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Watershed-scale changes in terrestrial nitrogen cycling during a period of decreased atmospheric nitrate and sulfur deposition

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HIGHLIGHTS

- Changes in terrestrial N cycling between 1980 and 2010 were inferred from declining tree-ring natural abundance ^{15}N values.
- Changes in terrestrial N cycling were not solely influenced by decreasing atmospheric N deposition.
- Declining tree-ring $\delta^{15}N$ trends did not always coincide with decreased stream nitrate yields.

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ABSTRACT

Recent reports suggest that decreases in atmospheric nitrogen (N) deposition throughout Europe and North America may have resulted in declining nitrate export in surface waters in recent decades, yet it is unknown if and how terrestrial N cycling was affected. During a period of decreased atmospheric N deposition, we assessed changes in forest N cycling by evaluating trends in tree-ring $\delta^{15}N$ values (between 1980 and 2010; $n = 20$ trees per watershed), stream nitrate yields (between 2000 and 2011), and retention of atmospherically-deposited N (between 2000 and 2011) in the North and South Tributaries (North and South, respectively) of Buck Creek in the Adirondack Mountains, USA. We hypothesized that tree-ring $\delta^{15}N$ values would decline following decreases in atmospheric N deposition (after approximately 1995), and that trends in stream nitrate export and retention of atmospherically deposited N would mirror changes in tree-ring $\delta^{15}N$ values. Three of the six sampled tree species and the majority of individual trees showed declining linear trends in $\delta^{15}N$ for the period 1980–2010; only two individual trees showed increasing trends in $\delta^{15}N$ values. From 1980 to 2010, trees in the watersheds of both tributaries displayed long-term declines in tree-ring $\delta^{15}N$ values at the watershed scale ($R = -0.35$ and $p = 0.001$ in the North and $R = -0.37$ and $p < 0.001$ in the South). The decreasing $\delta^{15}N$ trend in the North was associated with declining stream nitrate concentrations (-0.009 mg N L^{-1} yr^{-1}, $p = 0.02$), but no change in the retention of atmospherically deposited N was observed. In contrast, nitrate yields in the South did not exhibit a trend, and the watershed became less retentive of atmospherically deposited N (-7.3% yr^{-1}, $p < 0.001$). Our $\delta^{15}N$ results indicate a change in terrestrial N availability in both watersheds prior to decreases in atmospheric N deposition, suggesting that decreased atmospheric N deposition was not the sole driver of tree-ring $\delta^{15}N$ values at these sites. Other factors, such as decreased sulfur deposition, disturbance, long-term successional trends, and/or increasing atmospheric CO_2 concentrations, may also influence trends in tree-ring $\delta^{15}N$ values. Furthermore, declines in terrestrial N availability inferred from tree-ring $\delta^{15}N$ values do not always correspond with decreased stream nitrate export or increased retention of atmospherically deposited N.

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1. Introduction

Nitrogen and sulfur oxide emissions (NO_x and SO_x, respectively) from fossil fuel combustion have contributed to atmospheric acid deposition (defined herein as the wet and dry deposition of nitric and sulfuric acids) and the acidification and eutrophication of many terrestrial and aquatic ecosystems throughout Europe and North America for more than a century (Driscoll et al., 2001). To prevent further ecosystem deterioration and protect human health, regulations requiring NO_x and SO_x emission reductions were implemented in many industrialized nations, resulting in declines in acid deposition in recent decades (Vet et al., 2014). Observational studies indicate that resultant long-term declines in NO_3-N deposition have sometimes occurred concomitantly with decreased NO_3-N export in surface waters, suggesting potential declines in ecosystem N availability (e.g. Eshleman et al., 2013; Rogora et al., 2012; Waller et al., 2012; Kothawala et al., 2011). Catchment-scale clean roof experiments have also demonstrated that ecosystem N availability and stream NO_3-N yields can decline in response to decreased N and S inputs (Corre and Lamersdorf, 2004; Corre et al., 2003). Experimental approaches, however, cannot be easily replicated in multiple watersheds across broad spatial scales. In addition, factors such as forest succession (e.g., McLauchlan et al., 2007), changing denitrification rates (Morse et al., 2015), insect-caused defoliation (e.g., Eshleman et al., 1998), disturbance (e.g., Bernal et al., 2012), in-stream processes (e.g., Peterson et al., 2001), and timber harvest (e.g., Vitousek and Melillo, 1979) can also influence stream NO_3-N yields, which may make it difficult to detect a direct influence of declining NO_3-N deposition on stream NO_3-N yields or to infer changes in terrestrial N availability (Kopáček et al., 2016, Argerich et al., 2013). A proxy that captures information about past changes in N availability within catchments is needed to help assess the influence of decreased NO_3-N deposition on N cycling in terrestrial ecosystems (Tomlinson et al., 2015).

Recent theoretical and empirical advances indicate that the nitrogen isotope ($\delta^{15}N$; $^{15}N/^{14}N$ ratio of a sample relative to a standard) values of tree rings provide an integrated metric of historical changes in soil N availability, defined as the supply of N relative to its demand by plants (e.g. Howard and McLauchlan, 2015; Gerhart and McLauchlan, 2014; McLauchlan et al., 2007). Tree-ring $\delta^{15}N$ values record changes in multiple pathways that fractionate N isotopes, including gaseous N losses during denitrification and nitrification, nitrate leaching, and transfer of N to plants via mycorrhizal fungi (Craine et al., 2009). Overall, greater N availability tends to result in relatively low $\delta^{15}N$ values in the N that is lost (e.g. through denitrification or nitrification followed by leaching of NO_3-N), which results in more positive $\delta^{15}N$ values within residual soil inorganic nitrogen (IN) pools, and thus more positive $\delta^{15}N$ values in plant tissues. Furthermore, high N availability tends to cause plants to be less dependent on mycorrhizal fungi, which are known to provide them with N that has low $\delta^{15}N$ values (Michelsen et al., 1998; Hobbie et al., 2000). High $\delta^{15}N$ values typically occur in soil and leaves of forests with high rates of nitrification (Pardo et al., 2007), denitrification (Templer et al., 2007; Nadelhoffer et al., 1996), nitrate leaching (Pardo et al., 2002), and low input of N from mycorrhizal fungi (Pardo et al., 2006).

