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Combination of factors rather than single disturbance drives perturbation of the nitrogen cycle in a temperate forest

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Abstract Nitrogen (N) is a critical element in many ecological and biogeochemical processes in forest ecosystems. Cycling of N is sensitive to changes in climate, atmospheric carbon dioxide (CO_2) concentrations, and air pollution. Streamwater nitrate draining a forested ecosystem can indicate how an ecosystem is responding to these changes. We observed a pulse in streamwater nitrate concentration and export at a long-term forest research site in eastern North America that resulted in a 10-fold increase in nitrate export compared to observations over the prior decade. The pulse in streamwater nitrate occurred in a reference catchment in the 2013 water year, but was not associated with a distinct disturbance event. We analyzed a suite of environmental variables to explore possible causes. The correlation between each environmental variable and streamwater nitrate concentration was consistently higher when we accounted for the antecedent conditions of the variable prior to a given streamwater observation. In most cases, the optimal antecedent period exceeded two years. We

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assessed the most important variables for predicting streamwater nitrate concentration by training a machine learning model to predict streamwater nitrate concentration in the years preceding and during the streamwater nitrate pulse. The results of the correlation and machine learning analyses suggest that the pulsed increase in streamwater nitrate resulted from both (1) decreased plant uptake due to lower terrestrial gross primary production, possibly due to increased soil frost or reduced solar radiation or both; and (2) increased net N mineralization and nitrification due to warm temperatures from 2010 to 2013. Additionally, variables associated with hydrological transport of nitrate, such as maximum stream discharge, emerged as important, suggesting that hydrology played a role in the pulse. Overall, our analyses indicate that the streamwater nitrate pulse was caused by a combination of factors that occurred in the years prior to the pulse, not a single disturbance event.

Keywords Nitrogen · Temperate forest · Long-term research · Streamwater nitrate

Introduction

Nitrogen (N) plays a critical role in plant, microbial, and animal nutrition (Vitousek and Howarth 1991), and is typically a limiting nutrient in temperate forest ecosystems. As a result, N is typically tightly retained by forest ecosystems. Thus, monitoring N inputs and outputs in small catchments can be a powerful tool for tracking how the catchment N cycle responds to disturbance and changes over time (Aber et al. 2002). Streamwater nitrate is responsive to disturbance (Goodale et al. 2000; Ohte et al. 2003) and thus nitrate patterns can provide an integrated view of N biogeochemical processes occurring within a catchment.

This study focuses on the variability of streamwater nitrate concentrations at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire, USA; a site where streamwater nitrate patterns have helped produce fundamental understanding of forest N dynamics (Likens 2013). Prior disturbances in the reference watershed, such as drought, defoliation events, soil frost, an ice storm, and high atmospheric deposition of N, have led to periods of elevated streamwater nitrate concentration and export (Bernhardt et al. 2003; Bernal et al. 2012). Over the past 20 years at the HBEF, and across the region, streamwater nitrate concentration and export have declined. This decline has been attributed to decreases in atmospheric N deposition, warming air temperatures, increasing atmospheric carbon dioxide (Groffman et al. 2018; Mason et al. 2022), and increased N immobilization in coarse woody debris (Lajtha 2020). Within this long-term period of low streamwater nitrate export, a pulse in streamwater nitrate occurred in 2013-14 with sustained increases in nitrate concentrations and export during the winter months (Fig. 1). This pulse is unusual because, unlike past pulses of streamwater nitrate, there was no obvious disturbance to the forest that would cause nitrate to leach from the ecosystem.

The N cycle in forested catchments is too complex to explain with direct measurements and monitoring alone, so modeling, either simulation or empirical, is necessary. Simulation modeling has improved our understanding of how the N cycle may have changed in the past or will change in the future (Aber et al. 2002; Hong et al. 2005). In addition, simulation modeling allows the upscaling of processes documented at smaller scales to river basin scales (Mineau et al. 2015; Robertson and Saad 2021). However, often the full suite of data on environmental processes and how they interact with each other—and the N cycle—are limited, reducing the ability of the models to predict outcomes accurately. Empirical models such as machine learning models are increasingly applied to process and interpret correlated independent variables and non-linear processes, so that accurate predictive models can be constructed and used to identify the most important variables for predictions (Abbasian et al. 2022; Cai et al. 2023). Utilizing empirical models with comprehensive, long-term data sets can lead to new insights into multiple concurrent, interactive, and lagged factors that together contribute to changes in the N cycle.

In this study we attempt to explain the drivers of the almost 10-fold increase in streamwater nitrate export in water year 2013 compared to the decade prior to the pulse. We hypothesized that the nitrate pulse was due to one or more drivers, including: (1) elevated atmospheric N inputs, (2) increased N production within the catchment, (3) reduced biotic uptake or microbial immobilization, and/or (4) enhanced hydrologic transport of N (Fig. 2).

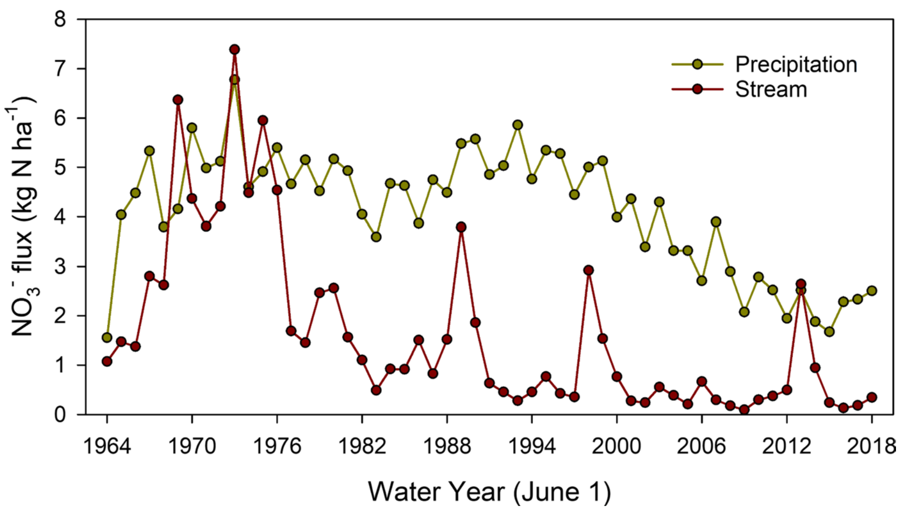


Fig. 1 Long-term annual streamwater nitrate export from a reference watershed at the Hubbard Brook Experimental Forest, Watershed 6, was high in the early record, likely due to high rates of atmospheric N deposition, and was followed by a decline in the 1980s that has persisted except for a few episodes. The streamwater nitrate export peak in water year 1989 was attributed to a soil frost event (Mitchell et al. 1996) and the peak in water year 1998 was attributed to canopy damage from an ice storm (Houlton et al. 2003). The peak in water year 2013 is the focus of our investigation. The water year runs from June 1 to May 31

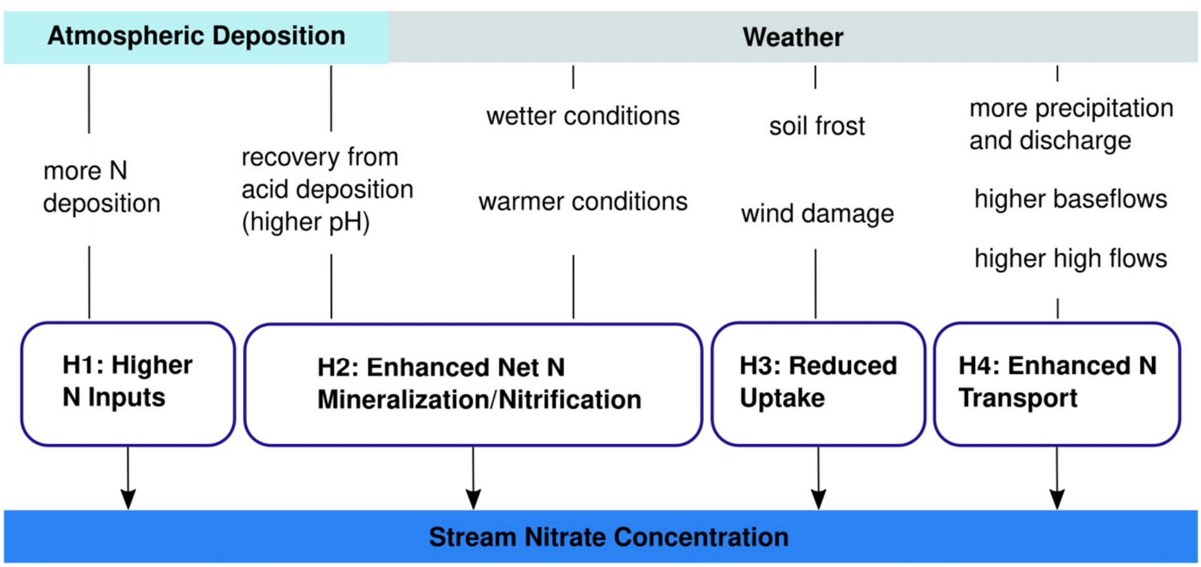


Fig. 2 Conceptual relationships between external drivers, responsive environmental variables, the four hypothesized reasons for the pulse in streamwater nitrate concentration and pulse

Methods

Reference watershed at the Hubbard Brook Experimental Forest (HBEF)

Watershed 6 (W6), a reference watershed at HBEF, is located within the White Mountains of central New Hampshire, USA (Fig. 3, 43°56′N, 71°45′W). The forest within W6 is mostly mixed hardwood

