

The isotopic composition of Sr in the stream water is dependent on the compositions and relative abundance of the sources of Sr. Figure 10 shows the changing trends in isotopic composition for the two watersheds. W6 is about 40% smaller, has slight variations in bedrock, soil, vegetation, topography relative to drainage, and has a lower isotopic composition in general. W5 is a larger watershed and thus has a greater chance of encompassing a region of soil or zone of bedrock with an unusually high ratio that might mix with inputs from the atmosphere and throughfall resulting in the consistently higher baseline composition.

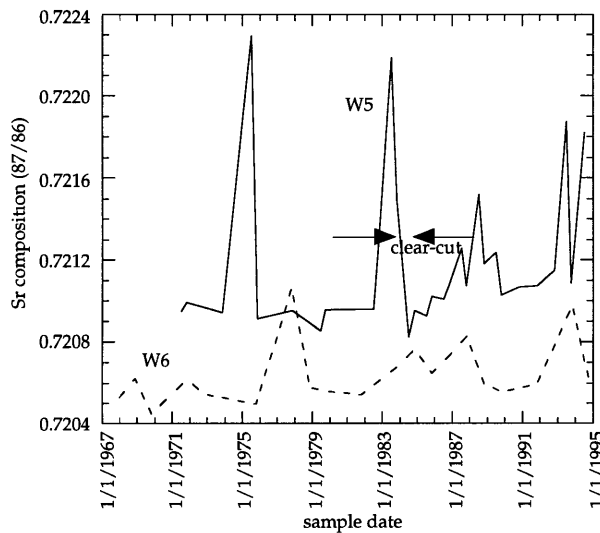


Figure 10: Isotopic composition of strontium plotted for W5 (solid line) and W6 (broken line) over time.

Examination of the data indicates that the deforestation event does not appear to affect the trend, rather the highs in the data correspond to lows in the streamflow, and precipitation events seem to be the primary control of the compositional variations. Most seasons of relative drought appear as

spikes in the composition data (Figure 10). Nineteen eighty-three was an especially dry year, with reduced streamflow in W5 from the fall of 1982 until the winter of 1983, but the low streamflow was not as pronounced in W6 as in some other parts of the HBEF. Assuming streamflow is generally indicative of precipitation, it appears that periods of high precipitation result in lower isotopic compositions (Figure 11). However, the trend in the data presented in Figure 11 asymptotically approaches a minimum of $^{87}\text{Sr}/^{86}\text{Sr}=0.7204$, with the minimum for W5 being even higher, and this value is much greater than that of precipitation. The bulk atmospheric isotopic composition of $^{87}\text{Sr}/^{86}\text{Sr} = 0.71031$ (Bailey *et al.*, 1993) at HBEF is dominated by the sea water value of $^{87}\text{Sr}/^{86}\text{Sr} = 0.7091$ (Jacks *et al.*, 1989) with a contribution from radiogenic continental dust. While precipitation controls relative variations in the isotopic composition of the stream waters, it does not greatly influence the overall compositional trends by pushing the lower limit of stream water composition close to that of bulk precipitation.

A plot of Sr concentration versus isotopic composition for W5 as in Figure 12a reveals clusters of data that correspond to distinct environmental conditions. The three samples taken during the harvesting period are less radiogenic and more concentrated with respect to Sr and Ca than samples taken during non-extreme conditions. Similarly, the samples taken during periods of relative drought have high isotopic ratios and moderate cation concentrations.

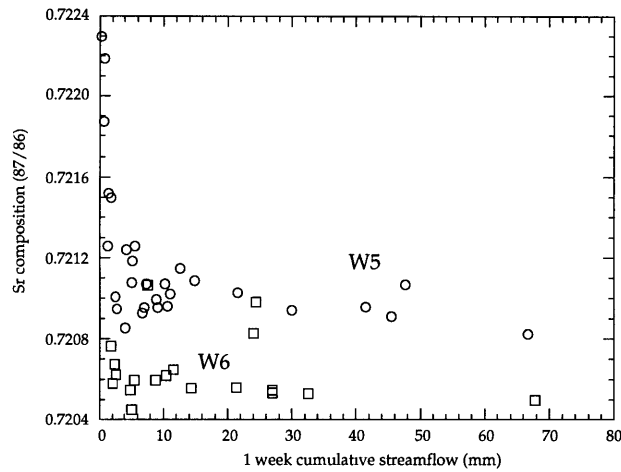
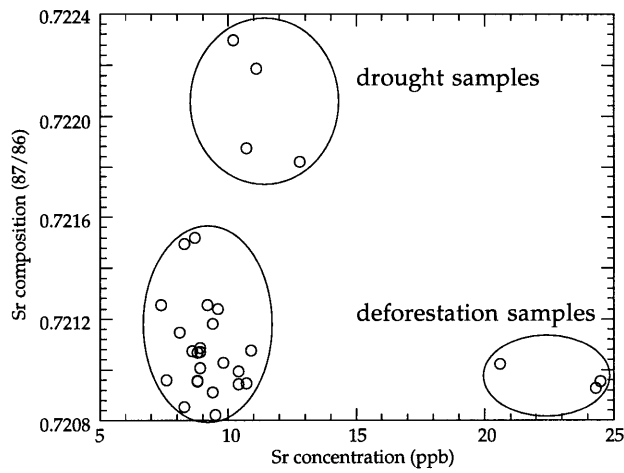