Some of the recent declines in stream NO_3-N yields attributed to decreased atmospheric N deposition in the northeastern US may be partly explained by declining terrestrial N availability (as recorded by tree-ring $\delta^{15}N$ values) due to decreased inorganic nitrogen (IN) inputs. However, the relative importance of declining N deposition on terrestrial N availability as recorded in plant $\delta^{15}N$ values is uncertain (Gerhart and McLauchlan, 2014). Declines in stream NO_3-N yields and tree-ring $\delta^{15}N$ values in a forested watershed in the northeastern United States over a 30 year period were attributed to successional processes that drove a decline in N availability (McLauchlan et al., 2007), suggesting that stream NO_3-N export and tree-ring $\delta^{15}N$ records may be complementary approaches that provide independent validation of each other in terms of changes in ecosystem N availability. However, species-specific tree ring $\delta^{15}N$ trends have also been observed (McLauchlan and Craine, 2012; Cairney and Meharg, 1999), indicating that species may exhibit temporal variation in their partitioning of available forms of N due to changing factors such as nitrification rates, ammonium deposition, and/or changes on reliance of mycorrhizal fungi (Gerhart and McLauchlan, 2014). Comparison of tree-ring $\delta^{15}N$ and stream N datasets can help to disentangle the influence of local changes in terrestrial N cycling from larger, regional factors, such as decreased IN inputs via declines in atmospheric N deposition, to explain catchment-scale trends in terrestrial N availability and stream NO_3-N yields (Eshleman et al., 2013; McLauchlan et al., 2007).

We conducted a comparative analysis at two well-studied forested watersheds (North and South Tributaries of Buck Creek) in the Adirondack Mountains, New York, USA (Ross et al., 2012; Lawrence, 2002). Hydrologic and stream water-quality monitoring have been carried out at these Buck Creek tributaries since the fall of 1999, along with periodic vegetative and soil surveys (Ross et al., 2012; NYSERDA, 2012; Lawrence, 2002). Stream NO_3-N yields in the North Tributary (North) are typical of other forests in New England and the Adirondacks (~1.2 kg N ha^{-1} yr^{-1}), whereas stream NO_3-N yields in the South Tributary (South) are elevated (~5.10 kg N ha^{-1} yr^{-1}) relative to other northeastern forests (Ross et al., 2012). Trends in acid deposition (1986–2011), $\delta^{15}N$ in tree cores (1980–2010), and stream NO_3-N export (2000–2011) were evaluated and compared. A multiple regression model was also constructed to assess the relationship between IN and sulfate deposition and stand-level tree-ring $\delta^{15}N$ values. We hypothesized that tree-ring $\delta^{15}N$ values would only begin to decline following decreased atmospheric N deposition (~post-1995), and that trends in stream NO_3-N export and retention of atmospherically deposited N would mirror changes in tree-ring $\delta^{15}N$ values. Specifically, we expected watershed-scale tree-ring $\delta^{15}N$ values to remain stable for the 1980–1995 period, but decline due to declining N availability following declines in atmospheric IN deposition. We also hypothesized that stream NO_3-N export would show a decline and thus coincide with a declining trend in tree-ring $\delta^{15}N$ values between 2000 and 2010.

2. Methods

2.1. Site description

The North and South Tributaries of Buck Creek (referred to as North and South below; Fig. 1) have been continuously gaged since October 1999. They have been the subject of multiple hydro-biogeochemical investigations assessing the impacts of acid deposition on Adirondack forests (e.g., Ross et al., 2012; Lawrence et al., 2011; Burns et al., 2009). These mountainous catchments were last logged in the early 1900s, and currently contain mature forests typically found throughout the northeastern United States (NYSERDA, 2012). The climate of the Buck Creek watershed (Fig. 1) is characterized by cold winters and cool summers with mean monthly temperatures in January and July averaging −10 °C and 18 °C, respectively (Lawrence et al., 2004; PRISM, 2015). Over the period of record (1986–2013), mean annual precipitation was ~1300 mm according to data extracted from NADP/PRISM gradient maps (NADP, 2015; PRISM, 2015). The typical growing season for the forest surrounding Buck Creek extends from late May to mid-September, and is followed by the development of a significant

