

Review

Utilizing $\delta^{15}\text{N}$ of biomonitors to assess N emission sources and deposition chemistry?Meaghan I. Petix^{a,*}, Michael D. Bell^b, David G. Williams^c, R. Dave Evans^a^a School of Biological Sciences and Stable Isotope Core Facility, Washington State University, P.O. Box 644236, Pullman, WA 99164, USA^b National Park Service, Air Resources Division, 111 Kipling St., Building 50, Lakewood, CO 80226, USA^c Department of Botany, University of Wyoming, 1000 E. University Ave., Laramie, WY 82071, USA

ARTICLE INFO

Keywords:

Stable isotope
Nitrogen
Anthropogenic emissions
Lichen
Moss

ABSTRACT

Anthropogenic nitrogen (N) emissions and subsequent deposition can cause harm to ecosystem function and processes. Identifying emission sources of atmospheric N deposition (N_{dep}) is critical for land management and policy development to understand what N species are impacting an area and where action can be taken to reduce loading. Measuring and monitoring deposition is time intensive and expensive, but biomonitors, such as mosses and lichens, can be used to evaluate finer-scale deposition patterns and source attribution using stable isotope analysis. The N stable isotope composition ($\delta^{15}\text{N}$) of N_{dep} provides unique insight into emission sources and chemistry at different temporal and spatial scales because it is determined in part by the $\delta^{15}\text{N}$ of contributing N emission sources that vary at a local, regional, and global level. The $\delta^{15}\text{N}$ of biomonitor organisms can be used to monitor N_{dep} at these diverse scales capturing the spatial and temporal heterogeneity of N_{dep} rates and source chemistries. However, the $\delta^{15}\text{N}$ of biomonitors integrates not only source effects, but also isotopic effects associated with canopy dynamics and organism biology, thus interpretation of biomonitor $\delta^{15}\text{N}$ needs to consider multiple factors including emission source, atmospheric transformations, and canopy and physiological effects. Despite local scale and organism specific responses, lichens and mosses from herbaria collections document coherent anthropogenically driven shifts in N_{dep} $\delta^{15}\text{N}$ signals over the last century consistent with observations from lake sediments and ice cores.

1. Introduction

Atmospheric nitrogen (N) deposition (N_{dep}) is a major driver of global change. Emissions and subsequent deposition of reactive N (N_r) has increased since the industrial and agricultural revolutions and is now dominated by anthropogenic processes such as fossil fuel combustion, fertilizer use, and biomass burning (Bobbink et al., 2010). Increased emissions of N_r have resulted in higher atmospheric N_{dep} rates onto terrestrial and aquatic ecosystems, leading to ecological effects across the globe (Fenn et al., 2003a; Pardo et al., 2011). Tracking levels of N_{dep} requires local measurements or generalized values from chemical transport models that may not capture local environmental variability. Here we evaluate how biomonitors, organisms used to assess pollution, can be used to understand local N_{dep} gradients and emission sources based on their nitrogen stable isotope composition ($\delta^{15}\text{N}$) (see

Box 1).

Monitoring N_{dep} is challenging as instrument-based monitoring networks are costly and time-intensive. Direct measures of N_{dep} chemistry require separate, expensive collectors for wet and dry deposition, and are thus sparsely located in remote regions (Root et al., 2013; NADP, 2023) and developing countries (Díaz-Álvarez et al., 2018). These sparse collectors often do not provide N_{dep} data at ecologically relevant scales (Jovan et al., 2021). However, the use of biomonitors, including mosses and lichens, can supplement existing monitoring networks (Geiser et al., 2010, 2021; Root et al., 2013, 2015; Jovan et al., 2021). These non-vascular organisms integrate cumulative amounts of N_{dep} and are ubiquitous in urban, exurban, and wildland ecosystems, allowing for monitoring at diverse spatial and temporal scales (Lakatos et al., 2007; Williams et al., 2007; Rai and Gupta, 2022).

* Corresponding author.

E-mail address: meaghan.petix@wsu.edu (M.I. Petix).<https://doi.org/10.1016/j.ecolind.2024.112866>

Received 13 August 2024; Received in revised form 15 November 2024; Accepted 16 November 2024

1470-160X/© 2024 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Box 1

Spatial and temporal variation in stable isotope composition integrates signals from sources and subsequent transformations that occur during physical and biological reactions

Stable isotope composition is expressed as the molar ratio (R) of the heavier to lighter isotope of an element. Using N as an example:

$$R = {}^{15}\text{N}/{}^{14}\text{N} \quad (1)$$

The R of a sample is normalized relative to an international standard and expressed as the deviation from unity:

$$\delta^{15}\text{N} = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \quad (2)$$

Values are expressed as parts per thousand or per mil (‰) by multiplying (2) by 1000.

Stable Isotopes Inform About Sources.

