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► **To cite this version:**

Bérangère A Leys, Gene E Likens, Chris E Johnson, Joseph M Craine, Brice Lacroix, et al.. Natural and anthropogenic drivers of calcium depletion in a northern forest during the last millennium. Proceedings of the National Academy of Sciences of the United States of America, 2016, 113, pp.6934 - 6938. 10.1073/pnas.1604909113 . hal-04777142

HAL Id: hal-04777142

<https://hal.science/hal-04777142v1>

Submitted on 15 Nov 2024

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Natural and anthropogenic drivers of calcium depletion in a northern forest during the last millennium

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Submitted to Proceedings of the National Academy of Sciences of the United States of America

The pace and degree of nutrient limitation are among the most critical uncertainties in predicting terrestrial ecosystem responses to global change. In the northeastern United States, forest growth has recently declined along with decreased soil calcium (Ca) availability, suggesting that acid rain has depleted soil Ca to the point where it may be a limiting nutrient. Yet, it is unknown whether the past 60 years of changes in Ca availability are strictly anthropogenic or partly a natural consequence of long-term ecosystem development. Here, we report a high-resolution millennial-scale record of Ca and 16 other elements from the sediments of Mirror Lake, a 15-ha lake in the White Mountains of the New Hampshire surrounded by northern hardwood forest. We found that sedimentary Ca concentrations had been declining steadily for 900 years before regional Euro-American settlement. This Ca decline was not a result of serial episodic disturbances, but instead the gradual weathering of soils and soil Ca availability. As Ca availability was declining, nitrogen availability concurrently was increasing. These data indicate that nutrient availability on base-poor, parent materials is sensitive to acidifying processes on millennial timescales. Forest harvesting and acid rain in the post-settlement period mobilized significant amounts of Ca from watershed soils, but these effects were exacerbated by the long-term pattern. Shifting nutrient limitation can potentially occur within 10,000 years of ecosystem development, which alters our assessments of the speed and trajectory of nutrient limitation in forests, and could require reformulation of global models of forest productivity.

calcium | natural depletion | acidification | nutrients

Introduction

Elemental limitation of terrestrial primary productivity is a master variable that can determine key ecosystem processes such as carbon exchange, ecosystem biodiversity, and water quality (1). Terrestrial primary productivity is most frequently limited by the availability of nitrogen (N), but phosphorus (P) is generally recognized as the limiting nutrient in terrestrial ecosystems with older soils (2). Consequently, a paradigm of progression from N to P limitation has developed (3, 4), but this is far from a predictable phenomenon (5, 6). For example, Ca can also be a limiting element in base-poor ecosystems (7, 8) and experimental Ca addition can increase forest productivity (8, 9).

As a base cation, soil Ca²⁺ is highly sensitive to pH, and several mechanisms that acidify soil could lead to the development of Ca limitation (10). Understanding nutrient limitation requires consideration of multiple elements, including macronutrients and rock-derived elements such as Al, Si, Ca, Na, Mg, and K. Acid rain—atmospheric deposition of all wet and dry substances that cause acidification—commenced in Europe and eastern North America in the middle of the 20th century and caused nutrient leaching from soils (11). A decline in forest productivity has been observed in affected ecosystems since about 1980 C.E. (8, 12), demonstrating clear evidence of the effects of acid rain on forest ecosystems (11, 13). Non-anthropogenic Ca depletion in soils

also occurs in terrestrial ecosystems due to natural weathering of parent material in concert with plant uptake, long-term N enrichment, and inputs of organic acids produced by plants (14). Although some long-term records seem to indicate patterns of ecosystem acidification over millennial timescales (15), whether these processes were widespread or sufficient enough to cause Ca limitation is largely unknown.