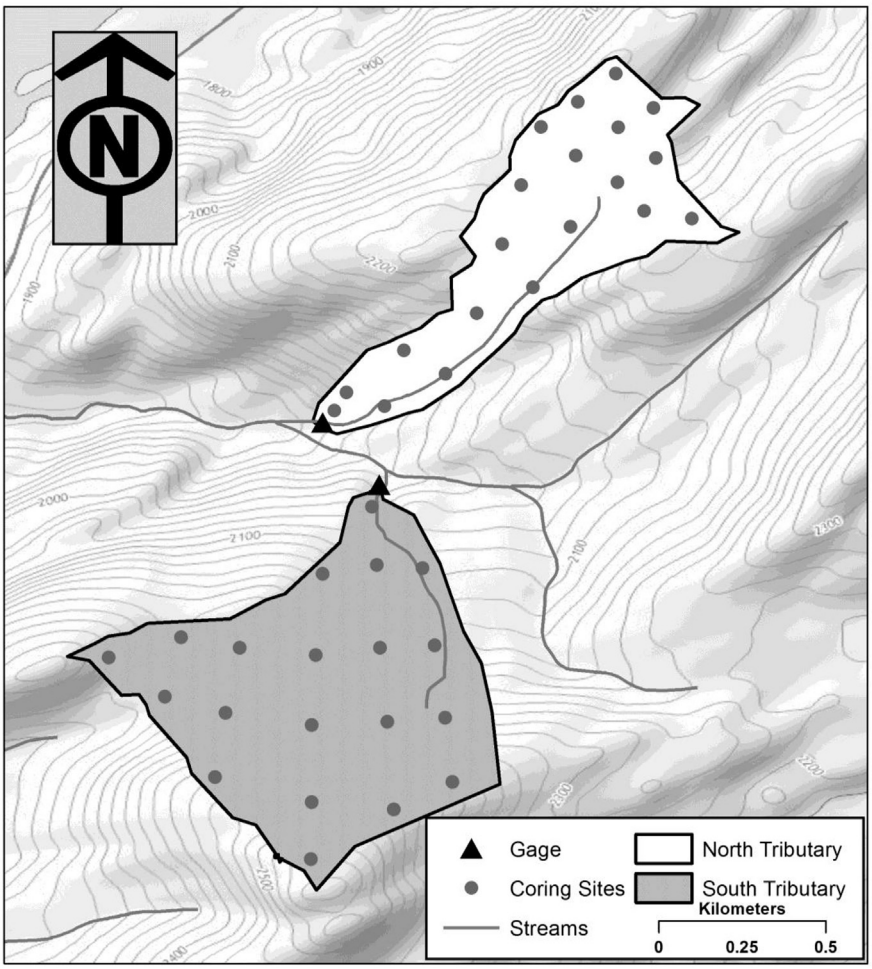

Fig. 1. Map of tree coring sites and stream gages in the North and South Tributaries of the Buck Creek watershed.

snowpack, which usually melts in mid-April.

The mixed forest of the North watershed (27 ha) is dominated by red spruce (*Picea rubens*), American beech (*Fagus grandifolia*), and red maple (*Acer rubrum*) with *Sphagnum*-dominated wetlands in the headwaters (NYSERDA, 2012; Lawrence, 2002). There was a reported decrease in basal area in this catchment between 2005 and 2010 due to (1) an unexplained red spruce decline across all size classes (DBH > 5 cm) and (2) beech bark disease, which is eliminating older beech trees in the watershed (NYSERDA, 2012). Beech bark disease is a fungal infection that makes beech trees vulnerable to drought and insect infestations (Houston, 1994). The North watershed contains well-drained Spodosol soils lying above metasedimentary rock and various forms of gneiss (Lawrence, 2002). Fractured bedrock is exposed at the surface in many locations within the catchment, which may result in a loss of water to deep groundwater before exiting the watershed. The stream tends to dry up for a few weeks in late summer with flow restarting in September. Stream NO_3-N yields in the North (~1.2 kg N ha^{-1} yr^{-1}) are close to the median values of forested watersheds in the northeastern U.S. (Ross et al., 2012). Potential mineralization and nitrification rates are also similar to those of other forests in the region, and nitrification potentially consumes up to ~22% of the mineralized ammonium (Ross et al., 2012).

American beech is the dominant tree species in the South watershed (52 ha). However, beech bark disease has infected virtually all beech trees in this catchment, with higher mortality rates among larger individuals (Ross et al., 2012). Despite the prevalence of beech bark disease, the total basal area of American beech increased from 2000 to 2010 (NYSERDA, 2012), because saplings increased in size to be included in the tree monitoring. The South contains well-drained Spodosol soils and generally has more till deposits than the North (Lawrence, 2002). Stream NO_3-N yields in the South (~5.10 kg N ha^{-1} yr^{-1}) are among the highest in the region, but potential mineralization and nitrification rates in the South are consistent with those in other regional forests (Ross et al., 2012). Potential nitrification rates are higher in the South than North watershed, and nitrification consumes a relatively greater proportion (~33%) of the mineralized ammonium in the South watershed (Ross et al., 2012).

2.2. Dendroisotopic records

Twenty mature trees were sampled in each watershed. The trees were randomly spread along transects that were perpendicular to the fall line and spaced approximately 200 m apart (Fig. 1). In the field, the largest tree nearest to the pre-selected sampling point was usually chosen to optimize time-series data per sampled tree, but trees that were apparently diseased or in decline (based on visual inspection of the bark) were not sampled; the next nearest healthy, co-dominant or dominant canopy tree was sampled instead. As a result of this sampling strategy, no beech trees were cored. Two cores were taken from opposite sides of each bole at

breast height using a 5.15 mm incremental borer and stored in paper straws. The cores were returned to the lab, dried in an oven at 60 °C, sanded, and stored until ring widths were measured using CooRecorder software (0.001 mm resolution; Larsson, 2009). A detailed visual examination of each increment bore was used to assign ages to each ring. Individual annual increments were cut from one bore per tree using a razor blade and stored in 96-well plates prior to $\delta^{15}N$ and %N analysis.

Approximately 10 mg of wood from every other annual increment for the 1980–2010 period was subsampled and used for $\delta^{15}N$ and %N analysis. In cases where the annual rings were too narrow to yield ~10 mg, multiple rings were aggregated (e.g., 2002–2004) and the midpoint of the aggregated range (e.g., 2003) was used in subsequent statistical analyses. Prepared samples (n = 580) were analyzed for $\delta^{15}N$ using a Carlo Erba NC2500 elemental analyzer (CE Instruments, Milano, Italy) interfaced with a Thermo Delta V+ isotope ratio mass spectrometer (Bremen, Germany). A Carbosorb trap was used to remove CO_2 and a magnesium perchlorate trap was used to remove water vapor after combustion in the elemental analyzer. The $\delta^{15}N$ data were normalized to the AIR scale using a two-point normalization curve with internal standards calibrated against USGS40 and USGS41 (Brand et al., 2014; Qi et al., 2003). The analytical precision among runs (1σ) of an internal wood standard was 0.3‰.