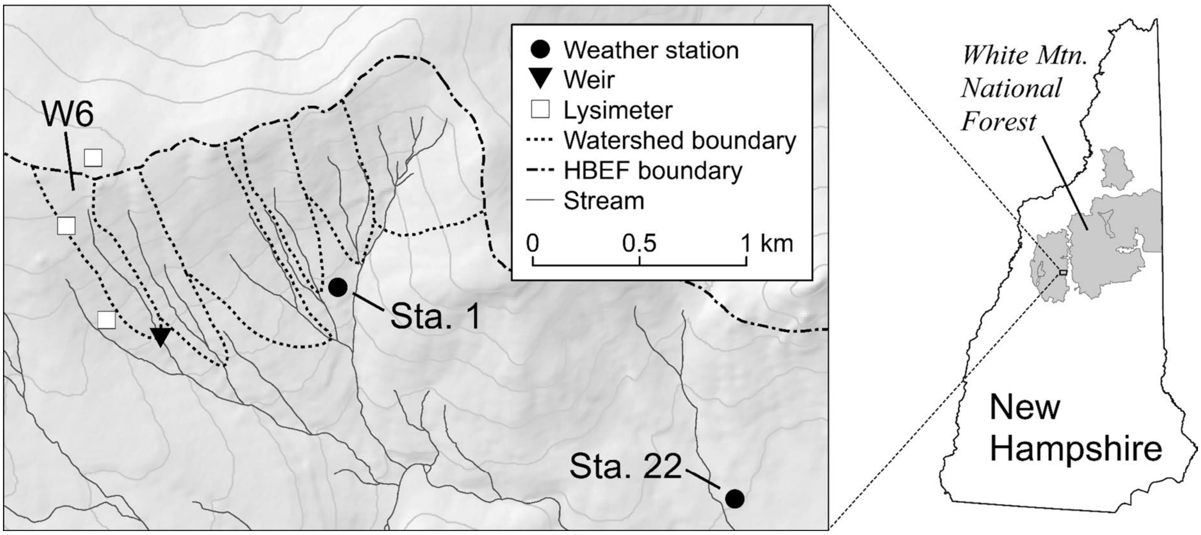


Fig. 3 Monitoring sites within the Hubbard Brook Experimental Forest where data used in this analysis were collected

species—sugar maple (*Acer saccharum*), American beech (*Fagus grandifolia*), and yellow birch (*Betula alleghaniensis*)—with some softwoods (balsam fir (*Abies balsamea*) and red spruce (*Picea rubens*) and white birch (*Betula papyrifera*) near the ridge top (Johnson et al. 2000). The climate is cool and moist with a seasonal snowpack (Likens 2013). Soils at HBEF are Spodosols, developed by soil water percolation or lateral flow resulting in distinct spatial variation along hillslopes (Bailey et al. 2014). Soils are underlain by glacial till and metamorphosed granitic bedrock.

Data

For this study, we used data from the HBEF for the period January 1, 2003 to May 30, 2018 (Table 1). This period was chosen to isolate several years of data around the period of high streamwater nitrate concentrations in 2013–2014. Streamwater nitrate at HBEF has experienced multiple systematic changes over its long-term record, due to long-term reductions in atmospheric deposition, increases in atmospheric CO_2, climate change, forest maturation, and disturbances (Bernal et al. 2012; Yanai et al. 2013). 2003 was chosen as the starting year for the analysis because 3 year lags were considered in relationships between variables, and the forest recovered from a 1998 ice storm around 2000 (Rhoads et al. 2002; Bernhardt et al. 2003). Thus, 2003 to 2018 represents a period when obvious forest disturbances were minimal.

Streamwater nitrate and other streamwater solutes are measured in samples collected at the outflow from W6 on a weekly basis, with periodic high frequency sampling during storm events (Hubbard Brook Watershed Ecosystem Record, 2022). The samples are stored in cool conditions until measurement in the laboratory. Major anion concentrations—NO_3^-, SO_4^{2-}, Cl^-—are measured on an ion chromatograph. Major cation concentrations—Ca^{2+}, Mg^{2+}, K^+, Na^+—are measured on an ICP-OES. Stream discharge is measured using a V-notch weir and a San Dimas flume for high flows (See et al. 2020). Runoff was calculated as the area-normalized discharge, summed over a specified period. Bulk atmospheric deposition is measured using the same lab analytical techniques as streamwater on cumulative weekly precipitation samples (Buso et al. 2000). Precipitation volume is measured with a series of precipitation collectors and is area-weighted to the catchment (Green et al. 2018).

We used other hydrometeorological measurements as independent variables for our analysis. Mean, minimum, and maximum daily air temperature is measured at a long-running meteorological station near W6 (Station 1), using recording temperature sensors (Bailey et al. 2003). Snow water equivalent

Table 1 Independent variables included in the analysis, their associated hypothesis, and data source. The mean, sum, maximum, minimum, or coefficient of variation was applied to the variable during the antecedent period prior to a streamwater sample

Variable	Description (units)	Hypothesis				Data source
DIN Dep	Sum of bulk deposition of dissolved inorganic N (g N/ha/month)	1				HBWatER (2022)
H^+ Dep	Sum of bulk deposition of H^+ (g/ha/month)		2	3		HBWatER (2022)
T_{cv}	Coefficient of variation of mean daily air T (°C/°C)			3		USDA Forest Service (2021a)
GPP_{mean}	Mean of the monthly modeled gross primary productivity (kg C/m^2/month)			3		Running et al. (2015)
T_{mean}	Mean of the mean daily air T (°C)		2			USDA Forest Service (2021a)
RO	Sum of stream runoff (mm of water)				4	USDA Forest Service (2020)
P	Sum of precipitation (mm of water)		2		4	USDA Forest Service (2021b)
q_{cv}	Coefficient of variation for specific discharge				4	USDA Forest Service (2020)
RO:P	Runoff ratio (mm:mm)				4	USDA Forest Service (2020, 2021b)
T_{min}	Minimum air T (°C)		2	3		USDA Forest Service (2021a)
T_{max}	Maximum air T (°C)		2			USDA Forest Service (2021a)
SWE_{mean}	Mean snow water equivalent (mm of water)		2	3	4	USDA Forest Service (2021c)
$Frost_{max}$	Maximum frost depth (cm)			3		USDA Forest Service (2021c)
q_{max}	Maximum specific discharge (mm/hour)				4	USDA Forest Service (2020)
q_{min}	Minimum specific discharge (mm/hour)				4	USDA Forest Service (2020)
Rad_{mean}	Mean incident solar radiation (MJ/m^2/day)			3		USDA Forest Service (2019)
Si_{mean}	Mean streamwater Si concentration (mg/L)				4	HBWatER (2022)
$Wind_{mean}$	Mean wind speed (m/s)			3		USDA Forest Service (2022)
$Wind_{max}$	Maximum wind speed (m/s)			3		USDA Forest Service (2022)
DOC_{lys}	Mean dissolved organic C in soil water (mg/L)		2	3		Driscoll (2022)
pH_{lys}	Mean pH in soil water		2	3		Driscoll (2022)

Some variables were relevant to multiple hypotheses

The hypotheses are numbered 1 to 4 to represent (1) increased N inputs, (2) increased N production within the catchment, (3) reduced biotic uptake/consumption, or (4) enhanced N transport

is measured weekly during the winter months using a Federal Snow Tube at Station 1 (Campbell et al. 2010). We linearly interpolated those weekly values to daily values. Soil frost is measured adjacent to the snow measurements by excavating a soil pit and determining the depth of the frost line by visual and tactile estimation (Campbell et al. 2010). Daily total solar radiation is measured at the nearby Hubbard Brook headquarters building, 3 km from W6 (Station 22), using a pyranometer (Bailey et al. 2003). Daily wind speed is measured at the same location using a digital anemometer (Bailey et al. 2003).

Soil water is collected monthly with zero-tension lysimeters at three elevations adjacent to W6 (LoRusso et al. 2021). We used nitrate, pH, and dissolved organic carbon (DOC) data from the lysimeters for this study. Nitrate concentration is measured with ion chromatography, pH is measured with a glass electrode, and DOC concentration is measured with a total organic carbon analyzer.

For estimates of GPP, we used NASA's MODIS gross primary productivity (GPP) data product (MOD17A2H version 6; Hasenauer et al. 2012). The data for the pixels within the HBEF valley were averaged on a monthly basis using Google Earth Engine.

Data analysis

To evaluate our four hypotheses, we conducted a univariate correlation analysis and constructed machine learning models, which were used to determine the independent variables that most impacted predictions of streamwater nitrate concentration. The dependent variable in all cases was nitrate concentration in W6 streamwater. Independent variables were those that were available from long-term monitoring that would allow us to assess the four hypotheses (Fig. 2 and Table 1).

Univariate correlation

The correlation between each independent variable and streamwater nitrate concentration in W6 was assessed using Spearman's rank correlation (ρ). To account for the time it takes for catchment biogeochemical and hydrological processes to produce nitrate and transport it to the catchment outlet, we calculated the antecedent conditions for each independent variable prior to a streamwater nitrate observation. The period prior to an observation was defined as the antecedent window, within which a summary metric was calculated, such as the mean, minimum, maximum, or coefficient of variation of daily values (Table 1). The optimum window was the period with the highest correlation (ρ) between streamwater nitrate concentration and the transformed independent variable. We tested antecedent windows from 7 to 1097 days (i.e., one week to 3 years), incremented by 10 days. The ρ often varied incrementally with antecedent window length, but was highly variable in some instances, so we smoothed the relationship using Lowess with the span parameter set to 0.75 (Cleveland 1979). The antecedent window length associated with the largest absolute value of ρ was accepted as the optimum window for that independent variable. We also report the ρ associated with a 157 day antecedent window because the median water residence time for the nearby HBEF hydrologic reference catchment (W3) is approximately 150 days (Benettin et al. 2015). The algorithm for this analysis is described in more detail in the Supplemental Methods.

Two multivariate data sets were produced from the univariate analysis, which were used in the multivariate analyses. The first included each independent variable transformed using its optimal antecedent window. The second included each independent variable transformed with a 157-d antecedent window. In both data sets, the maximum discharge using a 7-d antecedent window was included to account for nitrate flushing (e.g., Pardo et al. 2022).