Spatial and temporal variation in stable isotope composition integrates source substrates and subsequent transformations that occur during physical and biological reactions. The elemental content of a pool (B) reflects all inputs (A) and losses (C) of a given element.

$$A \rightarrow B \rightarrow C \quad (3)$$

If there is only one source, then the $\delta^{15}\text{N}$ of B will reflect that of its source, A, assuming no isotopic fractionation with uptake or loss. Reactants often vary in their stable isotope composition. For example, if A_1 and A_2 are two possible sources with $\delta^{15}\text{N}$ of -10‰ and $+10\text{‰}$, respectively, then the $\delta^{15}\text{N}$ of B will depend on the relative contribution of each source. For example,

$$A_1 \text{ 75\% and } A_2 \text{ 25\%, then } B \delta^{15}\text{N} = -5\text{‰} \quad (4)$$

$$A_1 \text{ 50\% and } A_2 \text{ 50\%, then } B \delta^{15}\text{N} = 0\text{‰} \quad (5)$$

$$A_1 \text{ 25\% and } A_2 \text{ 75\%, then } B \delta^{15}\text{N} = 5\text{‰} \quad (6)$$

Stable Isotopes Inform About Processes.

Fractionation (α) occurs when the different isotopes of an element have different reaction rates, leading to a difference in isotopic composition between the source and product. Discrimination (Δ) is the deviation of α from unity ($\alpha - 1$) and can be approximated by.

$$\Delta = \delta_{\text{source}} - \delta_{\text{product}} \quad (7)$$

The Δ will be 0‰ if $\alpha = 0$ for a reaction, or when, according to mass balance, all source is converted into product (Evans, 2001). The Δ provides very useful information when $\Delta > 0$, and when mechanisms behind the variation in Δ are known.

The $\delta^{15}\text{N}$ (see Box 1) of biomonitors can provide insights into N_{dep} chemistry as it varies among N emission sources and chemical forms (Elliott et al., 2007, 2019; Felix et al., 2014). The $\delta^{15}\text{N}$ of N_{dep} can be assessed using mosses (Bragazza et al., 2005; Solga et al., 2005; Zechmeister et al., 2008; Liu et al., 2008; Liu et al., 2012a) and lichens (Russow et al., 2004; Boltersdorf et al., 2014; Boltersdorf and Werner, 2014; Fogel et al., 2008; Lee et al., 2009) that rely solely on N_{dep} as their N source. The $\delta^{15}\text{N}$ of non-vascular bimonitor organisms should be closer to that of N_{dep} than vascular plants that take up N from the soil (Solga et al., 2005).

The chemical composition of N_{dep} is ecologically significant yet overlooked even though the relative amount of oxidized and reduced N has changed rapidly in the past few decades (Templer et al., 2012). The U.S. Clean Air Act focused on NO_x emissions from fossil fuel combustion and reduced N_{dep} over the past 30 years (Du et al., 2014; Du, 2016; Li et al., 2016). However, NH_3 emissions from agriculture are not regulated and have increased with increased agricultural production causing a shift in stoichiometry of wet N_{dep} from predominantly oxidized to reduced N forms (Du et al., 2014; Du, 2016; Li et al., 2016; Gilliam et al., 2019; Murray et al., 2022). Reduced N also increased with decreased scavenging of atmospheric NH_4^+ by NO_3^- and SO_4^{2-} (Du et al., 2014; Gilliam et al., 2019). The recent trend of increasing NH_x/NO_x has been observed at a continental scale (Du et al., 2014; Du, 2016; Li et al., 2016), but considerable regional and local-scale variability can occur due to spatially heterogeneous emission sources (Murray et al., 2022).

2. Emissions to ecosystem pathway

Mosses and lichens that derive their nutrition solely from atmospheric sources integrate the $\delta^{15}\text{N}$ of N_{dep} (Bragazza et al., 2005; Boltersdorf et al., 2014). Important assumptions inherent in the use of biomonitors are that the $\delta^{15}\text{N}$ of the bimonitor reflects that of the atmospheric source and the $\delta^{15}\text{N}$ of the atmospheric source conserves the $\delta^{15}\text{N}$ of source emissions (Section 4). Although a growing number of studies utilize $\delta^{15}\text{N}$ of biomonitors to assess N_{dep} , uncertainty remains as to whether biomonitors can be utilized as tracers of N emission sources. Here, we trace the pathway from N emission sources to biomonitors (Fig. 1), considering each process that may influence the $\delta^{15}\text{N}$ of biomonitors including atmospheric processes (Section 5), canopy effects (Section 6), and physiological effects (Section 7). We then discuss how $\delta^{15}\text{N}$ of biomonitors can be utilized to assess both current and historical trends in N_{dep} (Section 8).

