

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

Bérangère A. Leys<sup>a,1</sup>, Gene E. Likens<sup>b,c</sup>, Chris E. Johnson<sup>d</sup>, Joseph M. Craine<sup>e</sup>, Brice Lacroix<sup>f</sup>, and Kendra K. McLaughlan<sup>a</sup>

<sup>a</sup>Department of Geography, Kansas State University, Manhattan, KS 66506; <sup>b</sup>Cary Institute of Ecosystem Studies, Millbrook, NY 12545; <sup>c</sup>Department of Ecology and Evolutionary Biology, University of Connecticut, Storrs, CT 06269; <sup>d</sup>Department of Civil and Environment Engineering, Syracuse University, Syracuse, NY 13244; <sup>e</sup>Jonah Ventures, LLC, Manhattan, KS 66502; and <sup>f</sup>Department of Geology, Kansas State University, Manhattan, KS 66506

Edited by Peter M. Vitousek, Stanford University, Stanford, CA, and approved May 12, 2016 (received for review March 25, 2016)

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. However, it is unknown whether the past 60 y 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 New Hampshire surrounded by northern hardwood forest. We found that sedimentary Ca concentrations had been declining steadily for 900 y 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 postsettlement 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 y 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 | hardwood forest

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 Ca<sup>2+</sup> 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 CE (8, 12), demonstrating clear evidence of the effects of acid rain on forest ecosystems (11, 13). Nonanthropogenic 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 1,200-y-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 United States (16) (also see *Materials and Methods*). These forests were established ~10,000 y 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 CE, followed by abandonment and development of second-growth mixed hardwood forest (16) and chronic acid rain from the mid-20th century to present (12, 18), 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.

To determine sedimentary elemental concentrations, we used X-ray fluorescence (XRF) analysis of dried and homogenized sediments (Table S1 and Figs. S1 and S2). Before 1800 CE, four

## 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 our knowledge, 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.

Author contributions: B.A.L. designed research; B.A.L. performed research; B.A.L. contributed new reagents/analytic tools; B.A.L., J.M.C., and B.L. analyzed data; and B.A.L., G.E.L., C.E.J., and K.K.M. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

Freely available online through the PNAS open access option.

<sup>1</sup>To whom correspondence should be addressed. Email: berangerleleys@gmail.com.

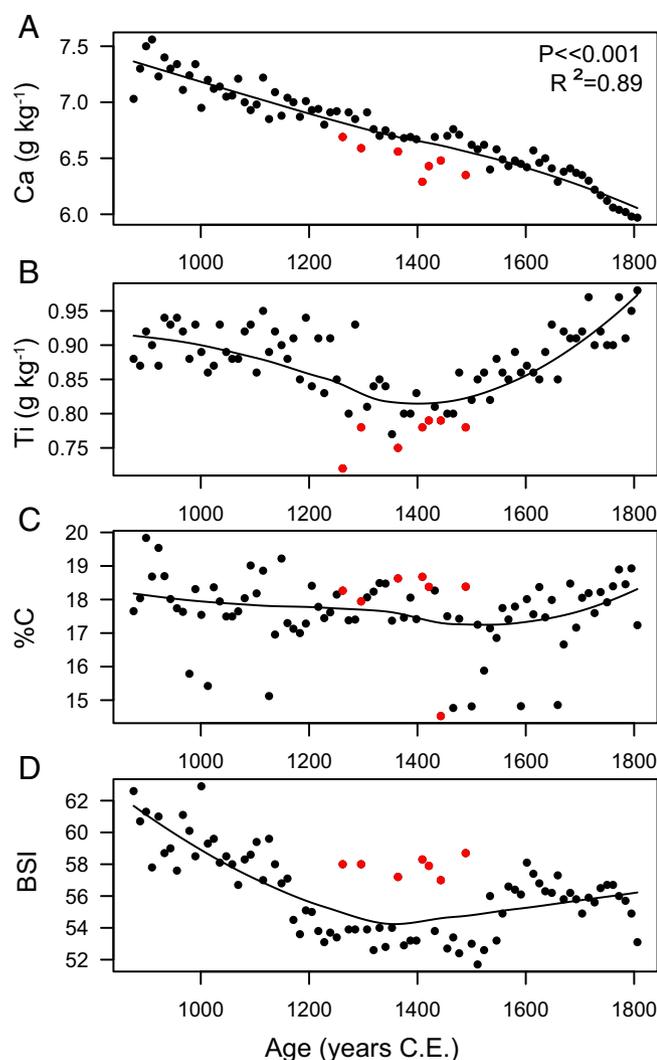
This article contains supporting information online at [www.pnas.org/lookup/suppl/doi:10.1073/pnas.1604909113/-DCSupplemental](http://www.pnas.org/lookup/suppl/doi:10.1073/pnas.1604909113/-DCSupplemental).

