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Give and Take: A Watershed Acid Rain Mitigation Experiment Increases Baseflow Nitrogen Retention but Increases Stormflow Nitrogen Export

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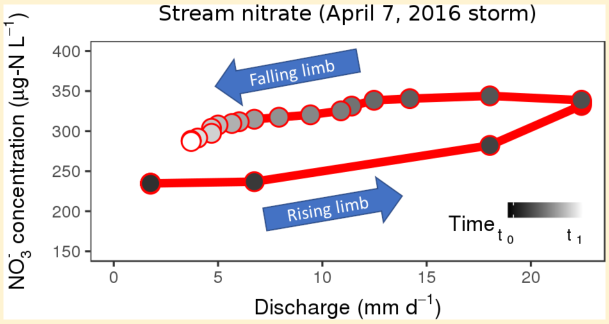
Supporting Information

ABSTRACT: In many temperate forested watersheds, hydrologic nitrogen export has declined substantially in recent decades, and many of these watersheds show enduring effects from historic acid deposition. A watershed acid remediation experiment in New Hampshire reversed many of these legacy effects of acid deposition and also increased watershed nitrogen export, suggesting that these two phenomena may be coupled. Here we examine stream nitrate dynamics in this watershed acid remediation experiment for indicators of nitrogen saturation in the terrestrial and aquatic ecosystems. Post-treatment, the (positive) slope of the relationship between nitrate concentration and discharge increased by a median of 82% (p = 0.004). This resulted in greater flushing of nitrate during storm events, a key indicator of early stage nitrogen saturation. Hysteretic behavior of the concentration-discharge relationship indicated that the mobilization of soil nitrate pools was responsible for this increased flushing. In contrast to this evidence for nitrogen saturation in the terrestrial ecosystem, we found that nitrogen uptake increased, post-treatment, in the aquatic ecosystem, substantially attenuating growing-season nitrate flux by up to 71.1% (p = 0.025). These results suggest that, as forests slowly recover from acid precipitation, terrestrial, and aquatic ecosystem nitrogen balance may be substantially altered.



1. INTRODUCTION

Many forested watersheds across northeastern North America and Europe have shown substantial, unexpected declines in inorganic nitrogen (N) export over the past two decades.[1−6] This reduced stream export coincides with long-term regional declines in soil inorganic N availability[7] and N mineralization rates,[8] suggesting a "tightening" of the N cycle. This tightening of the N cycle runs counter to predictions that anthropogenic N loading would eventually saturate plant N demand, increasing N export.[9] However, these predictions of increased N export fail to account for the accumulation of anthropogenic N in soils.[10] Soils have been shown to retain anthropogenic inputs of N even when plant demand is saturated,[11,12] but the mechanisms that determine this capacity for N retention remain unclear. Some authors have suggested that high N retention in recent decades is due to reaggradation of soil organic N stocks following catastrophic loss during logging, tillage, or other major disturbance.[13,14]

An alternative mechanism that has not been extensively examined is that soils have become more retentive of N due to persistent impacts of acid deposition. Levels of acid deposition in the United States and Europe have declined substantially since they peaked in the 1970s, yet forests and the streams that drain them remain severely impaired.[15] The legacy of over a hundred years of acid deposition has lowered soil pH and decreased the mobility of dissolved organic matter.[15−17] This decreased solubility of soil organic matter may reduce the bioavailability of soil organic N to microbes, reducing N

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mineralization in soils, as well as decreasing dissolved organic N export to streams. Further, low soil pH can suppress turnover of soil organic N due to impacts on soil microbial and faunal communities responsible for decomposition.[18−20]

A watershed acid remediation experiment at Hubbard Brook Experimental Forest (HBEF) (White Mountains National Forest, NH) resulted in a major increase in watershed N export, suggesting that the legacy effects of acid deposition may play a key role in suppressing N export from northern hardwood forests.[21] In this study, researchers applied wollastonite ($CaSiO_3$) to a watershed in order to increase soil Ca fertility and to moderately elevate soil pH,[22,23] countering two important legacy impacts of acid deposition that are linked to tree mortality, decreased primary productivity, and release of toxic aluminum species into aquatic ecosystems.[15] In the first 12 years of the experiment, upper soil horizons in the $CaSiO_3$-treated watershed lost 1333 kg N ha^{-1}, a 31% loss of soil organic N equivalent to ∼1.5 times the amount of N stored in biomass.[23] This loss of N occurred even as net primary productivity and forest biomass increased.[24,25] Nitrogen export in streams increased substantially but lagged the soil and biomass responses to the treatment. Beginning around 2008, almost nine years after treatment, N export from the $CaSiO_3$-treated watershed increased gradually such that, by 2013, N export from the $CaSiO_3$-treated watershed was 30-fold higher than from the reference watershed.[21]

These experimental results raise questions about how soil acidity and alkalinity constrain the mineralization and release of soil organic N. The $CaSiO_3$ treatment resulted in elevated export of N that is consistent with N saturation of the terrestrial ecosystem, despite appreciable declines in N deposition over the past 15 years[26] and presumed increased net plant uptake in biomass due to higher primary productivity.[25] The nitrogen saturation hypothesis proposes that chronic anthropogenic N deposition to an ecosystem will produce a predictable sequence of changes in ecosystem N retention, reflected in changes to the timing and magnitude of stream N export.[9,27,28] During the earliest stages of N saturation, stream N concentrations are elevated only during periods of high hydrologic flux, with enhanced primary productivity acting as a sink for elevated levels of N deposition during baseflow conditions. This results in a "flashy" pattern of watershed N export, in which a large proportion of the annual N export occurs during transient high flow events, analogous to hydrologic flashiness.[29] In later stages, the supply of soil inorganic N completely outstrips autotrophic demand, resulting in elevated baseflow stream N concentrations in addition to higher storm event concentrations. The progression of N saturation represents a shift from supply limitation of N, when N export from the watershed is limited by the mass of mobile N in soil pools, to transport limitation, where the conveyance of large standing pools of soil N to streams is limited only by the movement of water.[30] In-stream processing of N may also modify or obscure a terrestrial signal of N saturation, depending on whether aquatic ecosystem N demand is likewise saturated.[28]

