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Nitrogen wet deposition stoichiometry: the role of organic nitrogen, seasonality, and snow

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Abstract Wet deposition of dissolved inorganic nitrogen (N) is declining nationally, accompanied by a shift in stoichiometry from predominantly oxidized to reduced forms of N. Stoichiometric trends that include the organic fraction of N wet deposition have yet to be assessed in light of anthropogenic pressures and global change, including shifting seasonality. Here we use 17 years of weekly, year-round wet deposition data from a temperate watershed in New Hampshire (USA) to assess long-term and seasonal trends in NO_3^-, NH_4^+, and dissolved organic nitrogen (DON), and quantify the dependence of N stoichiometry on precipitation type (rain or snow). Concentration, load, and relative abundance of DON are increasing, a pattern previously unreported in the U.S. Deposition of total dissolved nitrogen at this site is declining, but is increasingly depleted in NH_4^+, contrary to national trends. The stoichiometry of inorganic N is highly sensitive to precipitation type with snow containing significantly more NO_3^- than rain, which was relatively enriched in NH_4^+. The effects of climate change on seasonality such as warmer winters could result in a greater proportion of precipitation entering the biosphere as rain that is relatively enriched in reduced N, with significant implications for watershed biogeochemical cycles at the regional scale. This study demonstrates variability in contemporary N deposition inputs including trends in stoichiometry and explores the role of organic N and seasonality in regulating inter- and intra- variability in N deposition stoichiometry.

Keywords Nitrogen · Deposition · Stoichiometry · Seasonality · Snow · Precipitation

Introduction

Atmospheric wet deposition of nutrients and pollutants has long been recognized as a chronic perturbation to ecosystems and biogeochemical cycles (Likens and Bormann 1974; Aber et al. 1998). The exchange of nitrogen (N) between the atmosphere and biosphere through precipitation represents the largest flux of N to minimally impacted ecosystems (Galloway et al. 2008). The industrial and agricultural revolutions have increased the magnitude of atmospheric N concentrations seven-fold (Bobbink et al. 2010) through fossil fuel combustion, fertilizer application (Lloret and Valiela 2016), and biomass burning (Neff et al. 2002).

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Federal legislation such as the U.S. Clean Air Act (CAA) has resulted in declines in anthropogenic emissions of oxidized N resulting in reduced dissolved inorganic N and nitrate (NO_3^-) concentrations across the U.S. (Du 2016). Nearly five decades have passed since the implementation of the CAA, with multiple amendments throughout the 1990's to early 2000's that have restricted reactive N emissions. Policies have been enacted in other countries with similar results (Vet et al. 2014). As emissions of NO_x decrease (Lloret and Valiela 2016) some watersheds that were historically N-saturated (Aber et al. 1998) are now experiencing recovery and returning to an N-limited state (Newcomer et al. 2021). Reduction in oxidized N inputs results in slower rates of terrestrial biomass accrual, higher soil C:N ratios, and stationary rates of soil N immobilization (Newcomer et al. 2021). Despite reductions in the deposition of inorganic N and oxidized forms such as NO_3^-, the absolute and relative rates of annual deposition of reduced N (e.g., NH_4^+) have increased or remained unchanged (Warner et al. 2017). This has resulted in a stoichiometric shift towards NH_4^+ enriched deposition at a continental scale (Gilliam et al. 2019). However, trends in NH_4^+ wet deposition exhibit significant regional and longitudinal variability (Ollinger et al. 1995; Feng et al. 2021). Because trends in N deposition are a product of spatially heterogenous emissions, some regions may be experiencing NH_4^+ enrichment while others may continue to see NO_3^- enrichment.

Although inorganic N deposition is consistently monitored due to its recognized importance in the N cycle, dissolved organic N (DON) is rarely quantified despite estimates that it may contribute approximately one-third of global N deposition (Neff et al. 2002). Organic N enters the atmosphere through a myriad of processes that directly and indirectly produce nitrogen-containing volatile organic compounds (NVOCs) such as transpiration (Sharkey et al. 2008; Nguyen et al. 2011), decomposition (Isidorov et al. 2010), biomass burning (Coggen et al. 2016), and airmass pollution (Neff et al. 2002). Because DON is not commonly monitored in national deposition programs, there are considerable gaps in our knowledge of long-term trends in DON deposition and its response to global change (Jickells et al. 2013). DON represents an important nutrient-containing fraction of the larger pool of dissolved organic matter (DOM; Wymore et al. 2015) which varies in chemical structure, reactivity, and capacity to stimulate N biogeochemical processes (Benner 2003).

In northern latitudes, seasonality and ecosystem phenology are shifting as a result of climate change (Contosta et al. 2017; Harrison et al. 2020; Green et al. 2021; Burakowski et al. 2022). Few studies report on the potential feedbacks between changing seasonality and atmospheric chemistry. Daylength, temperature, and precipitation can influence the composition of N deposition due to the roles these variables play in the formation and scavenging of ions in the atmosphere (Kotowski et al. 2020). For example, atmospheric concentrations of oxidized N vary throughout a year based on photolysis reactions (Khan et al. 2015). Rain and snow also have differing ion scavenging potential due to variability in surface area, porosity, size, and vapor pressure (Mitra et al. 1990; Sparmacher et al. 1993). With increasing frequency of warmer and shorter winters forecasted for northern latitudes, less precipitation is expected to fall as snow (Burakowski et al. 2022). Quantifying the form of precipitation entering a catchment and the associated ionic load is critical if we are to understand how global climate change will influence N deposition and stoichiometry.

Here, we quantify inter- and intra-annual trends in atmospheric N deposition at a northern New England site using long-term data (17 years) that includes both the inorganic and organic fraction of wet N deposition. We ask: (1) Is atmospheric deposition load and stoichiometry changing inter-annually for the three primary forms of dissolved N (NO_3^-, NH_4^+, DON), and (2) To what degree do seasonality and the form of winter precipitation influence wet deposition N stoichiometry? We hypothesize that NO_3^-depositional loads are decreasing with concurrent increases in NH_4^+ while DON remains static leading to a stoichiometric shift in inorganic N. We also expect that DON will show strong seasonal patterns due to its potential sources from biogenic VOCs and that the form of winter precipitation influences both inorganic and organic N in wet deposition due to different nucleating processes occurring in the atmosphere between snow and rain.