To assess the dynamics of Ca and other key nutrients linked to acidification processes during long-term ecosystem development, we examined the concentrations of 17 elements in a 1200-year-long sedimentary record from Mirror Lake, New Hampshire, a 15-ha oligotrophic lake in a temperate forest watershed in the White Mountains of the northeastern U.S. (16) (also see methods section). These forests were established approximately 10,000 years ago following deglaciation, and are situated on base-poor gneissic bedrock with relatively slow mineral weathering rates. Past research has suggested Ca limitation of productivity for these forests (8) as well as increasing N availability over the past millennium (17). The site has a typical history for the region: a period of Euro-American deforestation and agriculture beginning ~1770 C.E. followed by abandonment and development of second-growth mixed hardwood forest (16), and chronic acid rain from the mid-20th century to present (18, 12), which caused the export of large quantities of Ca from forests in this region *via* surficial streamflow (12).

Results and Discussion

Long-term calcium depletion reflects a decrease in weathered Ca

Significance

This research breaks new ground by showing that, contrary to generally accepted theories of ecosystem development, calcium depletion has been occurring for millennia as a natural consequence of long-term ecosystem development. This natural process predisposed forest ecosystems in the region to detrimental responses to acid rain in the 20th century. We also show that nitrogen availability was increasing concurrently with the depletion of calcium. This is the first study to reconstruct continuous changes in nutrient availability for a northern forest ecosystem on the millennial time scale. The results alter our assessments of the speed and trajectory of nutrient limitation in forests, and suggest that reformulation of global models of forest productivity may be necessary.

Reserved for Publication Footnotes

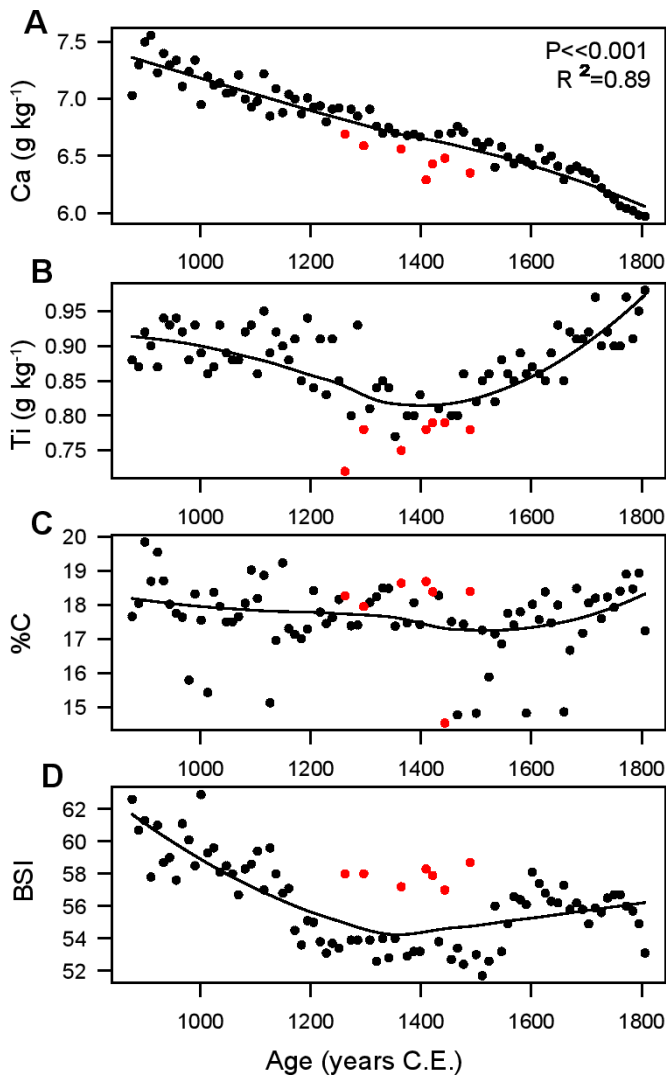


Fig. 1. Elemental composition of sediment deposited from 876 to 1800 C.E. Ca concentration, expressed in g kg^{-1} , P-value and r^2 are derived from a linear model (A). Ti concentration, expressed in g kg^{-1} , a proxy of erosion of the catchment (B). Percent organic C, a proxy of organic matter concentration (C). Base Saturation Index (BSI) calculated as the quotient of the sum of concentrations of Ca, Mg, K and Na and the sum of concentrations of Ca, Mg, K, Na and Al (D). Black curves are loess smooth splines. Seven events significantly different than baseline conditions signified by a principal component axis from 876 to 1800 C.E. are colored red.