While the N saturation hypothesis is commonly examined in ecosystems with high external inputs of N, it is also interesting to consider N saturation of an ecosystem driven by biogeochemical changes that cause extensive release of N from extant ecosystem pools, as is likely the case in the experiment at HBEF. If the changes to N cycling observed in this experiment presage changes that will occur as other forests gradually recover from acid precipitation, this experiment may have important implications for forest and freshwater resource management in temperate forests across the world. In this work, we examine evidence for N saturation in the $CaSiO_3$-treated watershed at HBEF by analyzing stream nitrate (NO_3^-) temporal dynamics, particularly during high flow events, complementing previous work that examined annual watershed N mass balance.[21] We focus on NO_3^- dynamics because the N saturation hypothesis predicts the greatest increases in export of this form of N,[9] and ammonium and organic nitrogen export were not elevated in the $CaSiO_3$-treated watershed (see Supporting Information (SI)).[21] We asked the following questions: 1. Do patterns of N export from the $CaSiO_3$-treated watershed at HBEF exhibit symptoms of N saturation? 2. Does an increase in the N export during high flow events in the early years of the experiment (1999−2007) act as a leading indicator of N saturation, prior to the period of greatly elevated N export (2007−present)? 3. To what extent does in-stream uptake of inorganic N alter the patterns of increased N export observed in the watershed?

2. MATERIALS AND METHODS

2.1. Study Site. The study was conducted within three small, hardwood forest watersheds at HBEF with areas ranging from 11.8 to 42.4 ha. The watersheds have podzolic soils underlain by glacial til and relatively impermeable bedrock, and are drained by first- and second-order streams. Hydrologic discharge is highest during the early spring snowmelt period, and lowest during the summer and during prolonged winter freezes. A site map and further site description are provided in the SI. Discharge is measured in each watershed by a v-notch weir.[31] Since 1963, the stream chemistry of major inorganic solutes has been measured weekly at the watershed outflows.[26] Stream volume-weighted NO_3^- concentrations at HBEF show a strongly seasonal, sinusoidal pattern, with highest concentrations observed during the early spring and the lowest concentrations observed in the late summer, a pattern attributed to the degree of biological N demand in each season.[26]

In October 1999, one of the gauged watersheds (the $CaSiO_3$-treated watershed) was treated with 1189 kg Ca ha^{-1} as powdered and pelletized wollastonite ($CaSiO_3$), applied aerially as an acid remediation treatment.[22] Two adjacent watersheds remained untreated, in a typical paired watershed experimental design. To be consistent with previous literature from the site, we refer to these reference watersheds as the biogeochemical reference and hydrologic reference watersheds, respectively, although the distinction is only nominal for the purpose of this study. Distinct but overlapping data sets have been collected from both of these watersheds throughout the years, and we use biogeochemical data from both watersheds in our analyses.

2.2. Storm Event Nitrate Dynamics in the Long Term Record. We used the long-term HBEF stream chemistry record to examine whether the $CaSiO_3$ treatment caused the relationship between streamwater NO_3^- concentration and discharge to become more strongly positive, leading to flashier N export at high flow. We analyzed the NO_3^- concentration-discharge relationships during high flow events in all three watersheds for three time periods: a pretreatment period (October 1991 to October 1999), the early post-treatment period (October 1999 to October 2007), and the recent post-treatment period (October 2007 to October 2014). The latter period corresponds to the occurrence of substantially elevated stream NO_3^- flux in the $CaSiO_3$-treated watershed. The strong seasonality of stream NO_3^- concentrations at HBEF complicates an examination of concentration-discharge relationships, so we seasonally detrended the data by evaluating concentration-discharge relationships over short intervals, comparing samples taken during high flow events to samples taken during baseflow conditions immediately prior to the events.

To identify stream chemistry samples taken during storms, we performed a hydrograph separation on the daily HBEF discharge data[32] using the Lyne-Hollick algorithm.[33] We identified high flow events as days in which baseflow comprised less than 50% of total discharge. We then paired all stream chemistry samples taken during a high flow event with the antecedent baseflow sample taken 1 week previously. We did not analyze pairs of samples where the antecedent sample was taken during zero flow (stagnant water) or also during high flow conditions. In total, 15% of samples met these criteria for a storm event. For each pair of samples, we calculated the slope of the concentration-discharge relationship as follows:

$$m = \frac{[NO_3]_{\text{highflow}} - [NO_3]_{\text{antecedent}}}{\log(Q_{\text{highflow}}) - \log(Q_{\text{antecedent}})} \qquad (1)$$

with $[NO_3^-]$ in units of mg L^{-1} and discharge (Q) in units of mm d^{-1}. A slope greater than zero indicates flushing behavior of the watershed, where stream NO_3^- concentrations increase with discharge, and a slope less than zero indicates diluting behavior. We used the Kruskal–Wallis test to test for differences in the median slope of the concentration–discharge relationship among watersheds and across time periods. We adopted this nonparametric approach as the frequency distributions of slopes were strongly positively skewed. To perform post hoc comparisons between watersheds and different time periods, we used Dunn's test, correcting for multiple comparisons using Holm's method. To examine the role of N uptake by terrestrial vegetation in driving event concentration–discharge relationships, we further divided the data into growing season (April–September) and nongrowing season events (October–March) and performed the same analyses.

2.3. High-Frequency Storm Nitrate Dynamics.

From August 2015 to December 2016, we employed SUNA optical NO_3^- analyzers (Sea-Bird Scientific, Halifax, NS) to measure stream NO_3^- concentrations at 3 h intervals. These measurements were cross-validated against laboratory analysis of samples, and the SUNA data were corrected for baseline drift. We identified the 12 highest discharge events for which data were available, and plotted these events in concentration-discharge space.