3. Methods

This review synthesizes current methodologies for assessing nitrogen emission sources and deposition chemistry using mosses and lichens. We conducted a comprehensive literature search across multiple scientific databases, including *Web of Science* and *Google Scholar*, focusing on studies published from 2000 to 2023. Key search terms included “nitrogen stable isotope”, “biomonitor”, “moss”, “lichen”, and “nitrogen

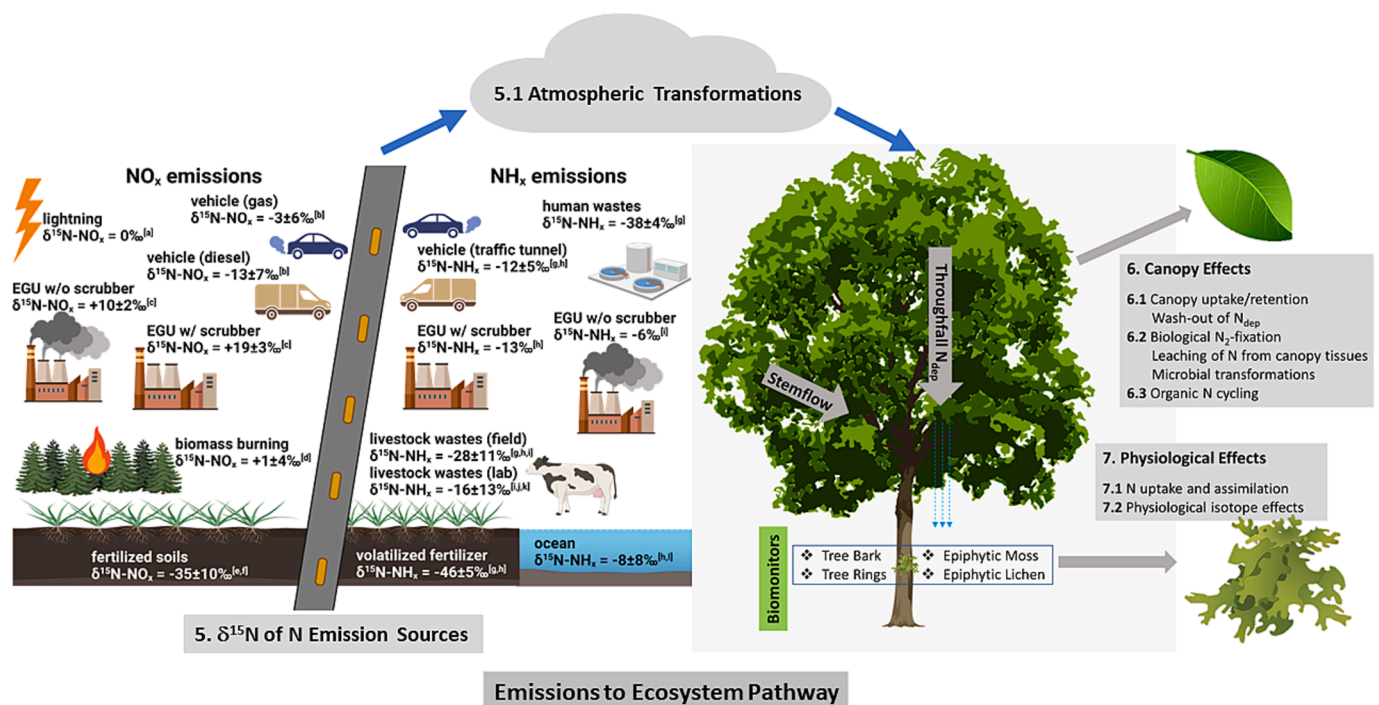


Fig. 1. Conceptual model of the emissions to ecosystem pathway where N compounds are emitted from natural and anthropogenic sources (Section 5), transformed in the atmosphere (Section 5.1), and then deposited back onto terrestrial ecosystems where they may interact with the forest canopy (Section 6) before uptake by biomonitor organisms (Section 7). The processes along this emissions to ecosystem pathway can influence the $\delta^{15}\text{N}$ of biomonitors. Display of $\delta^{15}\text{N-NO}_x$ and $\delta^{15}\text{N-NH}_x$ of N emission sources (mean $\pm$ 1 s.d.) adapted from Elliott et al. (2019). Source data: (a) Hoering (1957); (b) Walters et al. (2015a,b); (c) Felix et al. (2012); (d) Fibiger and Hastings (2016); (e) Li and Wang (2008); (f) Yu and Elliott (2017); (g) Chang et al. (2016); (h) Felix et al. (2013); (i) Freyer (1978); (j) Schulz et al. (2001); (k) Hristov et al. (2009); and (l) Altieri et al. (2014). Figure created with BioRender.com.

deposition". Relevant studies were selected based on criteria such as study design, geographic location, selection of biomonitors, and inclusion of $\delta^{15}\text{N}$ analyses within the studies. We reviewed 50 studies that investigated $\delta^{15}\text{N}$ of biomonitors, including lichens ($n = 29$), moss ($n = 16$), and both lichen and moss ($n = 5$) (Table 1). Details on methodologies for measuring $\delta^{15}\text{N}$ can be found in the original sources referenced in the text or relevant compilations of stable isotope analytical techniques (De Groot, 2004; De Groot, 2009).