To determine sedimentary elemental concentrations, we used X-ray fluorescence (XRF) analysis of dried and homogenized sediments (Table S1, Fig. S1, S2). Before 1800 C.E., four elements showed significant linear declines in concentrations over time: Ca, Mn, Rb and K (Fig. 1A; Fig. S1). Of these, Ca showed the strongest linear declines ($r^2 = 0.89$, Fig. 1A). Several lines of evidence indicate that the decline in Ca toward the present likely reflects lower inputs of weathered Ca from soils in the watershed. The decline is not solely due to a reduction only in plant-available forms of Ca. The amount of exchangeable Ca remained similar over this time period ($P > 0.3$; Table S2), indicating that the decrease of Ca concentration in the sediment is not due to labile Ca leached to the bottom of the core. There is also no evidence of a change in the Ca-bearing minerals being supplied to the lake. The estimation of mineral composition of the lake sediment by combining XRF and X-ray diffraction (XRD) shows that the relative abundances of quartz ($78 \pm 1.3\%$), albite ($11 \pm 0.5\%$), chlo-

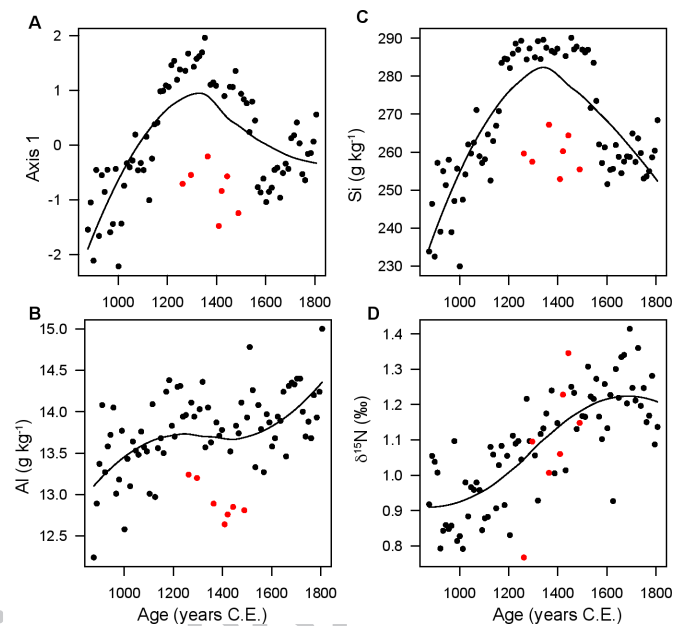


Fig. 2. Patterns of elemental composition of sediment deposited from 876 to 1800 C.E. Included are the first principal component axis of elemental concentrations ($\lambda = 17\%$) (A). Element concentrations of Al and Si (B, C). $\delta^{15}\text{N}$ in units of ‰ (D). Seven events significantly different than baseline (on PC1 from 876 to 1800 C.E.) are colored red.

rite ($8 \pm 0.5\%$), muscovite ($2 \pm 0.4\%$), and apatite ($0.5 \pm 0.05\%$) did not change significantly through time (Supplementary material, Table S3, S4). To assess whether the decline in Ca could be due to dilution from an increase in the concentration of other sedimentary components, we compared Ca concentrations with titanium (Ti, Fig. 1B), which is an erosion proxy (19), and organic carbon percentage (%C, Fig. 1C), used as an organic matter proxy (20). Both [Ti] and %C are independent of [Ca] over this period ($P > 0.15$ for both), indicating that the decline in [Ca] prior to 1800 C.E. was not due to dilution by other elements or change in the organic matter proportion of sediment samples. Together with low local atmospheric Ca inputs (12), these data indicate that the declines in sediment Ca concentrations did not reflect increases in erosion, increases in organic matter delivery, changes in sedimentation processes, or changes in the source of Ca. The decrease of Ca concentration thus most likely reflects a decrease of weathered Ca inputs to Mirror Lake.