Machine learning models

We built multivariate models to predict streamwater nitrate concentration with the Random Forest algorithm as implemented in R (Breiman 2001; Liaw and Wiener 2002). Four models were built using independent variables transformed with different antecedent windows: (1) the optimal antecedent window, (2) a 157-day antecedent window, (3) a 2-day antecedent window, and (4) all three of these antecedent windows together (three times the number of independent variables as the other models; referred to as the comprehensive model). The model goodness-of-fit was assessed using the Nash–Sutcliffe efficiency (NS; Nash and Sutcliffe 1970). The optimal set of independent variables for each model was determined as the variables chosen after the prediction step in the VSURF algorithm, as implemented in R (Genuer et al. 2010). The chosen set of variables is considered the most parsimonious set that captures redundant information in the full data set and effectively predicts the dependent variable. Once the optimal set of independent variables was chosen, the Random Forest model was run and the NS was calculated and the partial dependence of those independent variables with streamwater nitrate concentration were visualized using PDP library in R (Greenwell 2017).

Results

Documenting the nitrate pulse and concurrent environmental variation

Weekly streamwater nitrate concentrations increased starting from a low in 2010 and peaking during snowmelt of 2014 (Fig. 4a). Nitrate export followed a similar temporal pattern, with more distinct high peaks during large export events (Fig. 4b). High streamwater nitrate concentrations during this period were apparent across all watersheds at Hubbard Brook (Figure S1). The peak export occurred on April 14, 2014 and the peak concentration occurred on January 13, 2014. The January peak concentration occurred during a rain-on-snow event (43 mm of rain on a day with a maximum air temperature of 8 °C) and the April peak was associated with a warm rain during the seasonal spring snowmelt (40 mm of rain on a day with a maximum air temperature of 20 °C; Fig. 5).

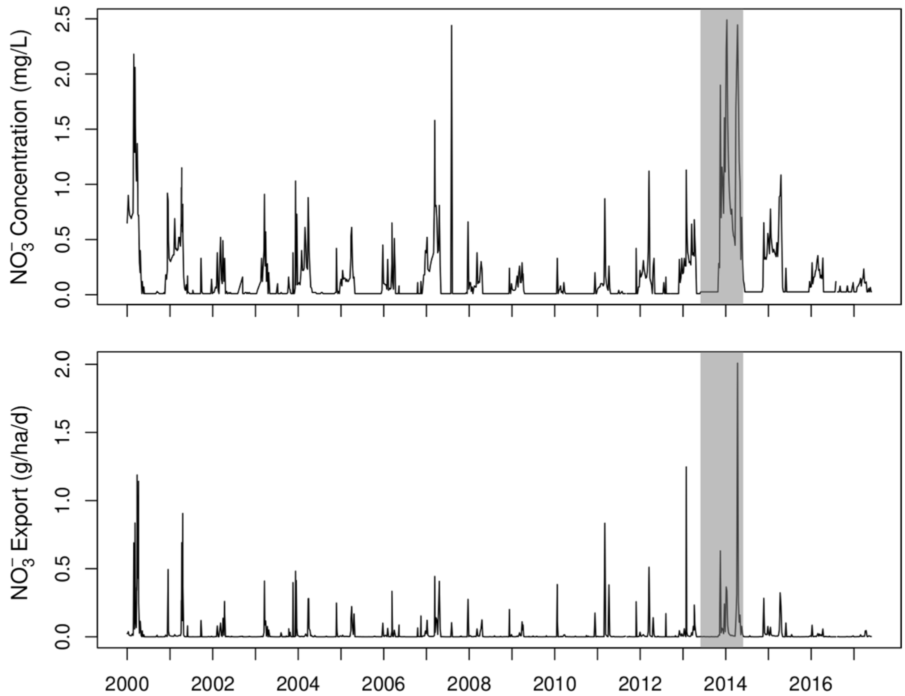


Fig. 4 Time series of weekly streamwater nitrate concentration and export in W6. The shaded area highlights the water year 2013 (June 1, 2013 to May 31, 2014). This shaded area is included for reference in subsequent figures

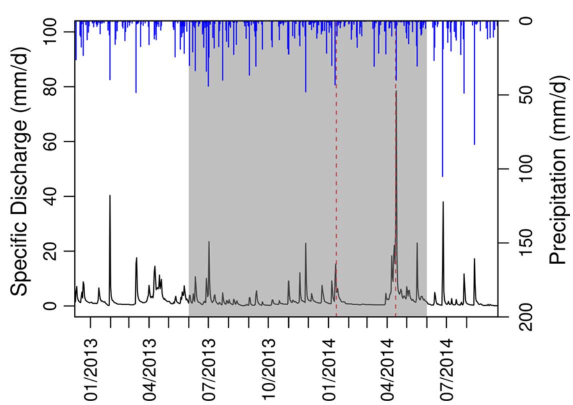
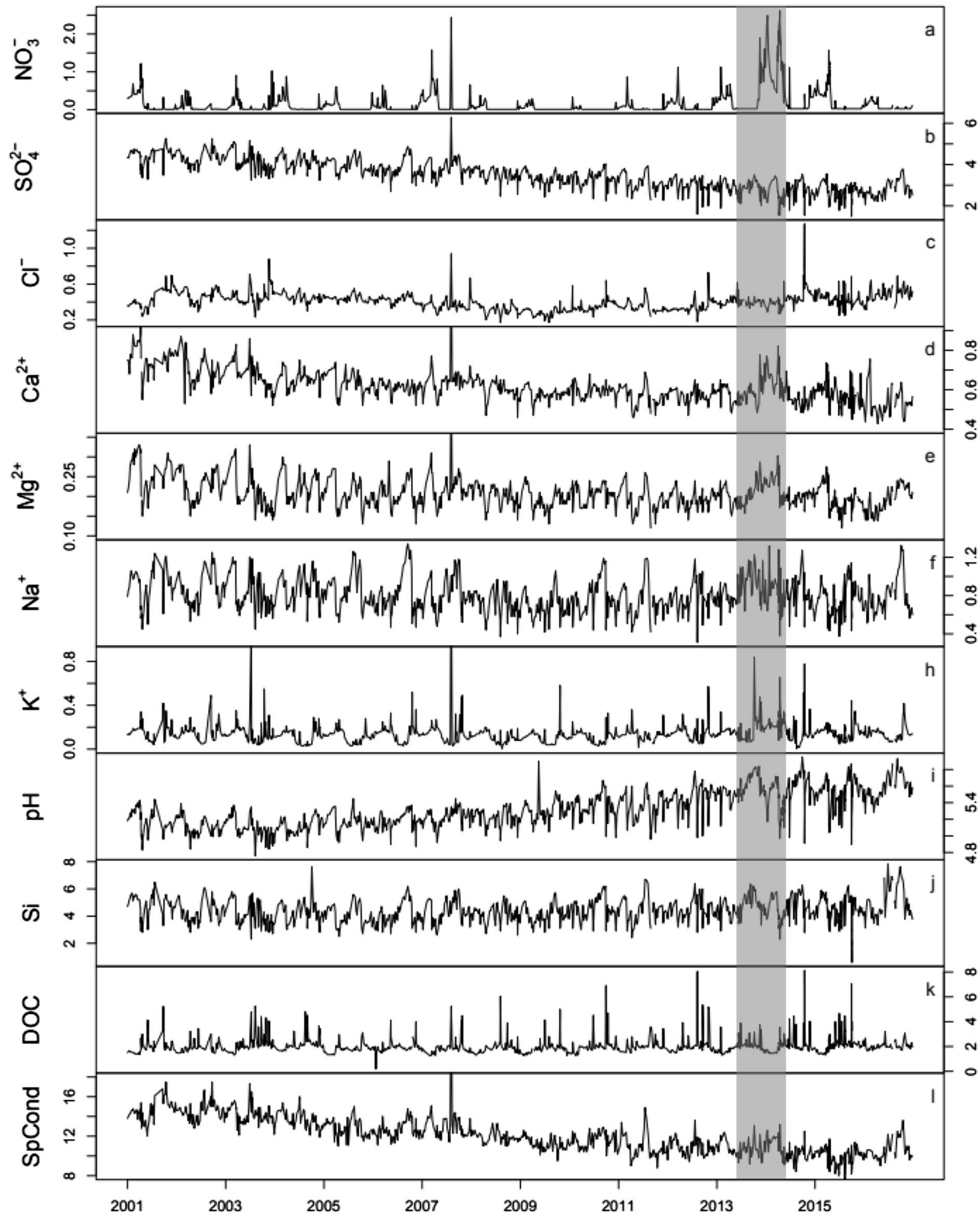


Fig. 5 Stream specific discharge (black line) and precipitation (blue bars) during the period of elevated nitrate concentrations. The red dashed lines show the date of the peaks in nitrate concentration and export. The shaded area highlights the water year 2013 (June 1, 2013 to May 31, 2014). (Color figure online)

Nitrate was the primary form of N that changed in streamwater during this period; ammonium and dissolved organic N did not peak with nitrate (Figure S2). Other streamwater solutes did not show major concentration peaks during the same period (Fig. 6). However, there were a few distinct patterns in temporal variability during this period. Calcium and magnesium concentrations were somewhat elevated during the nitrate pulse, and there was a notable concurrent spike in potassium and decrease in dissolved silica during an event in November 2013 (Fig. 6). Streamwater pH was lower during nitrate peaks than other periods. Similarly, streamwater DOC concentration storm peaks were lower during the period of elevated nitrate compared to other observations. Lysimeters adjacent to W6 show that the 2013–14 pulse was most apparent in the soil waters draining the Bs horizons in the low hardwood stands (Figures S3, S4, and S5). Soil water DOC concentration was relatively low and pH was higher prior to and during the streamwater nitrate concentration pulse. The environmental and ecological variables that we hypothesized would control streamwater nitrate (Table 1) did not show visibly different temporal patterns during this period of high nitrate concentrations and export (Figure S6).

Correlation results

Streamwater nitrate concentrations were most positively correlated with maximum discharge, maximum soil frost, and mean streamwater dissolved Si concentration and most negatively correlated with minimum



discharge, mean wind speed, and mean solar radiation. The optimal antecedent window was 1097 days for all variables except mean solar radiation (1037 days) and mean wind speed (737 days; Table 2).