Measurements of $\delta^{15}N$ were normalized by subtracting the mean $\delta^{15}N$ value of the 1980–2010 period from the $\delta^{15}N$ value of each sample from each bore such that each bore had a mean $\delta^{15}N$ value of 0‰ (McLauchlan et al., 2007). Pearson correlation values were calculated to assess trends in normalized $\delta^{15}N$ (n-$\delta^{15}N$) for the period of 1980–2010 for individual trees, species, watersheds, and both watersheds combined to facilitate comparison among sites, species, and scales. The significance of the correlation was evaluated using a block bootstrap and two-tailed significance test procedure in R (Tian et al., 2011). The procedure involved resampling time series of individual trees, species, watersheds, and both watersheds combined 10,000 times in blocks of three consecutive time periods (i.e., 1980–1981, 1982–1983, and 1984–1985) to generate a bootstrap distribution of Pearson correlation values. A two-tailed significance test was then used to assess if the correlation was still significant after accounting for temporal autocorrelation. In addition, trends for the 1980–1995 and 1995–2010 periods were assessed in both watersheds and the combined dataset. Complementing the correlation analysis (Table S1), a simple arithmetic two-year mean of all 20 individual trees (1980–1981, 1982–1983, etc.) sampled in each watershed was used to scale up from individual tree observations to further visualize trends in watershed-scale n-$\delta^{15}N$ and $\delta^{15}N$ values. Likewise, all 40 trees were used to calculate a two-year mean, combining the entire dataset.

2.3. Stream NO_3-N export and acid deposition

The annual wet atmospheric deposition rates and precipitation-weighted mean concentrations of NO_3-N, NH_4-N, IN, and sulfur (S) for the Buck Creek watershed were extracted using geographic information software from wet deposition annual gradient maps published by the National Atmospheric Deposition Program (NADP, 2015) for years 1986–2011. These continuous gradient maps are based on observations from the NADP National Trends Network and a high resolution precipitation model developed by the PRISM Climate Group (Latysh and Wetherbee, 2012). Trends through time in the wet atmospheric NO_3-N, NH_4-N, and IN deposition rates (1986–1995 and 1995–2011) and wet atmospheric S deposition rate (1986–2011) were assessed using simple linear regression analysis. Time periods for regression analysis were determined *a priori*, based on the observation of decreased SO_x emissions since the early 1970s following implementation of emissions reduction programs through the Clean Air Act of 1970 and implementation of NO_x emission reduction programs following implementation of Phase 1 of the Acid Rain Program in 1995 (Driscoll et al., 2003).

In addition, a multiple regression model was developed to estimate average n-$\delta^{15}N$ through time for the combined watershed dataset (1980–2010) using annual NH_4-N, NO_3-N, and S deposition rates reported at Huntington Wildlife Monitoring Station (NY20), which is about ~50 km from our study area. This dataset was used because it contains annual wet deposition values going back to 1980, whereas the NADP PRISM maps only extend to 1986. Similar deposition values and trends were found between NADP PRISM maps and measured deposition rates from NY20 for S deposition ($R^2 = 0.88$, y = 1.28x) and IN deposition ($R^2 = 0.77$, y = 1.27x) for the 1986–2011 period (data not shown). The annual deposition data were aggregated by calculating the 2-year mean deposition rate (1980–1981, 1982–1983), thus allowing direct comparison with n-$\delta^{15}N$ data. Analysis for multi-collinearity and model building was carried out in R using the **ltm**, **leaps**, and **car** packages (Rizopoulos, 2006; Fox and Weisberg, 2011; Lumley, 2009; R Core Team, 2016). Model selection was based on variance inflation factor (VIF), the Bayes' Information Criterion (BIC), and adjusted R^2 (Table S2).

Flow and stream NO_3-N concentration data for the North and South Tributaries were provided by the U.S. Geological Survey (USGS) and Adirondack Lake Survey Corporation (Lawrence, 2002; Lawrence et al., 2008) for the 2000–2012 period. Periodic (every two weeks, year round) and episodic (high flows between April and November) stream sampling has been carried out since 2000. Based on a time series of daily estimated concentration and daily mean discharge, a statistical load estimator (LOADEST) developed by the USGS (Runkel et al., 2004) was calibrated with inputs of time, daily flow and NO_3 concentration to estimate daily NO_3-N yields (kg ha^{-1} d^{-1}) for the same period. The same seven explanatory variables based on daily streamflow and time were used for each watershed. Observed daily concentrations were typically composed of an individual grab sample, but for days with multiple samples, a mean concentration was used to calibrate LOADEST to model daily NO_3-N concentrations on days when no sampling occurred. Some summer samples collected in the North (n = 21) were not included in the calibration because no flow was measured in the stream. In total, 394 and 455 daily concentrations for the North and South, respectively, were used to parameterize the LOADEST model. Estimates of the daily yields were summed to produce monthly and annual yields (kg N ha^{-1} mo^{-1} and kg N ha^{-1} yr^{-1}) and flow-weighted mean concentrations (mg N L^{-1}). For the dates when NO_3-N measurements were made, the LOADEST model explained 89% and 86% of the variation of natural-log daily NO_3-N yields in the South and North, respectively. Slopes of the graphs of observed versus predicted daily loads were 1.04 for the South and 1.08 for the North, which indicates only a small positive bias in the LOADEST estimates. Trends in annual NO_3-N yield, retention of wet IN deposition $\left(\frac{Wet\ Deposition - Yield}{Wet\ Deposition}\right)$, and flow-weighted mean concentrations were assessed using simple linear regression analysis.

3. Results

We observed declining n-$\delta^{15}N$ trends between 1980 and 2010 for 21 of the 40 sampled trees (Table S3-S4). Three of six sampled species displayed declining n-$\delta^{15}N$ values over time in the two watersheds (Fig. 2B and C; Table S2). Both maple species (red maple, n = 8; sugar maple, *A. saccharum*, n = 12) and red spruce (n = 12) declined over the period of record (Fig. 2, Table S2). Yellow birch (*Betula alleghaniensis*, n = 6), balsam fir (*Abies balsamea*,

n = 1) and eastern hemlock (*Tsuga canadensis*, n = 1) showed no trends over time. No species showed positive trends in n-δ^{15}N, and only two individual sugar maple trees in the South showed significant positive trends. Despite variation in n-δ^{15}N trends observed at the individual tree level, watershed-level n-δ^{15}N was similar in the North and South watersheds for the 1980–2010 period, respectively (Fig. 2A and Fig. S1; Table S1). At the watershed level, n-δ^{15}N trends were both declining for the 1980–1995 period in the North and South (Fig. S1, Table S1). Values of n-δ^{15}N continued a decline in the 1995–2010 period in both watersheds, but the trends were more apparent in the South (p = 0.001) than the North (p = 0.0895, Table S1). Despite similar trends, average non-normalized δ^{15}N values of the South were consistently higher than the North (Fig. S3).