Materials and methods

Study location

We used seventeen years (December 2003 to January 2021; $n = 858$) of year-round wet deposition data from Thompson Farm (TF; 43.11° N, 70.95° W) located within the Lamprey River Hydrological Observatory (Wymore et al. 2021), (Fig. 1) to assess inter-annual and seasonal trends in NO_3^-, NH_4^+, and DON wet deposition. The Lamprey River watershed is located in southeastern New Hampshire (USA) comprising an area of 554 km^2 low-elevation terrain before entering the Great Bay Estuary (Fig. 1). The landscape is primarily forested (73.6%) with agriculture (7.6%), wetlands (7.3%), scrub/shrubland (4.7%), and developed areas (3.4%) also present (Wymore et al. 2021). The TF deposition collection site is 23 m above sea level, 20 km from the Atlantic Ocean and surrounded by mixed deciduous and coniferous forests and agricultural fields (Fig. 1). Dominant tree species within the watershed include sugar maple (*Acer saccharum*), American beech (*Fagus grandifolia*), red oak (*Quercus coccinea*), birch (*Betula papyrifera*), and white pine (*Pinus strobus*). During the study period, mean annual air temperature was 9.2 ± 0.8 °C and the site received an average of 127 ± 6 cm of precipitation per year with 2–16% falling as snow.

Wet deposition sample collection

An Aerochem Metrics (ACM) 301 wet-only precipitation collector located in an open field was used from 2003 to 2008 and an N-CON Systems Company Inc. Atmospheric Deposition Sampler (Model 00-120) located on a 30 m walk-up tower was used from 2009 to present. The open field collector and tower collector are approximately 300 m apart. We conducted year-round event-based sampling through 2008. From 2009 to present samples were collected on a weekly basis. Collection buckets and lids were washed with a < 0.1% hydrochloric acid solution (HCl), soaked in deionized water and rinsed three or more times with deionized water before deployment. Buckets were changed after 7 days even if no precipitation occurred. Precipitation chemistry is representative of the cumulative conditions during the sampling window. Upon sample retrieval, the mass of precipitation in the bucket was recorded and used to verify the depth of rainfall collected (radius = 14.8 cm).

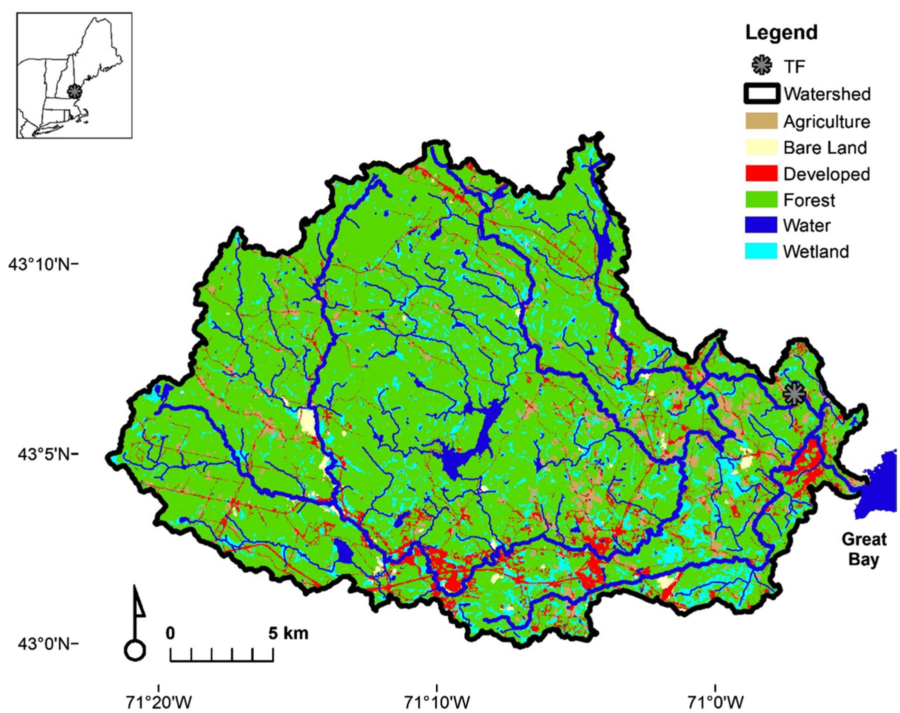

Fig. 1 Map of the Lamprey River Hydrological Observatory in southeastern New Hampshire (USA) and the Thompson Farm (TF) wet deposition collector. Land use data from NOAA Coastal Change Analysis Program (2016)

Wet chemistry analyses

Samples were analyzed at the University of New Hampshire Water Quality Analysis Lab. All samples were filtered through pre-combusted (450 °C for 4–6 h) 0.7 µm Whatman glass-fiber filters (GF/F), stored in acid-washed (10% HCl) HDPE bottles that were rinsed three times with deionized water and rinsed three times with filtered sample before filling, and frozen until analysis. Nitrate was measured using a Dionex Ion Chromatograph with suppressed conductivity detection (based on EPA 300.1; detection limit (DL) = 0.004 mg N/L). Analysis of NH_4^+ was done by colorimetric determination using the automated phenate method (based on EPA 350.1) on a Lachat Quickchem AE until 2004, and on a Smart Chem, Westco Scientific Instruments automated discrete analyzer from 2004 to present (DL = 0.004 mg N/L). TDN was analyzed on a high-temperature catalytic oxidation Shimadzu TOC-VCSH (Shimadzu Corporation, Kyoto, Japan) with a TNM-1 Total Nitrogen Module until 2014 (DL = 0.07 mg N/L), and on a Shimadzu TOC-LCSH with a TNM-1 (DL = 0.05 mg N/L) since 2014. Laboratory reagent blanks, laboratory duplicates, field duplicates, and certified reference materials are included in each analytical sequence to ensure quality control.