We analyzed each storm event visually for patterns of hysteresis in the concentration–discharge relationships. To qualitatively infer the source pools of NO_3^- export during storm events, we used the analytical framework of Evans and Davies.[34] This framework allows a coarse-scale inference into the concentrations of different ecosystem pools of dissolved solutes based on the direction and curvature of hysteresis in storm event solute concentrations. We classified high flow events based on whether the overall concentration–discharge relationship was positive (flushing) or negative (diluting), as well as if they displayed clockwise, anticlockwise or no hysteresis. For example, in a clockwise hysteresis, for any given discharge, the solute concentration on the rising limb of the hydrograph is higher than on the falling limb. A clockwise hysteresis indicates that proximal sources of water (e.g., channel interception, riparian groundwater) are higher in concentration than distal sources. We classified the event as showing no hysteresis when the difference in NO_3^- concentrations between the rising and falling limbs did not exceed the published accuracy of the SUNA instrument (± 28 μg NO_3–N L^{-1}).

2.4. In-Stream Nitrate Uptake.

To measure the impact of in-stream uptake on watershed NO_3^- export, we performed a mass balance for the stream channel, inferring net in-stream uptake of NO_3^- when a decrease in NO_3^- flux was observed between the headwaters and the weir of each watershed. Beginning in 1991, streamwater samples were collected approximately monthly at five sites along elevational gradients within the $CaSiO_3$-treated and biogeochemical reference watersheds. These gradients spanned first flowing water to the weir at the watershed outlet. Unfiltered samples were collected in HDPE bottles and analyzed for NO_3^- by ion chromatography. We calculated NO_3^- flux at each sampling location as the product of NO_3^- concentration and discharge. Discharge was estimated at ungauged sampling sites by using the mean daily discharge at the weir of each watershed and assuming that discharge at each sampling location was proportional to the upslope accumulated area. This method has been used previously for estimating solute fluxes for ungauged reaches at HBEF, where minimal groundwater recharge makes this method viable.[35] We estimated upslope accumulated area for each sampling location using a 1 m grid digital elevation model produced from a leaf-off light detection and ranging (LiDAR) flight,[36] coarsened to a 5 m grid and analyzed using ArcGIS 10.2 (ESRI, Redlands, CA).

For each sampling date, we calculated the net proportional decline in NO_3^- flux between the headwaters and the watershed weir following the approach of Bernhardt et al.[37] We calculated a ratio (r) as the NO_3^- flux at the weir of the watershed divided by the maximum NO_3^- flux observed upstream. A ratio below one indicates that $(1 - r)$ of the NO_3^- was removed from the water column by net in-stream NO_3^- uptake between the headwaters and the weir of the watershed on that day. A ratio above one indicates that there was no net retention of NO_3^- between the headwaters and the weir on that day (that is, NO_3^- flux increased between the two sampling locations.) This relative method allows comparison of NO_3^- uptake across years and widely varying flow conditions. This method is a calculation of net uptake for the entire stream length, and is thus a conservative floor of gross uptake rates, as it does not account for groundwater inputs of NO_3^- or in-stream nitrification. We aggregated net uptake measurements by month and split the data into pretreatment and post-treatment periods. Each set of aggregated ratios was tested to be significantly less than 1 using a one-way student's t test ($\alpha = 0.05$, corrected for multiple comparisons by Holm's method). This statistical test determined if the mean net retention of NO_3^- in a stream was nonzero for a given month. Four outliers out of a total of 373 ratio calculations were excluded from the analysis due to concerns over data quality; exclusion of these data did not impact the statistical significance of any results or our conclusions.

To better understand patterns of growing season net NO_3^- uptake over varying flow regimes, we also performed fine-scale longitudinal surveys of stream NO_3^- concentrations from June to August 2015. We performed eight surveys in the $CaSiO_3$-treated watershed and three surveys in the reference watersheds, over flow conditions ranging from 0.2 to 46 mm d^{-1}. Sampling locations were spaced ~50 m apart in stream reaches encompassing first flowing water to the weir of the watershed (550−700 m reaches, depending on flow conditions). We measured stream NO_3^- concentrations in situ using a SUNA optical NO_3^- analyzer placed in the main channel. Discharge at ungauged locations was estimated using the upslope area method previously described. We validated this method of discharge estimation by measuring discharge directly using a tracer slug injection method during the first four surveys performed.[38] For each survey, we calculated the flux ratio in the same manner as described above for the long-term data.

3. RESULTS

3.1. Storm Nitrate Concentration−Discharge Dynamics.

In the pretreatment and early post-treatment periods, instantaneous NO_3^- fluxes were similar among all watersheds (Figure 1), stream NO_3^- concentrations increased moderately with discharge (positive concentration-discharge slopes, flushing behavior), and there were no significant differences in median concentration-discharge slopes among the watersheds (Figure 2). In the recent post-treatment period, NO_3^- export was significantly "flashier" in the $CaSiO_3$-treated watershed due to greater slopes of the concentration−discharge relationship. During the recent post-treatment period, the median slope of the concentration−discharge relationship in the $CaSiO_3$-treated watershed (0.20, IQR: 0.05−0.43) was significantly higher than both the hydrologic reference watershed (0.06, IQR: 0.00−0.19; $p < 0.001$) and the biogeochemical reference watershed (0.00, IQR: 0.00−0.12; $p < 0.001$). Comparing across time within the $CaSiO_3$-treated watershed, the median slope in the recent post-treatment period (0.20, IQR: 0.05−0.43) was significantly higher than in the pretreatment period (0.11, IQR: 0.00−0.24; $p = 0.004$) and in the early post-treatment period (0.10, IQR: 0.00−0.25; $p = 0.003$). In both reference watersheds, there were no significant differences in median concentration-discharge slopes between time periods. All three watersheds showed a positive excursion in concentration-discharge slope in 1998 and 1999, during which time the forests in each watershed were recovering from a severe ice storm that destroyed up to 30% of the tree canopy.[39]

