JGR Biogeosciences

RESEARCH ARTICLE
10.1029/2024JG008403

Seasonal and Climatic Drivers of Wet Deposition Organic Matter at the Continental Scale

Desneiges S. Murray[1] and **Adam S. Wymore**[1]

[1]Department of Natural Resources and the Environment, University of New Hampshire, Durham, NH, USA

Key Points:

- Archived wet deposition samples from the US National Atmospheric Deposition Program are viable for hindcasting dissolved organic carbon (DOC) and dissolved organic nitrogen (DON)
- Highest concentrations of DOC and DON wet deposition correspond with the growing season in the northern hemisphere
- Climatic variables such as airmass range, air temperature, and precipitation seasonality explain variability in the spatial heterogeneity of Dissolved organic matter wet deposition

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

D. S. Murray,
desneiges.murray@unh.edu

Citation:

Murray, D. S., & Wymore, A. S. (2024). Seasonal and climatic drivers of wet deposition organic matter at the continental scale. *Journal of Geophysical Research: Biogeosciences*, *129*, e2024JG008403. https://doi.org/10.1029/2024JG008403

Received 6 AUG 2024
Accepted 17 OCT 2024

Author Contributions:

Conceptualization: Desneiges S. Murray, Adam S. Wymore
Data curation: Desneiges S. Murray
Formal analysis: Desneiges S. Murray
Funding acquisition: Desneiges S. Murray, Adam S. Wymore
Investigation: Desneiges S. Murray
Methodology: Desneiges S. Murray, Adam S. Wymore
Project administration: Desneiges S. Murray
Resources: Desneiges S. Murray, Adam S. Wymore
Software: Desneiges S. Murray
Supervision: Desneiges S. Murray, Adam S. Wymore
Validation: Desneiges S. Murray
Visualization: Desneiges S. Murray

Abstract Dissolved organic matter (DOM) concentrations and composition within wet deposition are rarely monitored despite contributing a large input of bioavailable dissolved organic carbon (DOC) and nitrogen (DON) to the Earth's surface. Lacking from the literature are spatially comprehensive assessments of simultaneous measurements of wet deposition DOC and DON chemistry and their dependencies on metrics of climate and environmental factors. Here, we use archived precipitation samples from the US National Atmospheric Deposition Program collected in 2017 to 2018 from 17 sites across six ecoregions to investigate variability in the concentration and composition of depositional DOM. We hypothesize metrics of DOM chemistry vary with ecoregion, season, large-scale climate drivers, and precipitation geographic source. Findings indicate differences in DOC and DON concentrations and loads among ecoregions. The highest wet deposition concentrations are from sites in the Northern Forests and lowest concentrations from sites in Marine West Coast Forests. Summer and autumn samples contained the highest DOC concentrations and DON concentrations that were consistently above detection limit, corresponding with seasonality of peak air temperatures and the phenology of the growing season in the northern hemisphere. Compositional trends suggest lighter DOM molecules in autumn and winter and heavier molecules in spring and summer. Climate drivers explain 51% of variation in DOM chemistry, revealing differing drivers on the concentrations and loads of DOC versus DON in wet deposition. This study highlights the necessity of incorporating DOC and DON measurements into national deposition monitoring networks to understand spatial and temporal feedbacks between climate change, atmospheric chemistry and landscape biogeochemistry.

Plain Language Summary Organic matter concentrations in wet deposition–or rain–are rarely reported, even though they contribute significantly to the dissolved organic matter (DOM) reaching the Earth's surface. We particularly lack insight into trends in the dissolved organic nitrogen (DON) portion of DOM. In this study, we examine how wet deposition DOM concentration, composition, and source change over time and across different regions. We hypothesize that the concentrations and composition of dissolved organic carbon (DOC) and DON in wet deposition will vary by region, show seasonal patterns, and be influenced by large-scale climate factors. To test these hypotheses, we use archived samples from the US National Atmospheric Deposition Program to analyze wet deposition DOM from samples collected in 2017 to 2018 across the U.S. Our results show that the concentrations of wet deposition DOM varied among regions, with most sites showing the highest values during the summer and fall seasons. Climate factors explained much of the variation in DOM wet deposition, but the carbon and nitrogen fraction of organic matter were related to different climate factors. Monitoring the exchange of organic matter between the atmosphere and the land surface provides valuable insights into the role of deposition in carbon and nitrogen cycles.

1. Introduction

Atmospheric wet deposition (e.g., precipitation) of organic carbon (C) and nitrogen (N) represents a critical proportion of bioavailable elements exchanged between the atmosphere and land surface. The composition of wet deposition is a function of landscape emissions, in-atmosphere chemical transformations, airmass transport, in and below cloud precipitation scavenging, and precipitation rate. Both natural and anthropogenic processes emit volatile organic compounds (VOCs) some of which contain N (N-VOCs). Processes that introduce organic C and N into the atmosphere include decomposition (Isidorov et al., 2010), pollen dispersal, tree leaf-out/senescence (Neff et al., 2002), biomass burning (Coggon et al., 2016), as well as anthropogenic practices such as agriculture (Cornell et al., 1995, 2001; Mace et al., 2003; Seitzinger & Sanders, 1999). Different emission sources of organic aerosols contain distinct types of organic functional groups, some of which can dissolve within precipitation directly via dissolution or indirectly via aerosol scavenging (Cape et al., 2011; Lee et al., 2022). The atmospheric

Writing – original draft: Desneiges S. Murray
Writing – review & editing: Desneiges S. Murray, Adam S. Wymore

residence time of (N)VOCs varies, depending on molecular weight and reactivity (Cape et al., 2012; Millet et al., 2004). Molecules may be transported to distant ecosystems via long-range airmasses, persisting in the atmosphere for weeks at a time, while others persist for only a few days, likely deposited to closer ecosystems via short-range airmasses.

Dissolved organic matter (DOM) within wet deposition represents a diverse and complex pool of molecules (Altieri et al., 2009, 2012; Gorzelska et al., 1992; Raymond, 2005). Concentrations and loads of dissolved organic carbon (DOC) are more commonly reported in deposition assessments relative to dissolved organic nitrogen (DON) (Iavorivska et al., 2016; Liptzin et al., 2022). Quantification of DON in wet deposition concurrently with DOC is important as it is a quantitatively significant fraction of wet deposition N contributing on average 30% and up to 92% of the total N load in precipitation (Cornell, 2011). Within the biosphere, DOC and DON fate and stoichiometry are not necessarily parallel (Brookshire et al., 2007; McDowell et al., 2004; Rodríguez-Cardona et al., 2022; Vanguelova et al., 2010; Verstraeten et al., 2016; Wymore et al., 2015) necessitating the specific quantification of DON. Wet deposition of DON contributes bioavailable compounds to terrestrial ecosystems (Scudlark et al., 1998; Seitzinger & Sanders, 1999; Vet et al., 2014) and can stimulate biologic uptake to the same extent as inorganic N (Mladenov et al., 2012; Russell et al., 1998; Violaki et al., 2010). DON can also serve as an energy or nutrient source in ecosystems driving an array of ecosystem and biogeochemical processes (Murray et al., 2023; Neff et al., 2002; Wymore et al., 2015).

While assessments on the spatial and decadal trends of depositional DOC and DON have been conducted independently (Cornell, 2011; Cornell et al., 2003; Jickells et al., 2013; Liptzin et al., 2022; Murray et al., 2022; Neff et al., 2002), spatially comprehensive data sets containing simultaneous measurements of both the C and N fraction of DOM in wet deposition are lacking. In the U.S., the National Atmospheric Deposition Program National Trends Network (NADP NTN) measures weekly wet deposition chemistry at 384 sites and has focused on quantifying dominant cation and anions in wet deposition (pH, conductivity, Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, NH_4^{+}, NO_3^{-}, Cl^{-}, SO_4^{2-}). This program was largely motivated by the impacts of acid rain and implementation of the U. S. Clean Air Act and equivalent policies in Europe such as the Directive on Ambient Air Quality Assessment and Management. Previous efforts quantifying the spatiotemporal variability of wet deposition have understandably focused on inorganic N due to the clear connection between anthropogenic emissions and ecosystem effects of inorganic N producing useful management guidelines such as ecosystem-specific nitrogen critical loads (CL; Aber et al., 1998; McDowell et al., 2004; Lovett & Goodale, 2011). Ecosystem CLs assess whether inputs of N via deposition exceed nutrient threshold tolerable to the ecosystem without adverse impacts (Kuylenstierna et al., 2001; Schulze et al., 1989). The calculation of ecoregion-specific CLs currently only considers inorganic N deposition (Pardo et al., 2011) due to the sparsity of monitoring DON. The lack of DOC and DON measurements were historically justified based on the assumption that organic molecules in wet deposition are sourced from short-range airmasses reflecting local background recycling processes, complemented by the analytical challenges and expense in measuring DON (Cornell, 2011; Cornell et al., 2003). In recent decades, however, studies have found the potential for long-range deposition of organic matter, and analytical resources have improved (Cape et al., 2011).

The few continuous published long-term records of wet deposition DOM indicate that both DOC and DON concentrations have increased over the last 2 decades while displaying distinct phenology (Benedict, Carrico, et al., 2013; Murray et al., 2022; Verstraeten et al., 2016). These observations evoke questions pertaining to the role these molecules play in terrestrial and aquatic biogeochemical cycles. Understanding the dynamics and drivers of wet deposition DOC and DON concentration, relative abundance, and molecular characteristics is important for understanding the full suite of deposition inputs into global ecosystems and their potential effects on surface water chemistry (e.g., Murray et al., 2023). Because wet deposition DOC and DON concentrations are rarely reported alongside one another, considerable gaps remain in understanding how long-term trends may be influenced by global climate change. It remains unknown, for example, how changes in ecosystem seasonality, airmass patterns, precipitation intensity, and air temperature may influence emissions and delivery of organic matter to the Earth's surface. Shifts in precipitation phase from snow to rain because of warming winters (Contosta et al., 2017) may also be a potential factor affecting the composition of wet deposition (Murray et al., 2022), with rain potentially favoring smaller, more labile DOM compounds (Lei & Wania, 2004; Mitra et al., 1990). Determining the relationship between wet deposition DOM concentration and composition and climate drivers is critical for interpreting the role of global climate change within the growing library of long-term trends on wet deposition chemistry (Du et al., 2024).

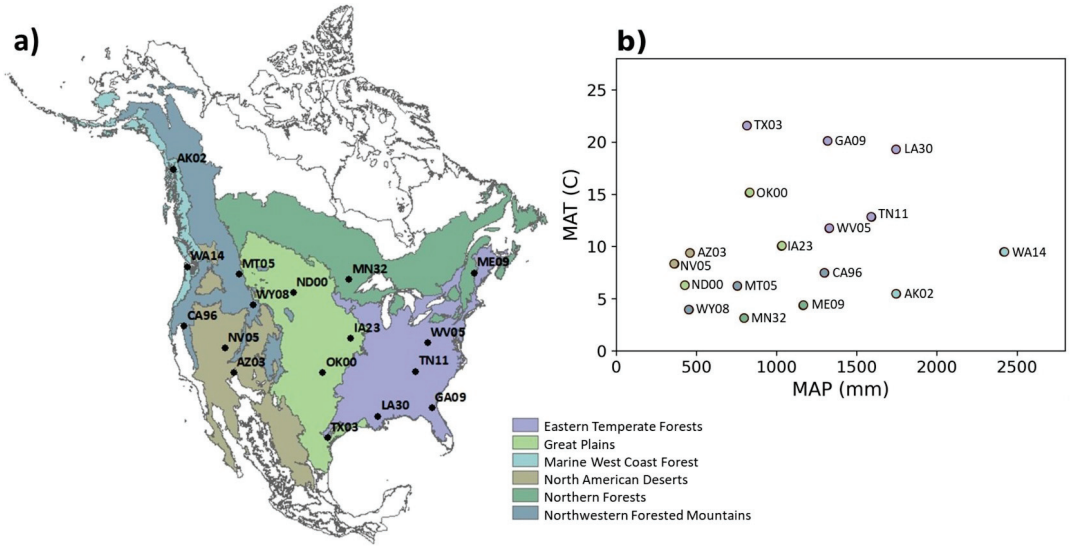

Figure 1. (a) Map of selected NADP study sites for archived sample analysis shown with level 1 EPA ecoregion boundaries and (b) the relationship between site-level mean annual precipitation (mm) and air temperature (°C) with site colors grouped by level 1 EPA ecoregion.