Figure 11: W6 data (squares) and W5 data (circles) plot as a curve asymptotically approaching a minimum concentration against cumulative streamflow. Streamflow measurements are discussed in Figure 7 caption.

The rapid flux of water through the watershed during the reduced evapotranspiration means that the water has less time with which to interact with the soil and mineral particles. Thus, although the acid conditions cause larger quantities of Sr to be removed from the soil-exchangeable cation sites whose composition reflects that of soil water, little of the input is from radiogenic sources indicative of mineral weathering. During the dry seasons, the water has time to interact with the soil minerals and till due to diminished flow velocities and may percolate deeper into the till. Interestingly, however, the two bedrock fracture water samples analyzed as part of this study have relatively low isotopic compositions (Figure 13), so unless the groundwater has a spatially variable ratio, dry periods do not show an increase in bedrock or deep groundwater interactions.

a)



b)

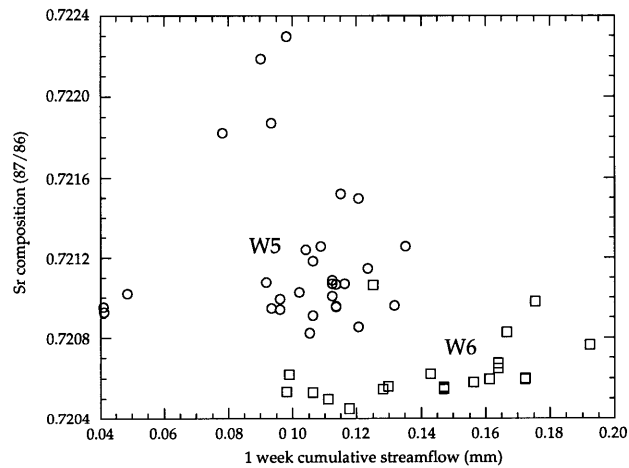


Figure 12: a) Concentration versus composition for W5. Included are the environmental conditions corresponding to groups of samples. b) Plotting $1/[Sr]$ versus composition for both watersheds reveals that a linear relationship for W6 is more pronounced than for W5.

Figure 12b demonstrates a more pronounced linear relationship for W6 than W5 when composition is plotted against the inverse of concentration. This corresponds to the hyperbolic relationship expected for a simple two-component mixing system as described by Faure (1986) when

composition is plotted against concentration. In a mixing hyperbola, the addition of a small quantity of an end-member composition such as the mineral contribution will have a non-linear impact on the composition of the output given that the concentration of the end-members strongly influences the weighting of their compositions in the mixture.

4.3.2 Composition of end members

Isolating the sources of environmental Sr is an intricate task, and this study provides some constraints on the problem. Figure 13 plots a few available end member sources relative to the measured samples for W5 and W6. Some of the data are from Bailey *et al.* (1993). Most of the samples have compositions that fall in the range of the soil water. The lower boundary is the value for the control watershed, and the upper is for the treated watershed, reflecting the trend in stream water compositions discussed previously. It is important to note that the soil water samples were taken with lysimeters during the snowmelt of 1994. Because the acid depresses the freezing point of the water, the most acid portion of the snow melts first, fluxing low pH waters through the system (Likens *et al.*, 1985).