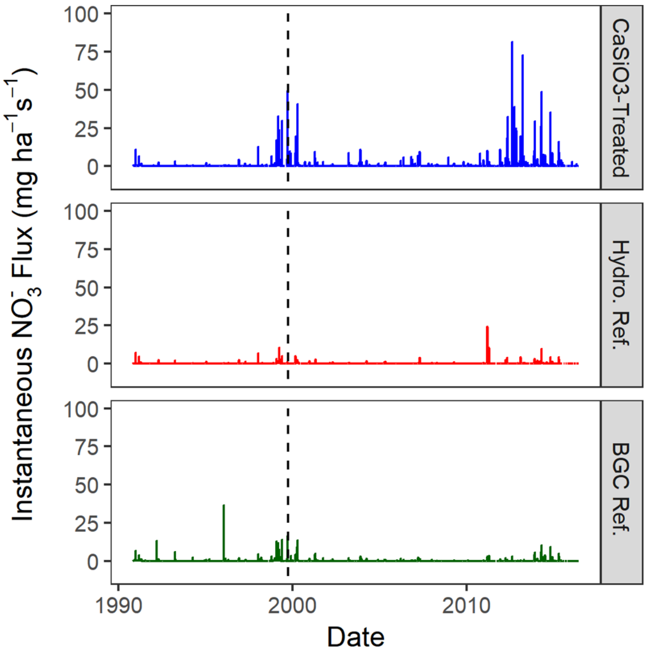

Figure 1. Instantaneous NO_3^- flux in three watersheds at Hubbard Brook Experimental Forest from 1 January 1991 to 30 June 2016. The dashed line indicates the date that the acid mitigation treatment was applied in the $CaSiO_3$-treated watershed. The watershed color scheme used here is maintained throughout the article. "Hydro ref." refers to the hydrologic reference watershed and "BGC ref." refers to the biogeochemical reference watershed (see Materials and Methods: Study Site).

The higher concentration−discharge slopes of NO_3^- export in the $CaSiO_3$-treated watershed during the recent post-treatment period were particularly apparent during the growing season (Figure 3). In the recent post-treatment period, the median growing season concentration−discharge slope in the $CaSiO_3$-treated watershed (0.15, IQR: 0.00−0.22) was significantly higher than in both the pretreatment period (0.00, IQR: 0.00−0.00, $p < 0.001$), and the early post-treatment period (0.00, IQR: 0.00−0.11; $p = 0.033$), when NO_3^- concentration was essentially invariant with discharge. In both reference watersheds, median growing season stream NO_3^- concentrations were at or near the detection limit (50 μg NO_3^--N L^{-1}), both during baseflow and event conditions. In the nongrowing season, concentration-discharge slopes were modestly higher in the $CaSiO_3$-treated watershed during the recent post-treatment period ($p < 0.1$).

During the 12 storms analyzed using high-frequency sensor data, concentration-discharge relationships showed markedly different patterns of hysteresis in the $CaSiO_3$-treated watershed compared to the hydrologic reference watershed (Figure 4). In all 12 events for the $CaSiO_3$-treated watershed, stream NO_3^- concentrations exhibited positive concentration-discharge slopes and strong anticlockwise hysteresis. This pattern suggests the mobilization of distal sources of NO_3^- containing substantially higher concentrations than near-streamwater and channel interception water. By contrast, the hydrologic reference watershed exhibited no consistent pattern of concentration-discharge hysteresis. We observed two winter events with anticlockwise concentration-discharge hysteresis (Figure 4b, events 3 and 6) although the magnitude of the hysteresis in the reference watershed was smaller than in the $CaSiO_3$-treated watershed. Four events showed clockwise concentration-discharge hysteresis (Figure 4b, events 1, 2, 11, and 12) and in the remaining six events there was no measurable hysteresis.

3.2. In-Stream Uptake of Nitrate.

The net rate of in-stream NO_3^- uptake was substantially increased in the $CaSiO_3$-treated watershed during the post-treatment period. In the pretreatment period (1991−1997), the flux ratio (r) was not significantly less than 1 for any month in the record, for either the $CaSiO_3$-treated or biogeochemical reference watersheds. This pattern indicates that there was no consistent signal of net N retention in either watershed in the pretreatment period (Figure 5). In the post-treatment period (1999−2012), net in-stream NO_3^- uptake significantly reduced the NO_3^- flux from the $CaSiO_3$-treated watershed during three growing-season months: June, July, and September. During these months, net

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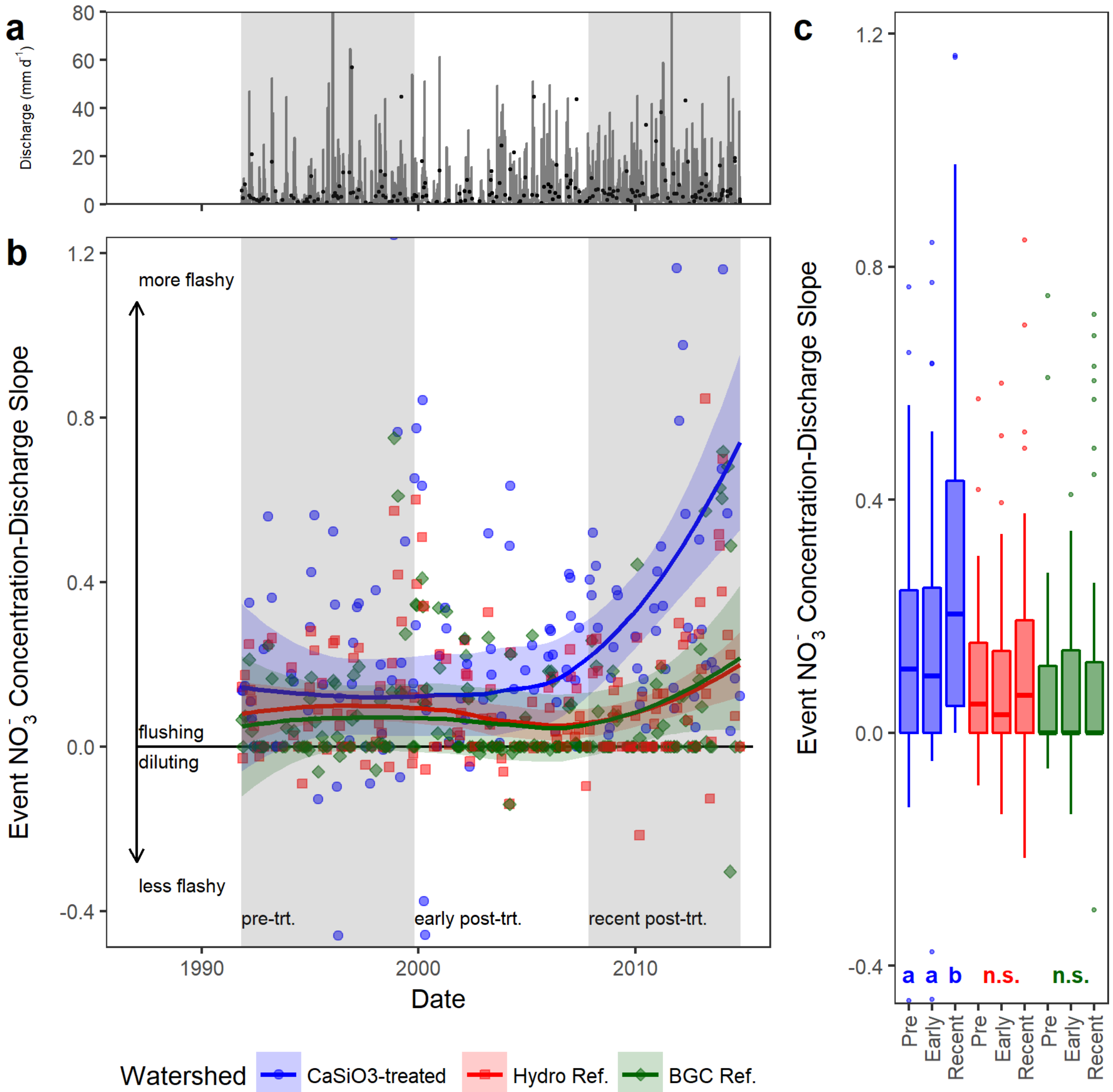

