

Decreased water flowing from a forest amended with calcium silicate

Mark B. Green^{a,b,1}, Amey S. Bailey^b, Scott W. Bailey^b, John J. Battles^c, John L. Campbell^b, Charles T. Driscoll^d, Timothy J. Fahey^e, Lucie C. Lepine^f, Gene E. Likens^{g,h,1}, Scott V. Ollinger^f, and Paul G. Schabergⁱ

^aCenter for the Environment, Plymouth State University, Plymouth, NH 03264; ^bNorthern Research Station, US Forest Service, Durham, NH 03824; ^cDepartment of Environmental Science, Policy, and Management, University of California, Berkeley, CA 94720; ^dDepartment of Civil and Environmental Engineering, Syracuse University, Syracuse, NY 13244; ^eDepartment of Natural Resources, Cornell University, Ithaca, NY 14853; ^fComplex Systems Research Center, University of New Hampshire, Durham, NH 03824; ^gCary Institute of Ecosystem Studies, Millbrook, NY 12545; ^hDepartment of Ecology and Evolutionary Biology, University of Connecticut, Storrs, CT 06269; and ⁱNorthern Research Station, US Forest Service, Burlington, VT 05403

Contributed by Gene E. Likens, February 21, 2013 (sent for review March 23, 2012)

Acid deposition during the 20th century caused widespread depletion of available soil calcium (Ca) throughout much of the industrialized world. To better understand how forest ecosystems respond to changes in a component of acidification stress, an 11.8-ha watershed was amended with wollastonite, a calcium silicate mineral, to restore available soil Ca to preindustrial levels through natural weathering. An unexpected outcome of the Ca amendment was a change in watershed hydrology; annual evapotranspiration increased by 25%, 18%, and 19%, respectively, for the 3 y following treatment before returning to pretreatment levels. During this period, the watershed retained Ca from the wollastonite, indicating a watershed-scale fertilization effect on transpiration. That response is unique in being a measured manipulation of watershed runoff attributable to fertilization, a response of similar magnitude to effects of deforestation. Our results suggest that past and future changes in available soil Ca concentrations have important and previously unrecognized implications for the water cycle.

Transpiration by trees represents a major loss of water from forested watersheds (1–4) that is sensitive to forest nutrition (5–9). Plot-scale chemical amendments to forest soils can result in 16–155% increases in transpiration during the first 60 d to 11 mo (5–9), yet it is unclear how these responses are expressed at the whole-watershed scale over longer periods. The magnitude of change in transpiration at the plot scale suggests that water yield from forested watersheds may be impacted by forest nutritional status. Watershed-scale soil amendments present a unique opportunity to improve understanding of hydrologic changes resulting from altered forest nutrition because of their larger scale and often more detailed and accurate water budgets.

Calcium (Ca) is an essential plant nutrient. For trees in particular, Ca is important for structural integrity and physiological functions, including cell division, cell-wall maintenance, stomatal regulation, and stress signaling and response (10). The importance of Ca supply for individual trees emerges at the ecosystem scale where Ca can limit forest primary production, influence forest nitrogen uptake, change cation exchange capacity, and alter other ecosystem dynamics (10–15). The critical role of Ca in forests has highlighted the need to understand better the consequences of available soil Ca depletion. Acid deposition has caused rates of Ca leaching to far exceed rates of replenishment through weathering and atmospheric deposition, making soil Ca loss a threat to long-term forest vitality in regions prone to acid deposition (13, 16–21).