Ca depletion as a natural consequence of long-term ecosystem development

To determine whether declining pre-settlement Ca availability was due to serial large-scale disturbances that depleted Ca stocks or gradual weathering, we tested whether Ca concentrations increased during any disturbance events identifiable in the sediment record before 1800 C.E. A principal component analysis of the elemental concentration data before 1800 C.E. and calculation of a Base Saturation Index identified seven disturbance events between 1250 and 1550 C.E. (Fig. 1D, Fig. 2A, see also supplementary material). The Base Saturation Index (BSI) indicated that sediments deposited during the seven events exhibit slightly more basic characteristics during an overall acidic period. This period corresponds to the glacierization phase of the Little Ice Age in Europe and North America, a period characterized by cool summers and wet winters (21). These conditions would be favorable to the formation of ice storms, which are documented as common disturbances in this region, and have been shown to damage trees and increase the flux of nutrient elements from forests (22). During the seven disturbance events, the concentrations of five elements are significantly lower ($P = 0.001$) than the

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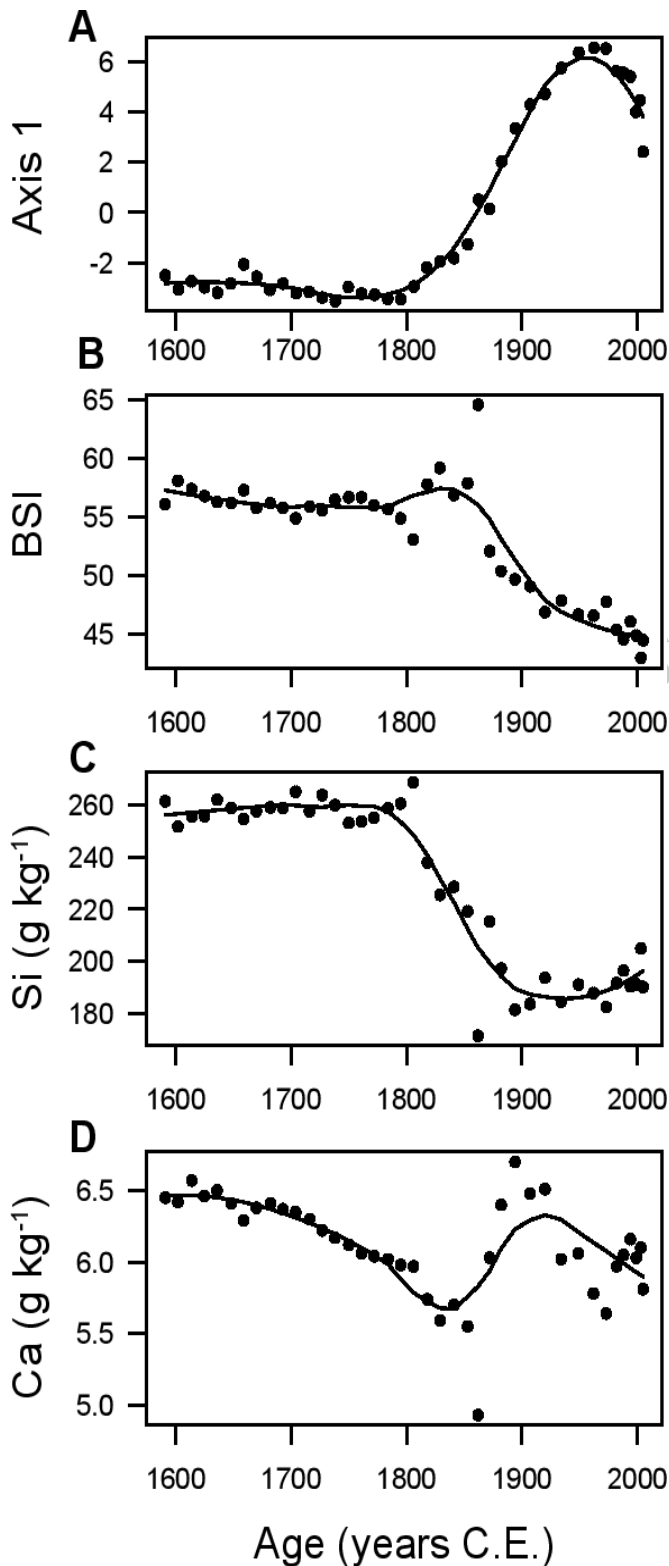