Figure 2. Slopes of the concentration−discharge relationship for high-flow events captured in the weekly stream chemistry record at Hubbard Brook Experimental Forest. Plots show only slopes in the 0.025 to 0.975 quantiles to facilitate viewing of detail, but all points are included in statistical analyses. (a) Hydrograph showing sampled events. The gray line shows the daily discharge of the $CaSiO_3$-treated watershed and black points show instantaneous discharge when the event sample was taken. (b) Time series of event concentration-discharge slopes, showing the three time periods analyzed. Curves shown for each watershed are LOESS models (tricubic weights, $\alpha = 0.75$) showing means and 95% CIs. (c) Summary statistics by period and watershed of event concentration−-discharge slope data. Groups that do not share a letter have significantly different medians.

in-stream uptake decreased net NO_3^- flux from the acid-remediated watershed by a mean of 71.1% in June (SE: ± 15.9%; $p = 0.025$), 63.0% in July (SE: ± 10.7%; $p = 0.023$) and 68.0% in September (SE: ± 9.7%, $p = 0.005$). There was no consistent in-stream uptake of NO_3^- in the biogeochemical reference watershed during these months of the post-treatment period, although significant in-stream uptake was detected in the month of November.

The fine-scale longitudinal surveys conducted from June to August 2015 showed that in-stream uptake continued to result in reduced NO_3^- fluxes from the $CaSiO_3$-treated watershed during the growing season. Net in-stream uptake reduced net NO_3^- flux from the watershed by 0−77.1% (median: 28.9%) across the eight surveys. The flux ratio was strongly positively correlated with the logarithm of discharge ($p < 0.001$) (Figure 6). The greatest proportional in-stream uptake was therefore observed during low-flow conditions, whereas during high flow conditions, there was no detectable in-stream uptake of NO_3^-. In each of the fine-scale surveys performed in the reference watersheds, there was no observed net in-stream uptake, regardless of discharge.

4. DISCUSSION

We found several lines of evidence indicating that the $CaSiO_3$-treated watershed shifts from supply limitation to transport limitation of NO_3^- in the stream, consistent with symptoms of N saturation. Foremost, we found that streams demonstrated a pronounced increase in the positive relationship between discharge and streamwater NO_3^- concentrations, resulting in substantially increased NO_3^- export during high flow events. Previous studies conducted in the 1960s at HBEF showed a positive relationship between discharge and stream NO_3^-

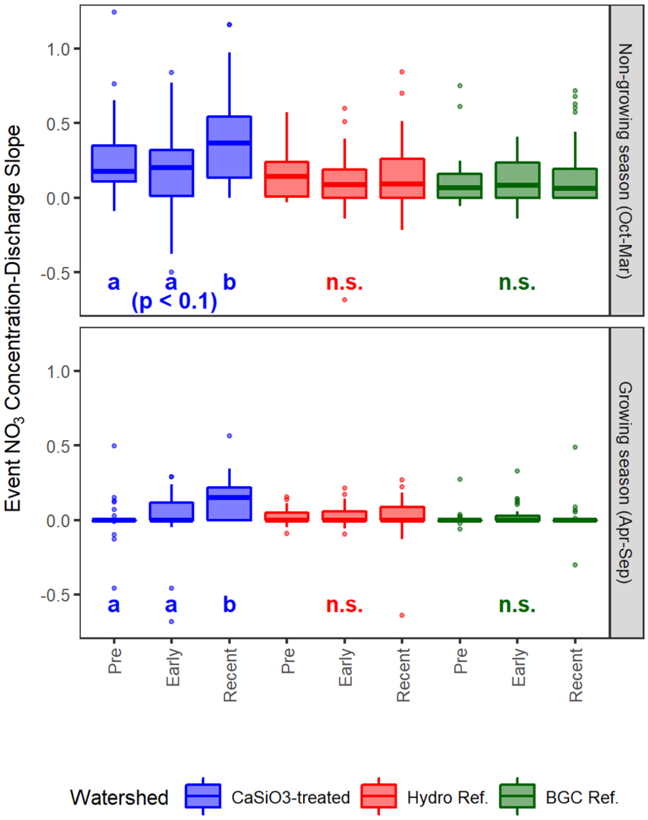

Figure 3. Summary statistics by period and watershed of event concentration-discharge slope data, disaggregated by season. Groups that do not share a letter have significantly different medians.