elements showed significant linear declines in concentrations over time: Ca, Mn, Rb, and K (Fig. 1A and 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 ( $11 \pm 0.5\%$ ), chlorite ( $8 \pm 0.5\%$ ), muscovite ( $2 \pm 0.4\%$ ), and apatite ( $0.5 \pm 0.05\%$ ) did not change significantly through time (Tables S3 and S4). To assess whether the decline

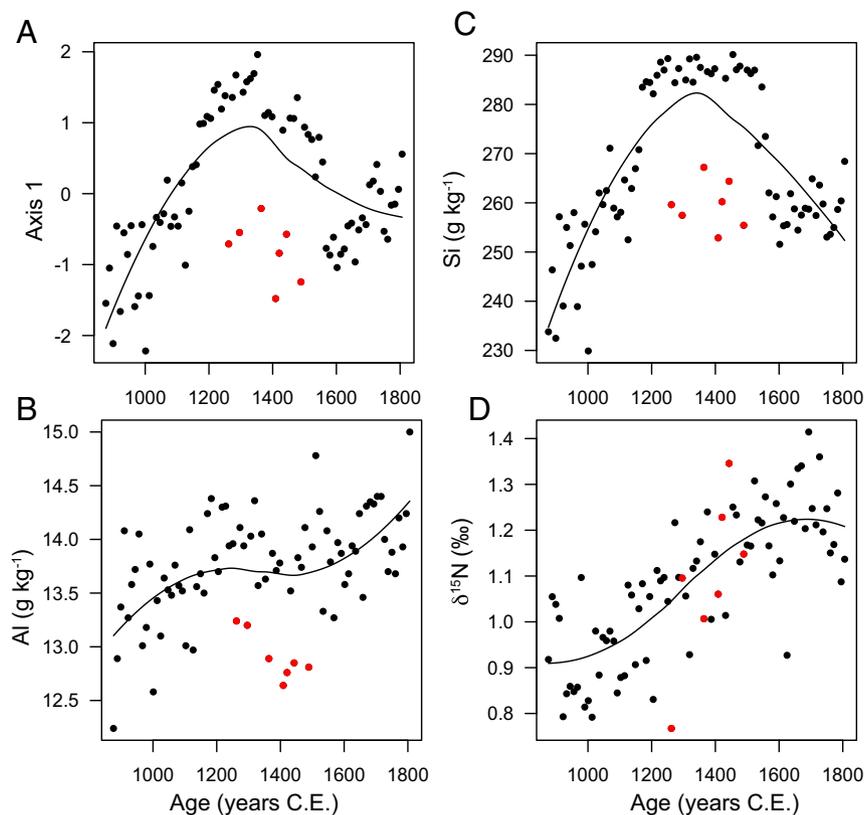
in Ca could be due to dilution from an increase in the concentration of other sedimentary components, we compared Ca concentrations with titanium (Ti; Fig. 1B), which is an erosion proxy (19), and organic carbon percentage (%C; Fig. 1C), used as an organic matter proxy (20). Both [Ti] and %C are independent of [Ca] over this period ( $P > 0.15$  for both), indicating that the decline in [Ca] before 1800 CE 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 presettlement 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 CE. Principal component analysis (PCA) of the elemental concentration data before 1800 CE and calculation of a Base Saturation Index (BSI) identified seven disturbance events between 1250 and 1550 CE (Fig. 1D, Fig. 2A, and Supporting Information). 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 intervening periods between 1250 and 1550 CE, including Al and Si, two elements that are weak acids in their dissolved forms (Fig. 2B and C and 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., refs. 21–24).

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  $\sim 876$ –1800 CE, 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 and 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 CE. The BSI also displays a long-term decline since 876 CE, 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  $\sim 10,000$  y postglacial retreat and before the onset of significant human activities in the region.