In October 1999, a catchment-scale experiment was initiated at the Hubbard Brook Experimental Forest (HBEF) in the White Mountains of New Hampshire. (Fig. S1) to understand the biogeochemical and ecological consequences of the depletion of available soil Ca. The objective of the experiment was to restore soil Ca concentrations to preindustrial levels by applying finely ground and pelletized wollastonite at 1,062 kg Ca ha⁻¹ across an 11.8-ha watershed. Vegetation on Watershed 1

(W1) is dominated by multiaged, second-growth northern hardwoods with sugar maple (*Acer saccharum*), yellow birch (*Betula alleghaniensis*), and American beech (*Fagus grandifolia*) making up about 80% of the basal area. At the higher elevations, the forest canopy includes significant components of two coniferous tree species—red spruce (*Picea rubens*) and balsam fir (*Abies balsamea*)—along with deciduous paper birch trees (*Betula papyrifera* Marsh. var. *papyrifera*). The current forest has developed without further management since the end of the last major logging activity in 1917. A more recent disturbance occurred in 1998 when an ice storm caused localized structural damage to the forest. Most of the damage was restricted to an elevation band between 600 and 800 m (22), and by 2001 leaf area had recovered in affected areas (23). The forest was monitored before and after the 1999 wollastonite addition to evaluate biogeochemical, ecological, and physical responses.

Results

Here, we report on an unexpected alteration of the W1 water balance following wollastonite addition. Five months after wollastonite was applied, W1 evapotranspiration (*ET*; calculated as the difference between precipitation and runoff) (*Methods*) substantially increased relative to *ET* at the nearby hydrologic reference watershed (W3) at the HBEF (Fig. 1A). Other untreated watersheds at the HBEF did not show a similar *ET* response. The W1 *ET* deviations in 2000, 2001, and 2002 were 25%, 18%, and 19% higher, respectively, than mean annual *ET* before wollastonite addition. Cumulative daily *ET* deviation from the hydrologic reference watershed demonstrates that the W1 *ET* deviation occurred between March 2000 and May 2002 (Fig. 1B). The beginning of the hydrologic response in March 2000 coincided with the onset of the first substantial sapflow after the wollastonite treatment, suggesting that the Ca addition stimulated transpiration. Notably, the cumulative daily *ET* deviation ceased increasing in May 2002 and abruptly began decreasing thereafter, indicating less *ET* in W1 compared with W3. Previously at HBEF, catchment-scale *ET* deviations have occurred three times, each following experimental deforestation: at W2 (1965–1967), W4 (1970–1974), and W5 (1983–1984). The *ET* response to wollastonite reported here was of a similar magnitude to the changes that followed deforestation, and is unique in being a report of a runoff decrease induced by alteration of a nutrient cycle (Fig. 1A).

Author contributions: S.W.B., C.T.D., T.J.F., and G.E.L. designed research; J.J.B., C.T.D., T.J.F., L.C.L., G.E.L., and S.V.O. performed research; M.B.G., A.S.B., J.J.B., T.J.F., L.C.L., and S.V.O. analyzed data; and M.B.G., S.W.B., J.J.B., J.L.C., C.T.D., T.J.F., L.C.L., G.E.L., S.V.O., and P.G.S. wrote the paper.

The authors declare no conflict of interest.

¹To whom correspondence may be addressed. E-mail: mbgreen@plymouth.edu or likensg@ecostudies.org.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1302445110/-DCSupplemental.