S deposition declined between 1986 and 2011, whereas no trend in precipitation amount was detected during this period (Fig. 3A). Deposition of IN declined during 1995–2011 despite substantial variability in precipitation amount, but no IN deposition trend was observed during 1985–1995 (Fig. 3A). Decreases in IN deposition were driven by declining NO_3-N deposition (data not shown). Deposition of NH_4-N was constant throughout the period of record, and its proportion of total IN deposition increased from ~30 to ~50% as NO_3-N deposition declined (data not shown).

Both SO_4-S and NO_3-N deposition rates from the NY20 NADP station displayed a positive relationship with the combined n-δ^{15}N dataset (SO_4-S: $R^2 = 0.78$, $p < 0.01$; NO_3-N: $R^2 = 0.54$, $p < 0.01$), whereas NH_4-N had little influence ($R^2 = 0.07$, $p = 0.76$). Both SO_4-S and NO_3-N deposition were highly correlated and failed the VIF test (calculated value > 5), so these variables could not be included together in the same multiple-regression model. NH_4-N deposition showed no issues of multi-collinearity with either SO_4-S and NO_3-N deposition variables. After model building, a combined NH_4-N and SO_4-S deposition model generated the lowest BIC score and highest adjusted R^2 of the seven models, with no issues of multi-collinearity among parameters (BIC = −22.38, $R^2 = 0.83$; Fig. 3B;

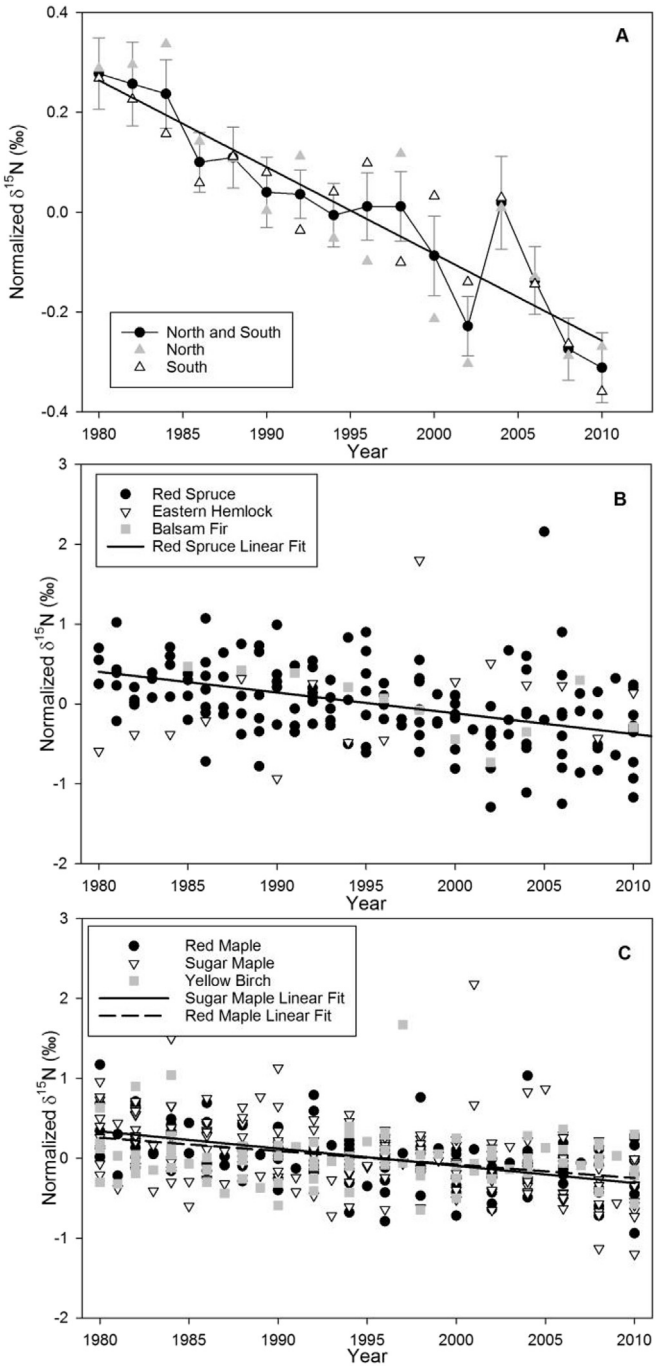

Fig. 2. A) Two-year mean n-δ^{15}N values (±1 S.E.) in the North (grey triangles), South (white triangles), and both watersheds combined (black circles; along with the linear line of best fit). Species-specific time series of n-δ^{15}N in coniferous (B) and deciduous trees (C) along with linear lines of best fit for significant negative correlations (Table S1-S4).

