Atmospheric Environment xxx (2016) 1–9

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

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

Robert D. Sabo [a,*], Sara E. Scanga [b], Gregory B. Lawrence [c], David M. Nelson [a], Keith N. Eshleman [a], Gabriel A. Zabala [b], Alexandria A. Alinea [b], Charles D. Schirmer [d]

[a] University of Maryland Center for Environmental Science, Appalachian Laboratory, 301 Braddock Road, Frostburg, MD, 21532, USA
[b] Department of Biology, Utica College, 1600 Burrstone Road, Utica, NY, 13502, USA
[c] New York Water Science Center, U.S. Geological Survey, 425 Jordan Road, Troy, NY, 12180, USA
[d] Department of Forest and Natural Resources Management, State University of New York, College of Environmental Science and Forestry, 1 Forestry Drive, Syracuse, NY, 13210, USA

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.

ARTICLE INFO

Article history:
Received 13 February 2016
Received in revised form
17 August 2016
Accepted 18 August 2016
Available online xxx

Keywords:
Terrestrial N cycling
Nitrate
Tree rings
Acid deposition
Temperate forest
Stable isotopes
Streams

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.

* Corresponding author.
E-mail address: rsabo@umces.edu (R.D. Sabo).

http://dx.doi.org/10.1016/j.atmosenv.2016.08.055
1352-2310/© 2016 Elsevier Ltd. All rights reserved.

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

Please cite this article in press as: Sabo, R.D., et al., Watershed-scale changes in terrestrial nitrogen cycling during a period of decreased atmospheric nitrate and sulfur deposition, Atmospheric Environment (2016), http://dx.doi.org/10.1016/j.atmosenv.2016.08.055