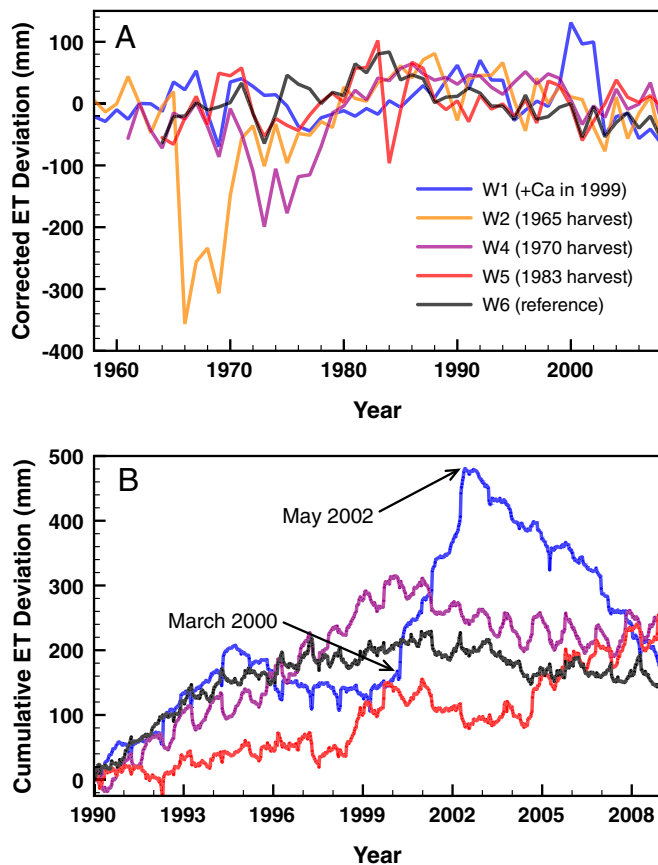


Fig. 1. Evapotranspiration deviations from W3 at an (A) annual scale and corrected by the median deviation, and (B) cumulative daily deviation between January 1, 1990 and December 31, 2008. The different HBEF watersheds are shown for context and the initiation year of forest harvests are noted in the legend.

Streamwater and soil water-chemistry data indicate strong retention of Ca by the ecosystem after the wollastonite application (24). Dissolved silicon (Si) concentrations in streamwater and soil water increased after the wollastonite application, followed by a gradual and consistent decrease after the peak (Fig. 24). Streamwater Ca concentrations in W1 increased immediately after the wollastonite application, as some wollastonite pellets began to dissolve, but declined rapidly over a 3-y period and stabilized thereafter (25) (Fig. 2B). Soil water Ca concentrations in both organic and mineral soil horizons show a lagged peak, occurring sometime in 2002 or 2003. The lack of an initial peak in soil water Ca concentration, like Si concentration, is attributed to Ca immobilization in the soil either by soil cation exchange or plant uptake (24). Soil water Ca began increasing in late 1998, after a significant ice storm and before the wollastonite application (22, 23). The impact of the ice storm with the wollastonite treatment remains unknown; however, the lack of a similar hydrological response in other watersheds disturbed by the ice storm suggests that our results are because of wollastonite application (Fig. 14). The Ca and Si dynamics result in streamwater Ca:Si ratios that show a rapid increase followed by a steep decline from November 1999 to April 2002, a period that matches the change in W1 *ET* deviations (Fig. 2C). The apparent uptake of Ca caused soil water Ca:Si ratios to decline initially because of increased Si concentrations relative to Ca, followed by a peak in late 2002. Both the streamwater and soil water Ca:Si ratios and mass balances suggest that Ca from wollastonite was strongly retained relative to Si (24).

The content of Ca in tree foliage also increased from 2000 to 2002, suggesting that biological processes influenced the Ca retention, as indicated by streamwater Ca:Si ratios. Sugar maple, which comprises ~35% of the W1 biomass and has high Ca requirements (20, 26), increased in foliar Ca between 1999 and 2002, followed by stable but elevated Ca concentrations thereafter (Fig. 3A). Foliar Ca concentrations at the time of treatment were at 0.54% Ca, slightly below a threshold where sugar maple is susceptible to decline disease (16). However, by 2001 foliar Ca had increased to 0.76%. Yellow birch, comprising 21% of the W1 tree biomass, showed a similar pattern for foliar Ca concentration, with the exception of a secondary peak in 2006. These Ca accumulation patterns are similar to previous observations of other vegetation in W1 (27).

