## Decreased water flowing from a forest amended with calcium silicate

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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<sup>-1</sup> 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

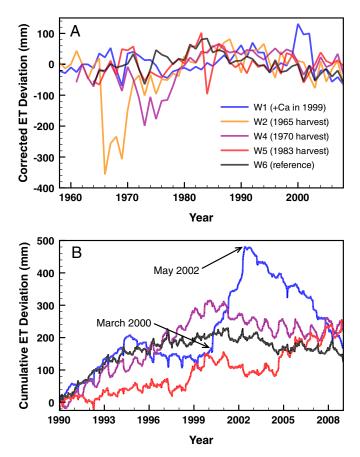
Here, we report on an unexpected alteration of the W1 water balance following wollastonite addition. Five months after wollastonite was applied, W1 evapotranspiration (ET; calculated as the difference between precipitation and runoff) (Methods) substantially increased relative to ET at the nearby hydrologic 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).

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**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. 2A). 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. 1A). 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. 3.4). 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  $2 \text{ m}^2 \text{ m}^{-2}$ 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,

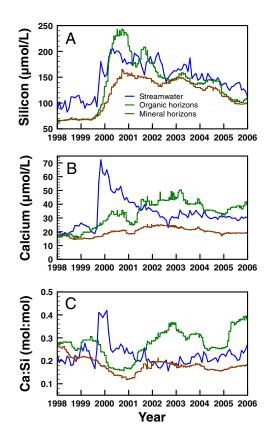
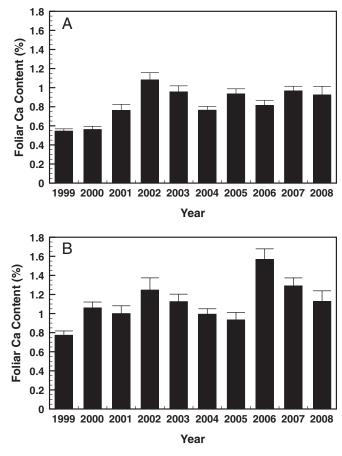


Fig. 2. Time series of streamwater and soil water in W1 (A) Si concentrations, (B) Ca concentrations, and (C) Ca:Si ratios.



**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<sup>-1</sup>, respectively), the difference in aboveground biomass between W1 and W6 increased (2.0, 4.3, and 13.0 Mg·ha<sup>-1</sup> 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.

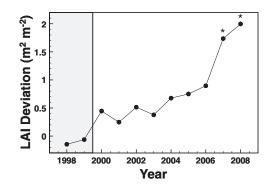
## Discussion

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. 1*B*), 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 xy-lem 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.

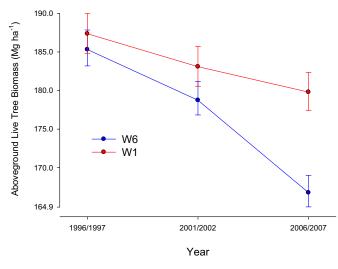


Fig. 5. Trends in aboveground live tree biomass in W1 and W6 for all trees ≥ 10 cm in diameter at breast height (1.37 m). Mean values with 95% confidence intervals shown.

acquisition and improved transport capacity within trees because greater xylem growth would make transpiration-induced leafwater deficits less likely or less intense. Persistent ET deviation throughout the fall and winter suggests a significant response of coniferous species to Ca fertilization. The health and foliar function of red spruce, the dominant conifer on W1, was notably improved by Ca addition there (29, 33, 34), and this species is known to photosynthesize and transpire on a year-round basis given favorable environmental conditions (40). Deficiencies of Ca impair guard cell physiology in red spruce (41), thus the Ca from wollastonite likely improved stomatal function and enhanced winter transpiration.

Other studies have shown that fertilization can stimulate forest transpiration (5, 38–41), including fertilization by Ca (41); however, the impact on hydrology at this spatial and temporal scale has not been witnessed previously. The watershed-scale response to fertilization demonstrates that ecosystem available Ca can be depleted to levels where it becomes physiologically limiting not only to specific plant populations but also to the biogeochemical functioning of the watershed. Our results demonstrate that under conditions of Ca depletion, a substantial increase in available soil Ca can stimulate uptake and primary production, and thereby alter forest hydrology. However, questions remain about whether a proportional decrease of available soil Ca would cause a proportional decrease in ET. If so, the 20th century depletion of available soil Ca from acid deposition may

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have caused a corresponding decrease in ET and increase in streamwater yield, whereas forest recovery from acid deposition may show a decrease in water yield.

The *ET* change in W1 was apparent in stream flow [because *ET* is calculated as the difference between precipitation and stream flow (42)], which is significant because it demonstrates that a transpiration response to fertilization can have a profound effect on a part of the hydrologic cycle that humans most readily interact with: flowing water. As the human need for carbon sequestration, biofuels, and other forest products increases, fertilization becomes a more likely tool to maintain or enhance forest productivity. Unintended forest fertilization is already occurring because of enhanced atmospheric CO<sub>2</sub> concentration and nitrogen deposition (43, 44). Whether intentional or unintentional, alleviation of limiting factors to forest productivity will likely broadly alter the water-provisioning ecosystem service (45), which must be recognized as a trade-off for the enhanced ecosystem services provided by fertilization.

## Methods

Watershed scale ET was estimated by subtracting runoff from precipitation, which assumes that groundwater exchange and interannual water storage is negligible (42). Interannual ET dynamics were demonstrated by calculating annual scale ET deviations from W3-the hydrologic reference watershedand subtracting the median annual ET deviation of a watershed from W3 for the entire monitored record (so that the ET deviation varied around zero). Finer-scale ET dynamics were analyzed by calculating the cumulative daily ET deviation from W3 beginning in January 1, 1990. Streamwater sampling, soil water sampling, foliar sampling, laboratory chemical methods, and aboveground biomass determination are described in detail by previous authors (38, 46-49). The composite soil water curve was produced with all soil lysimeter data (13 lysimeter plots) by calculating the daily running median Si and Ca concentrations and Ca:Si ratios with a 365-d moving window (Figs. S2 and S3). The LAI data were collected by measuring the area of freshly fallen leaves (50). The median LAI for three W1 plots was subtracted from the median LAI for seven reference plots to calculate the deviation of W1 LAI from the reference. Statistical significance of LAI differences between W1 plots and reference plots were assessed with a two-way ANOVA with year and treatment as the variables.

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