concentrations during the nongrowing season,[31,40] but since the 1990s this relationship has nearly disappeared as N deposition and stream N export have decreased markedly.[26] While we did find evidence that the concentration–discharge relationship became more positive during the nongrowing season in the $CaSiO_3$-treated watershed, the most striking changes were evident during the growing season. This pattern suggests that in the $CaSiO_3$-treated watershed, NO_3^- is produced in excess of biological demand and is retained in hydrologically isolated pools which then become mobilized during storm events. Even during the 1960s, when annual watershed export of N at HBEF was an order of magnitude higher than today, growing-season stream NO_3^- concentrations were uniformly low and did not vary with discharge,[40] likely due to strong terrestrial biotic demand for N.[41] This shift in the $CaSiO_3$-treated watershed toward flashy growing-season NO_3^- export thus represents a profound shift in ecosystem N balance.

Following Stoddard's model of N saturation,[27] we had initially hypothesized that an increase in the flashiness of NO_3^- export in the $CaSiO_3$-treated watershed would appear in the early post-treatment period (1999–2007) as a leading indicator of the greater annual NO_3^- flux observed in the recent post-treatment period (2007–2014). We did not find support for this hypothesis, however, as the median concentration-discharge slope in the early post-treatment period was no different than in the pretreatment period. Instead, the observed increased flashiness of NO_3^- export was coincident with the increase in total annual NO_3^- flux, with the watershed rapidly transitioning from very low annual N stream flux in the early post-treatment period to symptoms of intermediate N saturation in the recent post-treatment period.

The patterns of NO_3^- concentration-discharge hysteresis observed during storm events offers some suggestion as to the character and location of the concentrated NO_3^- pools that are mobilized during high flow events. The anticlockwise hysteresis pattern that we document indicates that high-NO_3^- waters from distal sources arrive to the stream late during storm events. Perhaps the most likely mechanism driving this pattern is that NO_3^- is being mobilized late in the storm from large standing pools in surficial soils throughout the watershed. This mechanism has been demonstrated to be plausible in modeling and empirical work if the hydrologic routing of a watershed has a large preferential flow component.[42] In this framework, water on the rising limb and at peakflow is efficiently routed to the stream through preferential flowpaths, with minimal contact time and exchange with soil porewater. The water that arrives on the falling limb of the hydrograph then represents matric flow with much longer travel times and exchange with surficial soil porewater. The late-arriving water is thus, in a sense, vertically distal from the stream, arriving from top soil layers. Extensive preferential flow has been documented at HBEF,[43,44] and NO_3^- concentrations in organic horizon lysimeter samples increased substantially in response to the $CaSiO_3$ treatment,[45] making this mechanism plausible. Patterns of hysteresis in the $CaSiO_3$-treated watershed remained constant regardless of season, suggesting that these high NO_3^- source areas remain active even in periods of high plant demand.

The reference watershed showed greater seasonal variability in patterns of hysteresis, similar to patterns observed in other headwater catchments throughout the region. During the nongrowing season there was a slightly positive concentration–discharge relationship and some examples of anticlockwise hysteresis, but during the growing season the concentration–discharge relationship became near-zero and displayed clockwise or no hysteresis. Koenig et al.[46] found that this seasonal pattern was common across forested watersheds in the region. Inamdar et al.[47] also showed flushing but clockwise NO_3^- storm hysteresis during the growing season in Adirondack headwater catchments, and still other regional examples[48] show strongly negative concentration-discharge relationships during the growing season. We do not have pretreatment data to show conclusively that the atypical patterns of hysteresis in the $CaSiO_3$-treated watershed are due to the treatment rather than intrinsic differences in the watersheds, though we have demonstrated that the overall concentration–discharge relationship changed positively compared to pretreatment conditions. Overall, the $CaSiO_3$-treated watershed now exhibits NO_3^- export characteristics that are atypical for headwaters in the region, both in the magnitude of the concentration–discharge relationship, hysteresis, and the aseasonality of these relationships. Taken together, these differences suggest a substantial alteration of N cycling in the $CaSiO_3$-treated watershed, occurring at a lag of almost a decade to the initial treatment.

The reasons behind the delayed but pronounced change in watershed N cycling remain unclear, but we speculate that it may be related to gradual changes in forest community composition and litter quality. The $CaSiO_3$ treatment resulted in a slow but pronounced recovery of sugar maple (*Acer saccharum*), attributable to higher Ca fertility, that roughly tracked the timing of the increase in N export from the