**Fig. 1.** Elemental composition of sediment deposited from 876 to 1800 CE (A) Ca concentration, expressed in  $\text{g}\cdot\text{kg}^{-1}$ ,  $P$  value, and  $r^2$  are derived from a linear model. (B) Ti concentration, expressed in  $\text{g}\cdot\text{kg}^{-1}$ , a proxy of erosion of the catchment. (C) Percent organic C, a proxy of organic matter concentration. (D) 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. Black curves are loess smooth splines. Seven events significantly different from baseline conditions signified by a principal component axis from 876 to 1800 CE are colored red.



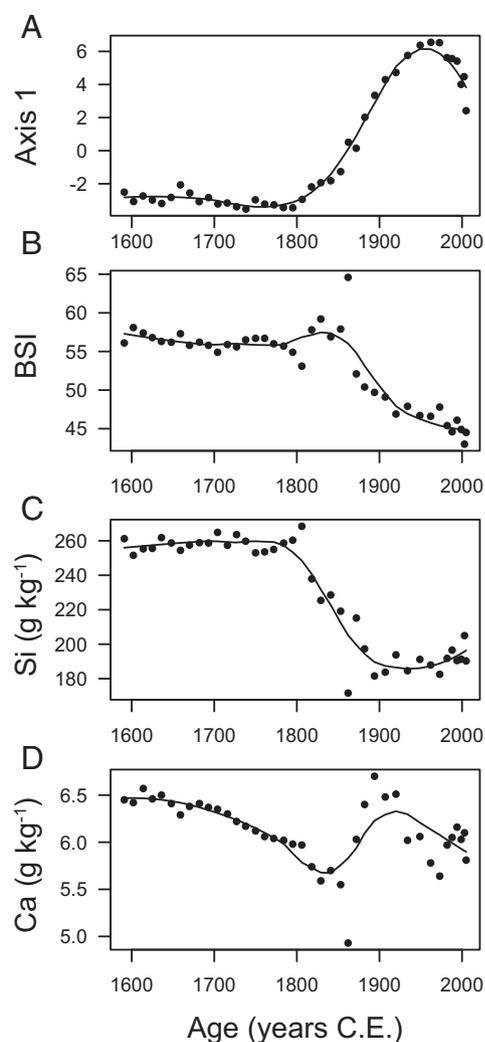
**Fig. 2.** Patterns of elemental composition of sediment deposited from 876 to 1800 CE (A) Included are the first principal component axis of elemental concentrations ( $\lambda = 17\%$ ). (B and C) Element concentrations of Al and Si. (D)  $\delta^{15}\text{N}$  in units of ‰. Seven events significantly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

### Large Changes in Nutrient Concentration After Euro-American Settlement.

Sedimentary elemental concentrations changed markedly after Euro-American settlement in the region began  $\sim 1770$  CE. As the Mirror Lake watershed experienced deforestation and agricultural activities (16), all 17 elements exhibited large changes. PCA reveals that the concentrations of 11 elements increased logistically after 1800 CE, reaching 95% of their upper asymptote by 1930 CE (Fig. 3A and 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 CE, there is no record of a significant increase in Ca flux as recorded in the sediments relative to other elements (Fig. 3D). Although 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 1800s 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  $\sim 1955$  CE 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 before 1800. Calcium concentrations were declining before 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 CE to the beginning of the presettlement period reflects a large depletion of the total Ca pool from upper soil horizons, and this pool remains a particular concern, as it is larger than the entire exchangeable Ca pool in the soil and the forest floor pool (10, 25).



**Fig. 3.** Elemental composition of sediment deposited from 1600 to 2000 CE, including post-Euro-American settlement and regional industrial activity. (A) First principal component axis ( $\lambda = 62\%$ ). (B) 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. Low values indicate acidic conditions. Also shown are Si concentrations (C) and Ca concentrations (D).

## 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 y 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  $\text{Al}^{3+}$  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 y 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 (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 CE, 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 *P. 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 ref. 17.

**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 <40- $\mu\text{m}$  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 XRF spectrometry (Bruker Tracer III). The major elements were measured during 3 min per sample at 15 kV with a vacuum attached to the instrument, limiting the background noise. The trace elements were measured during 2 min per sample at 40 kV, 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 (Figs. S1 and S2 and Table S1). Of the 102 samples, 70 were measured three times for major and three times for trace elements. Because iron is quantified by both the major and trace element protocols,

we chose the value with the smallest SD. Analytical error was  $\pm 2\%$  for both major and trace elements.