Measures of NO_3^- and NH_4^+ represent the atomic portion of N and are reported as NO_3-N and NH_4-N. Concentrations of DON were determined as the difference between TDN and dissolved inorganic nitrogen (DIN), where DIN is the sum of NO_3^- and NH_4^+. A detection limit of 0.01 mg N/L was assigned to DON. Data below the DL were included in data analysis and assigned ½ the DL. Relative abundance was calculated by dividing DL-corrected NO_3^-, NH_4^+, and DON concentrations by TDN concentrations (as the sum of DL-correction DIN and DON concentrations).

Precipitation and air temperature

Precipitation volume is measured at the Climate Reference Network (CRN; GHCND: USW00054795; NH Durham 2 SSW) weather station located 22 m from the ACM 301 collector and 295 m from the N-CON collector. Hourly precipitation and air temperature (NOAA National Centers for Environmental Information, 2001) from this co-located CRN station were merged with the wet deposition sampling intervals. For each sampling interval, we hindcasted the proportion of precipitation in the sampling bucket sourced from rain, snow, or a combination of rain and snow. We applied a surface air temperature threshold of 0.33 °C to define whether precipitation fell as rain or snow. This temperature threshold is the 50% rain-snow threshold for the region and represents the temperature at which precipitation occurs as rain and snow with equal frequency and below which precipitation is primarily snow (Jennings et al. 2018).

Dimensional analyses

To account for data gaps, we scaled measured wet deposition concentrations to monthly volume weighted mean concentrations by:

$$\text{Volume Weighted}\frac{mgN}{L} = \frac{\sum_{i=1}^{j=month} C_{ij} \times P_{depth_{ij}}}{P_{depth_j}} \tag{1}$$

where C_{ij} is the concentration (mg N L^{-1}) of each sampling interval (i) in each month (j), P_{depth} is the sum of precipitation of each sampling interval (i) in each month (j) measured at the hourly CRN weather station. For samples that bridged two months, the end-date month was assigned. From volume-weighted concentrations, watershed deposition load of TDN, NH_4^+, NO_3^-, and DON was calculated by:

$$\text{Deposition Load}\frac{mgN}{had} = \frac{C \times P_{depth} \times \frac{1L}{10^3 cm^3} \times \frac{10^8 cm^2}{1ha}}{T} \tag{2}$$

where C is the volume-weighted monthly sample concentration expressed in mg N L^{-1}, P_{depth} is the total precipitation (cm) that occurred during the month as measured by the hourly CRN weather station, and T is the average number of days per month.

Inter-annual trends

To address the question of whether wet deposition is changing over time for the three forms of dissolved N, timeseries trend analyses were conducted on monthly volume-weighted mean ($n = 207$) concentrations (mg N L^{-1}), deposition load (mg N ha^{-1} day^{-1}), and relative abundance (% of TDN). Using the *trend* package for R in RStudio (version 1.1.442, RStudio, Inc. Team, Boston, MA 2016), we applied a seasonal Mann-Kendall test which is a rank-based non-parametric method that tests whether a significant trend exists, and the direction of the trend. To quantify the magnitude of the trend, we used the Sen slope test, a nonparametric method that produces a slope representing the median change of a parameter over time. Trends were considered significant if both the Mann-Kendall and Sen Slope tests had an alpha level of <0.05.

Pettit's non-parametric changepoint test was applied to detect any significant shifts to the central tendency of the timeseries. Trend analyses were then run for data before and after the changepoint. We quantified the number of occurrences in a given year where wet deposition samples contained higher concentrations of oxidized N (NO_3^-) compared to reduced N (NH_4^+; e.g., Kurzyka and Frankowski 2019).

Seasonality and snow

Deposition seasonality was determined using volume-weighted monthly means of concentration, load, and relative abundance. Data were pooled by season (e.g., autumn is October–December; winter is January–March; spring is April–June; summer is July - September) from 2003 to 2021. To determine differences among seasons we applied a nonparametric Kruskal-Wallis analysis of variance, with a Dunn post-hoc test, using the *stats* and *FSA* packages in R. To avoid type-I error, post-hoc *p*-values were adjusted using the Holm method. Significance was determined at the 0.05 alpha level.

To quantify the degree to which precipitation type—rain, snow, or mixed—influences N deposition relative abundance (% of TDN) and NO_3:NH_4 molar ratios, we subset the data to include all samples collected during the months when snow occurs (October–May, $n=564$) and employed a linear mixed effects ANOVA. The model structure used a random intercept approach with a fixed effect of precipitation type category (e.g., 100% Rain, Mixed, and 100% Snow) and random effects of year and week of year (WOY). The random effect of year and WOY are included because we show significant inter-annual trends in relative abundance and molar ratio, and because daylight length influences the ambient relative abundance of oxidized N in the atmosphere (Khan et al. 2015). Controlling for these factors allows us to determine if precipitation type influences the composition and stoichiometry of deposition. Relative abundance data were arcsine square root transformed, and molar ratio data were $\log_{10}$ transformed prior to analysis. Modelling was conducted in RStudio using the *lmerTest* and *multcomp* packages. A Tukey post-hoc test was employed and post-hoc *p*-values were adjusted using the Holm method. Significance was determined at the 0.05 alpha level.

Results

Inter-annual trends

Total dissolved N wet deposition concentration and load decreased by − 0.005 mg N L^{-1} $year^{-1}$ and − 281 mg N ha^{-1} $year^{-1}$, respectively (Fig. 2). No significant trends in TDN were detected before or after the changepoint in 2014/2015 identified by the Pettit changepoint test (Table 1). However, mean TDN deposition concentration and load are higher before the respective changepoints, explaining the overall decreasing trend in TDN (Table 1). DON concentration, load, and relative abundance increased by 0.001 mg N L^{-1} $year^{-1}$, 24 mg N ha^{-1} $year^{-1}$, and 0.5% per year, respectively (Table 1; Fig. 2); each of these measures of DON deposition was at least two times higher after its respective changepoint (Table 1). However, DON concentration was found to decrease by 0.002 mg N L^{-1} $year^{-1}$ after its 2011 changepoint (Table 1). In contrast, NH_4^+ deposition concentration, load, and relative abundance decreased by − 0.003 mg N L^{-1} $year^{-1}$, − 145 mg N ha^{-1} $year^{-1}$, and −0.4% per year, respectively (Fig. 2). Trends in NH_4^+ concentration and load were not different before and after their respective changepoints (July 2014 and October 2012), although NH_4^+ relative abundance increased by 1.4% per year from 2003 to 2012 but remained static from 2012 to 2021. All NH_4^+ deposition values were higher before the changepoint, explaining the overall decreasing trend in NH_4^+ (Table 1). Nitrate deposition concentration and load decreased by − 0.004 mg N L^{-1} $year^{-1}$ and −195 mg N ha^{-1} $year^{-1}$, respectively (Fig. 2). Trends in NO_3^- relative abundance were not considered significant because the Sen Slope *p*-value was