Only a hornblende found in the glacial till has a higher isotopic composition than any of the waters due to its relatively high Rb/Sr ratio. Hornblendes are comparatively insoluble and a less common mineral species. The plagioclases have a low Rb/Sr ratio, resulting in a lower isotopic composition, and they are common and more soluble. In various portions of HBEF, the surface waters have limited interactions with the bedrock because the fragipan is relatively impermeable. No whole-rock or bulk mineral weathering estimates are listed here because of the local variability of geology and the uncertainties in the relative weathering contributions from each mineral type. Leaching experiments are planned for a till sample, but further

study is necessary in order to characterize the watershed-scale weathering processes, because this data does not give information about the weathering end-member.

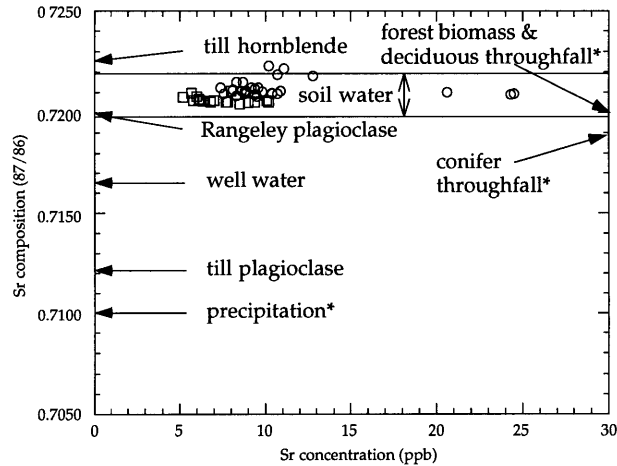


Figure 13: The composition of waters, minerals, and biota from the Hubbard Brook system plotted relative to concentration versus composition for the stream waters of W5 and W6.
 * indicates data from Bailey *et al.* (1993)

Throughfall waters have high compositions, and their chemistry is dependent on vegetation type. The water passes through the forest canopy and changes composition by some combination of washing or leaching strontium from the leaves and incorporating aerosols from the surfaces of the vegetation. The leached Sr has the approximate composition of the biomass and soil water, while the aerosols are derived from radiogenic continental dusts. It is notable that throughfall chemistry reflects the canopy composition even after the leaves have fallen, suggesting the much of the chemical interaction may be with the limbs and tree trunks (Bailey *et al.*, 1994). On the other hand, water pumped from bedrock fractures has a considerably lower composition than soil water, while the bulk precipitation is influenced

primarily by the composition of the oceans. It is generally assumed that bulk precipitation composition dilutes the ratios of the radiogenic sources to the values found in surface waters.

For many environmental systems including HBEF, a linear mixing model is used to describe the mixing of two compositionally distinct end-members in order to calculate the relative contribution of each source to the output (Graustein, 1988). For instance, the composition of bulk precipitation is mixed linearly with that of a presumed weathering end-member in order to evaluate their contributions to the composition of the other Sr reservoirs in the system (Bailey *et al.*, 1993 and 1994). However, when bulk precipitation interacts with the canopy and becomes throughfall, its composition is changed to approximately that of the biomass, which in turn is similar to that of soil water (Figure 13). In other words, the composition of atmospherically derived water that interacts with the system is not $^{87}\text{Sr}/^{86}\text{Sr} = 0.71013$ but is closer to 0.72. It is no longer compositionally distinct from soil water and the mixing relationship used in the linear modeling becomes difficult to evaluate (Equation 1).

$$\left(\frac{^{87}\text{Sr}}{^{87}\text{Sr} + ^{86}\text{Sr}}\right)_{\text{mix}} = \left(\frac{^{87}\text{Sr}}{^{87}\text{Sr} + ^{86}\text{Sr}}\right)_{r1} (1 - x) + \left(\frac{^{87}\text{Sr}}{^{87}\text{Sr} + ^{86}\text{Sr}}\right)_{r2} (x)$$

Equation 1: r1 and r2 are distinct sources (Graustein, 1988).

Figure 14 compares the mixing of hypothetical end-members for both linear and hyperbolic mixing curves. The single mixing hyperbola is an alternative approach to the linear model, and it approximates the two-stage mixing problem evidenced by the HBEF data. The parameters used in this model are a crude approximation; future work would include the acquisition of more data from W6 to characterize the concentration and composition of

the throughfall and the Sr budget of the canopy. Stage 1 corresponds to the interaction of bulk precipitation with the forest canopy to form throughfall, approximately indicated by the asterisk. Bailey *et al.*'s data (1994) show a dramatic change in composition between bulk precipitation and throughfall and a small change in Sr concentration. They also record a small composition change between throughfall and surface waters and a large concentration difference between the weathering end-members and surface waters. The latter condition corresponds to stage 2. Figure 14 is a modeled mixture in which the composition of the end-members is taken as $^{87}\text{Sr}/^{86}\text{Sr} = 0.710$ and 0.725 , and the concentration of the Sr reservoir is chosen to be 60 times that of bulk precipitation.