Here, we leverage archived samples collected from 17 NADP NTN sites across six North American ecoregions spanning 2 years. We use this data set to ask: what is the spatiotemporal variability in wet deposition DOM concentration, composition, and geographic source? We hypothesize that **(H1)** DOM wet deposition concentration, load, and composition will differ among ecoregions that represent a gradient of temperature and precipitation conditions; **(H2)** DOM wet deposition concentration, load, and composition will display seasonality, with values most different during warmer months due to heightened biogenic emissions during the northern hemisphere growing season correlated with higher air temperature; and **(H3)** short-range airmasses will be associated with higher DOM concentrations, and short- and long-range airmasses will differ in DOM composition. We also examine the relationship between climatic variables and DOM wet deposition chemistry using a multivariate redundancy analysis. Results from this study highlight whether, and at what scale, measurements of DOC and DON should be included in deposition monitoring networks and provides hypotheses for the abiotic and biotic controls on wet deposition DOM.

2. Materials and Methods

2.1. Site Selection

We used archived samples from 17 NADP NTN sites distributed across the continental U.S. (Figure 1) to hindcast DOM wet deposition concentration and composition. The subset of NADP NTN sites selected for this study were based on level 1 EPA ecoregions that represent a gradient of temperature and precipitation conditions (Figure 1), specifically Marine West Coast Forests (AK02, WA14), Northwestern Forested Mountains (MT05, WY08, CA96), North American Deserts (NV05, AZ03), Great Plains (ND00, IA23, OK00), Eastern Temperate Forests (TX03, LA30, GA09, TN11, WV05) and Northern Forests (MN32, ME09). Study sites were located within national or state parks, research stations, wildlife refuges, or U.S. Forest Service land. Sites were selected based on distance from a major city center (e.g., >50 miles from populations >10,000), and overlapping sampling dates within 1 January 2017, to 31 December 2018, with approximately one sample from each site per month in 2017 to 2018. Anomalous meteorological patterns, such as El Nino/La Nina, were classified as neutral during 2017 and 2018.

2.2. Wet Deposition Chemistry Analyses

2.2.1. Archived Sample Validation

Wet deposition samples were collected according to NADP standard operating procedures. Only samples with the highest NADP quality ranking were selected for this study. Filtered wet deposition samples were stored in HDPE

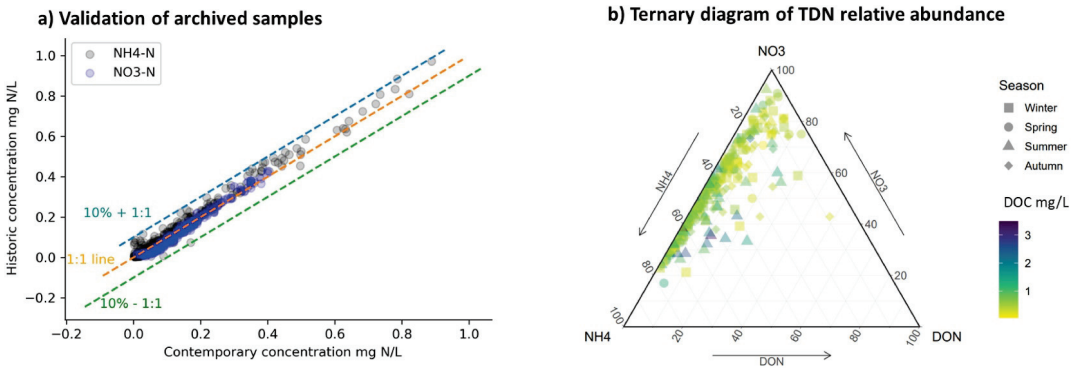

Figure 2. (a) Scatter plot between validated contemporary (i.e., measured at UNH WQAL). and historic (i.e., measured at NADP NTN lab at the University of Wisconsin) measurements of NH_4–N (black) and NO_3–N (blue) concentrations (mg N/L) ($n = 274$). The orange line is a 1:1 line, the blue and green lines are ±10% of the 1:1 line, respectively. Not shown are the 28 samples outside of the 1:1 ± 10% line which were excluded from statistical analyses; (b) Ternary diagram of relative abundance (%) of DON, NH_4, and NO_3 from all sites. Shapes represent the season during which each sample was collected with points colored by dissolved organic carbon concentration (mg/L).

bottles in a dark fridge held at 4°C at the NADP Central Analytical Laboratory (Madison, WI) until selected samples were overnight shipped in September 2022 to the University of New Hampshire Water Quality Analysis Lab (UNH WQAL) where they were immediately stored in a dark fridge held at 4°C until sample analyses in October 2022. Archived wet deposition samples are viable for reanalysis (Harvey, 2001; Nanus et al., 2018) because rain is generally nutrient dilute and absent of microbial activity, relative to surface waters for example, However, to test this assumption, we reanalyzed samples for NO_3^- and NH_4^+ to determine whether samples were viable for additional analyses of TDN, DOC, DON (by subtraction), and DOM spectral properties. The NADP NTN measures concentrations of NH_4^+ and NO_3^- using ion chromatography. For direct comparison we also measured these ions using automated ion colorimetry on a SmartChem 200 (NH_4^+ detection limit (DL) = 0.004 mg N/L and NO_3^- DL = 0.005 mg N/L). Measures of NO_3^- and NH_4^+ represent the atomic portion of N and are reported as NO_3–N and NH_4–N. We compared concentrations of NH_4^+ and NO_3^- measured at the UNH WQAL and to historical NADP measurements. We considered samples invalid and excluded them from the final data set if either NH_4^+ or NO_3^- contemporary concentrations had more than ±10% misalignment from the historic measurements. This threshold is used as an indicator for error in analytical chemistry QA/QC procedures at the UNH WQAL.

Inorganic N concentrations from archived samples showed strong agreement with contemporary measurements (Figure 2a), suggesting minimal to no deterioration of bioavailable N-containing compounds during sample storage. Out of the 298 archived samples analyzed, 8% (24 samples) were invalid, and were excluded from data analyses. For samples within the accepted 10% error range, NH_4^+ concentrations were overall lower and NO_3^- concentrations higher in contemporary measurements relative to historic concentrations (Figure 2a). No ecoregion- nor temporal-specific patterns were detected between historic and contemporary inorganic N concentrations.

2.2.2. DOM Analyses

Total dissolved N and DOC were analyzed using high-temperature catalytic oxidation on a Shimadzu TOC-LCSH with a TNM-1 Total Nitrogen Module (TDN DL = 0.05 mg N/L and DOC DL = 0.1 mg C/L). Concentrations of DON were determined as the difference between DL corrected TDN and dissolved inorganic nitrogen (DIN), where DIN is the sum of NO_3^-–N and NH_4^+–N. A DL 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^-–N, NH_4^+–N, and DON concentrations by TDN concentrations (as the sum of DL corrected DIN and DON concentrations; Figure 2b). Given our ability to recover DIN within 10% error (Figure 2a), our estimates of organic matter concentrations in the sampling bucket at the time of collection are representative of concentrations at the time of sample collection, however we recognize that values may be conservative based on some loss of DOM prior to sample collection (Walker et al., 2012). Loads of DOC and DON were calculated as

the product of DOC or DON concentration (mg/L) and the precipitation depth (mm) reported by NADP divided by the number of days within a sampling window, yielding units of load in mg per m^2 per day.

The composition of DOM wet deposition was assessed via optical properties and the molar stoichiometric ratio of DOC: DON was calculated for only those values where DON was above DL ($n = 39$). Ultraviolet (UV) absorbance of wet deposition samples was measured using a Thermo Genesys 150 UV-Vis Spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA) that scanned from 240 to 700 nm in 1-nm intervals. Log transformed absorption spectra in the ranges of 275–295 and 350–400 nm was fit nonlinearly to an exponential function to determine spectral slope (S) (Helms et al., 2008). Slope ratio (SR) was calculated as the ratio of slopes for the 275–295 and 350–400 nm ranges and is an indicator of DOM molecular weight (Helms et al., 2008). Slope ratio is negatively correlated to DOM molecular weight wherein a steeper SR slope is reflective of more low weight organic compounds while shallower slopes are heavier weight organic compounds. All contemporary measurements and historical NADP variables are available in the associated open-source data repository for this manuscript.

2.3. Spatial and Seasonal Scale Variability in DOM Wet Deposition

To test our first hypothesis, that DOM wet deposition concentration and load (DOC, DON) and composition (DOC: DON ratios, S_R) differ between ecoregions, we applied a linear mixed effects analysis of variance (ANOVA) using a random intercept approach. The model was implemented with ecoregion as a fixed effect and site as a random effect because multiple sites are nested within an ecoregion (Figure 1). Modeling was conducted in RStudio using the *lmerTest* and *multcomp* packages. If the overall ANOVA was significant (e.g., F-value >0.05), a Tukey HSD post-hoc test was employed to test specific differences between ecoregions and DOM variables. Post-hoc *p*-values were adjusted using the Holm method and significance was determined at the 0.05 alpha level. DOC and DON concentrations, DOC: DON and S_R were $\log_{10}$ transformed prior to analyses (Isles, 2020).

To test our second hypothesis, that DOM wet deposition concentrations, loads, and composition display seasonality, we used a nonparametric Kruskal-Wallis (KW) test between DOM wet deposition variables and month. A Dunn post-hoc test was used to determine differences between our response variables by month with significance determined at the 0.05 level and *p*-values transformed using the Holm method. Analyses were performed in RStudio using the FSA and stats package. Quantifying overall and site-specific seasonality of wet deposition DOM allows for understanding how trends at the local scale reflect trends at the continental scale. Site-level KW and post-hoc tests were also conducted on a seasonal scale (i.e., differences in values of DOM wet deposition between samples collected in winter, spring, summer, and autumn). Molar ratios of DOC: DON were not included in the site-level KW test due to lack of representation of valid data (i.e., DON concentrations > DL) occurring in all seasons across sites.

2.4. Climate Drivers of Wet Deposition DOM

To analyze the relationship between climatic drivers and DOM wet deposition, we performed a multivariate redundancy analysis (RDA; Legendre & Legendre, 1998) in RStudio using the vegan package (Jari Oksanen et al., 2018). Redundancy analysis allows for constraining not only the strength of explanatory variables with the canonical axes, indicated by the length of vectors, but also the correlation between explanatory and response variables, which are indicated by the direction and angles between these respective vectors (Legendre & Legendre, 1998). Response variables included $\log_{10}$ transformed site means of DOC and DON concentrations and loads, DOC: DON molar ratio, and S_R. Site TN11 was excluded from the analysis due to missing data needed to complete the matrix. Explanatory variables included the predominant cardinal direction of airmasses arriving to a site, frequency of samples derived from short-range or long-range airmasses, frequency of the type of precipitation (e.g., rain or snow) in deposition samples, precipitation seasonality index, site mean annual temperature (MAT) and precipitation (MAP). Derivation of predictor variables are described in detail below.

2.4.1. Modeling Airmass Backtrajectories and Directionality

Airmasses are the vector by which emissions of chemicals and aerosols are distributed to other systems and are therefore a proxy measurement for attributing the spatial trajectory of landscape emission sources to wet deposition chemistry. We used a "top down" approach to provide a general sense of the distance and cardinal

direction of precipitation-carrying airmasses arriving to a given site during our study period (Cape et al., 2011). Daily backward trajectory of airmasses to each NADP site was calculated using the NOAA HYSPLIT model version 5.2.1 (Draxler, 1999; Draxler & Hess, 1997, 1998; Stein et al., 2015). For each site, trajectories with a 24-hr run time were computed from 1 January 2017, to 31 December 2018, using the archived data from the Global Data Assimilation System (GDAS) meteorological data set at 1-degree resolution. The model output is a pair of latitude and longitude coordinates (e.g., X, Y) for each hour across the 24-hr period. The series of paired X and Y coordinates originate (i.e., hour −24) at the beginning of the airmass trajectory and terminate (i.e., hour 0) at the study site location.

For all subsequent analyses, we selected only those airmasses that contributed precipitation during a wet deposition sampling window (defined from sample deployment to collection). Detection of daily precipitation presence or absence was conducted using the Daymet Daily Surface Weather Data on a 1-km Grid for North America, Version 4 R1 (Thornton et al., 2022) accessed via the Python daymetpy package (version 1.0.0). Daily precipitation values were downloaded for the cell corresponding to the latitude and longitude of the study site. We then assigned a daily airmass as containing precipitation if the corresponding precipitation value accessed from Daymet was greater than zero.

To determine the predominant cardinal direction of airmasses arriving at a given site, we input the precipitation-containing 24-hr backtrajectories into the cluster analysis option in the HYSPLIT model. This analysis determines the mean path of dominant groups of airmasses, which allows for assigning common patterns of airmass delivery. The number of clusters chosen by the HYSPLIT model is based on the maximum reduction in total spatial variance and the output allows for each daily airmass backtrajectory input to be assigned a cluster value. We determined the predominant airmass direction as the cluster with the highest percentage of daily precipitating trajectories classified under a cluster value (Figure S1 in Supporting Information S1). The bearing of the predominant cluster trajectory at each NADP site was calculated using the Haversine formula and subsequently assigned a cardinal or intercardinal direction (e.g., north, south, east, west, northwest etc.). We visually assessed the geographic source of the predominant airmass cluster and directionality relative to each site.