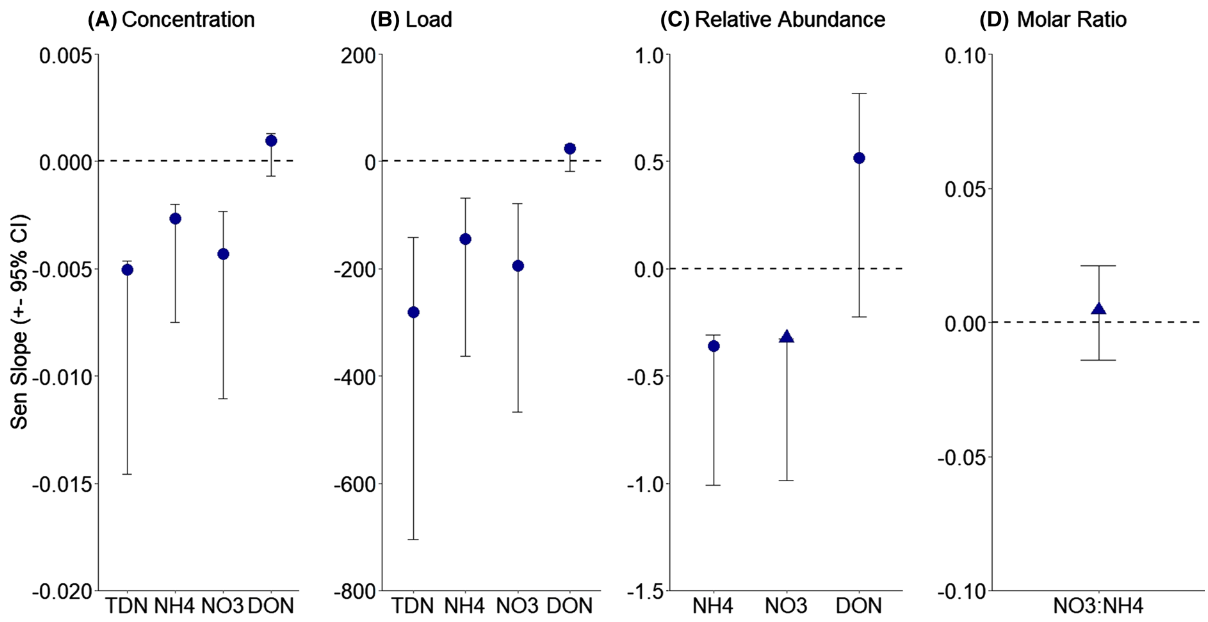

Fig. 2 Annual Sen slopes for wet deposition N **a** concentration (mg N L^{-1} $year^{-1}$), **b** load (mg N ha^{-1} $year^{-1}$), **c** relative abundance (% $year^{-1}$), and **d** molar ratio of NO_3:NH_4 at Thompson Farm from 2003 to 2021. Circles denote significant trends (Mann–Kendall and Sen Slope $p<0.05$) with 95% confidence intervals. Triangles represent the annual Sen slope of variables with non-significant trends (either Mann–Kendall or Sen Slope $p>0.05$)

Table 1 Summary of results from the Mann-Kendall and Sen Slope trends for wet deposition at Thompson Farm including volume-weighted mean monthly concentrations, loads, relative abundance, and oxidized to reduced N ratio. If not statistically significant ($p>0.05$) the result is denoted as (–)

Variable	N-species	2003–2020 (study record)		Change-point (mm-yyyy)	Before changepoint		After changepoint	
		Sen slope ($year^{-1}$)	Mean		Sen slope ($year^{-1}$)	Mean	Sen slope ($year^{-1}$)	Mean
Concentration (mg N L^{-1})	TDN	− 0.005	0.36	07-2015	–	0.39	–	0.30
	NH_4^+	− 0.003	0.15	07-2014	–	0.17	–	0.13
	NO_3-	− 0.004	0.18	07-2014	–	0.20	–	0.15
	DON	0.001	0.04	05-2011	–	0.02	− 0.002	0.06
Load (mg N ha^{-1} day^{-1})	TDN	− 281	11,118	05-2014	–	12,467	–	8950
	NH_4^+	− 145	4650	10-2012	–	5603	–	3599
	NO_3-	− 195	5685	08-2011	–	7003	–	4580
	DON	24	1226	05-2011	–	761	–	1593
Relative abundance (%)	NH_4^+	− 0.4	38.3	10-2012	1.4	41.3	–	34.9
	NO_3-	–	50.4	02-2010	–	54.0	–	48.3
	DON	0.5	11.3	07-2011	–	6.6	–	15.2
Molar ratio	NO_3^-: NH_4^+	–	1.6	09-2013	− 0.07	1.4	–	1.8

Mean values and trend results are also reported before and after the Pettit's changepoint

>0.05, however the Mann-Kendall result indicated a significant decline in $\%NO_3^-$ ($S = -191$; $p = 0.02$). No significant trends were detected before or after the changepoint for any descriptors of NO_3^- deposition, although NO_3^- concentration values were higher before the changepoint explaining the overall decreasing trend in NO_3^- (Table 1).