4. Effective biomonitors for N_r

Mosses and lichens are the most common biomonitors to assess N_{dep}. Both lack roots and a cuticle and accumulate N and other water-soluble nutrients roughly in proportion to their abundance in the atmosphere. Epiphytic mosses growing on trees and shrubs, epilithic mosses growing on rock or concrete, and *Sphagnum* peat mosses that comprise the ground layer of ombrotrophic bogs receive all their nutrition from N_{dep}, while terrestrial mosses may receive N from both atmospheric sources and the soil (Turetsky, 2003; Liu et al., 2012a). Epiphytic lichens with a green algal photobiont are well-suited as biomonitors of N_{dep} as they also derive their nutrition solely from N_{dep} (Nash, 1996). Lichens with a cyanobacterial photobiont, herein referred to as *cyanolichens*, provide useful estimates of N derived from N₂-fixation. Quantitative relationships between paired observations from deposition collectors and epiphytic lichens allow prediction of N_{dep} from lichen tissue N concentration (Root et al., 2013). Diazotrophs growing in close association with mosses can provide significant N to mosses through N₂-fixation (reviewed in Rousk et al., 2013; Rousk 2022). These associations are not obvious during field collections, so careful assessment of samples for the presence of cyanobacteria are necessary before attributing variation in moss $\delta^{15}\text{N}$ to N_{dep}. Tree rings (Poulson et al., 1995; Saurer et al., 2004; Saurer and Siegwolf, 2007; Savard et al., 2009; Guerrieri et al., 2009) and tree bark (Schulz et al., 2001; Boltersdorf et al., 2014) can also be utilized as

biomonitors of amount and sources of N_{dep}. Analyzing tree rings can allow for interpretation of $\delta^{15}\text{N}$ over long time periods, providing information about both current and past N_{dep} (Savard et al., 2009). Airborne pollutants can be adsorbed to tree bark when exposed either directly from the atmosphere or via throughfall deposition and stemflow (Schulz et al., 2001). Although tree rings and bark have been shown to reflect anthropogenic N_{dep} sources, we focus on mosses and lichens for this review as their effectiveness as biomonitors has been better studied and substantiated by existing literature (Boltersdorf et al., 2014). The $\delta^{15}\text{N}$ of vascular plants, including tree rings/bark and leaf tissue, are influenced by mixing of atmospheric and soil N pools, and thus, may not reflect N_{dep} as well as non-vascular biomonitor organisms such as mosses and lichens.

5. $\delta^{15}\text{N}$ of anthropogenic N emission sources

The $\delta^{15}\text{N}$ of N_r species are thought to be quantitative tracers of NO_x and NH_x source chemistries (Fig. 1). Reactive N is biologically, photochemically, and radiatively active (Galloway et al., 2003). It is emitted from transportation, industry, and agriculture, and includes reduced forms such as ammonia [NH₃] and ammonium [NH₄⁺], referred to collectively as NH_x, oxidized forms including nitrogen oxides [NO + NO₂ = NO_x], nitric acid [HNO₃], nitrous oxide [N₂O], and nitrate [NO₃⁻], and organic compounds such as urea, amines, proteins, and nucleic acids (Galloway et al., 2003). Emissions from transportation and industry are dominated by NO_x, while those from agriculture are mainly NH_x (Fenn et al., 2003b).

The $\delta^{15}\text{N}$ of N_r exhibits considerable variation across the globe (Fig. 1) due to differences in substrate and technologies associated with emission reductions. Both factors are more consistent on local and regional scales, providing more reliable estimates of source attribution using the $\delta^{15}\text{N}$ of N_r. The dominant source of NO_x to the atmosphere is fossil fuel combustion by electricity generating units (EGU) and vehicles

Table 1
Studies investigating $\delta^{15}\text{N}$ of lichens (n = 29), moss (n = 16), and both lichen and moss (n = 5).

Biomonitor	Reference
Lichen	Ellis et al., 2003
Lichen	Russow et al., 2004
Lichen	Asada et al., 2005
Lichen	Purvis et al., 2005
Lichen	Tozer et al., 2005
Lichen	Fogel et al., 2008
Lichen	Proemse and Mayer, 2012
Lichen	Boltersdorf and Werner, 2013, 2014
Lichen	Bermejo-Orduna et al., 2014
Lichen	Crittenden et al., 2015
Lichen	Ciężka et al., 2016, 2022
Lichen	Cocozza et al., 2016
Lichen	Munzi et al., 2016, 2017, 2019
Lichen	Hogan et al., 2017
Lichen	Pinho et al., 2017
Lichen	Manninen, 2018
Lichen	Barre et al., 2018
Lichen	Simonova et al., 2018
Lichen	Hoffman et al., 2019
Lichen	Dörter et al., 2020
Lichen	Hurtado et al., 2020
Lichen	Xu et al., 2021
Lichen	Wieder et al., 2022
Lichen	Niepsch et al., 2021, 2023
Lichen + Moss	Lee et al., 2009
Lichen + Moss	Cipro et al., 2011
Lichen + Moss	Boltersdorf et al., 2014
Lichen + Moss	Díaz-Álvarez and de la Barrera, 2018
Lichen + Moss	Bokhorst et al., 2019
Moss	Pearson et al., 2000
Moss	Peñuelas and Filella, 2001
Moss	Gerdol et al., 2002
Moss	Bragazza et al., 2005
Moss	Solga et al., 2005, 2006
Moss	Liu et al., 2008
Moss	Zechmeister et al., 2008
Moss	Wilson et al., 2009
Moss	Xiao et al., 2010
Moss	Foan et al., 2010
Moss	Liu et al., 2012a
Moss	Delgado et al., 2013
Moss	Skudnik et al., 2014
Moss	Nielsen et al., 2017
Moss	Donovan et al., 2022