To assign the frequency of wet deposition derived from short-range or long-range airmasses, we classified each precipitation-containing airmass backtrajectory as short-range (e.g., origin of airmass < 100 km from study site; Aliaga et al., 2021) or long-range (origin of airmass > 100 km from study site). Most weekly deposition samples correspond to more than one daily precipitation event; therefore each observation of wet deposition was categorized as being sourced from short-range airmasses, long-range airmasses, or a combination of short-and-long-range airmasses.

To test our third hypothesis, we subset the data by site and calculated the mean of DOC and DON concentrations and the slope ratio for each airmass category (i.e., short, long, or combination of short-and-long) which were used to calculate the ratio between the short and long airmass categories (e.g., $\mu[DOM]_{short}$: $\mu[DOM]_{long}$). If the ratio is greater than 1, the site has on average greater DOM values in short-range airmasses, and if the ratio is less than 1 the site has on average greater DOM values in long-range airmasses. Seven out of 17 sites contained samples only sourced from long-range or only sourced from short-range airmasses in combination with the mixed bin of short- and long-range airmasses, which prevented us from calculating the short: long ratio for these sites.

2.4.2. Precipitation Phase

Precipitation phase can influence the concentration and composition of C and N in deposition (e.g., Murray et al., 2022) because of the greater capacity of snow particles to scavenge heavier molecules due to increased surface area relative to rain (Lei & Wania, 2004; Mitra et al., 1990). To determine how precipitation phase of our archived samples influences organic matter in wet deposition, we hindcasted the frequency of whether samples are sourced from rain, snow, or mixed precipitation at a given site. Daily air temperature values were downloaded for the cell corresponding to the latitude and longitude of the study site from Daymet. For each deposition collection window, we hindcasted the proportion of precipitation in the sampling bucket sourced from rain, snow, or a combination of rain and snow (e.g., 100% Rain, Mixed, and 100% Snow). We applied a site-specific surface air temperature threshold to define whether daily precipitation fell as rain or snow. This temperature threshold is the 50% rain-snow threshold for the region (cell size = 50 km^2) 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).

Table 1
Response and Predictor Variables Used in the RDA Analysis

Ecoregion	Site	DOC mg/L	DOC mg m-^{2}d^{-1}	DON mg/L	DON mg m-^{2}d^{-1}	DOC: DON	S_R	Elevation (m)	Seasonality index	MAP (mm)	MAT (ºC)	Dominant precipitation airmass direction	Frequency of airmass range (%)	Frequency of precipit-ation phase (%)
Marine West Coast Forest	AK02	0.37	1.94	0.006	0.03	30.8	2.9	25	0.22	1,746	5.5	S		
	WA14	0.52	3.78	0.008	0.05	45.0	2.3	182	0.40	2,416	9.5	SW		
Northwestern Forested Mountains	CA96	0.42	2.55	0.007	0.07	15.5	2.4	1,754	0.48	622	7.5	S		
	MT05	0.95	2.31	0.01	0.02	57.4	2.2	964	0.09	754	6.2	S		
	WY08	0.65	1.95	0.01	0.02	37.2	1.9	1,912	0.08	454	3.9	W		
North American Deserts	NV05	1.02	2.59	0.009	0.02	72.7	2.2	2,066	0.08	363	8.3	NW		
	AZ03	0.69	1.69	0.005	0.01	73.4	1.7	2,071	0.11	460	9.4	SW		
Great Plains	ND00	0.98	2.63	0.01	0.02	59.2	2.6	863	0.42	427	6.3	S		
	OK00	0.74	4.32	0.008	0.04	22.5	1.6	344	0.26	829	15.2	S		
	IA23	0.84	3.95	0.007	0.04	61.7	1.8	320	0.32	1,030	10.0	S		
Eastern Temperate Forests	TX03	0.48	1.97	0.007	0.05	30.4	1.6	82	0.14	815	21.6	SE		
	LA30	0.71	4.00	0.009	0.06	42.6	1.9	77	0.06	1,743	19.3	SW		
	GA09	0.83	3.54	0.01	0.05	54.9	1.3	45	0.18	1,316	20.1	SW		
	WV05	0.74	2.90	0.006	0.02	44.8	2.4	210	0.09	1,328	11.7	SW		
Northern Forests	MN32	0.99	2.79	0.02	0.03	32.1	2.2	421	0.34	797	3.1	S		
	ME09	0.82	2.65	0.02	0.05	37.7	2.1	322	0.09	1,164	4.4	S		

Note. MIXED RANGE, SHORT RANGE, LONG RANGE; MIXED, RAIN, SNOW

2.4.3. Precipitation Seasonality and Mean Annual Temperature and Precipitation

Wet deposition fluxes depend on meteorological conditions (Benedict, Carrico, et al., 2013). For example, precipitation seasonality, MAT, and MAP all reflect the climatic and meteorological positioning of a given site. To determine how these variables influence organic matter in wet deposition, we used Daymet values of air temperature and precipitation volume to calculate the long-term (1980–2019) MAT and MAP for each site. We also calculated a long-term precipitation seasonality index (SI), which expresses the degree to which precipitation is concentrated in time, for each site using daily Daymet precipitation values from 1980 to 2019, following Markham (1970). Values range from 0.06 to 0.5 (Table 1). Sites that are a-seasonal with respect to precipitation have a lower SI while sites that are highly seasonal in precipitation frequency will display a higher number.

3. Results

3.1. Ecoregion Variability in DOM Wet Deposition

As hypothesized, wet deposition DOM concentration and load differed among ecoregions (Figure 3). Dissolved organic C concentrations were nearly twice as low in the Marine West Coast Forest ecoregion ($\mu = 0.4$ mg C/L) compared to Eastern Temperate Forests ($\mu = 0.8$ mg C/L; $p < 0.001$), Great Plains ($\mu = 0.8$ mg C/L; $p < 0.001$), and Northern Forests ($\mu = 0.9$ mg C/L; $p = 0.002$). The highest DOC and DON concentrations occurred in the Northern Forests (Figure 3). Dissolved organic N concentrations were nearly 3-fold lower in the North American Deserts ecoregion ($\mu = 0.007$ mg N/L) and the Great Plains (0.008 mg N/L) compared to the Northern Forests ($\mu = 0.02$ mg N/L; $p = 0.05$). Loads of wet deposition DOC did not necessarily correspond to patterns of DOC concentrations (Figure 3). For example, while DOC concentrations were relatively high at sites in the North American Desert, DOC loads ($\mu = 14$ mg C/m^2) were on average nearly half of the highest DOC loads occurring at sites in the Eastern Temperate Forests ($\mu = 25$ mg C/m^2; $p = 0.01$) and Great Plains ($\mu = 26$ mg C/m^2; $p = 0.001$). Similarly, DON loads at sites within the North American Deserts ($\mu = 0.1$ mg N/m^2) were a third lower than the highest DON loads found at sites within the Northern Forests ($\mu = 0.3$ mg N/m^2; $p = 0.04$), Eastern Temperate Forests ($\mu = 0.3$ mg N/m^2; $p = 0.007$), and Marine West Coast Forests ($\mu = 0.3$ mg N/m^2; $p = 0.006$). Some sites showed mirroring trends for both DOC and DON loads and concentrations, such as the Great Plains, which displayed high DOC concentrations and load (Figure 3). Sites within the Great Plains receive a relatively low amount of annual precipitation (427–1000 mm) compared to the other ecoregions considered (Figure 1c; Table 1) yet still reflect significantly high DOC loads (Figure 3). No significant differences in DOM composition (DOC: DON or S_R) were detected at the ecoregion level (Figure 3).

3.2. Seasonality of DOM Wet Deposition

Consistent with our hypothesis, we found significant differences in pair-wise comparisons among months for DOC and DON wet deposition concentrations, loads, and S_R ($p < 0.001$), corresponding with trends of daily average air temperature (Figure 4). Across all sites, peak daily mean air temperature occurred during June, July, and August (Figure 4). Similarly, DOC concentrations in July and August were significantly higher compared to concentrations in months from October to April ($p < 0.01$). Monthly pair-wise comparisons for DOC concentrations also showed significantly higher values in May, June, and September, compared to January, February, and March ($p < 0.01$), with a generally increasing trend from April to September and decreasing trend from August to December (Figure 4a). Loads of DOC (mg C/m^2) were significantly higher in June, July, and August as compared to loads occurring during months from January to April (Figure 4c). Distinct seasonality in DOC wet deposition was also reflected in the site-level KW tests (Figure S2 in Supporting Information S1). Specifically, DOC concentrations at MN32, ME09, AZ03, WV05, and GA09 had significantly ($p = 0.005$–0.03) lower DOC concentrations in the winter (0.3–0.5 mg C/L) as compared to summer (1.2–1.5 mg C/L). However, DOC loads were only significantly different between winter and summer for site MN32 ($p = 0.03$).

Wet deposition DON concentrations were generally low at many sites, with many values at DL, except during the summer and autumn seasons (Figure 5). Dissolved organic N concentrations were highest in August compared to most other months except July, September, November, and December ($p < 0.001$–0.03). Concentrations of DON in wet deposition progressively increased from June to August (Figure 4b) with concentrations five-fold greater in August, matching increases in daily average temperature (Figure 4). Loads (mg N/m^2) and concentrations (mg/L) of DON wet deposition were significantly lower ($p = 0.02$) in September than the highest concentrations and loads observed in August (Figure 4d) likely due to the low precipitation all sites experienced during September 2017 and 2018. No site-level seasonality was observed for DON concentrations, however, DON loads at WY08 were significantly higher ($p = 0.03$) in summer compared to autumn (Figure S2 in Supporting Information S1). Only one site in winter (ME09), and five sites in spring, (MN32, AK02, IA23, OK00, TX03) had 20%–40% of samples above the DON DL (Figure 5). In contrast, 12 sites in summer (DON concentrations ranged from 0.006 to 0.08 mg/L), and eight sites in autumn, had 20%–80% of samples above the DON DL (Figure 5).

Metrics of DOM composition also varied seasonally. Ratios of DOC: DON displayed a similar trend to DOC concentrations (Figure 4e). Peak DOC: DON ratios (e.g., relatively enriched in DOC) corresponded to peak daily temperature in July (Figure 4e), however monthly pairwise comparisons were not significant. At the site level, no significant seasonality trends were detected for S_R. Across all sites, S_R had significantly shallower slopes in June compared to the steeper spectral slopes detected in January ($p < 0.02$), October ($p < 0.01$), and November

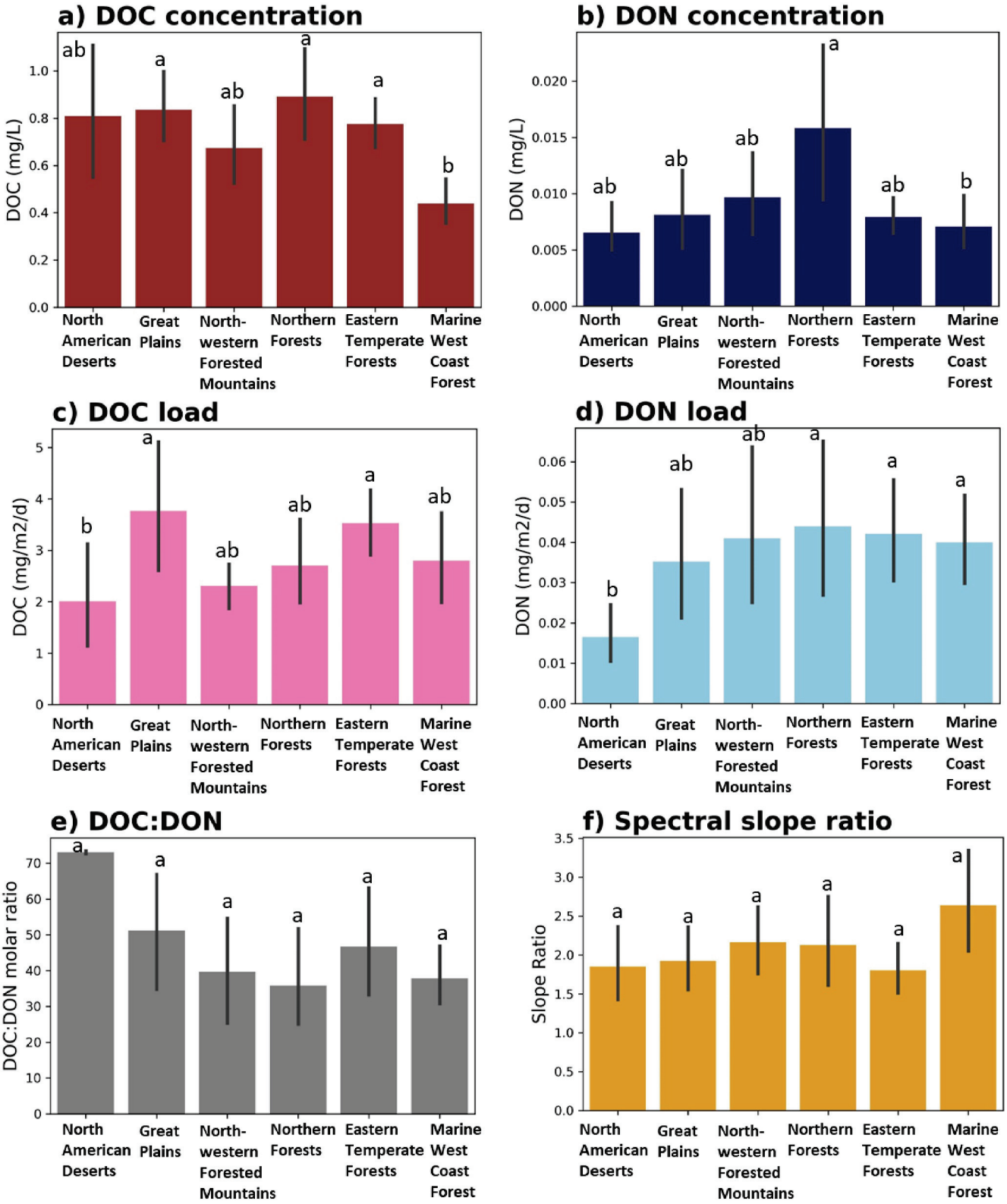

Figure 3. Bar plots of mean (±1SE) (a) DOC concentrations, (b) DON concentrations, (c) DOC load, (d) DON load, (e) DOC: DON molar ratio, and (f) slope ratio (S_R). Statistical significance among ecoregions is noted with letters.