Despite declines in loads of TDN and inorganic N across the study period, the molar ratio of inorganic N (NO_3^-:NH_4^+) displayed no significant change over time (Fig. 2d). However, a significant changepoint was detected for NO_3^-:NH_4^+ in 2013 (Table 1), with significant declines in this ratio prior to the September 2013 changepoint and static trend thereafter. Mean NO_3^-: NH_4^+ was higher after the changepoint, indicating recent NO_3^- enrichment relative to NH_4^+ over the last seven years of the data record (Table 1). Within a given year, the percent of samples in which wet deposition contained higher NO_3^- than NH_4^+ concentrations ranged from 30 to 80% of samples (Fig. 3c). From 2004 to 2012, the number of samples with higher NO_3^- than NH_4^+ concentrations declined (Fig. 3c). However, from 2012 to 2013 a distinct shift occurred wherein the number of samples with high NH_4^+ sharply declined, and from 2015 to 2020 deposition samples have shifted toward increasingly NO_3^- enriched returning to values similar to the beginning of the record (Fig. 3c). This finding is consistent with the changepoints detected for inorganic N, load, concentration, and molar ratio (Table 1).

Seasonal trends

Wet N deposition composition at TF displayed significant variation with season (Fig. 4). Concentrations of TDN follow a distinct seasonal pattern wherein autumn concentrations are lower than spring and summer ($p < 0.001$), and winter concentrations are higher than autumn ($p < 0.001$) but lower than spring ($p < 0.001$; Fig. 4a). Concentration, load, and relative abundance of NH_4^+ are generally lowest in autumn and winter, and highest in spring and summer, respectively ($p < 0.001$; Fig. 4b). In contrast, NO_3^- relative abundance is highest in winter ($p < 0.001$), with the largest difference occurring between autumn-winter

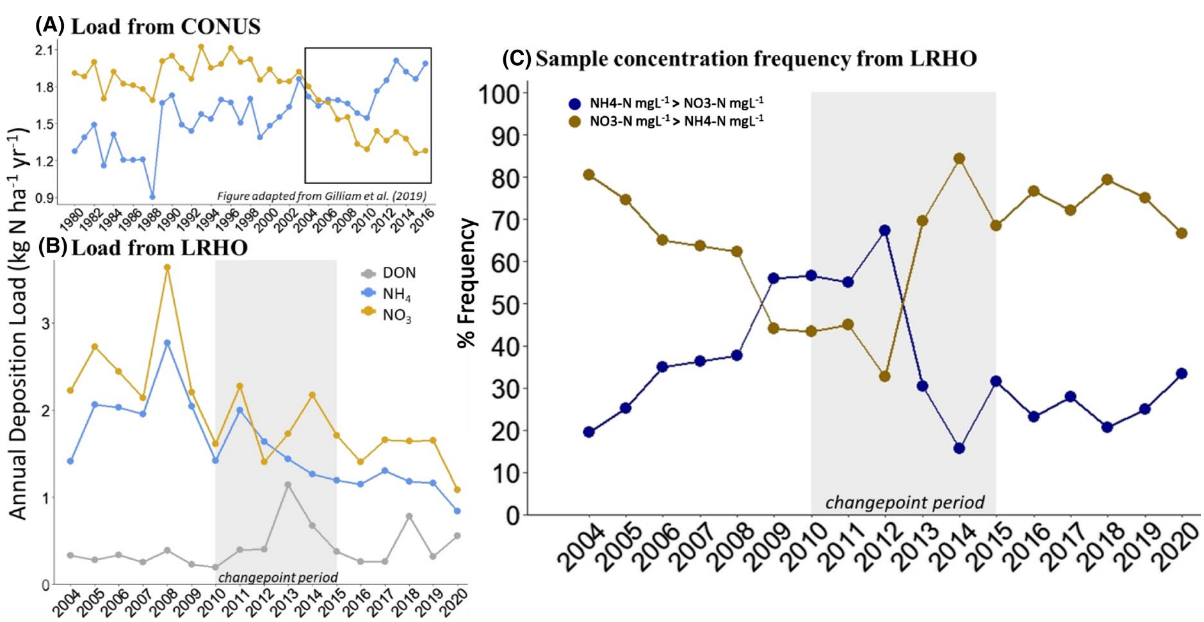

Fig. 3 **a** Average annual wet deposition N load (kg N/ha/year) across all NADP sites in the U.S., as reported in Gilliam et al. (2019), compared with **b** annual wet deposition N load (kg N/ha/year) at Thompson Farm and the Lamprey River Hydrological Observatory (LRHO) for NO_3^- (orange), NH_4^+ (turquoise) and DON (gray); and **c** frequency (%) of deposition samples in a given calendar year where NO_3^- concentrations exceeded NH_4^+ (brown), and where concentrations of NH_4^+ exceeded NO_3^- (blue) within the LRHO. The shaded region in panel **b** and **c** represents the range of years for which significant changepoints were found (see Table 1). Data within the square in panel **a** compared to panel's **b** and **c** show opposite trends