Leaf area index (LAI) increased and spectral responses were consistent with enhanced photosynthetic capacity after wollastonite addition in W1 relative to reference watersheds. LAI was measured between 1998 and 2008 in reference areas west of W6 and W1. The deviation of W1 from the reference areas was slightly negative ($-0.1 \text{ m}^2\cdot\text{m}^{-2}$) in 1998 and 1999 before wollastonite addition, followed by almost linear increase to $2 \text{ m}^2\cdot\text{m}^{-2}$ in 2008 (Fig. 4). The deviation became statistically significant in 2007. Evidence of enhanced photosynthetic capacity comes from observations using aircraft remote sensing. In 1997 and 2003, high spectral-resolution imagery was obtained at 17-m spatial resolution for the entire HBEF by the National Aeronautics and Space Administration's Airborne Visible/Infrared Imaging Spectrometer. We evaluated changes in reflectance properties related to canopy nitrogen concentration (%N) using reflectance data across watersheds and calculating the ratio of estimated canopy %N for each watershed to canopy %N for W3, and analyzed changes in this ratio over time (28). From 1997 to 2003,

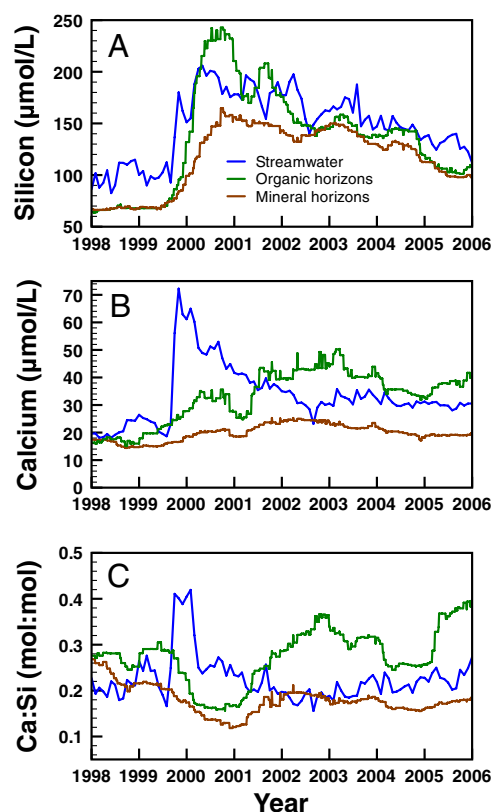


Fig. 2. Time series of streamwater and soil water in W1 (A) Si concentrations, (B) Ca concentrations, and (C) Ca:Si ratios.

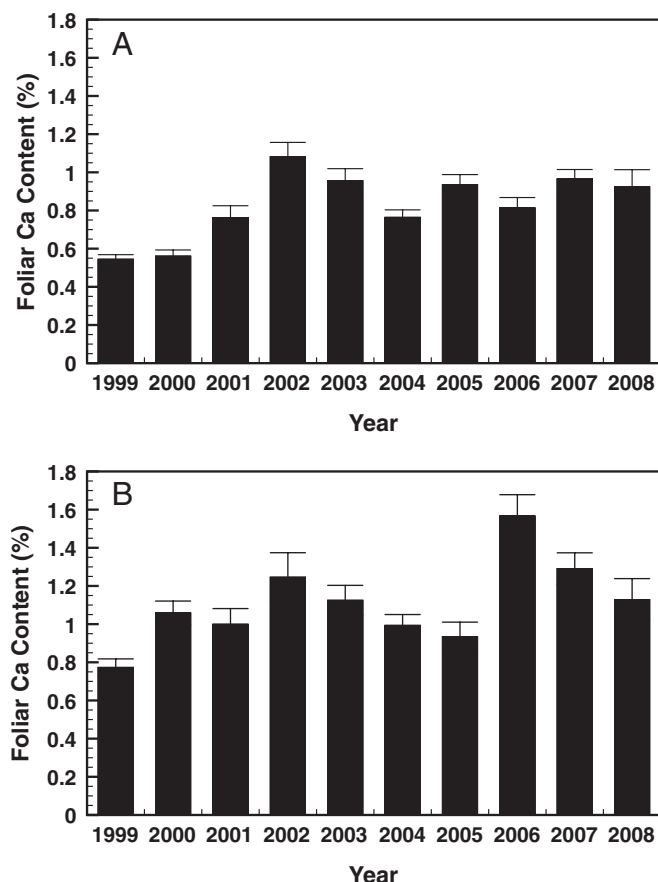


Fig. 3. Mean spring foliar calcium content in W1 (A) sugar maple and (B) yellow birch between 1999 (before the wollastonite addition) and 2008. Error bars show 1 SE.