◂**Fig. 6** Streamwater solute concentrations, pH, and specific conductivity (SpCond) in Watershed 6 during the period of this study. The gray shaded region highlights the 2013 water year. One sample during very low flow conditions was not shown for Ca^{2+}, Mg^{2+}, K^{+}, and SpCond because concentrations were elevated and obscured temporal patterns. The units for each of the solute concentrations is mg/L, except for SpCond. The SpCond units are μS/cm at 25 °C. (Color figure online)

When a 157 day window was used across all variables, only stream dissolved silica concentration and H^+ deposition had Spearman ρ values greater than 0.2 or less than − 0.2.

Soil water nitrate concentrations were not consistently correlated with streamwater nitrate concentrations (Table S1). Three sites had positive Spearman ρ values greater than 0.2: the Bh horizon in the spruce/fir/birch area, the Bs horizon in the low elevation hardwood area, and the Oa horizon in the low elevation hardwood area. The optimum antecedent windows were 457, 1097, and 707 days, respectively. Two sites had negative ρ values less than − 0.2: the Bh and Bs horizons in the high elevation hardwood area. The optimum antecedent windows were 967 and 1097 days, respectively. The soil water nitrate concentration was consistently negatively correlated with DOC and positively correlated with pH (Table 3).

Machine learning results

The machine learning models effectively predicted the streamwater nitrate concentration during the period prior to and during the pulse, although they generally underestimated the peaks, including the 2014 nitrate concentration pulse (Fig. 7). The model using an optimum antecedent window for each independent variable had a NS = 0.56, and the most important variables—from most important to least important—were mean air T, mean stream dissolved Si concentration, sum of DIN deposition, sum of H^+ deposition, mean snow water equivalent, maximum T, and mean GPP in the antecedent window prior to a stream sample. The model using independent variables with a 157-day antecedent window had a NS = 0.53, and the most important variables were minimum air T, maximum air T, solar radiation, CV of air T, mean GPP, and mean air T. The model using a 2 day antecedent window had a NS of 0.28, and the most important variables were minimum discharge, the sum of runoff, the runoff ratio, the sum of H^+

Table 2 Correlations between environmental drivers and streamwater nitrate concentration, listed in order of the absolute value of their Spearman ρ for the optimum antecedent window length

Variable	ρ (optimum window)	Optimum window length (d)	ρ (157 d window)
Max discharge	0.46	967	0.11
Max frost	0.38	987	0.00
Min discharge	− 0.34	1097	− 0.08
Mean solar radiation	− 0.32	1097	− 0.16
Mean wind speed	− 0.31	707	− 0.13
Mean stream [Si]	0.31	1097	0.26
Max wind speed	− 0.29	1097	− 0.09
Max air T	− 0.29	337	− 0.14
Mean air T	0.28	1097	0.00
Sum H^+ deposition	− 0.26	487	− 0.21
Mean SWE	− 0.26	1097	− 0.09
Sum DIN deposition	− 0.22	827	− 0.15
Mean runoff ratio	− 0.22	377	− 0.15
Sum runoff	− 0.21	457	− 0.16
Sum precip	− 0.19	657	− 0.13
Mean GPP	− 0.16	1097	−0.08
Min air T	− 0.12	317	− 0.09
CV of air T	0.11	1097	0.06

The Spearman ρ for the 157 day window (the approximate median water residence time in a nearby catchment) is included to illustrate how correlations compare with a similar duration antecedent window

Table 3 Correlation between streamwater nitrate concentration and soil water solution dissolved organic carbon (DOC) concentration and pH

Soil horizon	Vegetation zone	Independent variable	Optimum window length (d)	ρ (optimum window)
Bs	HH	DOC	1097	– 0.42
Bh	HH	DOC	1097	– 0.35
Bh	HH	pH	877	0.33
Bs	LH	pH	447	0.33
Bh	LH	pH	427	0.32
Oa	HH	DOC	387	– 0.3
Bh	SFB	pH	447	0.3
Bh	LH	DOC	427	– 0.3
Oa	HH	pH	437	0.29
Oa	SFB	pH	1097	0.29
Bs	HH	pH	437	0.28
Bs	SFB	DOC	557	– 0.2
Oa	SFB	DOC	467	– 0.19
Bs	LH	DOC	7	0.16
Bh	SFB	DOC	7	0.14
Bs	SFB	pH	517	0.13
Oa	LH	pH	7	– 0.12
Oa	LH	DOC	1097	0.07

The vegetation zone abbreviations are: *HH* high hardwood, *LH* low hardwood, *SFB* spruce/fir/birch

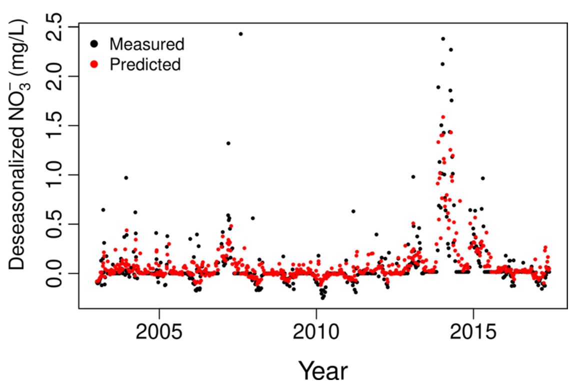


Fig. 7 Time series of the deseasonalized streamwater nitrate concentration observations (black) and the predicted concentration from the random forest model that used all three antecedent windows (red). The Nash-Sutcliffe efficiency of this model was 0.67. (Color figure online)

deposition, mean snow water equivalent, the sum of DIN deposition, and mean GPP. The comprehensive model where each independent variable was summarized (e.g., mean, max, sum) within a 2 day, 157 day, and optimum antecedent window produced a NS of 0.67 (Fig. 7). When this model was analyzed for the most important variables, the following variables emerged: mean wind speed (optimum window), mean air T (optimum window), maximum air T (157 day window), maximum air T (optimum window), sum of runoff (2 day window), maximum discharge (2 day window), maximum discharge (157 day window), and GPP (optimum window) (Fig. 8). The partial dependence of these variables with streamwater nitrate concentration were generally non-linear. Streamwater nitrate concentration was highest at the extreme lowest wind speeds, highest mean air temperatures, lowest maximum air temperatures, highest runoff, highest 2 day and 157 day maximum discharge rates, and highest GPP (Fig. 9).

Discussion

Our analysis suggests that the 2013–14 streamwater nitrate pulse was not caused by one dominant factor, but rather multiple factors and their interactions, operating at multiple time scales. Our overall assessment is that the streamwater nitrate pulse resulted from the accumulation of nitrate in the subsurface due to increased N production (net mineralization and nitrification) and reduced microbial and/or plant uptake of N, combined with the subsequent enhanced hydrologic transport of the accumulated nitrate from