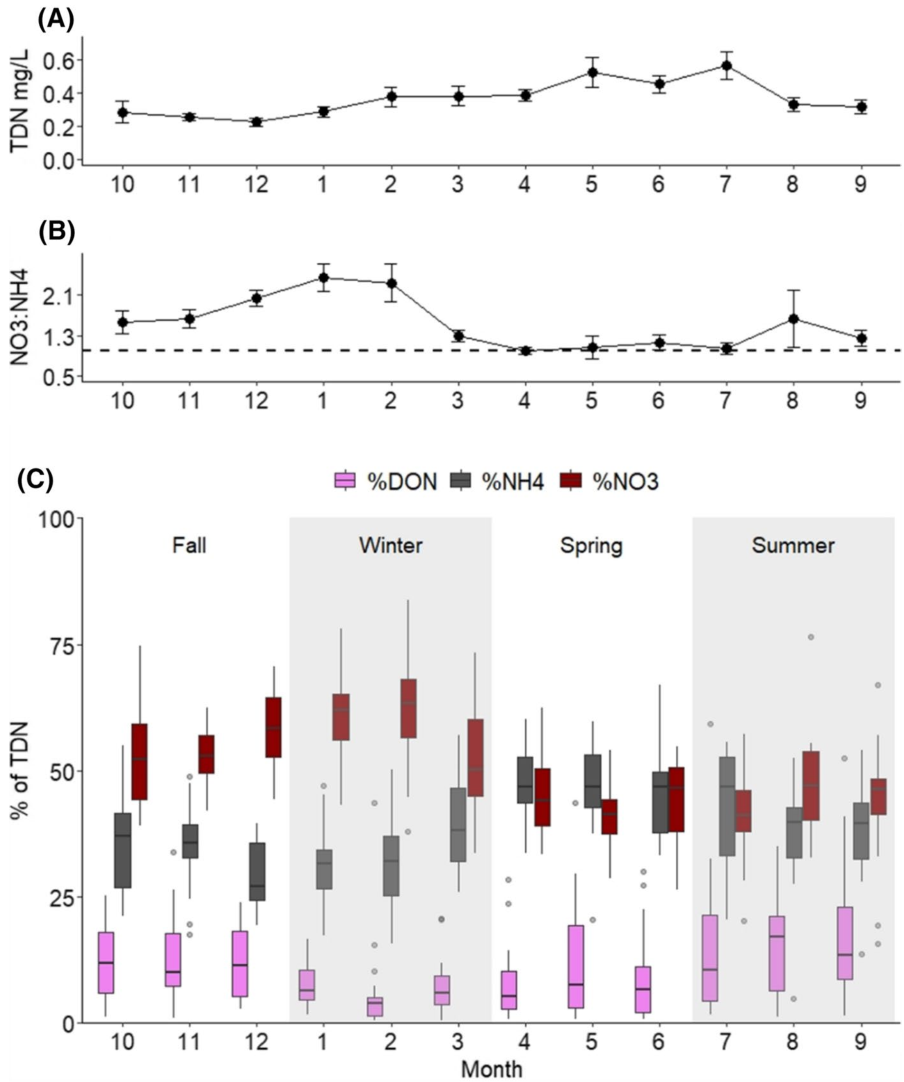

Fig. 4 Seasonality of **a** average (± 1 SE) monthly volume-weighted TDN concentration (mg L^{-1}), **b** average (± 1 SE) monthly volume-weighted molar NO_3:NH_4 ratio, and **c** relative abundance of %DON (violet), %NH_4^+ (gray), and %NO_3^- (red) from 2003 to 2020

and spring-summer (Fig. 4b). DON relative abundance and concentration are lowest in the winter and highest in the summer ($p<0.001$; Fig. 4b). NO_3^-:NH_4^+ ratios followed a seasonal pattern wherein the ratio was highest in winter and lowest in spring ($p=0.03$) followed by summer, then autumn.

Precipitation type

The ratio of NO_3^-:NH_4^+ in wet deposition varies with precipitation form (Fig. 5). As the percent of snow-derived deposition increases, the relative abundance of NO_3^- increases, while the relative abundance of NH_4^+ decreases and DON remains unchanged (Fig. 5a). Results from the mixed-effects ANOVA indicate that for the average year and daylength during months when snow falls, NO_3:NH_4 is significantly different when the sample is composed of 100% rain, mixed, and 100% snow ($p<0.0001$; Fig. 5b). That is, during the months of October–May, rain is more enriched in NH_4^+ whereas snow is significantly more enriched in NO_3^-.

Discussion

Inorganic nitrogen

The stoichiometry of wet deposition N is changing at both national and regional scales and may be explained by both shifting anthropogenic pressures

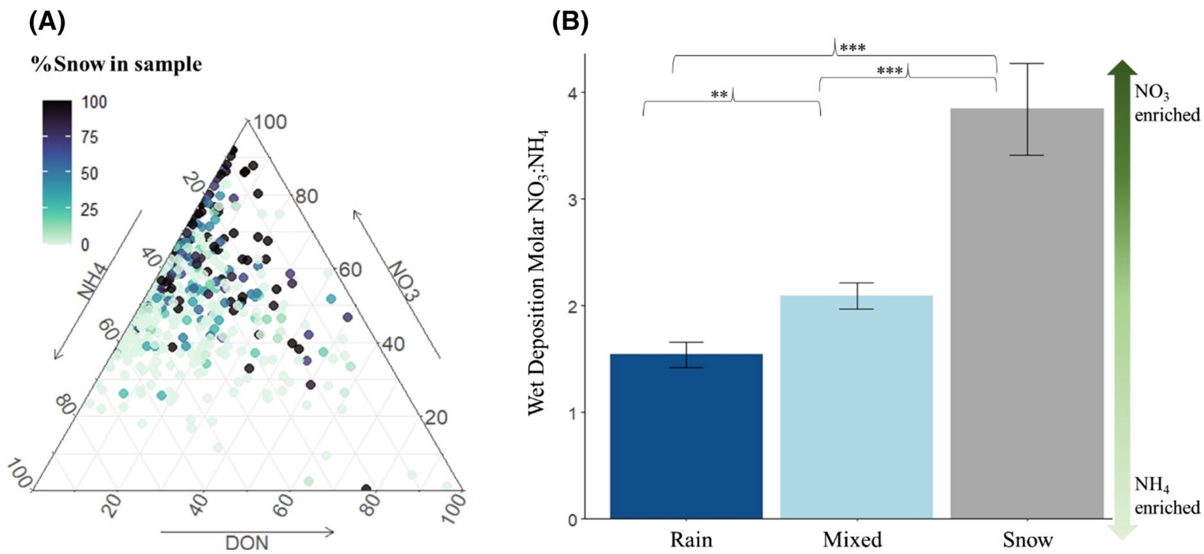

Fig. 5 **a** Ternary diagram of relative abundance (%) of DON, NH_4, and NO_3 during months where precipitation falls as snow (October–May; $n=564$), color gradient denotes percent of deposition sample sourced from snow. **b** Bar plot of mean (± 1 standard error) molar ratio of NO_3:NH_4 for deposition samples containing 100% rain ($n=359$), mixture of rain and snow ($n=196$) and 100% snow ($n=89$); asterisks denote significance of the mixed-effects ANOVA ($p<0.01$*, $p<0.0005$**, $p<0.00001$***)