Fig. 3. Elemental composition of sediment deposited from 1600 to 2000 C.E., including post-EuroAmerican settlement and regional industrial activity. First principal component axis ($\lambda=62\%$) (A). Base Saturation Index (BSI) equal to the ratio of sum of base cations (Na, Ca, Mg, K) divided by the sum of base cations and Al, no unit (B). Low values indicate acidic conditions. Also shown are Si concentrations (C) and Ca concentrations (D).

intervening periods between 1250 and 1550 C.E., including Al and

Si, two elements that are weak acids in their dissolved forms (Fig. 2 B,C; Fig. S1). Higher Ca concentrations in sediments during these events would have suggested an increase in loss rates of Ca from the bulk soil in the watershed during disturbance, but Ca concentrations are actually 4% lower during these events than the surrounding time ($P=0.05$). Therefore, the decline in Ca does not appear to be driven by these events, but instead seems to be a consequence of sustained weathering stimulated by plant uptake of Ca during ecosystem development (e.g., 21, 22).

To understand the interactions between forest Ca availability and N dynamics better, we examined patterns of sedimentary $\delta^{15}\text{N}$, an index of N availability. In general, in Mirror Lake, high sedimentary $\delta^{15}\text{N}$ appears to indicate high N availability in the terrestrial ecosystem as enriched plant material, soil organic matter, and inorganic N enter the lake (17). From the beginning of the sedimentary record in ~ 876 to 1800 C.E., the decline in Ca concentrations in sediment was directly associated with increasing N availability. As Ca declined over this time period, sedimentary $\delta^{15}\text{N}$ increased ($r=-0.68$, Fig. 2D, Fig. S3), suggesting increasing Ca limitation and declining N limitation. Alternatively, the different dominant sources of these two elements—the atmosphere for N and bedrock weathering for Ca—can explain the different trajectories recorded in Mirror Lake sediment since 876 C.E. The BSI also displays a long-term decline since 876 C.E., reflecting increasingly acidic conditions (Fig. 1D). This long-term decline in BSI suggests that watershed soils were becoming increasingly base-poor through this time period. Thus, these data seem to indicate changes in nutrient availability for both N and Ca after only $\sim 10,000$ years post-glacial retreat, and before the onset of significant human activities in the region.

Large changes in nutrient concentration after Euro-American settlement

Sedimentary elemental concentrations changed markedly after Euro-American settlement in the region began ~ 1770 C.E. As the Mirror Lake watershed experienced deforestation and agricultural activities (16), all 17 elements exhibited large changes. Principal components analysis reveals that the concentrations of 11 elements increased logistically after 1800 C.E., reaching 95% of their upper asymptote by 1930 C.E. (Fig. 3A, Fig. S2). The identity of these elements indicates a signature of increased atmospheric pollution (e.g. increases in [Pb], [Zn]), an increase in erosion ([Ti]), and an increase in acidification (BSI: Fig. 3B), which may have increased leaching of Al from the forest floor and upper soil horizons. The increases in concentrations of heavy metals (e.g. Pb, Zn) are a general phenomenon in northern temperate lakes, and have been documented in Mirror Lake previously, coupled with the increase in atmospheric deposition, and the absence of change in lake productivity (16). In concert with these increases, six elements had lower concentrations in sediments after 1800 than before. Most notably, Si concentrations declined by 24% (Fig. 3C), likely reflecting the decline in biogenic silica concentration (16) rather than a diminution of rock weathering, as estimated mineral proportions indicate no increase in silicate-rich rock inputs (Table S4). In addition to the increase in heavy metal concentrations, the increases in erosion processes and acidification indicate that other pre-Industrial human activities such as forest clearance were strongly influencing the biogeochemistry of the lake and its watershed.