BSI 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,  $\text{Al}^{3+}$ ). 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 (Table S2). The analysis was run on 2-g sediment samples, previously dried and powdered. Cations ( $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$ ) were extracted by ammonium acetate solution (1 M, 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 Spectrometer, Model 720-ES Inductively Coupled Plasma Optical Emission Spectrometer (Varian Australia Pty Ltd.).

**XRD Method.** Thirty of the 102 sediment samples from the Mirror Lake core were analyzed for mineral composition by XRD. Each sample powder was pressed into a sample holder and analyzed at 40 kV, 20 mA volume with a copper X-ray source,  $K\alpha$  of 1.54. Data are first presented as count peaks on a  $2\theta$  angle scale, from 2 to 80°. The mineral composition was assessed by the software HighScore Plus, version 4.0. Because 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. Because 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, 10 samples, which were previously dried and powdered, were heated to 1000 °C for 2 h (Table S3). This procedure removed organic matter, composition water from clays, hydrated minerals, and the  $\text{CO}_2$  from carbonates. The resultant material thus reflected only crystalline-form minerals. On these samples, 12 element concentrations from XRF after a loss-on-ignition (LOI) at 1,000 °C were transformed to oxide-form concentrations ( $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{MnO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{NiO}$ ) to match mineral composition according to the valence of the chemical formula of each mineral (Table S4).

**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) Delta Plus mass spectrometer interfaced with a Carlo Erba NC2500 elemental analyzer. Analytical error was  $<0.1\%$  for  $\delta^{15}\text{N}$  (more information in ref. 17).

**Statistical Analysis.** PCAs were conducted to assess the relationship among elements and to compare Ca trends to other nutrients over two different periods: (i) from 873 to 1800 CE and (ii) from 1600 to 2000 CE. PCA from 873 to 1800 CE 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 those elements that are decreasing in concentration from 876 to 1800 CE (Ca, Mn, K) versus those that increase over this period (Al, Si; Fig. S2). A Kruskal–Wallis rank-sum test was used to test whether elemental concentrations during the seven 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 seven 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 (Grant NSF-DEB-1145815). Funding for long-term data on precipitation, stream water, and lake chemistry was provided by the National Science Foundation, including the Long Term Research in Environmental Biology and Long-Term Ecological Research programs, and The Andrew W. Mellon Foundation. The data reported in this paper are tabulated in *Supporting Information*. 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.