(Felix et al., 2012; Walters et al., 2015a,b; Elliott et al., 2019). The $\delta^{15}\text{N}$ varies with pollution control technologies; selective catalytic reduction (SCR) reduces NO_x emissions from EGUs (Srivastava et al., 2005) by reacting NO_x with NH_3 or urea over a catalyst to form N_2 and water vapor (Felix et al., 2012). Fractionation during the reaction between NO_x and NH_3 alters the $\delta^{15}\text{N}$ - NO_x as evidenced by differences in $\delta^{15}\text{N}$ of NO_x emitted from power plants with ($19 \pm 3 \text{ ‰}$) or without SCR ($10 \pm 2 \text{ ‰}$) (Felix et al., 2012) (Fig. 1). SCR is installed on > 1,000 point sources in the U.S. (ICAC, 2009) but is not universal causing spatial variation in $\delta^{15}\text{N}$ - NO_x for EGU sources. Three-way catalytic converters (TWC) on gasoline-powered vehicles also use a catalytic reduction of NO_x to N_2 and water vapor (DeFoort et al., 2004) causing differences in $\delta^{15}\text{N}$ - NO_x emitted from vehicles, with higher $\delta^{15}\text{N}$ - NO_x emitted from vehicles with TWC (Walters et al., 2015b). Differences may also exist among vehicles equipped with TWC as the effectiveness of TWC is dependent on stoichiometric combustion to successfully reduce NO_x , and thus can be variable in its effect on $\delta^{15}\text{N}$ - NO_x (DeFoort et al., 2004; Elliott et al., 2019). Agriculture is the dominant source of NH_x emissions (Felix et al., 2013; Chang et al., 2016; Elliott et al., 2019). The $\delta^{15}\text{N}$ of agricultural emissions are often very negative because the observed discrimination can be + 20 to + 27 ‰ for the $\text{NH}_4\text{:NH}_3$ equilibrium, and + 29 ‰ during NH_3 volatilization (Evans, 2007), but can also vary regionally as a

function of soil and environmental conditions (Elliott et al., 2019) (Fig. 1). Schulz et al. (2001) found the observed discrimination was temperature-dependent, suggesting $\delta^{15}\text{N}$ - NH_3 may vary seasonally and could differ depending on what time of year manure is applied, which is typically in the fall and spring (Schulz et al., 2001). The observed discrimination also varies as substrate is consumed; Evans (2007) modeled the $\delta^{15}\text{N}$ - NH_3 after application of urine with $\delta^{15}\text{N}$ of 0 ‰ (Frank et al., 2004) and observed an increase in $\delta^{15}\text{N}$ - NH_3 from ca. -35 to 0 ‰ over time. Variation in $\delta^{15}\text{N}$ - NH_3 has also been observed with different livestock housings, including between different animal sources (Schulz et al., 2001; Felix et al., 2014; Chang et al., 2016). Ammonia emissions can be released from EGUs although they constitute a small percent of overall NH_3 emissions. The $\delta^{15}\text{N}$ - NH_3 varies between power plants with (-13 ‰) or without SCR (-6‰) (Freyer, 1978; Felix et al., 2013; Elliott et al., 2019) (Fig. 1). Power plants with SCR can have ‘ NH_3 slip’ if all the supplied NH_3 does not react in the catalytic NO_x reduction process (Felix et al., 2013; Felix et al., 2014). Similarly, NH_3 can also be a byproduct in the catalytic NO_x reduction from vehicles equipped with TWC, thus NH_3 emissions from vehicles have increased in the past several decades with increasing usage of TWC (Felix et al., 2013). Felix et al. (2013) and Chang et al. (2016) found different ranges of $\delta^{15}\text{N}$ - NH_3 for vehicle emissions within a traffic tunnel in their respective study areas. Presumably, only vehicles equipped with TWC would be emitting NH_3 , so emission control technologies would not be the reason for differing $\delta^{15}\text{N}$ - NH_3 . Other factors potentially contributing to regional differences in $\delta^{15}\text{N}$ of NH_3 from vehicle emissions should be explored, as this emission source may be increasingly important, especially in urban centers.