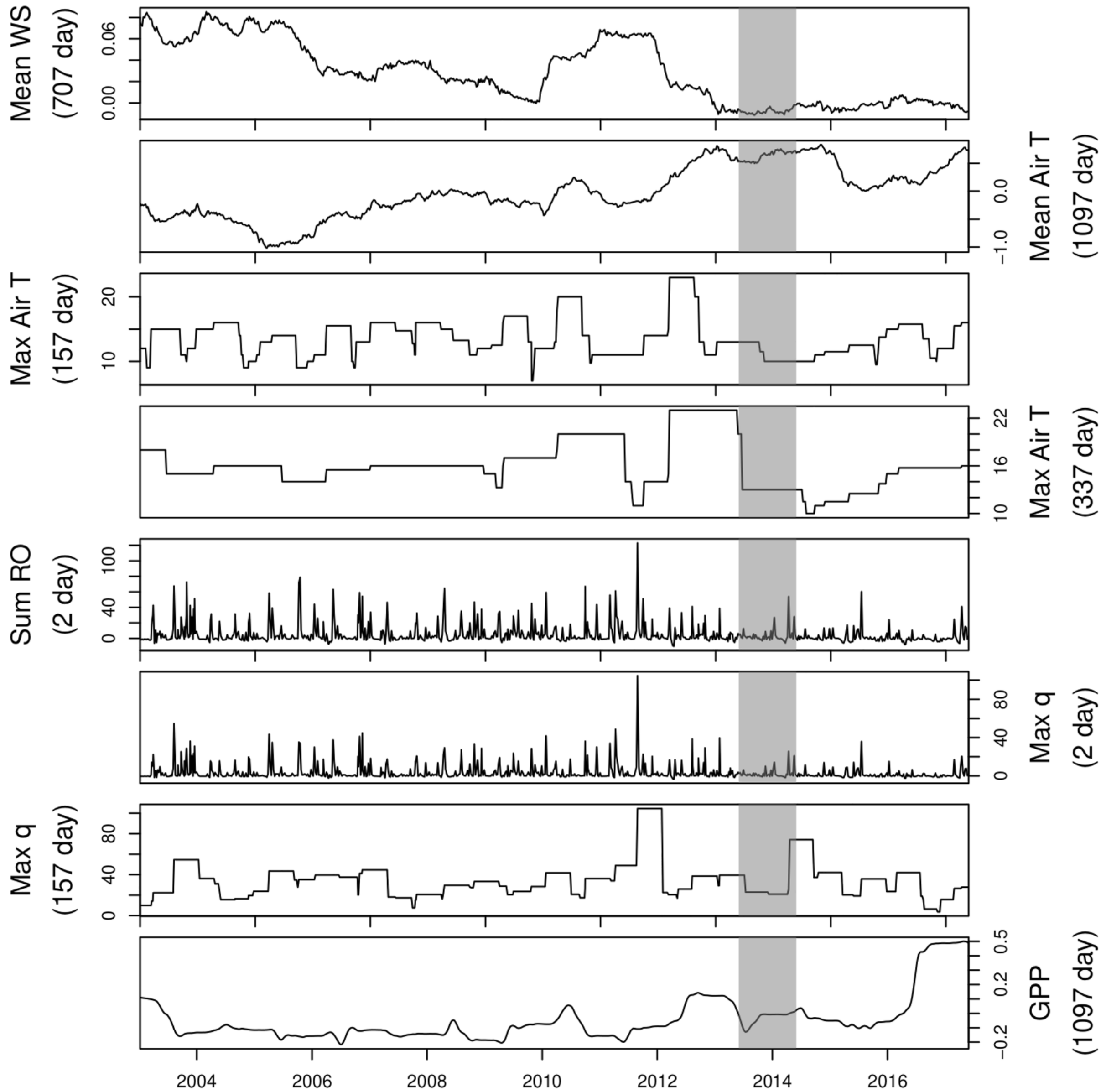
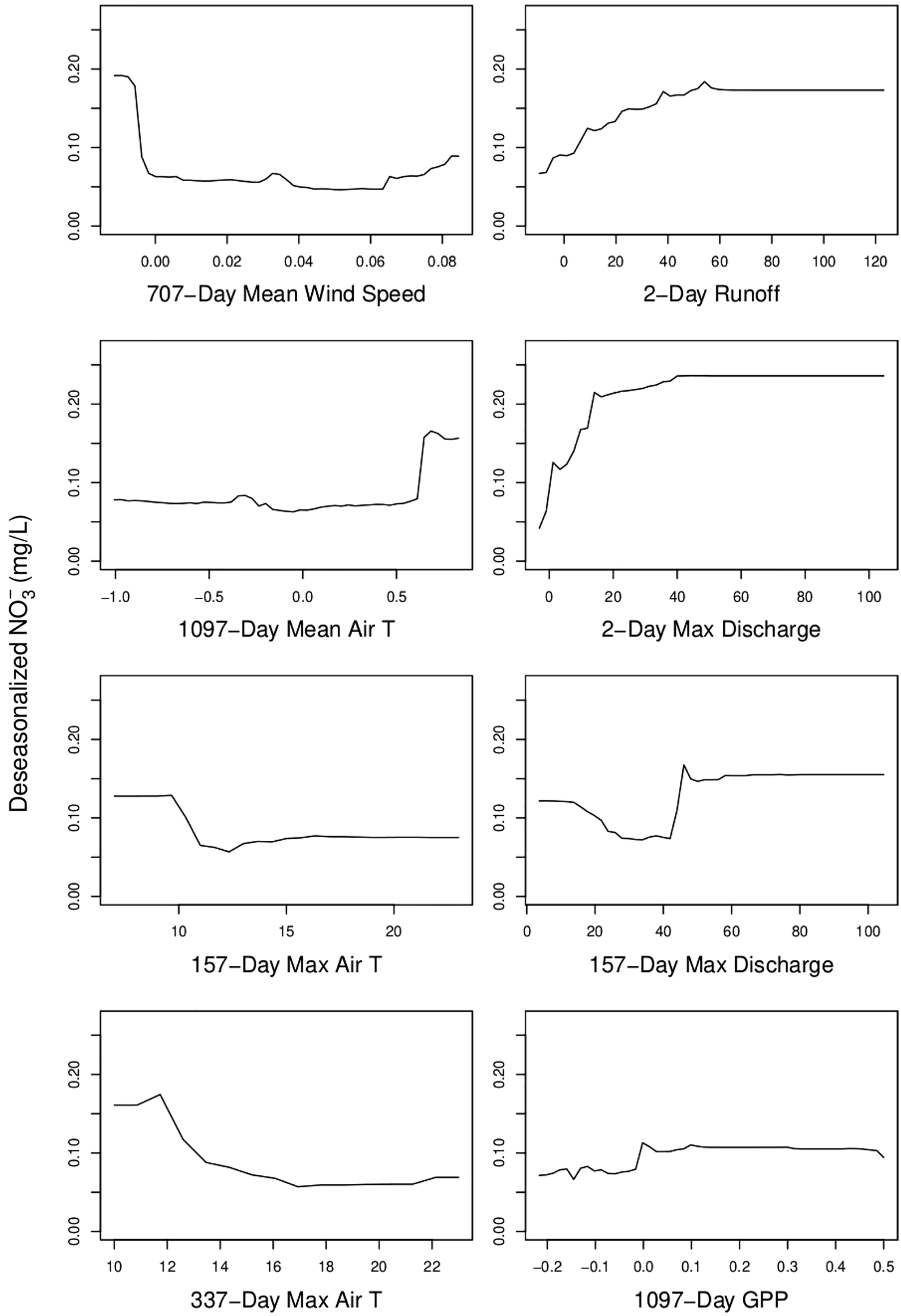


Fig. 8 Time series of the transformed independent variables that emerged as most important for the Random Forest model using all variables with multiple antecedent window transformations (2 day, 157 day, and optimum-day antecedent windows listed in Table 2). The panels are organized top to bottom by their relative importance to the Random Forest model. The abbreviations for the axis labels are: WS is wind speed, RO is runoff, q is specific discharge, and GPP is gross primary productivity. The grey shaded region is the period of the streamwater nitrate pulse

2010 to 2013. We hypothesize that the pulse arose from particular, coincidental timing of these factors. Here we synthesize the evidence from the univariate correlation and multivariate analyses to assess the evidence for our four general hypotheses (Fig. 2): a pulse of N inputs; increased N production within the catchment; reduced biotic uptake/consumption; or enhanced N hydrologic transport.

It is not surprising that our analysis did not find evidence of N deposition being an important driver of this pulse event, as atmospheric N deposition only emerges as a dominant direct control on stream


Deseasonalized NO_3^- (mg/L)
707−Day Mean Wind Speed
2−Day Runoff
1097−Day Mean Air T
2−Day Max Discharge
157−Day Max Air T
157−Day Max Discharge
337−Day Max Air T
1097−Day GPP

◂**Fig. 9** Partial dependence plots of the relationship between deseasonalized streamwater nitrate concentration and the independent variables from the comprehensive Random Forest model. The independent variables are transformed (first deseasonalized and then the antecedent value was calculated), and thus represent a deviation from their expected value

N export at very high deposition rates (Templer et al. 2022). Additionally, N deposition has declined significantly across the region in recent years which is one cause of lower N export from river basins in the Northeastern U.S. (Eshleman et al. 2013). In our analysis, N deposition is weakly correlated with streamwater nitrate concentration and is not an important variable in the Random Forest model with the best predictive power. Previous analyses of ecosystem net N retention have highlighted other factors like soil temperature (Bernal et al. 2012) or tree CO_2 fertilization response (Groffman et al. 2018) are likely controlling long-term N export in more recent decades. If our analysis included the full long-term record at Hubbard Brook, the impact of declining N deposition might emerge as an important driver of N export during the last 60 years. However, we intentionally limited our analyses to only include the period from 2003 to 2018 since we aimed to isolate the cause of the recent pulse in nitrate.

Soil nitrate production was likely enhanced by warmer soil temperatures and soil recovery from acidification in the years leading up to 2013–14. Soil net N mineralization and nitrification rates are strongly regulated by soil temperature (Johnsson et al. 1987), which is influenced by air T, and thus we interpret that these linkages may be why mean air T emerged as an important independent variable across most of our models. The partial dependence in the comprehensive Random Forest model showed a positive relationship, with a step increase in predicted streamwater nitrate concentration when the mean air T over the antecedent 3 years was 0.5 °C warmer than typical (Fig. 9). The higher pH in the Bh and Bs horizon soil waters leading up to and during the streamwater nitrate pulse may indicate that the soil environment was conducive to more nitrification (Figures S4 and S5; DeForest and Otuya 2020). Additionally, the lower DOC concentrations in soil water leading up to the higher streamwater nitrate concentration might suggest that a lack of labile organic carbon availability limited microbial immobilization of nitrate (Figures S3, S4, and S5; Goodale et al. 2005). Lysimeters from some, but not all soil horizons and vegetation zones also showed a pulse in nitrate concentration during the period of interest.

The analysis suggests that diminished N uptake by soil microbes and/or trees played a role in the streamwater nitrate pulse. The univariate correlation was high between streamwater nitrate concentration and soil frost, which has a known negative effect on microbial biomass and activity, and tree N uptake (Fig. 10). There were year-over-year increases in the maximum soil frost from 2009 to 2013 that may have caused reduced N uptake (Figure S6). Soil frost can reduce soil microbial biomass during the subsequent spring (Sorensen et al. 2018) and damage tree roots (Cleavitt et al. 2008; Comerford et al. 2013; Campbell et al. 2014) decreasing microbial and plant N uptake (Campbell et al. 2014), which has been suggested as a cause of a previous streamwater nitrate pulse in the northeastern U.S. around 1990 (Fig. 1; Mitchell et al. 1996). While the disturbance to the microbial community by soil frost reduces N uptake in the spring, the microbial biomass can recover by the summer (Sorensen et al. 2018). Solar radiation emerged as an important variable for predicting streamwater nitrate concentration. We hypothesize that this variable is related to its impact on soil temperature and thus increasing soil frost, and possibly decreasing GPP (e.g., Chen et al. 2021). The role of GPP was not clear in our analysis—it was an important variable in the Random Forest models, but the partial dependence suggested a weak relationship with streamwater nitrate. We expect GPP to be positively related to soil N uptake, reducing the availability of N to be transported to streams, and thus lower solar radiation would result in lower N uptake. Changes in algal N uptake in Hubbard Brook streams can cause changes in streamwater nitrate concentrations when reduced canopy cover increases the incident light in a stream (Bernhardt et al. 2003). However, the 2013–14 streamwater nitrate pulse did not coincide with a punctuated reduction in light to the stream or a visible reduction in the stream algae biomass.