Despite these observed changes in elemental concentrations after 1800 C.E., there is no record of a significant increase in Ca flux as recorded in the sediments relative to other elements (Fig. 3D). While there are no records of direct human manipulation of Ca inputs in the Mirror Lake watershed, Euro-American land use changes affected Ca concentrations in the sediment. After 1800, there is a decline in sedimentary [Ca] associated with a decline in %C and organic matter inputs (Fig. S2) during extensive forest harvest, followed by a reestablishment of organic Ca

inputs in the late 1800's during a period of reforestation. The sedimentary Ca concentration was further marked by increases in the early to mid-20th century, consistent with elevated Ca levels in streamwater flux as an effect of acid rain, and decreases after 1970 possibly reflecting the reduced deposition of acid rain and the depletion of Ca in soils (12). To contextualize the sedimentary elemental record with the long-term stream chemistry data from nearby Hubbard Brook watersheds, the onset of acid rain ~1955 C.E. led to significant leaching of base cations— up to 50% of exchangeable Ca— from upland forests (12). This hydrologic loss pathway of dissolved Ca would not necessarily be recorded in lake sediments that are composed of organic and clastic material, and thus more closely reflect Ca concentration of organic material entering to the lake. However, the two records are complementary. On average, sedimentary Ca concentrations were 12% less after 1800 than during the period prior to 1800. Calcium concentrations were declining prior to Euro-American settlement and it is difficult to assess the role of anthropogenic activities in the 20th century from these sedimentary data alone. Nevertheless, this decrease in sedimentary Ca from 876 C.E. to the beginning of the pre-settlement period reflects a large depletion of the total Ca pool from upper soil horizons, and this pool remains a particular concern since it is larger than the entire exchangeable Ca pool in the soil, and the forest floor pool (10, 25).

Conclusions

Our data indicate that nutrient availability on base-poor parent materials is sensitive to acidifying processes on millennial timescales. Long-term acidification of the system from natural processes has led to changes in both Ca and N dynamics, which may have affected nutrient limitation. Long-term acidification coincided with a steady decline of [Ca] and an increase of [Al] in lake sediments. Further, anthropogenic activities caused rapid (decadal) acidification in the 20th century, affecting many aspects of ecosystem biogeochemistry. Although Ca addition experiments at Hubbard Brook have demonstrated the reversibility of some of the modern Ca loss (26), there was also a decrease in N availability and no effect on Al concentration for 10 years after Ca application (8). Thus, at Hubbard Brook, additions of Ca alone are not sufficient to stop acidification on a long-time scale. Regulations to minimize acidic precipitation are important to maintain, because mineral weathering rates are too low to neutralize additional acidic input to these forest ecosystems (12, 27), and currently there are minimal aerosol and precipitation inputs of Ca to sustain productivity (12). Thus, trajectories of increased acidification are likely to continue in this base-poor system.

Two major components of ongoing global change— increased atmospheric carbon dioxide concentrations and production of reactive N— both lead to ecosystem acidification. Global N additions may have already shifted soils from base cation buffering to Al³⁺ buffering (28). Nonetheless, Ca limitation is considered rare in temperate forest systems because of the relatively young age of most temperate-zone soils. However, our results demonstrate that shifting nutrient limitation can potentially occur within 10,000 years of ecosystem development. Lacustrine sedimentary records can be used to assess terrestrial nutrient dynamics, and due to the widespread occurrence of lakes, continuous depositional processes, and good chronological control, these records could help us build more generalized understandings of slow processes like the development of nutrient limitation in terrestrial ecosystems.