(e.g., source of N emissions) and shifting seasonality due to climate change (e.g., warming winters). The decline in wet deposition TDN and NO_3^- load and concentration in the Lamprey River watershed is consistent with national trends (McHale et al. 2021). However, wet deposition in the Lamprey River watershed is also increasingly depleted in NH_4^+ (Fig. 2), a pattern opposite that of continental scale analyses (Gilliam et al. 2019). Deposition trends of NH_4^+ vary by region, with some parts of the northeastern U.S. displaying declines in NH_4^+ while the northwest and Midwest regions show increased or static NH_4^+ concentrations (Warner et al. 2017; Feng et al. 2021). Airmasses arriving to the Lamprey River watershed generally contain aerosols derived from marine, agricultural, and anthropogenic sources (Jordan and Talbot 2000). Regional variation in NH_4^+ deposition can be attributed to differences in automobile emissions, agricultural land use (e.g., ammonium volatilization during fertilizer application), soil temperatures, and variation in NO_3^- and SO_4^{2-} atmospheric concentrations which scavenge NH_4^+ (Du et al. 2014).

We found a distinct changepoint in the ratio of NO_3:NH_4 in 2013 (Table 1). Prior to 2013, wet deposition samples had a progressively increasing contribution of NH_4^+ relative to NO_3^-, a stoichiometric shift consistent with national trends (Fig. 3). Findings from Europe (Kurzyka and Frankowski 2019) and the U.S. (Li et al. 2016) also indicate wet deposition increasingly enriched in NH_4^+. But from 2013 to 2020, wet deposition samples in the Lamprey River watershed were more frequently enriched in NO_3^-, with depositional stoichiometry shifting toward those recorded at the beginning of the record. An increase in the frequency of deposition samples enriched in NO_3^- relative to NH_4^+ is a trend contrary to the most recent studies at the continental scale (e.g., Gilliam et al. 2019; Feng et al. 2021; McHale et al. 2021). However, these previous studies use data up to 2016/2017, which are just after the changepoints detected in our study (Table 1). Changes in land use and land management practices in the vicinity of the TF collector have occurred during the study period including the use of organic fertilizers at local dairy farms (Aber et al. 2020). However, with the placement of the NCON collector on the 30-m tall tower in 2009, we believe the site tends to reflect regional rather than local conditions. For example, NADP sites within 150 km of TF show similar changes in wet deposition nitrogen trends (*see supplemental materials*). Specifically, concentrations of NO_3^- are declining while NH_4^+ is static or slightly increasing with significant changepoints falling within the same range reported in this study (see associated online resource and Table 1). Our results emphasize the importance of continually reporting wet deposition trends in nitrogen at both national and regional-scales, and that a changepoint analysis is useful for identifying whether long-term trends are shifting in response to changing emissions of NO_x which have occurred in New England since 2020.

Changes in inorganic N stoichiometry appear to be occurring in concert with the widely reported declines in N deposition load. Recovery of ecosystems that have historically experienced chronic N deposition in the Northeastern U.S. (Likens and Bormann 1974) may follow a hysteretic recovery pathway that describes the process of ecosystem recovery with declining N depositional loads (Aber et al. 1998; Gilliam et al. 2019). The hysteresis recovery model is predicated on the concept that declining trends in ecosystem N input are not immediately paralleled in ecosystem-scale processes due to lags in response times and turnover of various N pools. But in regions experiencing static NO_3^- deposition trends, such as this study, the rate of recovery (e.g., slope of the hysteretic loop) could be slower. The stable $\%NO_3^-$ relative abundance trends (Table 1) suggests that NO_3^- may not decline to reach an assumed baseline of pre-anthropogenic inputs but rather may reach a new alternative stable state. This possibility of alternative equilibria is further reinforced by climate warming, which introduces considerable uncertainty in whether decreasing inputs of atmospheric N will continue over the next few decades due to atmosphere-biosphere feedbacks (Gilliam et al. 2019).

The role of snow

Given the dependence of N deposition composition on climate-sensitive variables such as precipitation, we examined the potential feedbacks between changing seasonality and atmospheric N stoichiometry. Climate change predictions for the northeast suggest warmer winters and a lengthening vernal window (Contosta et al. 2017) resulting in less precipitation falling as snow (Burakowski et al. 2022). In the Lamprey River watershed, inorganic N deposition displayed the largest differences in oxidized and reduced concentrations during winter (Fig. 4) and precipitation type had a significant effect on ratios of inorganic N (Fig. 5). In this study, 2–16% of total precipitation fell as snow across the study record. But snowfall can constitute up to 46% of total N deposition input to some forest ecosystems (Cao et al. 2019). Rain and snow have differing physical mechanisms controlling in-cloud and below-cloud aerosol scavenging. Snow is up to five times more efficient at ion scavenging compared to rain (Sparmacher et al. 1993). Heavier ions, such as NO_3^- (molar mass NO_3^- = 62.00 g/mol; NH_4^+ = 18.04 g/mol), are more likely to be scavenged by snow due to snow crystals containing increased surface area, porosity, size, and vapor pressure gradient (Mitra et al. 1990). Although the relative abundance of DON showed no significant dependence on precipitation type in this study, differences in snow-rain organic compound scavenging have been recorded at air temperatures < -10 °C (Lei and Wania 2004) which is below the temperature threshold considered for rain-snow partitioning in this study (0.33 °C). The direct comparison of wet deposition N in snow versus rain represents a relatively novel approach in the study of N deposition especially given patterns of shifting seasonality with global change (e.g., *this study*; Cao et al. 2019; Kurzyca and Frankowski 2019; Kotowski et al. 2020) with potentially meaningful consequences for biogeochemical cycles and microbial communities (Moore et al. 2021).