Finally, we hypothesize that catchment hydrology influenced streamwater nitrate concentration through event-scale flushing of soil N to the stream and by vertical percolation of nitrate into groundwater (Fig. 11). Streamflow generation of high flows

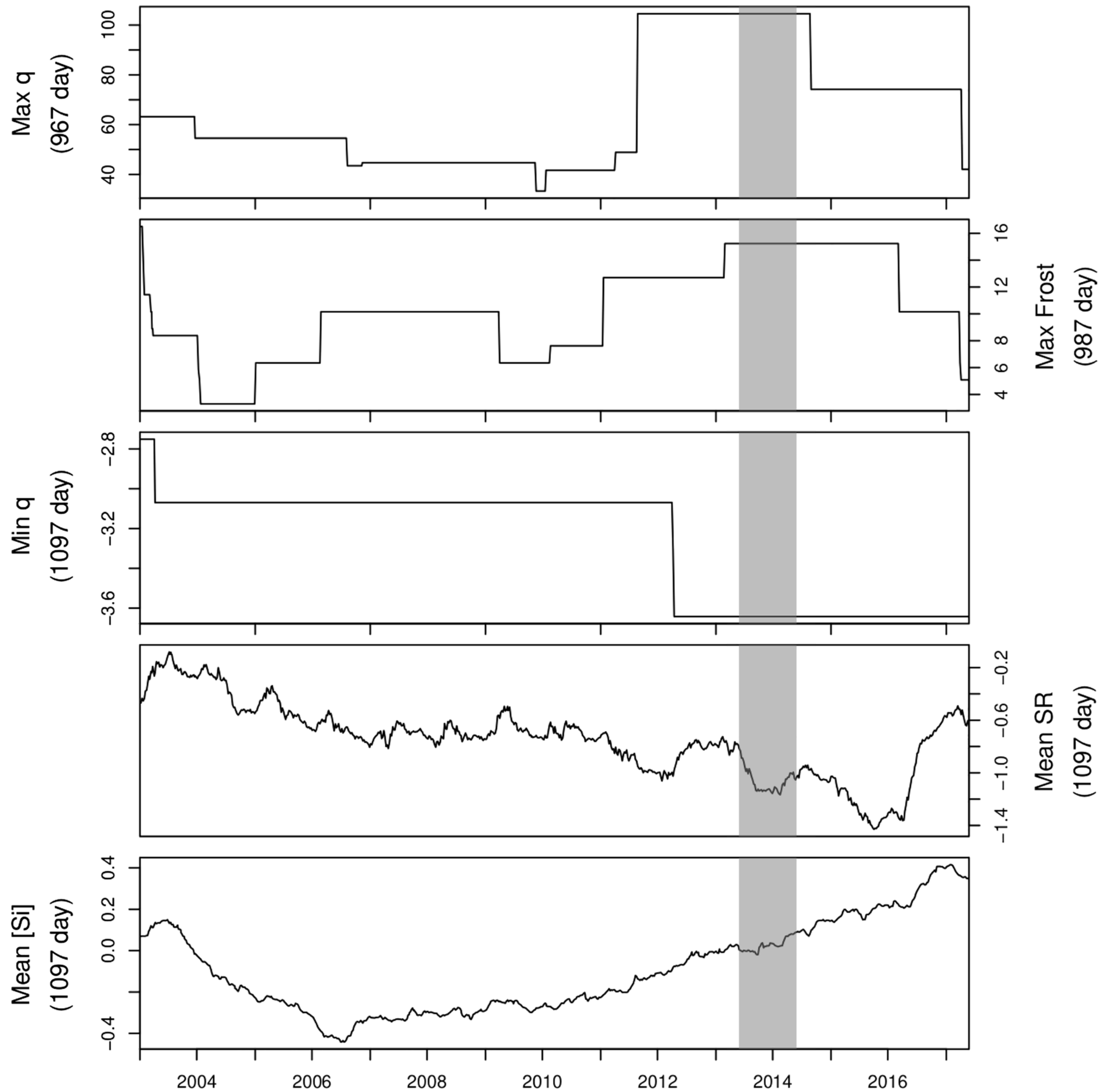


Fig. 10 Time series of the five independent variables that emerged as important for the univariate correlation analysis but did not emerge as important for the Random Forest models. These variables are transformed with their optimum antecedent window length, which is noted in the axis label. The abbreviations for the axis labels are: q is specific discharge, SR is solar radiation, and [Si] is dissolved silica concentration

activates the full range of flow paths from perched water table-generated shallow paths to piston flow generated by vertical percolation (Gazis and Feng 2004; Zhao et al. 2013). Shallow flow paths would rapidly flush some shallow soil nitrate to the catchment outlet (e.g., Creed et al. 1996, Pardo et al. 2022), while some of the nitrate from the same source could be transported to shallow groundwater with percolating water generated during the event. We propose that this is the likely reason that maximum discharge at two time scales emerged as important in our analysis. The correlation analysis produced the strongest relationship (positive) with maximum discharge over the almost three

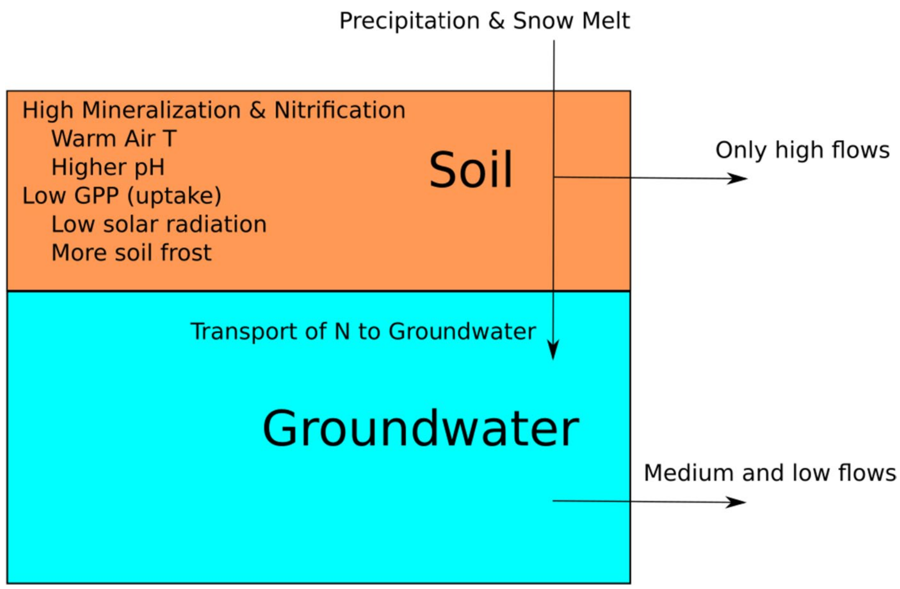


Fig. 11 Conceptual model nitrate accumulation and transport pathways to streamwater. Nitrate accumulates in the soil from either mineralization/nitrification or low plant and microbial uptake or both, and is then available for transport to the stream during episodes that produce lateral flow (short flow paths) or to the groundwater during percolation events. The groundwater nitrate then constitutes a greater fraction of the streamflow during non-storm periods and thus streamwater is more likely to reflect groundwater nitrate

years prior to when a water sample was collected. The high correlation between streamwater nitrate concentration and minimum discharge and streamwater dissolved Si concentration also suggests that nitrate concentration increased as flows decreased and deeper flow paths were a greater contributor to stream flows. Streamwater dissolved Si is mostly derived from bedrock weathering, and thus concentrations are higher in deep flow paths, resulting in a strong negative concentration-discharge relationship (Hooper and Shoemaker 1986; Benettin et al. 2015; Aulenbach et al. 2016). Inspection of the nitrate concentration time series (Fig. 4) shows increasing peak concentrations during snowmelt in 2011, 2012, and 2013, and measurable pulses of nitrate in the summers of 2011 and 2012. The summer peaks are unusual, since biotic demand for N is highest during summer, so high summer nitrate concentration in the years prior to the major nitrate pulse suggests that there was an increase in the soil N pool. We hypothesize that the smaller snowmelt and summer pulses in 2009 and 2010 indicate that enhanced soil nitrate production started increasing in 2011 and transported N vertically into shallow groundwater during snowmelt and large storm events (tropical storms in August 2011 and October 2012). We suggest that the multiple years of vertical transport of nitrate from shallow soils where mineralization and nitrification are most active, to shallow groundwater, the main source of water to streams at Hubbard Brook, caused nitrate to accumulate in groundwater. This groundwater most visibly contributed to streamwater during water year 2013 but continued into water year 2014 (Fig. 4).

Some independent variables in the analysis emerged as important for predicting streamwater nitrate concentration but are challenging to explain. The negative correlation of maximum temperature and streamwater nitrate concentration was unexpected. Rates of net nitrification can be reduced at high soil temperatures (Gubry-Rangin et al. 2017) and GPP is often operating at suboptimal air T in mixed forests (Huang et al. 2019). Thus, low antecedent maximum air temperature during the streamwater nitrate pulse (Fig. 8) could have caused there to be higher rates of nitrification and lower rates of GPP and associated N uptake, however, these responses to lower air temperatures are highly uncertain. The relatively strong negative correlation of streamwater nitrate concentrations and H^+ deposition was also unexpected. This may be related to pH sensitivity of soil N production (Curtin et al. 1998; DeForest and Otuya 2020). The Bs soil horizon in the low hardwood zone showed the nitrate pulse the clearest, experienced some coincident spikes in pH during the nitrate pulse and increased in pH after the nitrate pulse, hinting that pH may be associated with a change in the soil N transformation processes (Fig. S5). The most unexpectedly important independent variable was mean wind speed which was negatively correlated to streamwater nitrate concentration. We included wind in the analysis because of the possible influence of wind-associated forest damage on reduced forest N uptake which would lead to a positive relationship between wind speed and streamwater nitrate. In particular, a microburst windstorm in June 2013 caused severe, localized canopy damage in forest stands west of W6 (Battles et al. 2017), but no subsequent decrease in leaf biomass in the monitored catchment was observed (Fahey et al. 2022). Mean wind speed may, instead, be a proxy for synoptic meteorological conditions. It is possible that there were unusual regional weather patterns, which are known to impact stream chemistry (Siegert et al. 2021) and hydrologic conditions (Kingston et al. 2007; Suriano et al. 2018). Climate teleconnections such as the North Atlantic Oscillation and the Pacific Decadal Oscillation have been related to streamflow and a suite of ecological processes in eastern North America (Detenbeck 2018), and thus could be related to the observed nitrate pulse. Further research is needed to explore these connections and the mechanisms behind these unexpected independent variables influencing streamwater nitrate concentrations and watershed nitrate export.