Materials and Methods

Study site

Mirror Lake is a 15-ha oligotrophic lake in the White Mountains of New Hampshire, USA (16). The surrounding vegetation is northern hardwood forest containing deciduous and coniferous tree species. Common tree species

in the watershed include *Pinus strobus*, *Tsuga canadensis*, *Fagus grandifolia*, *Fraxinus americana*, *Acer saccharum*, and *Betula alleghaniensis*. There are three stream inlets that drain the watershed and one outlet from the lake. Elevation in the watershed ranges from 213 m at lake level to 469 m at ridge tops.

Parent material in the watershed is primarily sandstone and mudrock deformed and metamorphosed from the Littleton Formation. The most abundant primary minerals are quartz, plagioclase, biotite and sillimanite in a coarse-grained matrix. In the southwest corner of the watershed, there is an inclusion of the Kinsman Formation, a metamorphosed granitic material. The minerals oligoclase, andesite, potassium feldspar, biotite and muscovite define this medium- to coarse-grained formation. Soils in most of the watershed are Spodosols, generally acidic (pH is less than 4.5) and infertile (16). At pH 5.5 and under, the concentration of dissolved aluminum increases and limits plant root growth (16). At pH 5.5 and less, soil water concentrations of aluminum increase, limiting plant root growth. More generally acid rain in this region has caused nutrient leaching in the soil, and a decline in forest productivity has been observed since 1980, demonstrating clear evidence of the effects of acid rain on forest ecosystems (11, 29).

Historical context of the study site

The first Euro-American settlers in the watershed were recorded around 1770 C.E., and soil tillage for row-crop agriculture, grazing by sheep in pastures, and selective logging all occurred subsequently. The activities of the settlers and their descendants resulted in clear-cutting of most of the watershed, as well as conversion of a substantial portion to pasture and arable land in the late 1800s and early 1900s. The subsequent abandonment of agricultural land led to replacement by natural succession, and was coupled with forest plantations such as *Pinus strobus* in the 1930s (16). Since the 1980s, a dramatic decline in forest growth has been recorded, coupled with a large decline in calcium in various components of the ecosystem, including the forest floor. The causes of this ecosystem change come from several factors such as natural factors, disease, nutrient limitation and pollution effects. The emergent hypothesis is that the deficiency of available calcium in the soil is a result of the effects of acid rain (29).

The collection of the sediment core and the construction of the age-depth model are described in (17).

X-Ray fluorescence (XRF) method and calibration

The 102 sediment samples were dried at 60° C until no further mass loss was observed, ground to pass through a <40µm sieve, and analyzed for the 11 major elements traditionally listed as oxides (Na, Mg, Al, Si, P, S, K, Ca, Ti, Mn and Fe) and 6 trace elements (Cu, Zn, As, Pb, Rb and Mo) by handheld wavelength-dispersive X-ray fluorescence (XRF) spectrometry (Bruker Tracer III). The major elements were measured during 3 minutes per sample at 15kV with a vacuum attached to the instrument, limiting the background noise. The trace elements were measured during 2 minutes per sample at 40kV, with a yellow filter increasing the magnitude of the trace element spectra. Data were first recorded in counts, and then were calibrated with the mudrock calibration (30), which is a combination of 200 standards of similar matrix (grain-size, homogeneity) and composition, to obtain quantitative data (Supplementary Fig. S1, S2; Supplementary Table 1). Of the 102 samples, 70 were measured 3 times for major and 3 times for trace elements. Because iron is quantified by both the major and trace element protocols, we chose the value with the smallest standard deviation. Analytical error was ±2% for both major and trace elements.

The base saturation index was calculated as the ratio of elements that form the basic cations (Na, Ca, Mg, and K) to those elements and Al (which produces an acidic cation, Al³⁺). Thus, this index reflects the balance between base and acidic cations in a sample. A decrease in this index will be due to an increase in the acidic cation and/or a decrease of base cations, and decreases in the index can be interpreted as increased acidification of the system.