As winter rain increases in frequency, the net proportion of N entering the biosphere as NH_4^+ is likely to increase (Fig. 4). Future increases in NH_4^+ deposition have been proposed by previous studies (e.g., Warner et al. 2017) but have not been attributed to mechanisms associated with 'winter-warming'. The ecological consequences of increased reduced N deposition loads will be a function of ecosystem N-status (Aber et al. 2003; Newcomer et al. 2021). If the receiving ecosystem is N-saturated due to chronic N deposition, increased NH_4^+ deposition in winter and spring may result in higher loads of reduced N to receiving waterbodies due to lack of soil adsorption sites as well as higher runoff capacity of rain-dominated winter precipitation events (Creed et al. 2015). On the other hand, if the ecosystem remains N-limited, a higher proportion of reduced N deposition may stimulate microbial N assimilation or nitrification with ramifications for net ecosystem productivity or increase the production of nitrous oxide (N_2O; a potent greenhouse gas). However, these hypothetical responses may be offset by other consequences of warming winters such as increased frequency of soil freeze-thaw events due to lack of insulating snow cover (Groffman et al. 2001) which can reduce the capacity of soil microbial communities to process N in low elevation watersheds (Duran et al. 2016). The exact consequences of this shifting stoichiometry for the Lamprey River watershed remains an open question as the N status of many ecosystems is shifting due to changes in land use and other pressures associated with increased urbanization.

Despite the established dependency of inorganic N abundance on precipitation type, precipitation form is not accounted for in many national monitoring protocols including the National Atmospheric Deposition Program (NADP), the National Ecological Observatory Network (NEON), and the Long-Term Ecological Research (LTER) program. Until this type of meteorological data is reported alongside deposition chemistry, it will be necessary to use hindcasting approaches to estimate precipitation form when examining the role of shifting winter precipitation on seasonal and annual trends in N deposition. Hindcasting observations of meteorological conditions for each deposition sample presents some challenges such as locating climate data stations in close proximity to deposition collectors. However, identifying co-located climate and deposition sites (as practiced by NEON, for example) or applying gridded climate data may be a solution.

Organic nitrogen

The deposition of DON is also changing such that it is increasingly likely that N entering the Lamprey River watershed will be organic rather than inorganic. Although increases in wet deposition DON have been documented regionally in Europe (Verstraeten et al. 2016), to the best of our knowledge, this pattern has not been previously reported in the U.S. We recognize that calculating DON by subtraction, as is common practice (Cornell 2011), presents analytical challenges due to error propagation. However, we found that concentrations and loads of dissolved organic carbon (DOC) at TF have also been increasing at a rate of 0.03 mg C L^{-1} $year^{-1}$ and 557 mg C ha^{-1} $year^{-1}$ ($p < 0.05$), respectively, suggesting the entire pool of dissolved organic matter (DOM) is experiencing temporal variation. Whether this result is consistent across the U.S. remains to be tested, and accessibility to long-term data records that measure DON and DOC in wet deposition are limited.

One hypothesis for explaining increases in DON concentration and relative abundance (Fig. 2), as well as its seasonal variability (Fig. 4) and correspondence to DOC trends, is the feedback between climate warming and increased rates of decomposition and transpiration (Vanguelova et al. 2010). Forest chemical fluxes of volatile organic compounds (VOCs) are of similar magnitude to anthropogenic methane production (each comprising one-third of total annual VOC emissions; Guenther et al. 2006) and have the potential to significantly influence atmospheric fluxes of DOM. For example, leaf litter decomposition directly emits NVOCs (e.g., amino acids, thymine, uridine) and can constitute 10–15% of total VOC production resulting from decomposition (Isidorov et al. 2010). While the relationship between climate change and soil organic matter decomposition is dependent on many environmental factors (Davidson and Janssens 2006), there is increasing evidence to suggest that warming soil temperatures correspond with increased decomposition rates in the northeastern U.S. (Pold et al. 2015). Assuming the production of N-containing VOCs scale with decomposition rates, the increased load of depositional DON to the Lamprey River watershed may be explained by this mechanism.

Transpiration rates within the past decade have also increased in the northeast (Green et al. 2021) and have been attributed to warming air temperatures (Harrison et al. 2020) and lengthening of the vernal window and growing season (Contosta et al. 2017). VOCs released during plant transpiration are predominantly comprised of isoprene (C_5H_8; Sharkey et al. 2008), which does *not* contain N. Once isoprene is present in the atmosphere it is subject to reactions with OH and NO_3^-, undergoing rapid oxidation to produce secondary organic aerosols (SOA) that *are* N-containing VOCs (e.g., $C_{10}H_{14}NO_{10}^-$; Nguyen et al. 2011). We acknowledge that these mechanisms have yet to be directly tested; yet they offer an explanation for DON deposition seasonal patterns observed in this study and others (e.g., Keene et al. 2002) as well as long-term trends, and should be considered when interpreting components of the N cycle that result from feedbacks between ecosystems and the atmosphere.

Conclusion

There is a long history of measuring inorganic N in atmospheric deposition, but data records that also measure organic N are rare and valuable for understanding how different components of the global N cycle are changing. Seventeen years of weekly, year-round wet deposition data from the Lamprey River watershed in New Hampshire, USA were used to assess inter-annual and seasonal trends in NO_3^-, NH_4^+, and DON wet deposition. We found that wet deposition of TDN is decreasing, but that the stoichiometry is simultaneously becoming depleted in inorganic N and enriched in DON. We also show that the ratio of inorganic N (e.g., NO_3:NH_4) has recently shifted towards increasingly NO_3-enriched, a pattern contrary to reported national trends. Precipitation type also contributes to seasonal differences in inorganic N stoichiometry. We suggest that as winters warm in response to climate change and more precipitation falls as rain in northern latitudes, the relative abundance of NH_4^+ may increase with implications for assimilation, nitrification, organic matter decomposition, and N_2O production. Furthermore, the observed DON enrichment in the U.S. and Europe may be correlated to climate change-induced increases in transpiration and decomposition. The role of organic N, snow, and shifting seasonality should be increasingly recognized as drivers of N deposition stoichiometry.

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Data availability The meteorological datasets leveraged in the current study are available from NOAA National Centers for Environmental Information repository, https://www.ncei.noaa.gov/access/search/index. The wet deposition chemistry datasets generated during the current study are not publicly available but can be requested from the University of New Hampshire Water Quality Analysis Lab.

Declarations

Competing interests The authors have not disclosed any competing interests.

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