W1 showed a significant increase in estimated canopy %N, a change that was not evident in any other watershed (Tables S1 and S2). Between 2003 and 2009, the canopy %N ratio for W1 showed no change.

After the wollastonite addition, aboveground biomass in W1 appears to have stabilized relative to the declining biomass observed in a reference watershed (Fig. 5). Even though the aboveground biomass in W1 declined across 1996/1997, 2001/2002, and 2006/2007 (median aboveground live tree biomass of 187.4, 183.1, and 179.8 Mg·ha⁻¹, respectively), the difference in aboveground biomass between W1 and W6 increased (2.0, 4.3, and 13.0 Mg·ha⁻¹ more biomass in W1, respectively), indicating stimulation of net primary production in W1 relative to the biogeochemical reference watershed.

In aggregate, W1 experienced a transient whole-forest fertilization of physiological activity indicated by increased canopy reflectance, higher LAI, increased aboveground biomass, foliar Ca accumulation, soil water Ca increase, rapid streamwater Ca:Si ratio change, and enhanced *ET*. We hypothesize that the *ET* response was primarily a transient transpiration response during rapid Ca uptake and increased primary production by the forest. If the W1 forest were generally Ca-limited, we would expect rapid mycorrhizal-assisted uptake of Ca and water by trees as Ca became available from weathering of the wollastonite. This increase in Ca nutrition would stimulate an upswing in foliar mass (as indicated by LAI data) and water use associated with increased primary production. Transpiration could increase either because of an increased number of stomata (i.e., more foliage on existing trees and new regeneration) or increased water-loss rate from

stomata. Our evidence of increased LAI, and past measurements of greater crown density (11), foliar biomass (29), and seedling regeneration (30) at HBEF following Ca addition suggests that this *ET* response was because of an increased number of stomata.

Discussion

We see two possible reasons for the transient transpiration response: drastically improved water use efficiency beginning in 2002 because of enhanced stomatal function (10) or triggering of a secondary limitation to primary production in 2002. The lack of a foliar %N difference between 2003 and 2009, and the rapid decline in *ET* deviation after 2002 (Fig. 1B), suggest that secondary limitation to primary production was most likely. A transient physiological response is consistent with other field experiments that have shown a temporary improvement in physiological activity following fertilization that recedes as other nutrients become more limited (31, 32). Secondary nutrient limitations following the satiation of a primary deficiency are so common that applications of multinutrient fertilizers are the norm in high-production (e.g., agricultural) systems.

Recent studies support the hypothesis that Ca was a primary constraint on forest physiology at the HBEF. Responses to wollastonite application have included significantly improved photosynthetic function (33), larger sapwood area (an indicator of greater foliar biomass) (29), increased sugar storage and oxidative protection (34), higher phosphorus content of foliage (35), greater mycorrhizal abundance (30), and a more vigorous sugar maple population (30, 36) in W1 compared with other untreated HBEF watersheds. Other plot-scale wollastonite additions at the HBEF, but outside of W1, caused increased crown vigor and xylem basal area (11), stimulated fine-root length by ~300% (37), and resulted in generally more decline-resistant trees (11).

Initial wollastonite weathering was apparently rapid (24), making Ca quickly available to the Ca-limited forest. Within 1 y wollastonite application approximately doubled the pretreatment exchangeable Ca concentrations in the organic soil horizon (38), where sugar maple fine roots are most abundant and can grow quickly in response to increased nutrient resources (37). Based on previous studies, we expect that the initial wollastonite weathering rates were much higher than long-term rates because of the release of Ca with freshly broken bonds on surfaces artificially created by the wollastonite milling process (39).