5.1. Atmospheric transformations

Fractionation during atmospheric transformations can alter the original $\delta^{15}\text{N}$ of both reduced and oxidized N emissions. These transformations can be complex and exhibit seasonal and diurnal variation due to fluctuations in temperature, atmospheric moisture, solar radiation, and other atmospheric conditions (see review by Elliott et al., 2019). The challenge when interpreting $\delta^{15}\text{N}$ of N_{dep} is assessing the relative contributions of emission sources versus subsequent atmospheric transformations. For example, distinct seasonal patterns in $\delta^{15}\text{N}$ - NH_4^+ in precipitation were often attributed to seasonal changes in emission sources, but it is now clear that fractionation during aerosol NH_4^+ formation may also be a factor (Huang et al., 2019). The NH_4^+ in precipitation results from the dissolution of atmospheric NH_3 gas as well as the scavenging of aerosol NH_4^+ (Russell et al., 1998), thus the $\delta^{15}\text{N}$ - NH_4^+ in precipitation reflects both processes (Huang et al., 2019). Seasonal variation has been observed in $\delta^{15}\text{N}$ - NH_3 in agricultural regions and was likely influenced by fractionation, but $\delta^{15}\text{N}$ - NH_3 was seasonally consistent for rural non-agricultural areas (Felix et al., 2017). Thus, the relative importance of isotopic fractionation may vary seasonally (Huang et al., 2019) and regionally (Felix et al., 2017).

There is a gap in our ability to determine how atmospheric transformations alter $\delta^{15}\text{N}$ - NO_3 of N_{dep} . Atmospheric transformation of NO_x are complex with multiple competing reactions (Elliott et al., 2019), each of which has an associated fractionation factor that may alter the $\delta^{15}\text{N}$ of the original emitted N. Rapid photochemical cycling of NO_x occurs during the day and is controlled by O_3 concentrations and the NO_2 photolysis rate (Elliott et al., 2019). The oxidation of NO by O_3 has a kinetic isotopic effect (ϵ_k , defined as $(\alpha - 1) \times 1000$) of -7‰ at 298 K, resulting in lower $\delta^{15}\text{N}$ in NO_2 compared to NO and the total NO_x (Walters and Michalski, 2016). However, there is also a large equilibrium isotopic effect ($\epsilon_{\text{eq}} = +37 \text{ ‰}$ at 298 K) for the equilibrium reaction between NO and NO_2 , where the $\delta^{15}\text{N}$ of NO_2 is higher relative to NO and the total NO_x (Walters et al., 2016). Most NO_x is subsequently oxidized to HNO_3 via daytime or nighttime reactions that may be associated with additional isotopic fractionations (Elliott et al., 2019). The observed discrimination for the exchange reactions between NO_2 ,

NO_3 , and N_2O_5 has been investigated (Walters and Michalski, 2015), but the potential kinetic isotopic effects associated with the subsequent reactions leading to the formation of HNO_3 have not yet been quantified (Elliott et al., 2019). It is likely that isotopic effects during atmospheric transformations are influencing variability in $\delta^{15}\text{N}$ measured in N_{dep} (Elliott et al., 2019). However, the degree to which each of these factors contribute to variability is an active area of research using tools such as dual nitrate isotope analyses (Chen et al., 2019).

6. Canopy effects

Epiphytic lichens and mosses occurring on stem surfaces of woody plants are consequently only collected from within or under plant canopies. Transformations within the canopy may alter the amount and $\delta^{15}\text{N}$ of N_{dep} (Heaton et al., 1997; Hoffman et al., 2019). For example, Heaton et al. (1997) observed higher $\delta^{15}\text{N}\text{-NO}_3^-$ in throughfall (+0.3 to +4.7 ‰) compared to bulk rainfall (−1.5 to +0.9 ‰) and they attributed this to accumulation of dry N_{dep} in canopies. The $\delta^{15}\text{N}$ of NO_3^- formed as aerosols in dry deposition are higher than the $\delta^{15}\text{N}$ of their precursors and thus tend to be higher than $\delta^{15}\text{N}$ of NO_3^- in rainfall (Heaton et al., 1997). The $\delta^{15}\text{N}\text{-NH}_4^+$ was variable, with no consistent trend between throughfall and rainfall, which they hypothesized could be due to effects of pH and NH_3 concentrations (Heaton et al., 1997). In contrast, Hoffman et al. (2019) observed no differences between $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{15}\text{N}\text{-NH}_4^+$ in throughfall and bulk deposition, even though estimates of N_{dep} from throughfall were always much higher than bulk deposition at the same site. This suggests that the primary mechanism is accumulation and subsequent washout of dry deposition in throughfall, rather than selective leaching of different compounds. Contrasting results such as this emphasize that the canopy hosts a complex network of processes that contribute to and regulate forest N cycling (reviewed in Bortolazzi et al., 2021; Guerrieri et al., 2021), and canopy processes including uptake of N, wash-out and dissolution of dry deposition, biological N_2 -fixation, microbial transformations, leaching of N from canopy tissues, and organic N cycling can each alter the amount and $\delta^{15}\text{N}$ of N_{dep} (Fig. 1).