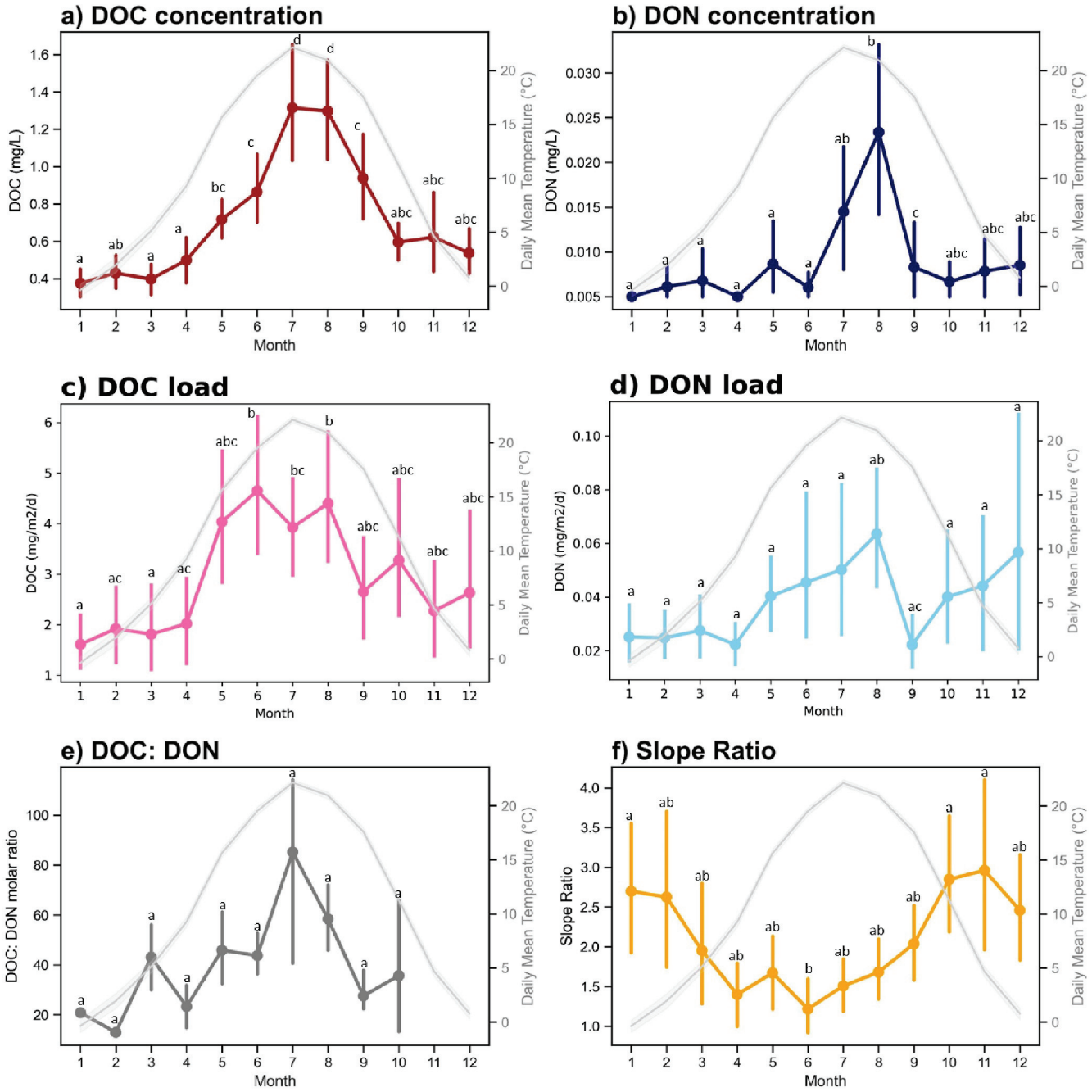

Figure 4. Monthly mean ±1 SE of (a) DOC concentration, (b) DON concentration, (c) **DOC loads;** (d) **DON load,** (e) DOC: DON molar ratio, and (f) spectral slope ratio, across 2017 and 2018 for all sites. The gray line represents the daily mean air temperature in a given month. Statistical significance of monthly pairwise comparisons are noted with letters. Missing data from months 11 to 12 in panel e reflects no valid data for DOC: DON (e.g., all DON values below DL).

($p < 0.03$), indicating the DOM deposition pool is comprised of lighter molecules when DOC concentrations are lowest (Figure 4f). Across all sites, DOC and DON concentrations were positively correlated (Pearson's $R = 0.64$; $p < 0.05$) while DOC and S_R were negatively correlated (Pearson's $R = -0.23$; $p < 0.05$).

3.3. Climate Drivers of DOM Wet Deposition

Results from the redundancy analysis indicate that metrics of climate variability are correlated with wet deposition DOM chemistry and composition (Figure 6). Climate drivers explained 51% of the variation in deposition DOC and DON concentrations and load, DOC: DON ratio, and S_R. The first redundancy axis (RDA1) explained

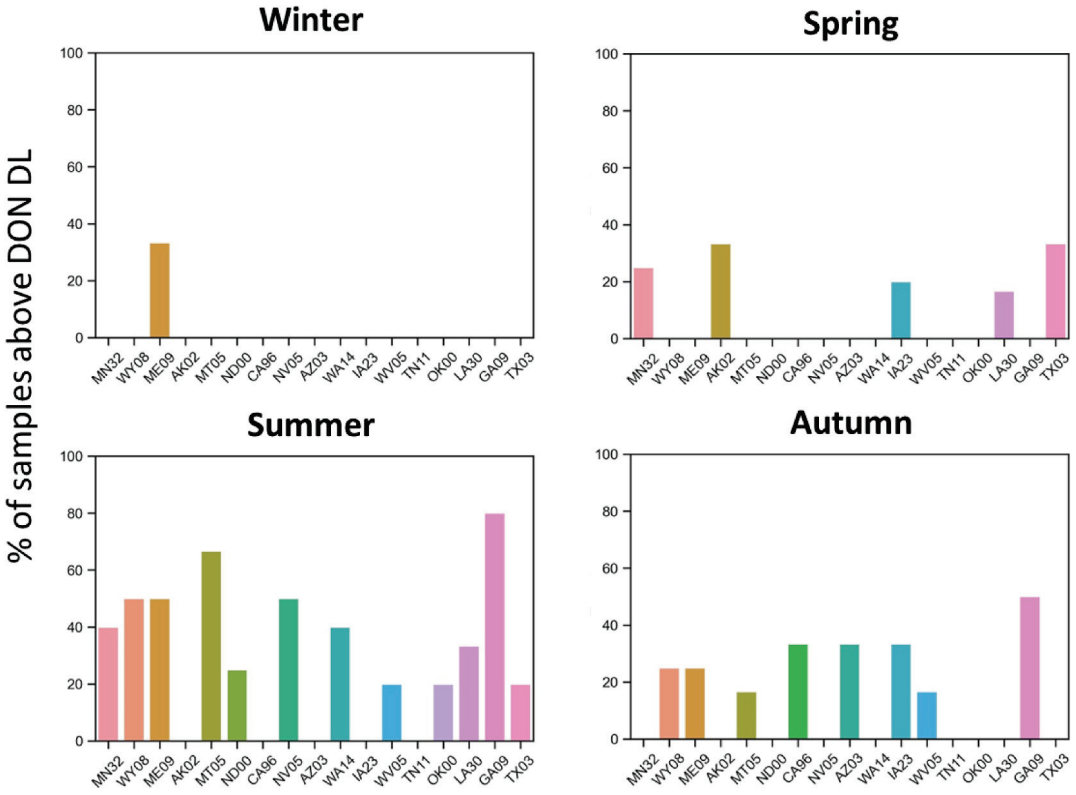

Figure 5. The percent of samples from each site with DON wet deposition concentrations above the detection limit (DL) in winter, spring, summer, and autumn.

32% of the variation in response variables, with frequency of shortrange airmasses and snow precipitation phase highly positively correlated, and MAP, MAT, rain precipitation phase, and precipitation seasonality index highly negatively correlated (Figure 6). The second redundancy axis (RDA2) explained 19% of the variation in response variables, with predominant airmass direction from the SE and SW (respective to each site) highly positively correlated, and MAT and the frequency of long-range airmasses negatively correlated (Figure 6). Mean annual temperature is equally negatively weighted on both RDA1 and 2. The vector representing the frequency of a site receiving long-range airmasses is the longest, displaying strong explanatory power of DOM wet deposition (Figure 6). Airmass directionalities were mostly distributed along the zero line for RDA1, with short vector lengths, indicating their relatively low power in explaining variability in DOM variables (Figure 6).

Results suggest the C and N fraction of DOM deposition may be influenced by different climate drivers. Except for S_R, all other DOM deposition variables were negatively correlated with RDA2 (Figure 6). Concentrations of DOC, DOC: DON, and S_R were positively correlated with RDA1 while DOC load, DON load, and DON concentration were negatively correlated to RDA1 (Figure 6). Vectors representing DOC loads and DON concentration plotted closely together and showed a tight positive association with MAT across the first axis and tight negative association with frequency of short-range airmasses (Figure 6), however the vector length for DON concentration is relatively small. The S_R vector was negatively correlated with the frequency of long-range airmasses and weakly positively correlated with the predominant airmass direction from the W (Figure 6). Vectors for concentrations of DOC and the DOC: DON ratio plotted near one another and were negatively correlated with precipitation seasonality index and MAP across the second axis (Figure 6), indicating that lower concentrations of DOC are associated with high MAP values that are also highly seasonal. Loads of DON plotted close to zero along the first axis and were negatively correlated with snow precipitation phase along the second axis (Figure 6). Some sites within ecoregions plotted together along the axes (e.g., sites within the Northwestern Forested Mountains), however no strong grouping patterns were apparent.

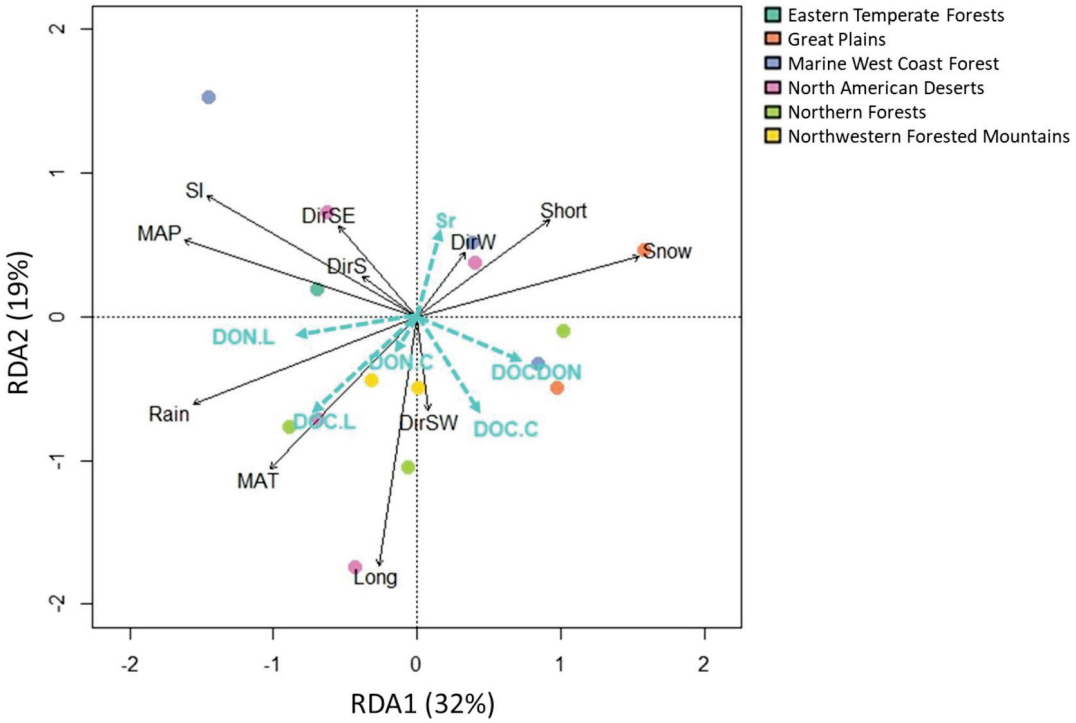

Figure 6. Redundancy analysis of selected explanatory variables: MAT, MAP, precipitation seasonality index (SI), predominant cardinal direction of airmasses (DirX), frequency of short-range or long-range airmasses, and frequency of precipitation phase for site means of dissolved organic carbon and dissolved organic nitrogen (DON) concentrations (DOX.C) and loads (DOX.L), DOC: DON molar ratio (DOC, DON), and spectral slope (Sr). Points are colored by ecoregion. The length of explanatory vectors (solid black) indicates strength of the relationship with the canonical axes. The angles between response (dashed turquoise) and explanatory vectors indicate their correlation and the direction of the explanatory arrows relative to the response arrows indicate the direction of correlation (Legendre & Legendre, 1998).