The pulse of Ca availability seemed to stimulate transpiration through fine root growth (37), uptake of Ca (and water), and primary production, as evidenced by a number of observations at HBEF. The enhanced springtime *ET* was facilitated by the addition of new leaves from stimulation of dormant buds (11) and establishment of new seedlings (30). During summer, Ca-induced rooting and mycorrhizal associations (30) would enhance water

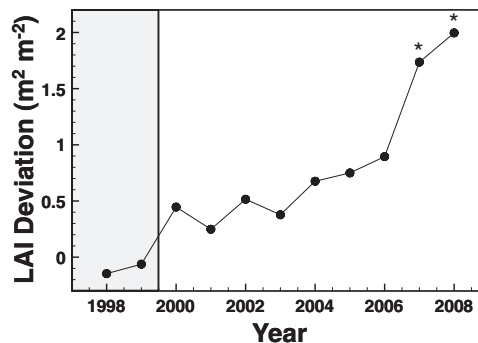


Fig. 4. Annual deviation of the median leaf area index in W1 from reference plots. The shaded area highlights the pretreatment period, and the starred points (*) indicate statistical significance from the reference plots.

16. Long RP, Horsley SB, Hallett RA, Bailey SW (2009) Sugar maple growth in relation to nutrition and stress in the northeastern United States. *Ecol Appl* 19(6):1454–1466.
17. Federer CA, Hornbeck JW, Tritton LM, Martin CW, Pierce RS (1989) Long-term depletion of calcium and other nutrients in Eastern US forests. *Environ Manage* 13(5): 593–601.
18. Likens GE, Driscoll CT, Buso DC (1996) Long-term effects of acid rain: Response and recovery of a forest ecosystem. *Science* 272(5259):244–246.
19. Schaberg PG, DeHayes DH, Hawley GJ (2001) Anthropogenic calcium depletion: A unique threat to forest ecosystem health? *Ecosyst Health* 7(4):214–228.
20. Warby RAF, Johnson CE, Driscoll CT (2005) Chemical recovery of surface waters across the northeastern United States from reduced inputs of acidic deposition: 1984–2001. *Environ Sci Technol* 39(17):6548–6554.
21. Rodhe H, Dentener F, Schulz M (2002) The global distribution of acidifying wet deposition. *Environ Sci Technol* 36(20):4382–4388.
22. Rhoads AG, et al. (2002) Effects of an intense ice storm on the structure of a northern hardwood forest. *Can J For Res* 32(10):1763–1775.
23. Weeks BC, Hamburg SP, Vadeboncoeur MA (2009) Ice storm effects on the canopy structure of a northern hardwood forest after 8 years. *Can J For Res* 39(8):1475–1483.
24. Cho Y, Driscoll CT, Johnson CE, Blum JD, Fahey TJ (2012) Watershed-level responses to calcium silicate treatment in a northern hardwood forest. *Ecosystems* 15(3):416–434.
25. Nezat CA, Blum JD, Driscoll CT (2010) Patterns of Ca/Sr and ⁸⁷Sr/⁸⁶Sr variation before and after a whole watershed CaSiO₃ addition at the Hubbard Brook Experimental Forest, USA. *Geochim Cosmochim Acta* 74(11):3129–3142.
26. Hallett RA, Bailey SW, Horsley SB, Long RP (2006) Influence of nutrition and stress on sugar maple at a regional scale. *Can J For Res* 36(9):2235–2246.
27. Dasch AA, et al. (2006) The relative uptake of Ca and Sr into tree foliage using a whole-watershed calcium addition. *Biogeochemistry* 80(1):21–41.
28. Ollinger SV, et al. (2008) Canopy nitrogen, carbon assimilation, and albedo in temperate and boreal forests: Functional relations and potential climate feedbacks. *Proc Natl Acad Sci USA* 105(49):19336–19341.
29. Schaberg PG, et al. (2011) Calcium addition at the Hubbard Brook Experimental Forest increases the capacity for stress tolerance and carbon capture in red spruce (*Picea rubens*) trees during the cold season. *Trees (Berl)* 25(6):1053–1061.
30. Juice SM, et al. (2006) Response of sugar maple to calcium addition to northern hardwood forest. *Ecology* 87(5):1267–1280.