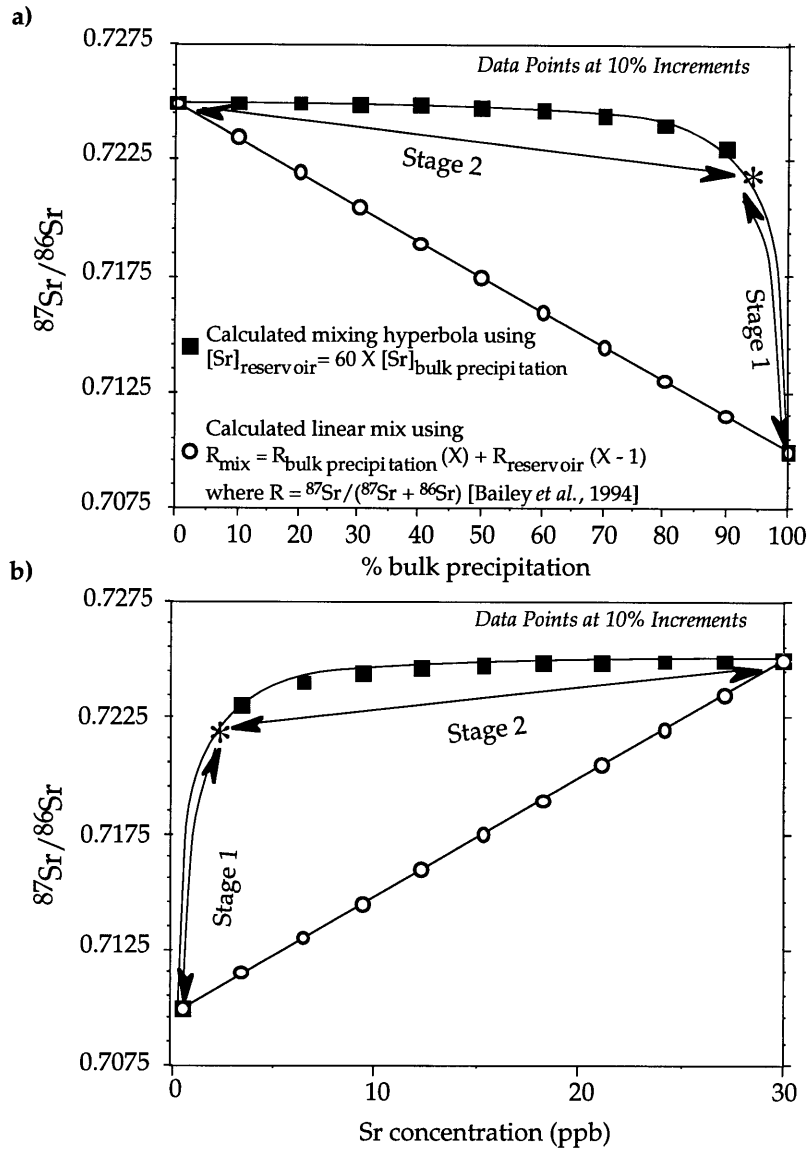


Figure 14: Hypothetical mixing of two concentration-composition separated end-members. The linear model versus a mixing hyperbola in two stages approximated by a single mixing curve.

Bailey *et al.* (1993, 1994) collected data for Cone Pond, a nearby watershed. Cone Pond is different enough in its physical characteristics that caution should be used when making comparisons to the data in this thesis; however, the trends in the Cone Pond data correspond closely to the model suggested here. Because the concentrations and isotopic compositions of bulk

precipitation and potentially interacting reservoirs are dramatically different, (Bailey *et al.*, 1994, and this study), isotopic mixing cannot be modeled as a linear equation, but is defined by a mixing hyperbola (Faure, 1986). The ratio of Sr bulk precipitation concentration to that of the weathering end-member is probably far greater than the hypothetical 60× modeled here, so the hyperbola would have an even higher degree of curvature. The influence of the addition of more weathering end-member is minimized regardless of the concentration differences because the compositions are so similar. Linear models do not account for large concentration differences. Figure 14a shows that for a mixed ratio of 0.7200, the linear model predicts an input of close to 40% bulk precipitation, whereas the hypothetical hyperbolic model shows that about 95% of the mixture must be bulk precipitation. This indicates that in first stage mixing, linear models may greatly underestimate the contribution of bulk precipitation.