Our analysis highlights that the 2013–14 nitrate pulse was associated with multiple factors operating over multiple years prior to the appearance of high streamwater nitrate concentrations. Water residence time in catchments is often months to years (Benettin et al. 2015) and thus it is not surprising that the ecosystem has inherent time lags due to transport of water and solutes in the catchment. Beyond hydrological time lags, sequences of biogeochemical processes also produce time lags in nitrate accumulation. For example, soil frost impacts microbial and/or plant N uptake in the following growing season, creating a multiple month time lag for soil N to accumulate (Campbell et al. 2014). Deterministic models of catchment N biogeochemistry and hydrology can simulate time lags as N moves between pools due to transformation, storage, and transport (e.g., Nguyen et al. 2021). Our empirical analysis required a way to include time lags and antecedent conditions so that the variables could be compared reasonably. Previous studies have used antecedent flow variables when analyzing stream solute export (Davis et al. 2014). Another example, where a particular sequence of events and antecedent conditions produced a large streamwater nitrate export event, was from the upper Mississippi River basin where soil water nitrate accumulated under drought conditions and then was rapidly flushed during major flooding after the drought (Loecke et al. 2017). Similarly, the particular seasonal timing of storm events or compounding effect of back-to-back events can have a disproportionate impact on solute export (Paerl et al. 2001; Lutz et al. 2012). In our case, we did not have a clear, major deviation of environmental conditions from the long-term norm that caused this nitrate pulse, however, the inclusion of antecedent variables helped identify the most likely causal set of conditions.

Our analysis was made possible by long-term, comprehensive research and monitoring at the HBEF which provided sufficient data to train a Random Forest model. There are likely opportunities to conduct similar analyses at other long-term research catchments to gain new insights into unexplained streamwater biogeochemical events and shed light on the role of multiple interacting variables driving catchment biogeochemical dynamics. Such information improves our understanding of ecosystem N budgets and how they are responding to global environmental changes. A more comprehensive understanding of unusually high N loss periods and its causes will help researchers use ecosystem N budgets to interpret changes in forest productivity and nutrition.

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Data availability The datasets analyzed during the current study are available in the Environmental Data Initiative repository. The streamwater chemistry data are at https://pasta.lternet.edu/package/eml/knb-lter-hbr/208/9. The atmospheric deposition data are at https://pasta.lternet.edu/package/eml/knb-lter-hbr/20/11. The solar radiation data are at https://pasta.lternet.edu/package/eml/knb-lter-hbr/60/11. The soil frost data are at https://pasta.lternet.edu/package/eml/knb-lter-hbr/27/18. The wind speed data are at https://pasta.lternet.edu/package/eml/knb-lter-hbr/56/11. The air temperature data are at https://pasta.

lternet.edu/package/eml/knb-lter-hbr/59/12. The precipitation data are at https://pasta.lternet.edu/package/eml/knb-lter-hbr/13/19. The discharge data are at https://pasta.lternet.edu/package/eml/knb-lter-hbr/2/12. The soil lysimeter data are at https://pasta.lternet.edu/package/eml/knb-lter-hbr/62/18.

Declarations

Competing interest The authors declare no competing interests.

References

Abbasian H, Solgi E, Hosseini SM, Kia SH (2022) Modeling terrestrial net ecosystem exchange using machine learning techniques based on flux tower measurements. Ecol Model 466:109901

Aber JD, Ollinger SV, Driscoll CT, Likens GE, Holmes RT, Freuder RJ, Goodale CL (2002) Inorganic nitrogen losses from a forested ecosystem in response to physical, chemical, biotic, and climatic perturbations. Ecosystems 5:0648–0658

Aulenbach BT, Burns DA, Shanley JB, Yanai RD, Bae K, Wild AD, Yi D (2016) Approaches to stream solute load estimation for solutes with varying dynamics from five diverse small watersheds. Ecosphere 7(6):e01298

Bailey AS, Hornbeck JW, Campbell JC, Eagar C (2003) Hydrometeorological database for Hubbard Brook experimental forest: 1955–2000. Gen. Tech. Rep. NE-305. Newtown Square, PA: U.S. Department of Agriculture, Forest Service, Northeastern Research Station. p 36

Bailey SW, Brousseau PA, McGuire KJ, Ross DS (2014) Influence of landscape position and transient water table on soil development and carbon distribution in a steep, headwater catchment. Geoderma 226:279–289

Battles JJ, Cleavitt NL, Saah DS, Poling BT, Fahey TJ (2017) Ecological impact of a microburst windstorm in a Northern Hardwood Forest. Can J For Res 47(12):1695–1701

Benettin P, Bailey SW, Campbell JL, Green MB, Rinaldo A, Likens GE, Botter G (2015) Linking water age and solute dynamics in streamflow at the Hubbard Brook experimental forest, NH, USA. Water Resour Res 51(11):9256–9272

Bernal S, Hedin LO, Likens GE, Gerber S, Buso DC (2012) Complex response of the forest nitrogen cycle to climate change. Proc Natl Acad Sci 109(9):3406–3411

Bernhardt ES, Likens GE, Buso DC, Driscoll C (2003) In-stream uptake dampens effects of major forest disturbance on watershed nitrogen export. Proc Natl Acad Sci 100(18):10304–10308

Breiman L (2001) Random forests. Mach Learn 45:5–32

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. Gen. Tech. Rep. NE-275. Newtown Square. U.S. Department of Agriculture, Forest Service, Northeastern Research Station, PA, p 52

Cai H, Shimoda Y, Mao J, Arhonditsis GB (2023) Development of a sensitivity analysis framework for aquatic biogeochemical models using machine learning. Ecol Inf. https://doi.org/10.1016/j.ecoinf.2023.102079

Campbell JL, Ollinger SV, Flerchinger GN, Wicklein H, Hayhoe K, Bailey AS (2010) Past and projected future changes in snowpack and soil frost at the Hubbard Brook Experimental Forest, New Hampshire, USA. Hydrol Process 24:2465–2480

Campbell JL, Socci AM, Templer PH (2014) Increased nitrogen leaching following soil freezing is due to decreased root uptake in a Northern Hardwood Forest. Glob Change Biol 20:2663–2673. https://doi.org/10.1111/gcb.12532

Chen S, Zhang Y, Wu Q, Liu S, Song C, Xiao J, Vose JM (2021) Vegetation structural change and CO2 fertilization more than offset gross primary production decline caused by reduced solar radiation in China. Agric for Meteorol 296:108207

Cleavitt NL, Fahey TJ, Groffman PM, Hardy JP, Henry KS, Driscoll CT (2008) Effects of soil freezing on fine roots in a Northern Hardwood Forest. Can J For Res 38(1):82–91

Cleveland WS (1979) Robust locally weighted regression and smoothing scatterplots. J Am Stat Assoc 74(368):829–836

Comerford DP, Schaberg PG, Templer PH, Socci AM, Campbell JL, Wallin KF (2013) Influence of experimental snow removal on root and canopy physiology of sugar maple trees in a Northern Hardwood Forest. Oecologia 171:261–269

Creed IF, Band LE, Foster NW, Morrison IK, Nicolson JA, Semkin RS, Jeffries DS (1996) Regulation of nitrate-N release from temperate forests: a test of the N flushing hypothesis. Water Resour Res 32(11):3337–3354

Curtin D, Campbell CA, Jalil A (1998) Effects of acidity on mineralization: pH-dependence of organic matter mineralization in weakly acidic soils. Soil Biol Biochem 30(1):57–64

Davis CA, Ward AS, Burgin AJ, Loecke TD, Riveros-Iregui DA, Schnoebelen DJ, Clair S (2014) Antecedent moisture controls on stream nitrate flux in an agricultural watershed. J Environ Qual 43(4):1494–1503

DeForest JL, Otuya RK (2020) Soil nitrification increases with elevated phosphorus or soil pH in an acidic mixed mesophytic deciduous forest. Soil Biol Biochem 142:107716

Detenbeck NE (2018) Statistical models to predict and assess spatial and temporal low-flow variability in New England rivers and streams. J Am Water Resour Assoc 54(5):1087–1108

Driscoll CT (2022) Chemistry of freely-draining soil solutions at the Hubbard Brook Experimental Forest, Watershed 6, 1982 - present ver 18. Environmental Data Initiative.https://doi.org/10.6073/pasta/90b588b9a04bfeefa29024929b0af1f4 Accessed 26 June 2022

Eshleman KN, Sabo RD, Kline KM (2013) Surface water quality is improving due to declining atmospheric N deposition. Environ Sci Technol 47(21):12193–12200

Fahey TJ, Cleavitt NL, Battles JJ (2022) Long term variation of leaf abundance in a Northern Hardwood Forest. Ecol Ind 137:108746

Gazis C, Feng X (2004) A stable isotope study of soil water: evidence for mixing and preferential flow paths. Geoderma 119(1–2):97–111