To test the potential exchange of cations within the sediment core, the exchangeable Ca in the sediment as well as K, Mg and Na were assessed (Supplementary Table 2). The analysis was run on 2-g sediment samples, previously dried and powdered. Cations (Ca²⁺, K⁺, Mg²⁺, and Na⁺) were extracted by ammonium acetate solution (1M, pH 7.0) following the method of Brown (31). A low-sodium filter paper was used, and the filtrate was analyzed by an Inductively Coupled Plasma (ICP) Spectrometer, Model 720-ES ICP Optical Emission Spectrometer (Varian Australia Pty Ltd, Mulgrave, Vic Australia).

X-Ray diffraction (XRD) method

30 of the 102 sediment samples from the Mirror Lake core were analyzed for mineral composition by X-ray diffraction (XRD). Each sample powder was pressed into a sample holder, and analyzed at 40 kV, 20 mA volume with a copper X-ray source, K α =1.54. Data are first presented as count peaks on a 2 θ angle scale, from 2 to 80°. The mineral composition was assessed by the software HighScore Plus, version 4.0. Since we were interested in the dominant mineralogy in the sediment, we did not target trace minerals and we stopped the peak assignment when the mineral composition explained at least 70% of the peaks. Since XRD reveals the same mineral phases within the 30 samples tested, but does not allow quantification of their proportion, we performed a normative calculation based on oxide element concentrations for five samples randomly distributed through the core. First, ten samples, which were previously dried and powdered, were heated to 1000 °C for two hours (Supplementary Table 3). This procedure removed

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organic matter, composition water from clays, hydrated minerals, and the CO₂ from carbonates. The resultant material thus reflected only crystalline-form minerals. On these samples, 12 element concentrations from XRF after LOI at 1000 °C were transformed to oxide-form concentrations (SiO₂, TiO₂, Al₂O₃, FeO, MnO, CaO, Na₂O, K₂O, P₂O₅, Cr₂O₃, and NiO) to match mineral composition according to the valence of the chemical formula of each mineral (Supplementary Table 4).

Nitrogen isotopes

To understand the relationship among calcium (Ca), nitrogen (N), and carbon (C) better, we used previously-published elemental and isotopic data for N that were produced at the Stable Isotope Lab at the University of Regina using standard methods on a Thermoquest (Finnigan- MAT, San Jose, CA) Delta Plus mass spectrometer interfaced with a Carlo Erba (Carlo Erba, Milan, Italy) NC2500 elemental analyzer. Analytical error was <0.1‰ for δ¹⁵N (more information in (17)).

Statistical analysis

Principal component analyses (PCA) were conducted to assess the relationship among elements, and to compare Ca trends to other nutrients, over two different periods: (1) from 873 to 1800 C.E. and (2) from 1600 to 2000 C.E. PCA from 873 to 1800 C.E. was rotated on correlations with a Varimax technique to strengthen contrasts. Examining the relationships among elements over the first time period (1), the first PCA axis describes

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those elements that are decreasing in concentration from 876 to 1800 C.E. (Ca, Mn, K) vs. those that increase over this period (Al, Si; Supplementary Fig. 2). A Kruskal-Wallis rank-sum test was used to test whether elemental concentrations during the 7 identified events in the first period differed significantly from concentrations at other times. A breakpoint analysis was used to identify (i) the overall period of the occurrence of the 7 events during period (1), and (ii) the date, when the 11 elements displaying an increase in concentration during period (2) reached 95% of their upper asymptote. All statistics were computed in R v. 3.1.2 (32).

Acknowledgments.

We thank Wyatt Oswald, Peter Leavitt, Bruce Kaiser, Pamela Kempton, Colleen Barbe, Emily Mellicant, Matthew Brueseke, Justin Hynicka, and Paul Bukaveckas for discussion and assistance. We are grateful for support from the Novus Research Coordinating Network (NSF-DEB-1145815). Funding for long-term data on precipitation, streamwater and lake chemistry was provided by the National Science Foundation, including the LTREB and LTER programs, and The A. W. Mellon Foundation. The data reported in this paper are tabulated in the Supplementary Material. This is a contribution of the Hubbard Brook Ecosystem Study. The Hubbard Brook Experimental Forest is administered by the USDA Forest Service, Northern Experiment Station.

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