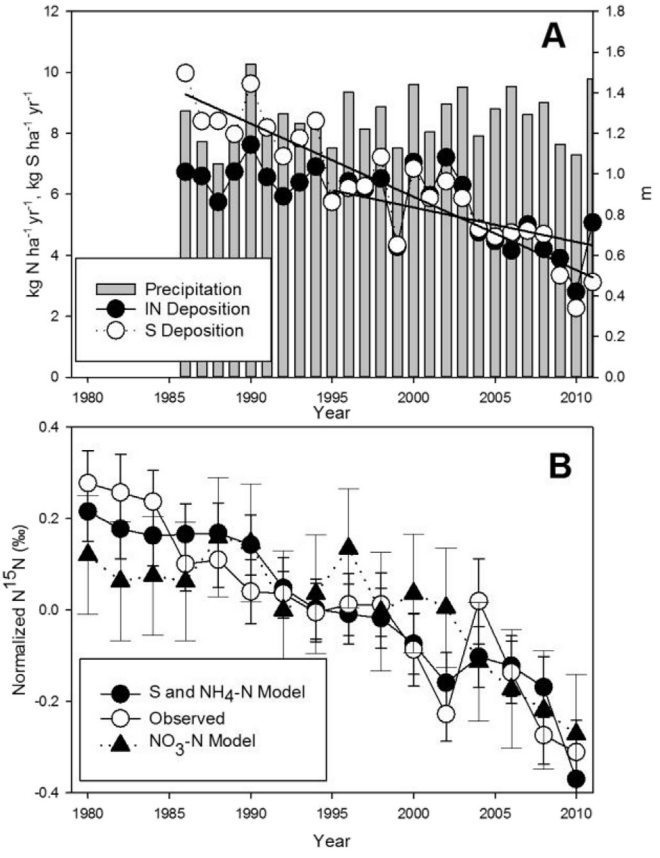

Fig. 3. A) Precipitation and wet deposition of inorganic nitrogen (IN) and sulfur (S). Wet S deposition decreased during 1986–2011 ($R^2 = 0.83$, $p < 0.0001$, n = 25) and IN deposition decreased during 1995–2011 ($R^2 = 0.49$, $p < 0.01$, n = 16). No trend in precipitation was observed in either period. B) Time series of predicted and observed combined watershed n-δ^{15}N values; NH_4-N and S deposition multiple regression model and simple NO_3-N model ($R^2 = 0.83$, $p < 0.01$, n = 30 and $R^2 = 0.51$, $p < 0.01$, n = 30, respectively; Table S5).

Table S5). This model demonstrated that lower annual n-$\delta^{15}N$ values were associated with higher NH_4-N deposition rates ($\beta_1 = -0.22$, $p = 0.03$) and lower SO_4-S deposition rates ($\beta_2 = 0.11$, $p < 0.01$). A NO_3-N and NH_4-N deposition model was also applied ($R^2 = 0.48$, BIC $= -4.4$), but NH_4-N deposition was not a significant parameter in this model ($p = 0.82$, data not shown); furthermore, this model explained less variance in the combined Buck Creek watershed n-$\delta^{15}N$ record than did a simplified NO_3-N deposition model ($R^2 = 0.51$, $p < 0.01$; Fig. 3B). Overall, annual n-$\delta^{15}N$ values in the North and South were declining prior to declines in atmospheric N deposition.

During the 2000s, the North typically yielded 30% of IN deposition on an annual basis, whereas the South retained little IN deposition, and even yielded more NO_3-N than wet-deposited IN in the latter half of the record (Fig. 4A). Stream-water mean annual flow-weighted NO_3-N concentrations declined in the North ($p = 0.02$; Fig. 4), whereas a weaker trend in concentration was observed in the South ($p = 0.09$; Fig. 4B). Stream NO_3-N yields and runoff showed no trends in the North or South (Fig. 4B; runoff data not shown). Mean monthly flow-weighted concentrations were lowest during the growing season and highest in the late winter and early spring (Fig. S2). Generally, the mean monthly flow-weighted concentrations for the dormant season in the North declined until ~2005–2006, after which they stabilized during the latter half of the record (Fig. S2). Monthly concentrations in the South displayed an initial decline (2000–2004) but peak dormant season concentrations have dramatically increased from ~1.0 mg NO_3-N L^{-1} in the mid-2000s to 1.4 mg NO_3-N L^{-1} after 2010 (Fig. S2).

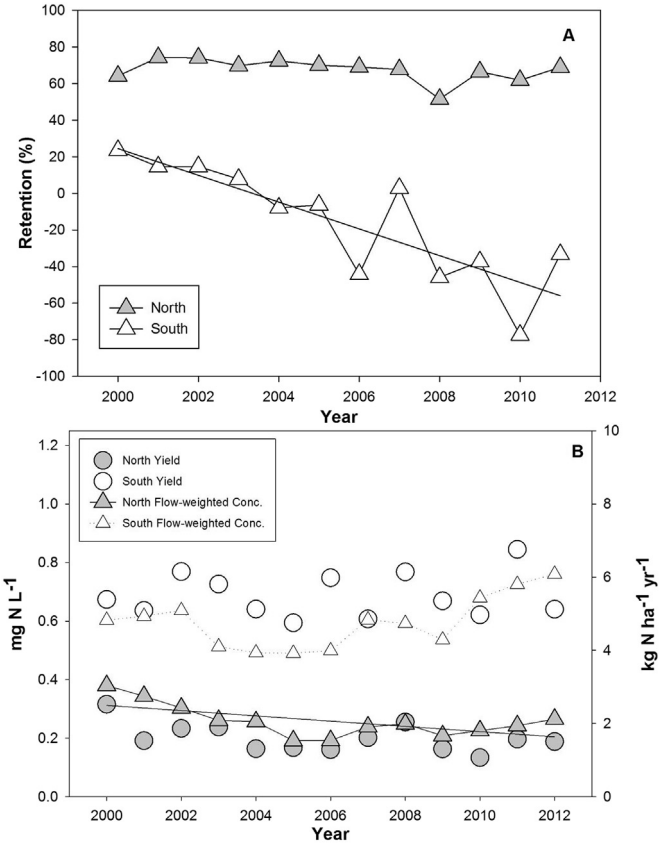

Fig. 4. A) Retention of wet IN deposition from 2000 to 2011. Retention has declined in the South ($R^2 = 0.68$, $p < 0.0001$), but has remained constant in the North. B) Annual stream runoff, NO_3-N yield, and mean flow-weighted concentration of NO_3-N for the North and South watersheds. Mean annual flow-weighted concentration of NO_3-N in the North has declined since 2000 ($R^2 = 0.33$, $p = 0.02$), but there was no trend in the South.