3.4. Role of Airmass Range

Coastal sites received precipitation predominantly from marine sources, specifically, the Pacific Ocean for AK02, WA14 and CA96, the Gulf of Mexico for TX03, LA30, and GA09, and the Atlantic Ocean for ME09 (Table 1; Figure S1 in Supporting Information S1). All but two sites, MN32 and NV05, received most precipitation from airmasses arriving from within the same ecoregion as the site (Table 1; Figure S1 in Supporting Information S1). In contrast, MN32 in the Northern Forests received 36% of airmasses (predominantly long-range) from the S corresponding to the Eastern Temperate Forests ecoregion, and NV05 in the North America Deserts received 60% of airmasses (predominantly long-range) from the NW corresponding to the Northwestern Forested Mountains ecoregion (Table 1; Figure S1 in Supporting Information S1).

Contrary to our hypotheses, we found that wet deposition DOM was predominantly sourced from long-range airmasses, and two sites (ND00 and IA23) had DOM sourced exclusively from long-range airmasses (Table 1; Figure 6). While no site was dominated by short-range airmasses (Table 1), most sites had higher DOC concentrations associated with short-range airmasses, consistent with our hypothesis. Contrary to our hypothesis, half the sites (AK02, CA96, AZ03, TN11) contained higher DON concentrations in samples from long-range airmasses compared to samples arriving from short-range airmasses. The majority of sites had $\mu[S_R]_{short}$: $\mu[S_R]_{long}$ ratios below one indicating lighter weight (i.e., steeper slopes) organic matter in deposition was associated with samples from long-range airmasses (Figure 7). No apparent seasonality was detected in the frequency of a given site receiving short- or long-range airmasses.

4. Discussion

Results from this study inform on the spatiotemporal variability of organic matter in wet deposition, with implications for constraining the role of atmosphere-terrestrial exchanges in C and N biogeochemical cycles.

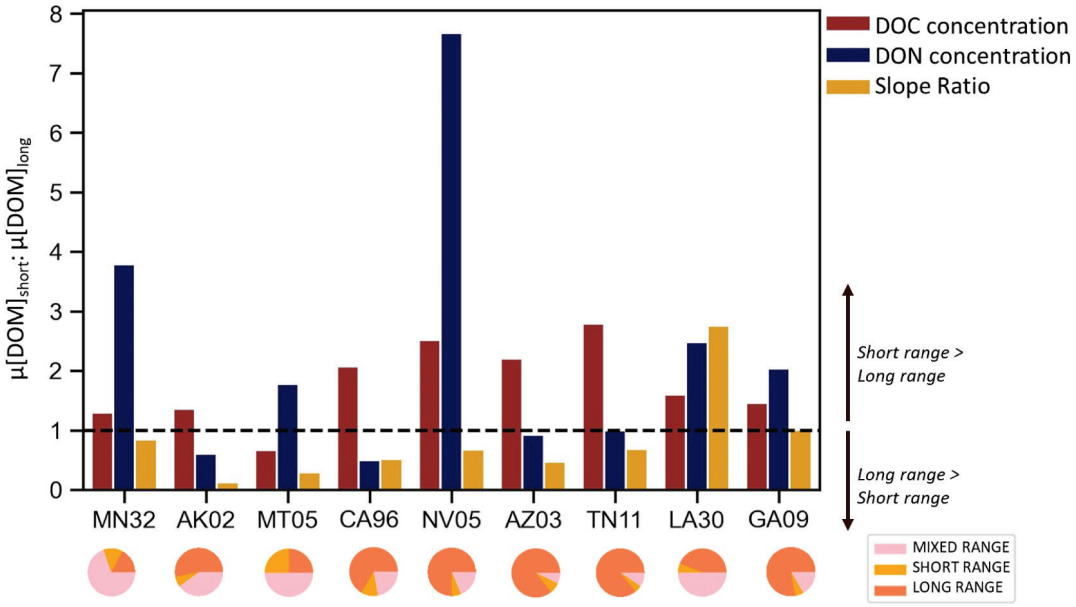

Figure 7. Ratio of mean volume-weighted concentrations of wet deposition dissolved organic carbon (red), dissolved organic nitrogen (blue) concentrations, and spectral slope ratio (yellow) between short-range and long-range airmasses for a given site ordered by MAT. Values above the black dashed line (e.g., >1) indicate the Dissolved organic matter (DOM) deposition metric is greater when sourced from short-range airmasses while values below the black dashed line (e.g., <1) indicate the DOM chemistry metric is greater when sourced from long-range airmasses, the frequency of which is indicated by the pie charts.

Concentrations of wet deposition DOC in this study (0.05–3.5 mg C/L) are on par with global average lake concentrations (Toming et al., 2020) and similar to the lower range of global stream and river concentrations (Kronholm & Capel, 2012; Wymore et al., 2021). The magnitude of DOM wet deposition, coupled with its distinct seasonal and spatial variability, are important to consider for biogeochemical models (e.g., PnET-BGC) that include wet deposition inputs (e.g., Benedict, Chen, et al., 2013; Boyer et al., 2002; Cambell et al., 2000; Gbondo-Tugbawa et al., 2001). Results suggest inputs of organic matter through deposition are not fixed through time and space. For example, the concentrations of DOM in wet deposition within the Northern Forests ecoregion were twice those in the Marine West Coast Forests. Increased concentrations and loads of DOM in wet deposition during warmer months indicate that current gridded annual estimates of wet deposition DOC (e.g., NADP TDep) may not reflect the strong seasonal variability of organic matter deposition.

Analyzing both the C and N fraction of organic matter in wet deposition revealed variability across ecoregions and the distinct influences of climate drivers. Although DON and DOC represent two ways to measure the same pool of DOM, they showed different ecoregional patterns. Many hypotheses regarding the drivers of DOM wet deposition have been proposed (Cape et al., 2001, 2011; Cornell, 2011; Murray et al., 2022; Neff et al., 2002), but few studies have directly tested relationships between abiotic processes and DOM chemistry. Our results show the spatial heterogeneity of DOM concentrations is somewhat predicted by climatic variables such as air temperature, MAP, precipitation seasonality, and precipitation phase. These relationships may allow for the development of hypotheses regarding the role of climate change to influence inputs of DOM via deposition. With the general observation that winter months are warming across the northern latitudes (Burakowski et al., 2022), we can expect changes in the chemistry of DOM at the seasonal scale. For example, wet deposition in winter months had generally lower weight organic matter and lower concentrations and loads; the frequency of winter precipitation phase (i.e., snow) negatively influenced DOC concentrations and DON loads. These results are in line with previous research that found rain collected smaller organic compounds compared to snow (Lei & Wania, 2004).

The phenology of multiple biological processes impacts wet deposition of both C and N (Cape et al., 2011; Jordon et al., 1995; Kieber et al., 2005; Mitra et al., 2013; Seaton et al., 2013). Concentrations and loads of DOC and DON in wet deposition display strong seasonality correlating with the growing season in the northern hemisphere. Because wet deposition concentrations and loads of DOC were at background levels (e.g., 0.3–0.7 mg/L) and DON below

detection limit for months outside summer, we interpret the controls on DOC and DON in wet deposition as binary, "turning on" in the spring and summer months and "turning off" in autumn and winter months (Murray et al., 2022). Biotic processes such as seasonal transpiration (Nguyen et al., 2011; Sharkey et al., 2007), biogenic VOC emission (Sindelarova et al., 2014), forest fires (Sricharoenvech et al., 2024) and decomposition (Isidorov et al., 2010) align with the seasonality detected in wet deposition DOM (Paulot et al., 2011; Zamora et al., 2011). It is important to connect seasonal trends of wet deposition organic chemistry with patterns of organic gaseous emissions because VOCs, when combined with atmospheric nitrogen oxides (NO_x), can produce tropospheric ozone (O_3), a regulated air pollutant (Jacob, 1999; Seinfeld & Pandis, 2012). Organic gaseous emissions directly from wildfires, or indirectly via isoprene emissions during plant transpiration are likely to exhibit increased variability with climate change (Contosta et al., 2017; Green et al., 2021; Harrison et al., 2020; Mansoor et al., 2022), which may impact background levels of organic matter emissions from landscapes (Schurman et al., 2015). Many questions remain regarding the impacts of climate change on biological processes, emissions and aerosol composition, and how these interactions translate to DOM wet deposition and subsequent ecosystem effects (Benedict et al., 2018).

Our results suggest that precipitation-carrying airmasses represent a vector for water and organic solutes to cross continental-to-ecosystem scale boundaries. It was historically assumed that DOM in wet deposition was sourced from short-range airmasses and local recycling processes (Cape et al., 2011; Cornell, 2011; Cornell et al., 2003). Pairing wet deposition chemistry with airmass backtrajectories allows for a direct test of this assumption. In contrast to our hypothesis, we found that atmospheric organic C and N is subject to long-range transport (Cornell et al., 1995, 2001; Matsumoto et al., 2018; Zamora et al., 2011). For about half of the sites, airmasses delivered precipitation sourced from a different ecosystem than the site, specifically coastal sites received precipitation from marine sources and MN32 to NV05 received precipitation from long-range airmasses from neighboring ecosystems. These results support previous findings that both marine and terrestrial environments emit VOCs that can be transported by long-range airmasses and eventually deposited via precipitation (Cornell, 2011). The relative role of short-range airmasses in transporting organic matter, however, appears to be site specific. While DOC and DON concentrations were often highest in short-range airmasses (88% and 55% of sites, respectively), no site was dominated by wet deposition sourced from short-range airmasses. Short-range airmasses are most frequent in sites within the Northwestern Forested Mountains, specifically, MT05 and WY08. This may indicate that wet deposition at these sites reflect local background recycling processes which are influenced by land use in the surrounding landscape (i.e., grasslands and crops in MT and WY; Nickerson et al., 2011). Attributing wet deposition chemical signals from a given airmasses to specific landscape sources is challenging because weekly deposition samples often capture multiple precipitation events, making it impossible to separate the chemical contributions of each event. Future studies that collect daily or event-scale samples would be well suited for detailed airmass source apportionment which could directly constrain the landscape (N)VOC emissions a given airmass accumulates as it travels from one ecosystem to another (e.g., Seaton et al., 2013).

The legacy of long-term monitoring of wet deposition chemistry originated out of efforts to understand the ecosystem impacts of acid rain (e.g., H_2SO_4 and HNO_3). Foundational studies focused on how the inorganic N and sulfate chemistry of wet deposition interacts with soil cation exchange capacity to cause ecosystem N saturation, C retention, and the acidification of freshwaters (Aber et al., 1998, 2003; Brookshire et al., 2007; Frey et al., 2014; Magill et al., 2000; McDowell et al., 2004; Oulehle et al., 2008). However, as the concentrations of NO_3^- and S have declined in precipitation, the source of H^+ ions has shifted toward organic acids (Feng et al., 2021; Lawrence et al., 2023; Vet et al., 2014). The implications for increased loading of organic acids via DOC wet deposition remains unclear. Much of the knowledge regarding the ecosystem impacts from wet deposition is framed within the concept of critical load's (CL), which assesses whether the deposition of a particular element in a given area exceeds the threshold that the ecosystem can tolerate without adverse impacts (Kuylenstierna et al., 2001; Schulze et al., 1989).