6.1. Canopy uptake/retention/wash-out of N_{dep}

Forest canopies accumulate dry deposition and retain a significant fraction of total N_{dep} (Fenn et al., 2013; Templer et al., 2015; Bortolazzi et al., 2021; Guerrieri et al., 2021). Foliar uptake can occur, primarily through stomatal diffusion, as well as passive diffusion through bark (Bortolazzi et al., 2021). Canopy biota, including leaf microbes, epiphytic lichens and mosses, and vascular epiphytic plants, also assimilate organic and inorganic N (Bortolazzi et al., 2021; Guerrieri et al., 2021). Conifer forests usually intercept more inorganic N from N_{dep} than deciduous forests partly due to higher canopy surface area and a lack of seasonal foliage loss (Vanguelova et al., 2010; Schwarz et al., 2014). Forests in the Pacific Northwest, USA, preferentially uptake NO_3^- from wet deposition, especially in winter (Klopatek et al., 2006; Fenn et al., 2013) so biomonitors lower in the canopy may be receiving less NO_3^- than in bulk N_{dep} , which may influence $\delta^{15}\text{N}$. However, studies in other regions have reported a higher efficiency of NH_4^+ retention than NO_3^- by forest canopies (Mustajärvi et al., 2008; Houle et al., 2015; Avila et al., 2017), which could have a differing influence on biomonitors $\delta^{15}\text{N}$.

6.2. Biological N_2 -fixation, leaching of N from canopy tissues, and microbial transformations

Cyanolichens may alter the chemistry and $\delta^{15}\text{N}$ of throughfall deposition. The N derived from N_2 -fixation has a $\delta^{15}\text{N}$ of −2 to 0 ‰ (Shearer and Kohl, 1993), which overlaps or exceeds the range of $\delta^{15}\text{N}$ for several anthropogenic N emission sources (Elliott et al., 2019) (Fig. 1). Leaching from cyanolichens can change the $\delta^{15}\text{N}$ of throughfall

deposition in canopies where rates of N_2 -fixation are high. Certain areas, including old-growth Douglas-fir forests of the Pacific Northwest, USA, have a substantial biomass of cyanolichens that contribute significant N inputs via nitrogenous leachates and decomposition (Pike, 1978; Carroll, 1980; Sollins et al., 1980; Antoine, 2004). Nitrogen can be readily leached from lichen tissues during heavy rainfall events (Millbank, 1982). Epiphytic mosses can be associated with N_2 -fixing prokaryotes that may also alter the $\delta^{15}\text{N}$ of throughfall deposition (Lindo and Whiteley, 2011; Wang et al., 2022). A confounding factor when using mosses as biomonitors is that unlike cyanolichens, epiphytic mosses with diazotroph-associations cannot be easily identified and separated out during field collections (Rousk et al., 2013; Rousk 2022). This can confound interpretation of moss $\delta^{15}\text{N}$ as moss that derives significant N from these associations should have $\delta^{15}\text{N}$ close to 0 ‰ (Deane-Coe and Sparks, 2016) although not in all cases (Stuart et al., 2021).

Nitrification by epiphytic microbes can also be significant in forest canopies (Guerrieri et al., 2015; Guerrieri et al., 2020). This can impact the amount and $\delta^{15}\text{N}$ of NO_3^- available to biomonitors. The observed discrimination for nitrification ranges from +5 to +35 ‰ (Delwiche and Steyn, 1970; Mariotti et al., 1981; Yu et al., 2021) producing NO_3^- with lower $\delta^{15}\text{N}$ than most anthropogenic sources.

6.3. Organic N cycling

Organic N deposition can be a significant component of total N deposition (Neff et al., 2002; Cornell et al., 2003; Cornell, 2011). Organic N comprised 56 % of total N measured in throughfall deposition in a mixed boreal forest in eastern Finland (Pirainen et al., 1998). Organic N may be a larger component of throughfall deposition than bulk deposition as throughfall deposition is enriched with amino acids as it is filtered through the canopy (Carlisle et al., 1966, 1967). Epiphytic biomonitors, including lichens and mosses, readily utilize amino acids and other organic N compounds (Smith, 1960; Dahlman et al., 2004; Liu et al., 2013) and Dahlman et al. (2004) suggests that the uptake of amino acids by lichens may rival that of NO_3^- . The question remains, however, how organic N uptake may influence the $\delta^{15}\text{N}$ of biomonitors. Accurate measures of organic N in most deposition collectors are problematic unless strict protocols are followed (Walker et al., 2012), and challenges associated with these measurements also apply to $\delta^{15}\text{N}$. Further development of protocols is necessary to better understand the $\delta^{15}\text{N}$ of organic N in throughfall deposition, whether it is altered through canopy processing, and to what extent it may influence the $\delta^{15}\text{N}$ of biomonitors.