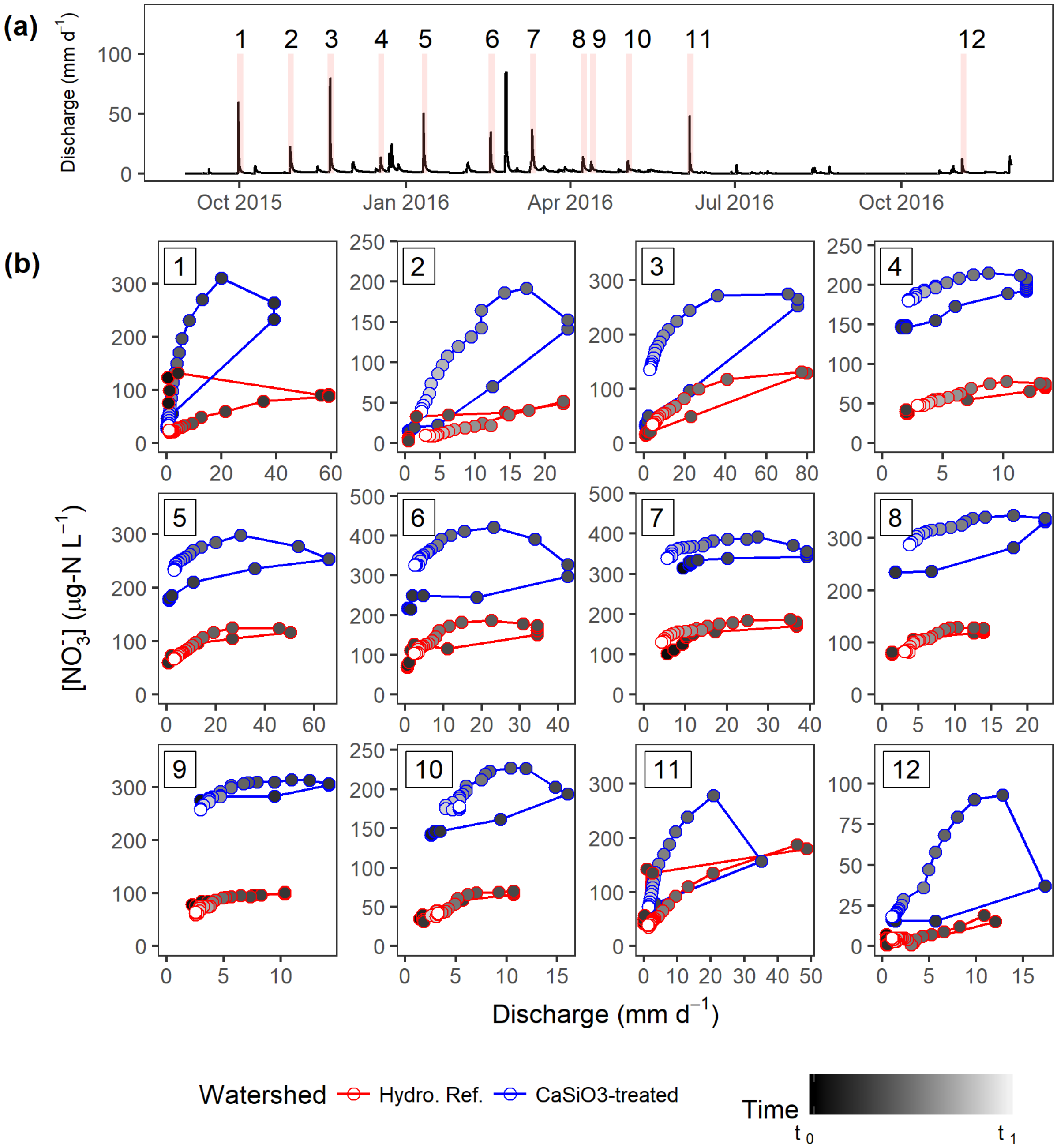

Figure 4. High-frequency NO_3^- concentration−discharge relationships for the 12 largest discrete storm events captured using optical NO_3 sensors. (a) Discharge of the hydrologic reference watershed, with the sampling periods of the plots in panel (b) indicated. (b) Time series of the NO_3^- concentration−discharge relationships for the $CaSiO_3$-treated and hydrologic reference watersheds. Direction of the hysteretic loops is indicated by greyscale shading. Note that scales of x and y axes are different for each event. Storms 1, 8, 9, 10, and 11 are growing season storms.

watershed.[25] Sugar maples are known to have highly labile litter which promotes faster N cycling and greater rates of nitrification.[49−51] Further, the treatment resulted in increased leaf litter N content for sugar maple and white birch,[52] likely driving greater turnover of N during litter decomposition. We thus hypothesize that declines in soil N stocks are coupled to enhanced watershed export of N through plant uptake and litter decomposition mechanisms that control the timing and magnitude of N export. Alternatively, the lagged effect may be the result of the slow migration of the Ca treatment into deep, hydrologically active soil horizons. The lysimeter data[45] showing enhanced fluxes of NO_3^- primarily from surficial soil horizons make this explanation less likely, though.

In addition to flushing of NO_3^--rich waters during storms, net in-stream NO_3^- uptake during baseflow conditions may also contribute to the enhanced flashiness of the NO_3^- concentration-discharge relationship in the $CaSiO_3$-treated watershed; a more strongly positive concentration-discharge relationship can result both from elevated event concentrations as well as suppressed baseflow concentrations. During the growing season, we documented a strong signal of net in-stream uptake of NO_3^- in the $CaSiO_3$-treated watershed and found that the proportional rate of NO_3^- uptake was strongly inversely correlated with discharge (Figure 5). This inverse relationship would be a prerequisite for in-stream uptake impacting the flashiness of stream N export. In-stream uptake

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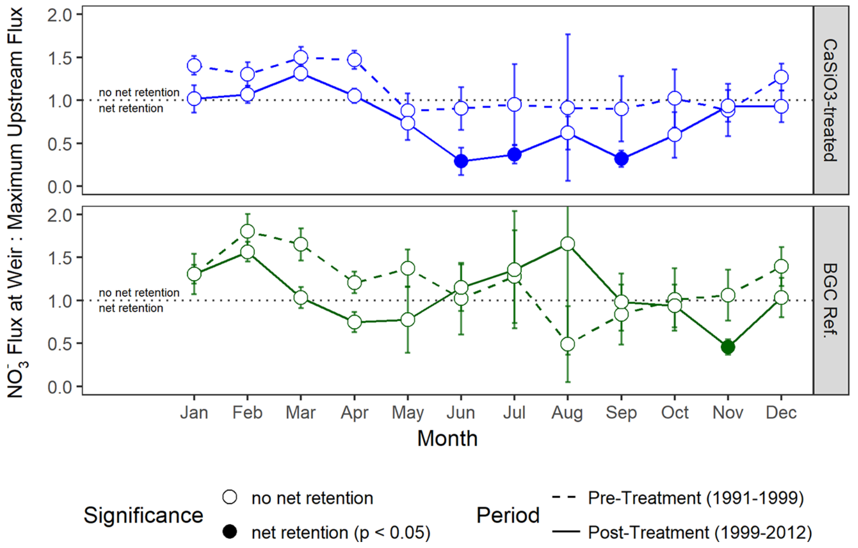

Figure 5. Mean NO_3^- flux by month observed at the weir of the $CaSiO_3$-treated and biogeochemical reference (BGC ref.) watersheds, relative to the maximum flux observed upstream of the weir. When this ratio is less than 1, there is net NO_3^- retention between the point of maximum NO_3^- flux and the weir. Filled circles indicate that the mean of the ratio was significantly less than 1, indicating net retention of NO_3^- in that month. Error bars are ±1 SE.