31. Nave LE, Vance ED, Swanston CW, Curtis PS (2009) Impacts of elevated N inputs on north temperate forest soil C storage, C/N, and net N-mineralization. *Geoderma* 153(1–2):231–240.
32. Oren R, et al. (2001) Soil fertility limits carbon sequestration by forest ecosystems in a CO₂-enriched atmosphere. *Nature* 411(6836):469–472.
33. Boyce RL (2007) Chlorophyll fluorescence response of red spruce and balsam fir to a watershed calcium fertilization experiment in New Hampshire. *Can J For Res* 37(8): 1518–1522.
34. Halman JM, Schaberg PG, Hawley GJ, Eagar C (2008) Calcium addition at the Hubbard Brook Experimental Forest increases sugar storage, antioxidant activity and cold tolerance in native red spruce (*Picea rubens*). *Tree Physiol* 28(6):855–862.
35. Fiorentino I, et al. (2003) Initial responses of phosphorus biogeochemistry to calcium addition in a northern hardwood forest ecosystem. *Can J For Res* 33(10):1864–1873.
36. Cleavitt NL, Fahey TJ, Battles JJ (2011) Regeneration ecology of sugar maple (*Acer saccharum*): Seedling survival in relation to nutrition, site factors, and damage by insects and pathogens. *Can J For Res* 41(2):235–244.
37. Naples BK, Fisk MC (2010) Belowground insights into nutrient limitation in northern hardwood forests. *Biogeochemistry* 97(2):109–121.
38. Cho Y, Driscoll CT, Johnson CE, Siccama TG (2010) Chemical changes in soil and soil solution after calcium silicate addition to a northern hardwood forest. *Biogeochemistry* 100(1–3):3–20.
39. Petrovich R (1981) Kinetics of dissolution of mechanically comminuted rock-forming oxides and silicates-I. Deformation and dissolution of quartz under laboratory conditions. *Geochim Cosmochim Acta* 45(10):1665–1674.
40. Schaberg PG, Shane JB, Cali PF, Donnelly JR, Strimbeck GR (1998) Photosynthetic capacity of red spruce during winter. *Tree Physiol* 18(4):271–276.
41. Borer CH, Schaberg PG, DeHayes DH (2005) Acidic mist reduces foliar membrane-associated calcium and impairs stomatal responsiveness in red spruce. *Tree Physiol* 25(6):673–680.
42. Likens GE, Bormann FH (1995) *Biogeochemistry of a Forested Ecosystem* (Springer, New York), 2nd Ed.
43. McMahon SM, Parker GG, Miller DR (2010) Evidence for a recent increase in forest growth. *Proc Natl Acad Sci USA* 107(8):3611–3615.
44. Thomas RQ, Canham CD, Weathers KC, Goodale CL (2010) Increased tree carbon storage in response to nitrogen deposition in the US. *Nat Geosci* 3(1):13–17.
45. Brauman KA, Daily GC, Duarte TK, Mooney HA (2007) The nature and value of ecosystem services: An overview highlighting hydrologic services. *Annu Rev Environ Resour* 32:67–98.
46. Buso DC, Likens GE, Eaton JS (2000) *Chemistry of Precipitation, Streamwater, and Lakewater from the Hubbard Brook Ecosystem Study: A Record of Sampling Protocols and Analytical Procedures* (US Department of Agriculture Forest Service, Newtown Square, PA).
47. Fahey TJ, et al. (2005) The biogeochemistry of carbon at Hubbard Brook. *Biogeochemistry* 75(1):109–176.
48. Siccama TG, et al. (2007) Population and biomass dynamics of trees in a northern hardwood forest at Hubbard Brook. *Can J For Res* 37(4):737–749.
49. Yanai RD, et al. (2010) Estimating uncertainty in ecosystem budget calculations. *Ecosystems (N Y)* 13(2):239–248.
50. Rhoads AG, et al. (2007) Comparing direct and indirect methods of assessing canopy structure in a northern hardwood forest. *Can J For Res* 47:584–591.