The calculation of ecoregion-specific CLs does not currently consider organic N deposition (Pardo et al., 2011). Critical loads of N are thresholds that indicate the maximum N input before adverse effects on different organisms such as lichens, herbaceous species, and trees, are observed (Kuylenstierna et al., 2001; Schulze et al., 1989). These adverse effects of excess N loading via wet deposition include N saturation, which occurs when the rate of N additions exceed rates of N removal via incorporation into biomass or soil (Lovett & Goodale, 2011). Including DON in critical load models is important because many organisms can directly assimilate DON at the same rate or higher than DIN in both marine and terrestrial environments (Antia et al., 1991; Dahlman et al., 2004; Paerl et al., 1999; Peierls & Paerl, 1997; Seitzinger & Sanders, 1999). Thus, incorporating depositional DON

concentrations in ecoregion-specific wet deposition CL calculations (e.g., Figures 4 and 5) could result in some regions exceeding their minimum CLs for longer than estimated (Benedict, Carrico, et al., 2013; Cape et al., 2011; Mladenov et al., 2012). To demonstrate this potential effect, we performed a conservative post-hoc estimate of how annual N deposition loads would change if the organic fraction of TDN loads were included. Assuming the site-specific DIN and DON loads reported here sufficiently represent TDN fluxes to landscapes within each studied ecoregion, the inclusion of DON would push sites within the Northern Forests and Eastern Temperate Forests ecoregions past their minimum CL (3 and 4 kg N ha^{-1} yr^{-1}, respectively, from Pardo et al., 2011) by an additional 0.3 kg N ha^{-1} yr^{-1}, and all sites (except those in North American Deserts) would exceed the minimum CL by an additional 1%–13%, as compared to DIN alone. This may lead to an extended ecosystem recovery time and hypothesized hysteresis of recovery (Gilliam et al., 2019) in response to periods of excess inorganic N deposition.

Simultaneous measurements of DOM wet deposition concentration and composition metrics may be helpful for predicting its eventual fate once deposited on the Earth's surface (Benedict et al., 2018; Schurman et al., 2015). For example, DON can either be an energy source or nutrient source (Orsi et al., 2016; Wymore et al., 2015). As such, depositional DOM with a higher C:N ratio (e.g., North American Deserts) may be more likely to be governed by different biogeochemical controls, depending on the ecosystem's nutrient status, than wet deposition organic matter that is richer in N (e.g., Northern Forests). The size of organic molecules can also determine the dominant biogeochemical pathways. Our finding of heavier weight molecules in the growing season may indicate that more deposition-derived organic matter persists in the environment in its depositional molecular form during this season because larger organic molecules are often more recalcitrant (Findlay & Sinsabaugh, 1999). Wet deposition DOC has also been shown to have positive associations with atmospherically derived Hg which contributes to the accumulation of Hg in litterfall (Navratil et al., 2021) and likely other organisms. Understanding what fraction of DON deposition is bioavailable would also be important for critical load calculations. DON wet deposition can be comprised of 20%–70% amino acids (Altieri et al., 2009; Cao et al., 2019; Finzi & Berthrong, 2005; Gorzelska et al., 1992; Seitzinger & Sanders, 1999). The labile N-containing proportion of DOM can be directly assimilated participating in the "short-circuit" of the terrestrial N cycle (Neff et al., 2003) via the direct uptake of amino acids by plants (Antia et al., 1991; Cao et al., 2019; Paerl et al., 1999; Peierls & Paerl, 1997; Seitzinger & Sanders, 1999) or provide a labile source of carbon driving denitrification (Murray et al., 2023). Wet deposition can also be further enriched in organic N during the process of throughfall (Cao et al., 2019; McDowell, 2023; Qualls et al., 2002), thereby contributing to the labile pool of soil organic N.

Wet deposition may contribute disproportionately to biogeochemical cycles in certain ecosystems relative to others. This may be especially important in places where depositional DOM inputs equal or exceed outputs. For example, high concentrations and loads of DOC and DON are prevalent in sites within the generally nutrient poor alpine zone of the Rocky Mountains, which may increase the relative influence of wet deposition DOM on catchment-scale biogeochemical cycling (Kaushal & Lewis, 2005; Mladenov et al., 2012). Low rates of DOC and DON loading to sites in the North American Deserts may reflect the minimal precipitation these landscapes receive (Figure 1c; Table 1). Further exploration on the lability of depositional DOM via molecular characterization and bioassays is needed as current efforts have only identified about 50% of potential molecules present (Cornell, 2011). More information is needed about what types of DOM compounds are retained versus transported in a catchment. Due to the strong continental patterns observed in this study, coupled with site-specific results regarding seasonality and role of airmass range, the monitoring of wet deposition organic matter at a spatiotemporal scale that captures the variability shown in our study is critical for understanding vectors by which ecosystems receive bioavailable nutrients.

5. Conclusions

Wet deposition organic matter originates from a combination of anthropogenic and natural processes, contributing nutrients to watersheds through precipitation. We used archived samples to investigate the variability of DOC and DON concentrations and composition in wet deposition. We found that DOM variables (DOC, DON, DOC: DON and S_R) are highly seasonal and vary across ecoregions. Contrary to historical assumptions, long-range airmasses can transport DOC and DON into ecosystems. Other climate drivers such as MAT and MAP appear to influence aspects of the DOM deposition pool. This study has begun to reveal the dynamics of wet deposition DOM across space and time, however the role of depositional DOM in global biogeochemical cycles is challenging to decipher. To address this gap, we need to continue adding organic solutes to programs that routinely monitor wet deposition. Opportunities may exist for hindcasting nation-wide DOM wet deposition

concentrations using archived samples from national depositional monitoring programs. These data could help determine the extent to which anthropogenic and biogenic emission sources contribute to the overall composition of organics in deposition and the fate of C and N entering the biosphere through precipitation.

Data Availability Statement

The raw wet deposition chemistry variables and airmass cluster analysis results supporting the results presented in this paper are openly available on Hydroshare at: http://www.hydroshare.org/resource/f1fc42978b4f4b64a90f198235d762e3 (Murray & Wymore, 2024).

Acknowledgments
Support for DSM was provided by the NASA FINESST program (Grant 80NSSC1441). Funding for this project was also provided by the National Science Foundation (NSF) Experimental Program to Stimulate Competitive Research (EPSCoR) program awards EPS-1929148 (Canary in the Watershed) and the United Stated Department of Agriculture (USDA) National Institute of Food and Agriculture Hatch Multi-State Project 1022291. This is scientific contribution number 3004. We thank David Gay and Amy Mager at the National Atmospheric Deposition Program for their assistance with acquiring archived samples and Mike Bell and Bret Schichtel at the National Park Service for additional insights on this manuscript.

References

Aber, J., McDowell, W., Nadelhoffer, K., Magill, A., Berntson, G., Kamakea, M., et al. (1998). Nitrogen saturation in temperate forest ecosystems. *BioScience*, *48*(11), 921–934. https://doi.org/10.2307/1313296

Aber, J. D., Goodale, C. L., Ollinger, S. V., Smith, M.-L., Magill, A. H., Martin, M. E., et al. (2003). Is nitrogen deposition altering the Nitrogen status of Northeastern forests? *BioScience*, *53*(4), 375. https://doi.org/10.1641/0006-3568(2003)053[0375:INDATN]2.0.CO;2

Aliaga, D., Sinclair, V. A., Andrade, M., Artaxo, P., Carbone, S., Kadantsev, E., et al. (2021). Identifying source regions of air masses sampled at the tropical high-altitude site of Chacaltaya using WRF-FLEXPART and cluster analysis. *Atmospheric Chemistry and Physics*, *21*(21), 16453–16477. https://doi.org/10.5194/acp-21-16453-202

Altieri, K. E., Hastings, M. G., Peters, A. J., & Sigman, D. M. (2012). Molecular characterization of water soluble organic nitrogen in marine rainwater by ultra-high resolution electrospray ionization mass spectrometry. *Atmospheric Chemistry and Physics*, *12*(7), 3557–3571. https://doi.org/10.5194/acp-12-3557-2012

Altieri, K. E., Turpin, B. J., & Seitzinger, S. P. (2009). Composition of dissolved organic nitrogen in continental precipitation investigated by ultra-high resolution FT-ICR mass spectrometry. *Environmental Science & Technology*, *43*(18), 6950–6955. https://doi.org/10.1021/es9007849

Antia, N. J., Harrison, P. J., & Oliveira, L. (1991). The role of dissolved organic nitrogen in phytoplankton nutrition, cell biology and ecology. *Phycologia*, *30*, 1–89. https://doi.org/10.2216/i0031-8884-30-1-1.1

Benedict, K. B., Carrico, C. M., Kreidenweis, S. M., Schichtel, B., Malm, W. C., & Collett, J. L. (2013). A seasonal nitrogen deposition budget for Rocky Mountain National Park. *Ecological Applications*, *23*(5), 1156–1169. https://doi.org/10.1890/12-1624.1

Benedict, K. B., Chen, X., Sullivan, A. P., Li, Y., Day, D., Prenni, A. J., et al. (2013). Atmospheric concentrations and deposition of reactive nitrogen in grand Teton national park. *Journal of Geophysical Research: Atmospheres*, *118*(20), 11–875. https://doi.org/10.1002/2013jd020394

Benedict, K. B., Prenni, A. J., Sullivan, A. P., Evanoski-Cole, A. R., Fischer, E. V., Callahan, S., et al. (2018). Impact of Front range sources on reactive nitrogen concentrations and deposition in Rocky mountain national park. *PeerJ*, *6*, e4759. https://doi.org/10.7717/peerj.4759

Boyer, E. W., Goodale, C. L., Jaworski, N. A., & Howarth, R. W. (2002). Anthropogenic nitrogen sources and relationships to riverine nitrogen export in the Northeastern U.S.A. In E. W. Boyer & R. W. Howarth (Eds.), *The Nitrogen cycle at regional to global scales* (pp. 137–169). Springer Netherlands. https://doi.org/10.1007/978-94-017-3405-9_4

Brookshire, E. N. J., Valett, H. M., Thomas, S. A., & Webster, J. R. (2007). Atmospheric N deposition increases organic N loss from temperate forests. *Ecosystems*, *10*(2), 252–262. https://doi.org/10.1007/s10021-007-9019-x

Burakowski, E. A., Contosta, A. R., Grogan, D., Nelson, S. J., Garlick, S., & Casson, N. (2022). Future of winter in Northeastern North America: Climate indicators portray warming and snow loss that will impact ecosystems and communities. *Northeastern Naturalist*, *28*(sp11), 180–207. https://doi.org/10.1656/045.028.s1112

Campbell, J. L., Hornbeck, J. W., McDowell, W. H., Buso, D. C., Shanley, J. B., & Likens, G. E. (2000). Dissolved organic nitrogen budgets for upland, forested ecosystems in New England. *Biogeochemistry*, *49*(2), 123–142. https://doi.org/10.1023/a:1006383731753

Cao, R., Chen, S., Yoshitake, S., & Ohtsuka, T. (2019). Nitrogen deposition and responses of forest structure to nitrogen deposition in a cool-temperate deciduous forest. *Forests*, *10*(8), 631. https://doi.org/10.3390/f10080631

Cape, J. N., Cornell, S. E., Jickells, T. D., & Nemitz, E. (2011). Organic nitrogen in the atmosphere—Where does it come from? A review of sources and methods. *Atmospheric Research*, *102*(1–2), 30–48. https://doi.org/10.1016/j.atmosres.2011.07.009

Cape, J. N., Coyle, M., & Dumitrean, P. (2012). The atmospheric lifetime of black carbon. *Atmospheric Environment*, *59*, 256–263. https://doi.org/10.1016/j.atmosenv.2012.05.030

Cape, J. N., Kirika, A., Rowland, A. P., Wilson, D. R., Jickells, T. D., & Cornell, S. (2001). Organic nitrogen in precipitation: Real problem or sampling artefact? *The Scientific World Journal*, *1*, 230–237. https://doi.org/10.1100/tsw.2001.278

Coggon, M. M., Veres, P. R., Yuan, B., Koss, A., Warneke, C., Gilman, J. B., et al. (2016). Emissions of nitrogen-containing organic compounds from the burning of herbaceous and Arboraceous biomass: Fuel composition dependence and the variability of commonly used nitrile tracers. *Geophysical Research Letters*, *43*(18), 9903–9912. https://doi.org/10.1002/2016GL070562

Contosta, A. R., Adolph, A., Burchsted, D., Burakowski, E., Green, M., Guerra, D., et al. (2017). A longer vernal window: The role of winter coldness and snowpack in driving spring transitions and lags. *Global Change Biology*, *23*(4), 1610–1625. https://doi.org/10.1111/gcb.13517

Cornell, S., Mace, K., Coeppicus, S., Duce, R., Huebert, B., Jickells, T., & Zhuang, L. Z. (2001). Organic nitrogen in Hawaiian rain and aerosol. *Journal of Geophysical Research: Atmospheres*, *106*(D8), 7973–7983. https://doi.org/10.1029/2000JD900655

Cornell, S., Randell, A., & Jickells, T. (1995). Atmospheric inputs of dissolved organic nitrogen to the oceans. *Nature*, *376*(6537), 243–246. https://doi.org/10.1038/376243a0

Cornell, S. E. (2011). Atmospheric nitrogen deposition: Revisiting the question of the importance of the organic component. *Environmental Pollution*, *159*(10), 2214–2222. https://doi.org/10.1016/j.envpol.2010.11.014

Cornell, S. E., Jickells, T. D., Cape, J. N., Rowland, A. P., & Duce, R. A. (2003). Organic nitrogen deposition on land and coastal environments: A review of methods and data. *Atmospheric Environment*, *37*(16), 2173–2191. https://doi.org/10.1016/S1352-2310(03)00133-X

Dahlman, L., Persson, J., Palmqvist, K., & Näsholm, T. (2004). Organic and inorganic nitrogen uptake in lichens. *Planta*, *219*(3), 459–467. https://doi.org/10.1007/s00425-004-1247-0

Draxler, R. R. (1999). HYSPLIT4 user's guide. In *NOAA Tech. Memo. ERL ARL-230*. NOAA Air Resources Laboratory.