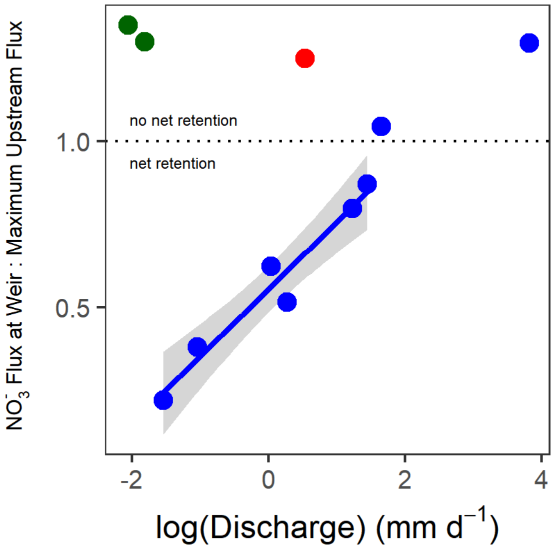

Figure 6. Relationship between the NO_3^- flux ratio (see Figure 5 caption and text) and discharge, calculated from longitudinal surveys performed in the $CaSiO_3$-treated watershed (blue points) from June to August 2015. Surveys performed in the biogeochemical reference (green points) and hydrologic reference (red point) watersheds are shown for comparison. For points above the dashed line, there was no net in-stream NO_3^- uptake. The coefficient of determination for the regression line shown is $r^2 = 0.938$ ($p < 0.001$).

of N is known to be tightly coupled to contact time between streamwater and benthic sediments.[53] Contact time is lower at high discharge due to higher stream velocity and a greater cross-sectional area to wetted perimeter ratio. We therefore conclude that the observed relationship between discharge and N uptake is consistent with increased uptake by benthic microbiota. This uptake resulted in lower baseflow stream NO_3^- concentrations that likely contributed to more positive, flashier NO_3^- concentration–discharge relationships during the growing season, although this contribution is difficult to quantify directly. While the terrestrial ecosystem in the $CaSiO_3$-treated watershed exhibited strong evidence of N saturation, the aquatic ecosystem showed continuing high levels of N demand, an interesting, contrasting response of the aquatic and terrestrial ecosystems to the $CaSiO_3$ treatment.

The high rates of net in-stream N uptake observed in the $CaSiO_3$-treated watershed are in contrast to the view that solute fluxes in the streams of small watersheds are almost always at steady state, with no net retention or release of solutes.[54] Among other studies that do show net in-stream uptake, our result is remarkable both for the amount of net uptake (up to 77% in the lowest flow conditions) and the lack of an obvious sink for this NO_3^-. Other work has shown moderate net in-stream uptake in conjunction with very high rates of algal primary productivity[55] or in conjunction with pulses of organic matter inputs, either during autumn or after a disturbance event.[56,57] In previous work at HBEF, high rates of net in-stream NO_3^- uptake were measured in the aftermath of the 1998 ice storm that resulted in a loss of ~30% of the forest canopy.[37] In this earlier instance, researchers speculated that high in-stream N retention was driven by the large inputs of terrestrial litter from downed trees and higher in-stream productivity resulting from increased light through the forest canopy. We measured similar rates of net NO_3^- uptake in the post-treatment period, despite no increase in detrital inputs and no algal productivity, as observed anecdotally during routine sampling.

Given the apparent lack of algal productivity or enhanced carbon inputs to the $CaSiO_3$-treated stream, we hypothesize that the higher in-stream NO_3^- uptake is due to an increase in denitrification. Denitrification can substantially attenuate N fluxes in streams,[58] and is favored under the conditions of higher stream pH and high NO_3^- availability observed in the $CaSiO_3$-treated watershed.[21,59,60] (Streamwater dissolved organic carbon concentrations were not elevated in the $CaSiO_3$-treated watershed,[21] so enhanced denitrification is presumably not driven by enhanced carbon supply.) Limited data (SI Figure S3) show elevated denitrification potential in the sediments of the $CaSiO_3$-treated stream, but further work would be required to quantify a potentially enhanced denitrification sink in the watershed. If the observed increase in N uptake were driven by denitrification, this would represent a permanent, dissimilatory sink of N, in contrast to assimilatory uptake, in which assimilated N could be rereleased as organisms die. This permanent sink of N could potentially alter the watershed N budget, particularly if in-stream processes are reliable proxies for metabolism also occurring in saturated soils.

Stream NO_3^- fluxes in the $CaSiO_3$-treated watershed are higher and substantially flashier post-treatment, consistent with saturation of ecosystem N demand. It is possible that this experiment may foreshadow changes in N cycling that will occur in acid-impacted forests over the coming decades during recovery from acid deposition. Many forests are showing incipient signs of recovery in soil acid−base properties,[61] and this recovery has been linked to enhanced loss of soil organic matter stocks, which are the largest pool of soil N in forested ecosystems.[62,63] This raises the intriguing possibility that acid precipitation, of which a large portion is deposited as nitric acid, may have paradoxically reduced watershed N export through stabilization of soil organic N at low soil pH (see Clarholm and Skyllberg[64] for a review of possible mechanisms). With declines in acid forcing on soils, this stabilized legacy N may be released, effectively resulting in ecosystem N saturation, a mechanism analogous to the internal eutrophication of lakes by remobilization of sediment phosphorus.[65] This hypothesized release of legacy N may alter forest productivity, cause further leaching of base cations (if the N is lost as NO_3^-), and negatively impact water quality. As ecosystems continue to recover from acid precipitation, this hypothesis should be examined across continental-scale gradients of severity in acid deposition, and it should be considered within the context of changing climate regimes that may also have dramatic impacts on N cycling.[8]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b03553.

> Additional data of annual stream dissolved N concentrations, additional site description, and stream sediment denitrification data. (nine pages with three figures) (PDF)

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Notes

The authors declare no competing financial interest.

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