- Gruber N, Galloway JN (2008) An Earth-system perspective of the global nitrogen cycle. *Nature* 451(7176):293–296.
- Porder S, Chadwick OA (2009) Climate and soil-age constraints on nutrient uplift and retention by plants. *Ecology* 90(3):623–636.
- Hedin LO, Vitousek PM, Matson PA (2003) Nutrient losses over four million years of tropical forest development. *Ecology* 84(9):2231–2255.
- Newman GS, Hart SC (2015) Shifting soil resource limitations and ecosystem retrogression across a three million year semi-arid substrate age gradient. *Biogeochemistry* 124(1–3):177–186.
- Menge DNL, Hedin LO, Pacala SW (2012) Nitrogen and phosphorus limitation over long-term ecosystem development in terrestrial ecosystems. *PLoS One* 7(8):e42045–e42045.
- Johnson MO, Gloor M, Kirkby MJ, Lloyd J (2014) Insights into biogeochemical cycling from a soil evolution model and long-term chronosequences. *Biogeosciences Discuss* 11(4):5811–5868.
- Balaria A, Johnson CE, Groffman PM (2014) Effects of calcium treatment on forest floor organic matter composition along an elevation gradient. *Can J Res* 44(8):969–976.
- Battles JJ, Fahey TJ, Driscoll CT, Jr, Blum JD, Johnson CE (2013) Restoring soil calcium reverses forest decline. *Environ Sci Technol Lett* 1(1):15–19.
- Mainwaring DB, Maguire DA, Perakis SS (2014) Three-year growth response of young Douglas-fir to nitrogen, calcium, phosphorus, and blended fertilizers in Oregon and Washington. *For Ecol Manage* 327(2014):178–188.
- Likens GE, et al. (1998) The biogeochemistry of calcium at Hubbard Brook. *Biogeochemistry* 41(2):89–173.
- Likens GE, Wright RF, Galloway JN, Butler TJ (1979) Acid rain. *Sci Am* 241(4):43–51.
- Likens GE (2013) *Biogeochemistry of a Forested Ecosystem* (Springer Science & Business Media, New York), 3rd Ed.
- Odén S (1968) *The Acidification of Air and Precipitation and Its Consequences on the Natural Environment* (State National Science Research Council, Washington, DC).
- Brady NC, Weil RR (1996) *The Nature and Properties of Soils* (Prentice-Hall Inc., Upper Saddle River, NJ).
- Oldfield F, et al. (2010) Terrestrial and aquatic ecosystem responses to late Holocene climate change recorded in the sediments of Lochan Uaine, Cairngorms, Scotland. *Quat Sci Rev* 29(7):1040–1054.
- Likens GE (1985) *An Ecosystem Approach to Aquatic Ecology: Mirror Lake and Its Environment* (Springer-Verlag, New York).
- McLaughlan KK, Craine JM, Oswald WW, Leavitt PR, Likens GE (2007) Changes in nitrogen cycling during the past century in a northern hardwood forest. *Proc Natl Acad Sci USA* 104(18):7466–7470.
- Likens GE, Driscoll CT, Buso DC (1996) Long-term effects of acid rain: Response and recovery of a forest ecosystem. *Sci Pap Ed* 272(5259):244–245.
- Kylander ME, Ampel L, Wohlfarth B, Veres D (2011) High-resolution X-ray fluorescence core scanning analysis of Les Echets (France) sedimentary sequence: New insights from chemical proxies. *J Quat Sci* 26(1):109–117.
- Kaushal S, Binford M (1999) Relationship between C:N ratios of lake sediments, organic matter sources, and historical deforestation in Lake Pleasant, Massachusetts, USA. *J Paleolimnol* 22(4):439–442.
- Matthews JA, Briffa KR (2005) The “Little Ice Age”: Re-evaluation of an evolving concept. *Geogr Ann, Ser A* 87(1):17–36.
- Houlton BZ, et al. (2003) Nitrogen dynamics in ice storm-damaged forest ecosystems: Implications for nitrogen limitation theory. *Ecosystems (N Y)* 6(5):431–443.
- Markewitz D, Richter DD, Allen HL, Urrego JB (1998) Three decades of observed soil acidification in the Calhoun Experimental Forest: Has acid rain made a difference? *Soil Sci Soc Am J* 62(5):1428–1439.
- Perakis SS, et al. (2013) Forest calcium depletion and biotic retention along a soil nitrogen gradient. *Ecol Appl* 23(8):1947–1961.
- Blum JD, et al. (2002) Mycorrhizal weathering of apatite as an important calcium source in base-poor forest ecosystems. *Nature* 417(6890):729–731.
- Johnson CE, Driscoll CT, Blum JD, Fahey TJ, Battles JJ (2014) Soil chemical dynamics after calcium silicate addition to a Northern hardwood forest. *Soil Sci Soc Am J* 78(4):1458–1468.
- Schaller M, Blum JD, Hamburg SP, Vadeboncoeur MA (2010) Spatial variability of long-term chemical weathering rates in the White Mountains, New Hampshire, USA. *Geoderma* 154(3):294–301.
- Tian D, Niu S (2015) A global analysis of soil acidification caused by nitrogen addition. *Environ Res Lett* 10(2):24019.
- Winter TC, Likens GE (2009) *Mirror Lake: Interactions Among Air, Land, and Water* (Univ of California Press, Berkeley, CA).
- Rowe H, Hughes N, Robinson K (2012) The quantification and application of handheld energy-dispersive x-ray fluorescence (ED-XRF) in mudrock chemostratigraphy and geochemistry. *Chem Geol* 324–325(2012):122–131.
- Brown JR (1998) *Recommended Chemical Soil Test Procedures for the North Central Region* (Missouri Agricultural Experiment Station, University of Missouri–Columbia, Columbia, MO).
- R Core Team (2014) *R: A Language and Environment for Statistical Computing* (R Foundation for Statistical Computing, Vienna, Austria).