Chapter 5

Conclusions

It is extremely difficult to characterize changes in an environmental system without a full development of all the processes influencing the elements in question. Other researchers have worked on the geochemical cycles of Ca, the mixing trends of Sr isotopes, and the impacts of environmental stress. Some have used compositing techniques, combining samples over periods of time, that obscure event information and can only indicate average conditions. This method is effective for developing nutrient cycles and element transport models, but it can obscure analysis of environmental impact because some of the stresses imposed on a system may be transient, seasonal, or variable in nature. On the other hand, this thesis is a long-term survey of discrete samples to evaluate trends and sudden shocks which environmental stresses can impose on a system. Whereas discrete sampling can indicate sudden changes, it can also show the long term trends presented by the composited sampling technique. However, outlying points on a trend become suspicious because of the event-sensitive nature of the sampling technique, but those points can be addressed in terms of the processes that control the variations of the system.

This data set also provides an argument against the assumption that atmospheric inputs strongly influence the Sr budget. The isotopic composition of the stream waters varies with the amount of rainfall, but the magnitude of this variation is lost when compared to the difference between stream water and precipitation compositions (Figures 12b and 13). The soil and till must, therefore, provide the bulk of Sr cations to the system. This has important implications for Ca budgets for the HBEF if we can actually assume

that Sr is a proxy for Ca. A comprehensive study of all the available Sr reservoirs using the Sr as an isotopic tracer would be necessary to evaluate the Sr-Ca systematics and confirm the conclusion that the atmosphere may not be a dominant reservoir in the Sr budget of these watersheds at Hubbard Brook. Figure 14a shows that using the rough estimate provided by the hyperbolic mixing relationship, estimating the atmospheric contribution during stage 2 mixing is difficult because large changes in percent input of bulk precipitation have little effect on the isotopic composition. The right data needs to be taken into account for future estimates. For instance, developing a detailed budget for the canopy by examining the aerosols and the leached products of the leaves might yield more information for separating the mixing lines in the composite hyperbola.

Acid rain, drought, and timber harvesting clearly impact the geochemical and nutrient cycles in the short-term. The data presented here expose some of the longer duration effects present at HBEF, but they say little that is definitive about the state of recovery from these stresses. Not enough time is encompassed by the samples to evaluate the recovery. A baseline of cation concentrations was never established prior to increased acid rain; the importance of diminishing cation concentrations is difficult to appreciate without a basis for comparison. On the other hand, there is a basis for comparison in the timber harvesting experiment, but the effects of the experiment have not gone to completion. The state of recovery is impossible to assess without this information.

Beyond the initial goals of this research, two other useful conclusions were discussed above. Unacidified, archived samples appear not to lose their integrity with respect to chemical analyses of cations such as Sr and Ca. This is useful for any future work on stored samples. Additionally, the frequent

assumption that Sr and Ca are interchangeable in geochemical cycles should be used with consideration for the possible exceptions. Adapting environments such as timber harvested watersheds may be an example of such a scenario.

Timber harvesting depletes a system of the nutrient pool contained in the biomass, and the flux of cations from the soil and till leads to fewer nutrients, higher acidity, and higher concentrations of deleterious substances such as Al. Ten years after the harvesting was completed, cation fluxes are still fluctuating. The acidification question is still open as to whether it is leading to the depletion of the available buffering pool. Cation concentrations are decreasing, but it is unclear which pool of cations is causing this trend: the atmosphere or the soil and till. Also, it is apparent that drought impacts the hydrology of a region that in turn influences the geochemical cycle. Streamflow chemistry during periods of lower precipitation is influenced more heavily by a combination of soil, till, and bedrock than during average conditions. From this data we can see that surface water chemistry is a valuable tool for evaluating the presence and effect of stress, but there are still many unknowns that must be characterized in order to appreciate the impact of changes on the system: weathering influences on bedrock minerals, the consequences of weathering on till and soil as a whole, and variables such as the extreme heterogeneity of a natural system. Using Sr isotopes as tracers to indicate the sources of cations into the system may not be a very efficient approach to nutrient modeling and mass balancing. Because of the uncertainties in the atmospheric input revealed by hyperbolic mixing models, the usefulness of isotopes prominent in weathering products and the atmosphere may be limited. A more detailed

budget of each of the interacting reservoirs is necessary to complete the evaluation of Sr isotopes as a tool for analyzing cation budgets.

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