Draxler, R. R., & Hess, G. D. (1997). Description of the HYSPLIT_4 modeling system. In *NOAA Tech. Memo. ERL ARL-224*. NOAA Air Resources Laboratory. 24.

Draxler, R. R., & Hess, G. D. (1998). An overview of the HYSPLIT_4 modeling system of trajectories, dispersion, and deposition. *Australian Meteorological Magazine*, *47*, 295–308.
Du, E., Clark, C. M., & de Vries, W. (2024). Forest remediation options in the face of excess nitrogen deposition. In *Atmospheric nitrogen deposition to global forests* (pp. 263–271). Academic Press.
Feng, J., Vet, R., Cole, A., Zhang, L., Cheng, I., O'Brien, J., & Macdonald, A. M. (2021). Inorganic chemical components in precipitation in the Eastern US and Eastern Canada during 1989–2016: Temporal and regional trends of wet concentration and wet deposition from the NADP and CAPMoN measurements. *Atmospheric Environment*, *254*, 118367. https://doi.org/10.1016/j.atmosenv.2021.118367
Findlay, S., & Sinsabaugh, R. L. (1999). Unravelling the sources and bioavailability of dissolved organic matter in lotic aquatic ecosystems. *Marine and Freshwater Research*, *50*(8), 781–790. https://doi.org/10.1071/mf99069
Finzi, A. C., & Berthrong, S. T. (2005). The uptake of amino acids by microbes and trees in three cold-temperate forests. *Ecology*, *86*(12), 3345–3353. https://doi.org/10.1890/04-1460
Frey, S. D., Ollinger, S., Nadelhoffer, K. E., Bowden, R., Brzostek, E., Burton, A., et al. (2014). Chronic nitrogen additions suppress decomposition and sequester soil carbon in temperate forests. *Biogeochemistry*, *121*(2), 305–316. https://doi.org/10.1007/s10533-014-0004-0
Gbondo-Tugbawa, S. S., Driscoll, C. T., Aber, J. D., & Likens, G. E. (2001). Evaluation of an integrated Biogeochemical Model (PnET-BGC) at a Northern hardwood forest ecosystem. *Water Resources Research*, *37*(4), 1057–1070. https://doi.org/10.1029/2000wr900375
Gilliam, F. S., Burns, D. A., Driscoll, C. T., Frey, S. D., Lovett, G. M., & Watmough, S. A. (2019). Decreased atmospheric nitrogen deposition in Eastern North America: Predicted responses of forest ecosystems. *Environmental Pollution*, *244*, 560–574. https://doi.org/10.1016/j.envpol.2018.09.135
Gorzelska, K., Galloway, J. N., Watterson, K., & Keene, W. C. (1992). Water-soluble primary amine compounds in rural continental precipitation. Atmospheric Environment. Part A. *General Topics*, *26*(6), 1005–1018. https://doi.org/10.1016/0960-1686(92)90032-G
Green, M. B., Bailey, S. W., Campbell, J. L., McGuire, K. J., Bailey, A. S., Fahey, T. J., et al. (2021). A catchment water balance assessment of an abrupt shift in evapotranspiration at the Hubbard Brook Experimental Forest, New Hampshire, USA. *Hydrological Processes*, *35*(8), e14300. https://doi.org/10.1002/hyp.14300
Harrison, J. L., Sanders-DeMott, R., Reinmann, A. B., Sorensen, P. O., Phillips, N. G., & Templer, P. H. (2020). Growing-season warming and winter soil freeze/thaw cycles increase transpiration in a northern hardwood forest. *Ecology*, *101*(11), 1–16. https://doi.org/10.1002/ecy.3173
Harvey, F. E. (2001). Use of NADP archive samples to determine the isotope composition of precipitation: Characterizing the meteoric input function for use in ground water studies. *Ground Water*, *39*(3), 380–390. https://doi.org/10.1111/j.1745-6584.2001.tb02322.x
Helms, J. R., Stubbins, A., Ritchie, J. D., Minor, E. C., Kieber, D. J., & Mopper, K. (2008). Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnology & Oceanography*, *53*(3), 955–969. https://doi.org/10.4319/lo.2008.53.3.0955
Iavorivska, L., Boyer, E. W., Miller, M. P., Brown, M. G., Vasilopoulos, T., Fuentes, J. D., & Duffy, C. J. (2016). Atmospheric inputs of organic matter to a forested watershed: Variations from storm to storm over the seasons. *Atmospheric Environment*, *147*, 284–295. https://doi.org/10.1016/j.atmosenv.2016.10.002
Isidorov, V. A., Smolewska, M., Purzyńska-Pugacewicz, A., & Tyszkiewicz, Z. (2010). Chemical composition of volatile and extractive compounds of pine and spruce leaf litter in the initial stages of decomposition. *Biogeosciences*, *7*(9), 2785–2794. https://doi.org/10.5194/bg-7-2785-2010
Isles, P. D. (2020). The misuse of ratios in ecological stoichiometry. *Ecology*, *101*(11), e03153. https://doi.org/10.1002/ecy.3153
Jacob, D. J. (1999). *Introduction to atmospheric chemistry*. Princeton University Press.
Jari Oksanen, F. G. B., Friendly, M., Kindt, R., Legendre, P., McGlinn, D., Minchin, P. R., et al. (2018). Community ecology package. *R package version*, *2*(6).
Jennings, K. S., Winchell, T. S., Livneh, B., & Molotch, N. P. (2018). Spatial variation of the rain–snow temperature threshold across the Northern Hemisphere. *Nature Communications*, *9*(1), 1148. https://doi.org/10.1038/s41467-018-03629-7
Jickells, T., Baker, A. R., Cape, J. N., Cornell, S. E., & Nemitz, E. (2013). The cycling of organic nitrogen through the atmosphere. *Philosophical Transactions of the Royal Society B: Biological Sciences*, *368*(1621), 20130115. https://doi.org/10.1098/rstb.2013.0115
Jordon, T. E., Correll, D. L., Weller, D. E., & Goff, N. M. (1995). Temporal variation in precipitation chemistry on the shore of the Chesapeake Bay. *Water, Air, and Soil Pollution*, *83*(3–4), 263–284. https://doi.org/10.1007/bf00477357
Kaushal, S. S., & Lewis, W. M. (2005). Fate and transport of organic nitrogen in minimally disturbed montane streams of Colorado, USA. *Biogeochemistry*, *74*(3), 303–321. https://doi.org/10.1007/s10533-004-4723-5
Kieber, R. J., Long, M. S., & Willey, J. D. (2005). Factors influencing nitrogen speciation in coastal rainwater. *Journal of Atmospheric Chemistry*, *52*(1), 81–99. https://doi.org/10.1007/s10874-005-8354-6
Kronholm, S., & Capel, P. (2012). Concentrations, loads, and yields of organic carbon in streams of agricultural watersheds. *Journal of Environmental Quality*, *41*(6), 1874–1883. https://doi.org/10.2134/jeq2012.0045
Kuylenstierna, J. C., Rodhe, H., Cinderby, S., & Hicks, K. (2001). Acidification in developing countries: Ecosystem sensitivity and the critical load approach on a global scale. *Ambio*, *30*(1), 20–28. https://doi.org/10.1579/0044-7447-30.1.20
Lawrence, C. E., Casson, P., Brandt, R., Schwab, J. J., Dukett, J. E., Snyder, P., et al. (2023). Long-term monitoring of cloud water chemistry at Whiteface Mountain: The emergence of a new chemical regime. *Atmospheric Chemistry and Physics*, *23*(2), 1619–1639. https://doi.org/10.5194/acp-23-1619-2023
Lee, J. Y., Peterson, P. K., Vear, L. R., Cook, R. D., Sullivan, A. P., Smith, E., et al. (2022). Wildfire smoke influence on cloud water chemical composition at Whiteface Mountain, New York. *Journal of Geophysical Research: Atmospheres*, *127*(19), e2022JD037177. https://doi.org/10.1029/2022jd037177
Legendre, L., & Legendre, P. (1998). *Numerical ecology*. Elsevier Scientific Pub. Co.
Lei, Y. D., & Wania, F. (2004). Is rain or snow a more efficient scavenger of organic chemicals? *Atmospheric Environment*, *38*(22), 3557–3571. https://doi.org/10.1016/j.atmosenv.2004.03.039
Liptzin, D., Boy, J., Campbell, J. L., Clarke, N., Laclau, J. P., Godoy, R., et al. (2022). Spatial and temporal patterns in atmospheric deposition of dissolved organic carbon. *Global Biogeochemical Cycles*, *36*(10), e2022GB007393. https://doi.org/10.1029/2022GB007393
Lovett, G. M., & Goodale, C. L. (2011). A new conceptual model of nitrogen saturation based on experimental nitrogen addition to an Oak forest. *Ecosystems*, *14*(4), 615–631. https://doi.org/10.1007/s10021-011-9432-z
Mace, K. A., Duce, R. A., & Tindale, N. W. (2003). Organic nitrogen in rain and aerosol at Cape Grim, Tasmania, Australia. *Journal of Geophysical Research*, *108*(D11). https://doi.org/10.1029/2002jd003051
Magill, A. H., Aber, J. D., Berntson, G. M., McDowell, W. H., Nadelhoffer, K. J., Melillo, J. M., & Steudler, P. (2000). Long-term nitrogen additions and nitrogen saturation in two temperate forests. *Ecosystems*, *3*(3), 238–253. https://doi.org/10.1007/s100210000023

Mansoor, S., Farooq, I., Kachroo, M. M., Mahmoud, A. E. D., Fawzy, M., Popescu, S. M., et al. (2022). Elevation in wildfire frequencies with respect to the climate change. *Journal of Environmental Management*, *301*, 113769. https://doi.org/10.1016/j.jenvman.2021.113769

Markham, C. G. (1970). Seasonality of precipitation in the United States. *Annals of the Association of American Geographers*, *60*(3), 593–597. https://doi.org/10.1111/j.1467-8306.1970.tb00743.x

Matsumoto, K., Takusagawa, F., Suzuki, H., & Horiuchi, K. (2018). Water-soluble organic nitrogen in the aerosols and rainwater at an urban site in Japan: Implications for the nitrogen composition in the atmospheric deposition. *Atmospheric Environment*, *191*, 267–272. https://doi.org/10.1016/j.atmosenv.2018.07.056

McDowell, W. H. (2023). DOM in the long arc of environmental science: Looking back and thinking ahead. *Biogeochemistry*, *164*(1), 15–27. https://doi.org/10.1007/s10533-022-00924-w

McDowell, W. H., Magill, A. H., Aitkenhead-Peterson, J. A., Aber, J. D., Merriam, J. L., & Kaushal, S. S. (2004). Effects of chronic nitrogen amendment on dissolved organic matter and inorganic nitrogen in soil solution. *Forest Ecology and Management*, *196*(1), 29–41. https://doi.org/10.1016/j.foreco.2004.03.010

Millet, D. B., Goldstein, A. H., Allan, J. D., Bates, T. S., Boudries, H., Bower, K. N., et al. (2004). Volatile organic compound measurements at Trinidad Head, California, during ITCT 2K2: Analysis of sources, atmospheric composition, and aerosol residence times. *Journal of Geophysical Research*, *109*(D23). https://doi.org/10.1029/2003jd004026

Mitra, S., Wozniak, A. S., Miller, R., Hatcher, P. G., Buonassissi, C., & Brown, M. (2013). Multiproxy probing of rainwater Dissolved Organic Matter (DOM) composition in coastal storms as a function of trajectory. *Marine Chemistry*, *154*, 67–76. https://doi.org/10.1016/j.marchem.2013.05.013