4. Discussion

4.1. Changes in terrestrial N cycling prior to declines in atmospheric IN deposition

Despite differences in tree species composition, soil composition, N retention, terrestrial N availability relative to plant demand (Fig. S3), and hydrology between the North and South (NYSERDA, 2012; Burns et al., 2009), both watersheds demonstrated near equivalent declines in tree ring n-$\delta^{15}N$ throughout the 30-year study period. The n-$\delta^{15}N$ values began to decline prior to decreases in atmospheric N deposition, which is inconsistent with our hypothesis that terrestrial N availability would only decline following declines in atmospheric N deposition. Thus factors other than declining atmospheric N deposition must have a greater relative influence on changes in terrestrial N availability (as inferred from tree-ring $\delta^{15}N$ values) at Buck Creek.

Decreased mineral acid (i.e., H^+) deposition, rather than N deposition, is one potential factor than may influence ecosystem N cycling in our study watersheds. For example, the clean-roof experiments of Corre et al. (2003) and Corre and Lamersdorf (2004) decreased the amount of both deposited N and acidity onto the catchments, so recovery from acidification may have at least partly driven the observed decline in N availability in the experimental catchment. Recovery of forests, soils, lakes, and streams from chronic acid deposition has been documented throughout the Adirondacks over the past three decades (Driscoll et al., 2003, 2016; Lawrence et al., 2013; Stoddard et al., 1999). At our study sites, decreases in soil aluminum (Al) mobilization as a result of decreased acidic deposition were indicated by pronounced decreases in exchangeable Al concentrations between 1997 and 2009–2010 in the North and between 1998 and 2014 in the South (Lawrence et al., 2015). Thus, the forests in the North and South may be experiencing reduced Al toxicity and enhanced nutrient cation availability (Ca, Mg, K) as the systems continue to recover from terrestrial acidification (Battles et al., 2014; Sullivan et al., 2013; Oulehle et al., 2011; Driscoll et al., 2001). Alleviation of these ecosystem stressors would potentially 1) enhance carbon accumulation in aboveground biomass and soil organic matter, thus increasing N immobilization and inducing N limitation (Monteith et al., 2007) and/or 2) increase decomposition rates in soils, in turn causing a shift in available N (Sawicka et al., 2016; McLauchlan and Craine, 2012).

Factors other than decreases in acid deposition may also contribute to explaining the declines in tree-ring $\delta^{15}N$ values in the North and South. Multiple studies have reported that the isotopic signature of atmospheric N deposition can be recorded in tree rings (Jung et al., 2013, Doucet et al., 2012; Savard et al., 2009; Saurer et al., 2004). Results from the multiple regression analysis indicated that atmospheric NH_4-N deposition was a significant and influential parameter when paired with SO_4-S deposition (Fig. 3B). $\delta^{15}N$-NH_4 values are typically quite negative, ranging from about −1 to −20‰ (Xiao et al., 2012; Jia and Chen, 2010; Garten, 1992), so it is possible that NH_4-N deposition may be depositing more negative $\delta^{15}N$-NH_4 into soil IN pools, thus influencing our observed tree-ring $\delta^{15}N$ trends. Yet, deposition typically comprises only a small proportion of tree N uptake, so the potential influence of $\delta^{15}N$-NH_4 on tree-ring $\delta^{15}N$ values requires further study (Gerhart and McLauchlan, 2014). Increased atmospheric CO_2 concentrations during the period of our study may also influence $\delta^{15}N$ trends by contributing to progressive N limitation through enhanced plant uptake and increased C:N ratios in plants and soils

(Norby et al., 2010; McLauchlan et al., 2010). However, neither watershed has progressively increased its N retention (Fig. 4A), suggesting that progressive N limitation may not be occurring in these watersheds. A recent study reported a decrease in nitrogen pools and mineralization rates at Hubbard Brook (Durán et al., 2016), and the authors posited that declining terrestrial N pools may be driven by warming temperatures and reduced snow accumulation. Reduced snowpack and warming temperatures have also been observed in the Adirondacks, but other studies have indicated that climate change may actually increase or have a minimal impact on terrestrial N availability and stream NO_3-N loss (Brookshire et al., 2011; Sebestyen et al., 2009) thus making the influence of climate change uncertain.

Forest successional processes are another plausible explanation for the declining n-δ^{15}N trends in the North and South. As forest succession proceeds, the N immobilization potential of a forest has been postulated to increase due to greater plant uptake, organic matter accumulation, and coarse woody debris production thereby contributing to declining N availability (McLauchlan et al., 2007). Disturbances ranging from low intensity surface fires to canopy gap formations, however, have been shown to disrupt any trends in N availability that may be brought about by successional processes (Howard and McLauchlan, 2015; Beghin et al., 2011; Bukata and Kyser, 2007). In the North, beech bark disease and spruce decline have caused a decline in tree basal area during the study period, whereas beech bark disease has killed a large proportion of mature beech trees in the South (NYSERDA, 2012). Disturbance has clearly happened in the North and South (as indicated by NYSERDA vegetative surveys from 2000 to 2010), yet n-δ^{15}N values declined between 1980 and 2010 at the watershed level. The ongoing disturbance in both watersheds thus reduces the likelihood that n-δ^{15}N trends observed in the North and South are being primarily driven by successional processes.

4.2. Individual tree and species-specific δ^{15}N trends

Downscaling observations to the level of individual trees revealed substantial variability in δ^{15}N trends. Only half of the trees exhibited long-term declines in δ^{15}N values in our study, and two trees actually demonstrated increased tree-ring δ^{15}N through time. Furthermore, some records displayed sudden and discordant positive peaks in δ^{15}N, which suggests relatively rapid and transient increases in N availability as the result of local-scale processes. Such processes may override the drivers of the declining δ^{15}N trends at the watershed scale. For example, the release of sub-canopy trees following canopy decline and/or mortality of dominant trees, due to disease or weather events, could increase access to nutrients due to 1) greater root production and coverage in the soil matrix and 2) possibly enhanced nutrient mineralization (e.g., Pickett and White, 1985). If local disturbances mask long-term trends in tree-ring δ^{15}N, then our results reinforce the importance of designing field sampling efforts to include high sampling density, multiple species, and extensive spatial coverage to assess changes in terrestrial N cycling across a watershed.