Genuer R, Poggi JM, Tuleau-Malot C (2010) Variable selection using random forests. Pattern Recognit Lett 31(14):2225–2236
Goodale CL, Aber JD, McDowell WH (2000) The long-term effects of disturbance on organic and inorganic nitrogen export in the White Mountains, New Hampshire. Ecosystems 3:433–450
Goodale CL, Aber JD, Vitousek PM, McDowell WH (2005) Long-term decreases in stream nitrate: successional causes unlikely; possible links to DOC? Ecosystems 8:334–337
Green MB, Campbell JL, Yanai RD, Bailey SW, Bailey AS, Grant N, Rustad LE (2018) Downsizing a long-term precipitation network: using a quantitative approach to inform difficult decisions. PLoS One 13(5):e0195966
Greenwell BM (2017) Pdp: an R package for constructing partial dependence plots. R J 9(1):421–436
Groffman PM, Driscoll CT, Durán J, Campbell JL, Christenson LM, Fahey TJ, Templer PH (2018) Nitrogen oligotrophication in Northern Hardwood Forests. Biogeochemistry 141:523–539
Gubry-Rangin C, Novotnik B, Mandič-Mulec I, Nicol GW, Prosser JI (2017) Temperature responses of soil ammonia-oxidising archaea depend on pH. Soil Biol Biochem 106:61–68
Hasenauer H, Petritsch R, Zhao M, Boisvenue C, Running SW (2012) Reconciling satellite with ground data to estimate forest productivity at national scales. For Ecol Manag 276:196–208
Hong B, Swaney DP, Woodbury PB, Weinstein DA (2005) Long-term nitrate export pattern from Hubbard Brook Watershed 6 driven by climatic variation. Water Air Soil Pollut 160:293–326
Hooper RP, Shoemaker CA (1986) A comparison of chemical and isotopic hydrograph separation. Water Resour Res 22(10):1444–1454
Houlton BZ, Driscoll CT, Fahey TJ, Likens GE, Groffman PM, Bernhardt ES, Buso DC (2003) Nitrogen dynamics in ice storm-damaged forest ecosystems: implications for nitrogen limitation theory. Ecosystems 6:431–443
Huang M, Piao S, Ciais P, Peñuelas J, Wang X, Keenan TF, Janssens IA (2019) Air temperature optima of vegetation productivity across global biomes. Nat Ecol Evol 3(5):772–779
Hubbard Brook Watershed Ecosystem Record (HBWatER) (2022) Continuous precipitation and stream chemistry data, Hubbard Brook Ecosystem Study, 1963 – present. ver 8. Environmental data initiative. https://doi.org/10.6073/pasta/5e9d1771f114913c2ca8c98520c230ad Accessed 16 September 2022
Johnsson H, Bergstrom L, Jansson PE, Paustian K (1987) Simulated nitrogen dynamics and losses in a layered agricultural soil. Agric Ecosyst Environ 18(4):333–356
Johnson C, Driscoll C, Siccama T et al (2000) Element fluxes and landscape position in a Northern Hardwood Forest watershed ecosystem. Ecosystems 3:159–184. https://doi.org/10.1007/s100210000017
Kingston DG, McGregor GR, Hannah DM, Lawler DM (2007) Large-scale climatic controls on New England river flow. J Hydrometeorol 8(3):367–379
Lajtha K (2020) Nutrient retention and loss during ecosystem succession: revisiting a classic model. Ecology 101(1):e02896
Liaw A, Wiener M (2002) Classification and regression by randomForest. R News 2(3):18–22
Likens GE (2013) Biogeochemistry of a forested ecosystem. Springer, Berlin
Loecke TD, Burgin AJ, Riveros-Iregui DA, Ward AS, Thomas SA, Davis CA, Clair MAS (2017) Weather whiplash in agricultural regions drives deterioration of water quality. Biogeochemistry 133(1):7–15
LoRusso NA, Bailey SW, Zeng T, Montesdeoca M, Driscoll CT (2021) Dissolved organic matter dynamics in reference and calcium-treated watersheds at Hubbard Brook experimental forest, NH, USA. J Geophys Res Biogeosci. https://doi.org/10.1029/2021JG006352
Lutz BD, Mulholland PJ, Bernhardt ES (2012) Long-term data reveal patterns and controls on stream water chemistry in a forested stream: Walker Branch, Tennessee. Ecol Monogr 82(3):367–387
Mason RE, Craine JM, Lany NK, Jonard M, Ollinger SV, Groffman PM, Elmore AJ (2022) Evidence, causes, and consequences of declining nitrogen availability in terrestrial ecosystems. Science 376(6590):eabh3767
Mineau MM, Wollheim WM, Stewart RJ (2015) An index to characterize the spatial distribution of land use within watersheds and implications for river network nutrient removal and export. Geophys Res Lett 42(16):6688–6695
Mitchell MJ, Driscoll CT, Kahl JS, Likens GE, Murdoch PS, Pardo LH (1996) Climatic control of nitrate loss from forested watersheds in the northeast United States. Environ Sci Technol 30(8):2609–2612
Nash JE, Sutcliffe JV (1970) River flow forecasting through conceptual models part I—a discussion of principles. J Hydrol 10:282–290
Nguyen TV, Kumar R, Lutz SR, Musolff A, Yang J, Fleckenstein JH (2021) Modeling nitrate export from a mesoscale catchment using storage selection functions. Water Resour Res 57(2):e2020WR028490
Ohte N, Tokuchi N, Katsuyama M, Hobara S, Asano Y, Koba K (2003) Episodic increases in nitrate concentrations in streamwater due to the partial dieback of a pine forest in Japan: runoff generation processes control seasonality. Hydrol Process 17(2):237–249
Paerl HW, Bales JD, Ausley LW, Buzzelli CP, Crowder LB, Eby LA, Ramus JS (2001) Ecosystem impacts of three sequential hurricanes (Dennis, Floyd, and Irene) on the United States' largest lagoonal estuary, Pamlico Sound, NC. Proc Nat Acad Sci 98(10):5655–5660
Pardo LH, Green MB, Bailey SW, McGuire KJ, McDowell WH (2022) Identifying controls on nitrate sources and flowpaths in a forested catchment using a hydropedological framework. J Geophys Res Biogeosci 127(2):e2020JG006140
Rhoads AG, Hamburg SP, Fahey TJ, Siccama TG, Hane EN, Battles J, Wilson G (2002) Effects of an intense ice storm on the structure of a Northern Hardwood Forest. Can J For Res 32(10):1763–1775
Robertson DM, Saad DA (2021) Nitrogen and phosphorus sources and delivery from the Mississippi/Atchafalaya

River basin: an update using 2012 sparrow models. JAWRA J Am Water Resour Assoc 57(3):406–429
Running S, Mu Q, Zhao M (2015) MOD17A2H MODIS/Terra Gross Primary Productivity 8-Day L4 Global 500m SIN Grid V006. Distributed by NASA EOSDIS Land Processes DAAC https://doi.org/10.5067/MODIS/MOD17A2H.006Accessed 29 Jan 2021
See CR, Green MB, Yanai RD, Bailey AS, Campbell JL, Hayward J (2020) Quantifying uncertainty in annual runoff due to missing data. PeerJ 8:e9531
Siegert CM, Suriano ZJ, Leathers DJ, Gold AJ, Addy K, Schroth AW, Levia DF (2021) Effects of atmospheric circulation on stream chemistry in forested watersheds across the Northeastern United States: part 1. Synoptic Scale Forcing J Geophys Res Atmos 126(13):e2020JD033413
Sorensen PO, Finzi AC, Giasson M, Reinmann AB, Sanders-DeMott R, Templer PH (2018) Winter soil freeze-thaw cycles lead to reductions in soil microbial biomass and activity not compensated for by soil warming. Soil Biol Biochem 116:39–47
Suriano ZJ, Benjamin AE, Leathers DJ, Schroeter D, Corradina V (2018) Northeast United States growing season moisture conditions: associations with a North American mid-tropospheric wave train. Int J Climatol 38(15):5542–5550
Templer PH, Harrison JL, Pilotto F, Flores-Díaz A, Haase P, McDowell WH, Taka M (2022) Atmospheric deposition and precipitation are important predictors of inorganic nitrogen export to streams from forest and grassland watersheds: a large-scale data synthesis. Biogeochemistry 160(2):219–241
USDA Forest Service, Northern Research Station (2019) Hubbard Brook experimental forest: daily solar radiation measurements, 1959 - present ver 11. Environmental data initiative. https://doi.org/10.6073/pasta/7486a33ab8549c262233ad3e4a8b42a3 Accessed 26 June 2022
USDA Forest Service, Northern Research Station (2020) Hubbard Brook Experimental Forest: Daily Streamflow by Watershed, 1956 - present ver 11. Environmental data initiative. https://doi.org/10.6073/pasta/d10220595119b502fe2ac14833fa4b9b Accessed 26 June 2022
USDA Forest Service, Northern Research Station (2021a) Hubbard Brook Experimental Forest: daily temperature record, 1955 - present ver 10. Environmental data initiative. https://doi.org/10.6073/pasta/3afab60d54d5f2fcb1112e71f4be2106 Accessed 26 June 2022
USDA Forest Service, Northern Research Station (2021b) Hubbard Brook Experimental Forest: daily precipitation rain gage measurements, 1956 - present ver 17. Environmental data initiative. https://doi.org/10.6073/pasta/453b49e8429a63b72419caf3b9ad6f98 Accessed 26 June 2022
USDA Forest Service, Northern Research Station (2021c) Hubbard Brook Experimental forest: weekly snow and frost measurements, 1955 - present ver 16. Environmental data initiative. https://doi.org/10.6073/pasta/f448b4b563d3f59b2058291459ce5926 Accessed 26 June 2022
USDA Forest Service, Northern Research Station (2022) Hubbard Brook experimental forest (USDA Forest Service): Wind speed and wind direction measurements, 1965 - present ver 9. Environmental data initiative. https://doi.org/10.6073/pasta/61b16218902a3ae764a3179c383132e0 Accessed 26 June 2022
Vitousek PM, Howarth RW (1991) Nitrogen limitation on land and in the sea: how can it occur? Biogeochemistry 13:87–115
Yanai RD, Vadeboncoeur MA, Hamburg SP, Arthur MA, Fuss CB, Groffman PM, Driscoll CT (2013) From missing source to missing sink: long-term changes in the nitrogen budget of a Northern Hardwood Forest. Environ Sci Technol 47(20):11440–11448
Zhao P, Tang X, Zhao P, Wang C, Tang J (2013) Identifying the water source for subsurface flow with deuterium and oxygen-18 isotopes of soil water collected from tension lysimeters and cores. J Hydrol 503:1–10