Mitra, S. K., Barth, U., & Pruppacher, H. R. (1990). A laboratory study of the efficiency with which aerosol particles are scavenged by snow Flakes. Atmospheric Environment. Part A. *General Topics*, *24*(5), 1247–1254. https://doi.org/10.1016/0960-1686(90)90089-6

Mladenov, N., Williams, M. W., Schmidt, S. K., & Cawley, K. (2012). Atmospheric deposition as a source of carbon and nutrients to an alpine catchment of the Colorado Rocky Mountains. *Biogeosciences*, *9*(8), 3337–3355. https://doi.org/10.5194/bg-9-3337-2012

Murray, D. S., Moges, E., Larsen, L., Shattuck, M. D., McDowell, W. H., & Wymore, A. S. (2023). Synchrony of nitrogen wet deposition inputs and watershed nitrogen outputs using information theory. *Water Resources Research*, *59*(10), e2023WR034794. https://doi.org/10.1029/2023WR034794

Murray, D. S., Shattuck, M. D., McDowell, W. H., & Wymore, A. S. (2022). Nitrogen wet deposition stoichiometry: The role of organic nitrogen, seasonality, and snow. *Biogeochemistry*, *160*(3), 301–314. https://doi.org/10.1007/s10533-022-00966-0

Murray, D. S., & Wymore, A. S. (2024). Dataset for seasonal and climatic drivers of wet deposition organic matter at the continental scale [Dataset]. *HydroShare*. http://www.hydroshare.org/resource/f1fc42978b4f4b64a90f198235d762e3

Nanus, L., Campbell, D. H., Lehmann, C. M. B., & Mast, M. A. (2018). Spatial and temporal variation in sources of atmospheric nitrogen deposition in the Rocky Mountains using nitrogen isotopes. *Atmospheric Environment*, *176*, 110–119. https://doi.org/10.1016/j.atmosenv.2017.12.023

Navrátil, T., Shanley, J. B., Rohovec, J., Dobešová, I., Matoušková, Š., Roll, M., et al. (2021). Mercury cycling during acid rain recovery at the forested Lesní potok catchment, Czech Republic. *Hydrological Processes*, *35*(6), e14255. https://doi.org/10.1002/hyp.14255

Neff, J. C., Chapin, F. S., & Vitousek, P. M. (2003). Breaks in the cycle: Dissolved organic nitrogen in terrestrial ecosystems. *Frontiers in Ecology and the Environment*, *1*(4), 205–211. https://doi.org/10.1890/1540-9295(2003)001[0205:BITCDO]2.0.CO;2

Neff, J. C., Holland, E. A., Dentener, F. J., McDowell, W. H., & Russell, K. M. (2002). The origin, composition and rates of organic nitrogen deposition: A missing piece of the nitrogen cycle? In E. W. Boyer & R. W. Howarth (Eds.), *The Nitrogen cycle at regional to global scales* (pp. 99–136). Springer Netherlands. https://doi.org/10.1007/978-94-017-3405-9_3

Nguyen, T. B., Laskin, J., Laskin, A., & Nizkorodov, S. A. (2011). Nitrogen-containing organic compounds and oligomers in secondary organic aerosol formed by photooxidation of isoprene. *Environmental Science & Technology*, *45*(16), 6908–6918. https://doi.org/10.1021/es201611n

Nickerson, C., Ebel, R., Borchers, A., & Carriazo, F. (2011). *Major uses of land in the United States, 2007. Economic information bulletin No. EIB-89*. U.S. Department of Agriculture, Economic Research Service. 67.

Orsi, W. D., Smith, J. M., Liu, S., Liu, Z., Sakamoto, C. M., Wilken, S., et al. (2016). Diverse, uncultivated bacteria and archaea underlying the cycling of dissolved protein in the ocean. *The ISME Journal*, *10*(9), 2158–2173. https://doi.org/10.1038/ismej.2016.20

Oulehle, F., McDowell, W. H., Aitkenhead-Peterson, J. A., Krám, P., Hruška, J., Navrátil, T., et al. (2008). Long-term trends in stream nitrate concentrations and losses across watersheds undergoing recovery from acidification in the Czech Republic. *Ecosystems*, *11*(3), 410–425. https://doi.org/10.1007/s10021-008-9130-7

Paerl, H., Willey, J., Go, M., Peierls, B., Pinckney, J., & Fogel, M. (1999). Rainfall stimulation of primary production in Western Atlantic Ocean waters: Roles of different nitrogen sources and co-limiting nutrients. *Marine Ecology Progress Series*, *176*, 205–214. https://doi.org/10.3354/meps176205

Pardo, L. H., Fenn, M. E., Goodale, C. L., Geiser, L. H., Driscoll, C. T., Allen, E. B., et al. (2011). Effects of nitrogen deposition and empirical nitrogen critical loads for ecoregions of the United States. *Ecological Applications*, *21*(8), 3049–3082. https://doi.org/10.1890/10-2341.1

Paulot, F., Wunch, D., Crounse, J. D., Toon, G. C., Millet, D. B., DeCarlo, P. F., et al. (2011). Importance of secondary sources in the atmospheric budgets of formic and acetic acids. *Atmospheric Chemistry and Physics*, *11*(5), 1989–2013. https://doi.org/10.5194/acp-11-1989-2011

Peierls, B. L., & Paerl, H. W. (1997). Bioavailability of atmospheric organic nitrogen deposition to coastal phytoplankton. *Limnology & Oceanography*, *42*(8), 1819–1823. https://doi.org/10.4319/lo.1997.42.8.1819

Qualls, R. G., Haines, B. L., Swank, W. T., & Tyler, S. W. (2002). Retention of soluble organic nutrients by a forested ecosystem. *Biogeochemistry*, *61*(2), 135–171. https://doi.org/10.1023/a:1020239112586

Raymond, P. A. (2005). The composition and transport of organic carbon in rainfall: Insights from the natural (13 C and 14 C) isotopes of carbon. *Geophysical Research Letters*, *32*(14), 2005GL022879. https://doi.org/10.1029/2005GL022879

Rodríguez-Cardona, B. M., Wymore, A. S., Argerich, A., Barnes, R. T., Bernal, S., Brookshire, E. J., et al. (2022). Shifting stoichiometry: Long-term trends in stream-dissolved organic matter reveal altered C:N ratios due to history of atmospheric acid deposition. *Global Change Biology*, *28*(1), 98–114. https://doi.org/10.1111/gcb.15965

Russell, K. M., Galloway, J. N., Macko, S. A., Moody, J. L., & Scudlark, J. R. (1998). Sources of nitrogen in wet deposition to the Chesapeake Bay region. *Atmospheric Environment*, *32*(14–15), 2453–2465. https://doi.org/10.1016/S1352-2310(98)00044-2

Schulze, E.-D., De Vries, W., Hauhs, M., Rosén, K., Rasmussen, L., Tamm, C.-O., & Nilsson, J. (1989). Critical loads for nitrogen deposition on forest ecosystems. *Water, Air, and Soil Pollution*, *48*(3–4), 451–456. https://doi.org/10.1007/BF00283342

Schurman, M. I., Lee, T., Sun, Y., Schichtel, B. A., Kreidenweis, S. M., & Collett Jr, J. L. (2015). Investigating types and sources of organic aerosol in Rocky Mountain National Park using aerosol mass spectrometry. *Atmospheric Chemistry and Physics*, *15*(2), 737–752. https://doi.org/10.5194/acp-15-737-2015

Scudlark, J. R., Russell, K. M., Galloway, J. N., Church, T. M., & Keene, W. C. (1998). Organic nitrogen in precipitation at the mid-Atlantic U.S. Coast—Methods evaluation and preliminary measurements. *Atmospheric Environment*, *32*(10), 1719–1728. https://doi.org/10.1016/S1352-2310(97)00458-5

Seaton, P. J., Kieber, R. J., Willey, J. D., Avery, G. B., & Dixon, J. L. (2013). Seasonal and temporal characterization of dissolved organic matter in rainwater by proton nuclear magnetic resonance spectroscopy. *Atmospheric Environment*, *65*, 52–60. https://doi.org/10.1016/j.atmosenv.2012.10.026

Seinfeld, J. H., & Pandis, S. N. (2012). *Atmospheric chemistry and physics: From air pollution to climate change*. Wiley.

Seitzinger, S. P., & Sanders, R. W. (1999). Atmospheric inputs of dissolved organic nitrogen stimulate estuarine bacteria and phytoplankton. *Limnology & Oceanography*, *44*(3), 721–730. https://doi.org/10.4319/lo.1999.44.3.0721

Sharkey, T. D., Wiberley, A. E., & Donohue, A. R. (2007). Isoprene emission from plants: Why and how. *Annals of Botany*, *101*(1), 5–18. https://doi.org/10.1093/aob/mcm240

Sindelarova, K., Granier, C., Bouarar, I., Guenther, A., Tilmes, S., Stavrakou, T., et al. (2014). Global data set of biogenic VOC emissions calculated by the MEGAN model over the last 30 years. *Atmospheric Chemistry and Physics*, *14*(17), 9317–9341. https://doi.org/10.5194/acp-14-9317-2014

Sricharoenvech, P., Edwards, R., Yaşar, M., Gay, D., & Schauer, J. J. (2024). Investigation of black carbon wet deposition to the United States from National Atmospheric Deposition Network samples. *Aerosol and Air Quality Research*, *24*(5), 230089. https://doi.org/10.4209/aaqr.230089

Stein, A. F., Draxler, R. R., Rolph, G. D., Stunder, B. J. B., Cohen, M. D., & Ngan, F. (2015). NOAA's HYSPLIT atmospheric transport and dispersion modeling system. *Bulletin America Meteorology Social*, *96*(12), 2059–2077. https://doi.org/10.1175/BAMS-D-14-00110.1

Thornton, M. M., Shrestha, R., Wei, Y., Thornton, P. E., Kao, S.-C., & Wilson, B. E. (2022). *Daymet: Station-level inputs and cross-validation for North America, version 4 R1*. ORNL DAAC. https://doi.org/10.3334/ORNLDAAC/2132

Toming, K., Kotta, J., Uuemaa, E., Sobek, S., Kutser, T., & Tranvik, L. J. (2020). Predicting lake dissolved organic carbon at a global scale. *Scientific Reports*, *10*(1), 8471. https://doi.org/10.1038/s41598-020-65010-3

Vanguelova, E. I., Benham, S., Pitman, R., Moffat, A. J., Broadmeadow, M., Nisbet, T., et al. (2010). Chemical fluxes in time through forest ecosystems in the UK – Soil response to pollution recovery. *Environmental Pollution*, *158*(5), 1857–1869. https://doi.org/10.1016/j.envpol.2009.10.044

Verstraeten, A., Verschelde, P., De Vos, B., Neirynck, J., Cools, N., Roskams, P., et al. (2016). Increasing trends of Dissolved Organic Nitrogen (DON) in temperate forests under recovery from acidification in Flanders, Belgium. *The Science of the Total Environment*, *553*, 107–119. https://doi.org/10.1016/j.scitotenv.2016.02.060

Vet, R., Artz, R. S., Carou, S., Shaw, M., Ro, C. U., Aas, W., et al. (2014). A global assessment of precipitation chemistry and deposition of sulfur, nitrogen, sea salt, base cations, organic acids, acidity and pH, and phosphorus. *Atmospheric Environment*, *93*, 3–100. https://doi.org/10.1016/j.atmosenv.2013.10.060

Violaki, K., Zarbas, P., & Mihalopoulos, N. (2010). Long-term measurements of Dissolved Organic Nitrogen (DON) in atmospheric deposition in the Eastern Mediterranean: Fluxes, origin and biogeochemical implications. *Marine Chemistry*, *120*(1–4), 179–186. https://doi.org/10.1016/j.marchem.2009.08.004

Walker, J. T., Dombek, T. L., Green, L. A., Gartman, N., & Lehmann, C. M. B. (2012). Stability of organic nitrogen in NADP wet deposition samples. *Atmospheric Environment*, *60*, 573–582. https://doi.org/10.1016/j.atmosenv.2012.06.059

Wymore, A. S., Johnes, P. J., Bernal, S., Brookshire, E. J., Fazekas, H. M., Helton, A. M., et al. (2021). Gradients of anthropogenic nutrient enrichment alter N composition and DOM stoichiometry in freshwater ecosystems. *Global Biogeochemical Cycles*, *35*(8), e2021GB006953. https://doi.org/10.1029/2021GB006953

Wymore, A. S., Rodríguez-Cardona, B., & McDowell, W. H. (2015). Direct response of dissolved organic nitrogen to nitrate availability in headwater streams. *Biogeochemistry*, *126*(1–2), 1–10. https://doi.org/10.1007/s10533-015-0153-9

Zamora, L. M., Prospero, J. M., & Hansell, D. A. (2011). Organic nitrogen in aerosols and precipitation at Barbados and Miami: Implications regarding sources, transport and deposition to the Western subtropical North Atlantic. *Journal of Geophysical Research*, *116*(D20), D20309. https://doi.org/10.1029/2011JD015660