Our results also highlight the importance of understanding how species-specific characteristics influence changes in forest N cycling. The growth of some species in our watersheds, including yellow birch and American beech, is thought to be insensitive to N deposition (e.g., Halman et al., 2015; Thomas et al., 2010). The results for the six yellow birch trees sampled in our study support this understanding, because they showed relatively constant δ^{15}N values over time despite significant decreases in N deposition. This lack of trend suggests that the amount of N available to yellow birch has not significantly changed through time. In contrast, other tree species, including the sugar maples in our study (Fig. 2C), may strongly respond to the reduced loss of base cations from soils and foliage as acid deposition declines (Huggett et al., 2007; Lovett and Mitchell, 2004). For example, in the northeastern United States, trees in sugar maple-dominated plots treated with lime to remediate acidified soils showed increased plant growth, greater recruitment, and reduced mortality (Halman et al., 2015; Groffman et al., 2006), which ultimately led to decreased ammonium available for nitrification (Groffman et al., 2006; Simmons et al., 1996). Soils at Buck Creek show signs of recovery from acidification (Lawrence et al., 2015), and similar declines in N availability may be occurring, at least for sugar maples, in the North and South.

4.3. Differing trends in watershed N retention

Declines in stream flow-weighted NO_3-N concentrations in the North were consistent with long-term declines in terrestrial N availability as inferred from declining watershed-scale tree-ring δ^{15}N values. This result was expected since a decline in terrestrial N availability would be associated with “tighter” N cycling thus minimizing the loss of N to streams (Aber et al., 1998). Relative to the South, the North was apparently more retentive of wet atmospheric N deposition for the period of record (Fig. 4), which is consistent with the North potentially having lower terrestrial N availability as indicated by dendroisotopic records (Fig. S3). The North is consistent with other mid-Atlantic forests that seem to retain a fixed proportion of wet deposited IN (~70%) over time (Eshleman et al., 2013), despite the fact that wet atmospheric IN deposition ranged from 3 to 7 kg N ha yr^{-1}. Although the hydro-biogeochemical mechanisms that can explain the relatively constant retention over time are uncertain (Eshleman et al., 2013; Grigal, 2012), it is clear from the mass balance that less total N is being deposited and retained in the North over time on an absolute basis. Somewhat inconsistent with stream NO_3-N trends in the North, however, was the negative but still not statistically significant δ^{15}N trend for the 1995–2010 period. Ongoing spruce decline and beech bark disease has caused a decrease in stand-level basal area in the North, and this disturbance may be masking the influence of N deposition on the short-term δ^{15}N trend by providing new sources of terrestrial N or depressing plant uptake of N in the North.

Unlike the consistent N retention over time in the North, the South displayed decreasing retentiveness during a period of declining N deposition and N availability, as inferred from declining watershed-scale tree-ring δ^{15}N values. These results indicate that dendroisotopic and stream NO_3-N records may not always provide similar information about terrestrial N availability (Tomlinson et al., 2015; Gerhart and McLauchlan, 2014; McLauchlan and Craine, 2012). The decline in N retention indicates that a source of N from within the catchment is being mineralized but not being retained by plants and soils in the South. At Buck Creek, a possible source includes the decomposition of more recalcitrant material in soils recovering from acidification (Sawicka et al., 2016; Lawrence et al., 2011, 2015). The decline of beech trees could also explain decreased N retention as a result of diminishing rates of plant uptake and death of older trees. However, the total basal area of beech in the South actually increased by 16% between 2000 and 2010 (NYSERDA, 2012), which argues against this explanation. Many other forested watersheds have also shown reductions in retentiveness of N during periods of decreased N and acid deposition (Kopáček et al., 2016, Argerich et al., 2013), yet the relative importance of the various factors contributing to declining retention remain unclear. Besides changes in terrestrial biogeochemical cycling, higher dormant season flows and increased flood peak frequency may be enhancing NO_3-N transport (Bernal et al., 2012). The inconsistency between declining tree-ring δ^{15}N values and

retention trends in the South could also originate from sampling bias during field collections of tree cores for $\delta^{15}N$ analysis. The sampling protocol required the sampling of healthy, large trees, so no mature American beech trees were sampled in this study. The extensive coverage of diseased beech in the South raises the prospect that the other randomly sampled species may not completely represent changes in tree-ring $\delta^{15}N$ values across the watershed. In previous studies, beech showed no particular sensitivity in growth or survival to atmospheric N deposition or calcium amendments (Halman et al., 2015; Thomas et al., 2010); so, similar to yellow birch, the changes in acid deposition over time may not have greatly influenced tree-ring $\delta^{15}N$ trends in beech. Thus, the apparent contradiction in the South between the streamwater NO_3-N and watershed-level dendroisotopic data should be interpreted with caution.

4.4. Conclusions

We observed that changes in N availability, as inferred from declining watershed-scale tree-ring $\delta^{15}N$ values, were occurring prior to decreases in atmospheric N deposition (pre-1995) in the North and South Tributaries of Buck Creek. Declines in N deposition cannot fully explain these trends and thus other factors, such as declines in acid deposition, may have greater influence on terrestrial N cycling in forests. Our data also indicate that trends in wood $\delta^{15}N$ values vary among tree species and individuals, and these differences may be due to species-specific sensitivity to acid deposition and local disturbance. Finally, decreased acid deposition and declining $\delta^{15}N$ trends in tree rings do not necessarily translate into decreased NO_3-N export in streams, as evidenced by the divergent trends in the North and South. The variable changes in ecosystem N cycling in the North and South highlight the need to further integrate terrestrial and stream datasets to comprehensively assess forest responses to decreased atmospheric pollution and other ongoing environmental changes.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2016.08.055.

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