6.4. Canopy impacts on biomonitors

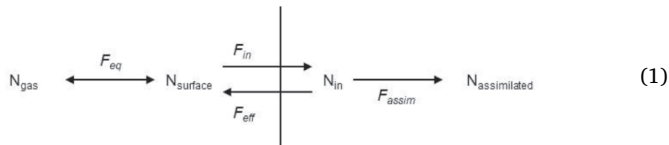
Canopy processes, including uptake of N, wash-out and dissolution of dry deposition, biological N_2 -fixation, microbial transformations, leaching of N from canopy tissues, and organic N cycling, are important to consider in studies using epiphytic mosses and lichens as biomonitors, as they can significantly alter the amount and $\delta^{15}\text{N}$ of N_{dep} available to these organisms. Best practices for collecting moss and lichen material should align with the study's objectives and research questions. For instance, harvesting from consistent heights and positions on trees can help account for vertical gradients in N inputs and transformations. While collecting samples from different vertical strata within the canopy can provide valuable data, this approach may not be practical at larger scales due to the time and effort required. The U.S. Forest Service Forest Inventory & Analysis (FIA) protocol is currently the standard methodology in the United States for lichen tissue collection for elemental analysis (Geiser, 2004; USFS, 2011). With this protocol, two target lichen species are collected from a minimum of six different locations, including from tree branches, tree/shrub boles, litterfall, or fallen branches, within a 34.7 m radius circular plot (Geiser, 2004; USFS, 2011). Sampling material from lower canopy positions and incorporating litterfall from mid- to upper-canopy levels can help capture the variation in $\delta^{15}\text{N}$ across a site, providing a more comprehensive

understanding of N dynamics. While the tissue pool of N in lichens and mosses is likely much larger than temporal additions or losses, with N turnover occurring over several years to more than a decade (Nash, 1996; Turetsky, 2003), minimizing potential bias from temporal dynamics should also be considered in sampling designs. By adopting best practices tailored to specific research objectives, researchers can more effectively interpret the complex interactions between N_{dep} , canopy processes, and biomonitors, leading to more robust and meaningful insights into N cycling and deposition patterns in forest ecosystems.

7. Physiological effects

7.1. N uptake and assimilation

Mosses and lichens can take up NO_3^- , NH_4^+ , and amino acids (Glime, 2007; Dahlman et al., 2004). Studies often assume that biomonitor $\delta^{15}N$ acts as a tracer where the isotope composition of biomonitor tissue reflects that of the N source. Inherent in this assumption is that fractionation events during physical and biological transformations are not important, thus the observed discrimination between N source and the organism is 0 ‰. The steps of N acquisition are uptake of N from the surface of the biomonitor, translocation to the site of assimilation, and assimilation into biomonitor tissue (Fig. 2).



Mosses and lichens absorb N across their entire surface (Glime, 2007; Hauck, 2010). Both have high surface cation exchange capacity (Bates, 1992; Bargagli et al., 1998; Gaio-Oliveira et al., 2001) that allows dry and wet deposition to be captured efficiently during precipitation events (Liu et al., 2012a; Carter et al., 2017). Moss sporophytes have stomata, but their role may be only to control desiccation for dehiscence of spores

rather than to optimize photosynthetic CO_2 uptake (Merced and Renzaglia, 2017). Uptake of NH_4^+ and amino acids bound to extracellular surfaces of mosses is via a proton antiport, while anion uptake occurs through a symport (Raven et al., 1998; Glime, 2007). Uptake of N_r by lichens is more complex; NH_3 and NO_2 can diffuse across the mycobiont cortex during dry conditions and subsequent uptake by algal cells occurs by both active and passive transport (Greaver et al., 2023). Gaseous NH_3 will often react with water when available and form NH_4^+ , and gaseous NO_2 will form HNO_3 , NO_3^- , or NO (Greaver et al., 2023). These reactions with water may occur in the surrounding atmosphere, on the surface of the lichen thallus, or in the cytosol. Assimilation of NH_4^+ and NO_3^- occurs via the same pathways as in vascular plants (Brown, 1982; Hauck, 2010). Assimilation of NH_4^+ occurs by the glutamine synthetase – glutamate synthase (GS-GS-GOGAT) pathway, while NO_3^- is first reduced to NO_2^- then NH_4^+ by nitrate and nitrite reductase, respectively, before the GS-GOGAT pathway.

7.2. Physiological isotopic effects

Isotopic fractionation during uptake and assimilation by diverse organisms has been described by Evans (2001)

$$\Delta = b - b \left(\frac{F_{assim}}{F_{in}} \right) \quad (2)$$

where F_{in} is the rate of N influx, F_{assim} is the rate of N assimilation, and b is fractionation associated with the assimilatory enzyme. Equations (1) and (2) predict that N from the surface ($N_{surface}$) is transported into N inside the organism (N_{in}), that in turn is being assimilated into organic N. The observed discrimination with F_{in} is 0 ‰, but nitrate reductase and glutamine synthetase both discriminate against ^{15}N during assimilation (Evans, 2001). For example, an isotope discrimination of +12.1 ‰ was measured for enzymatic nitrate reduction in a moss, *Hypnum plumaeforme*, similar to vascular plants (Liu et al., 2012b; Liu et al., 2020). The result is that ^{14}N is preferentially assimilated into organic N, causing the relative amount of ^{15}N in N_{in} to increase resulting in higher $\delta^{15}N$. Eq. (2)

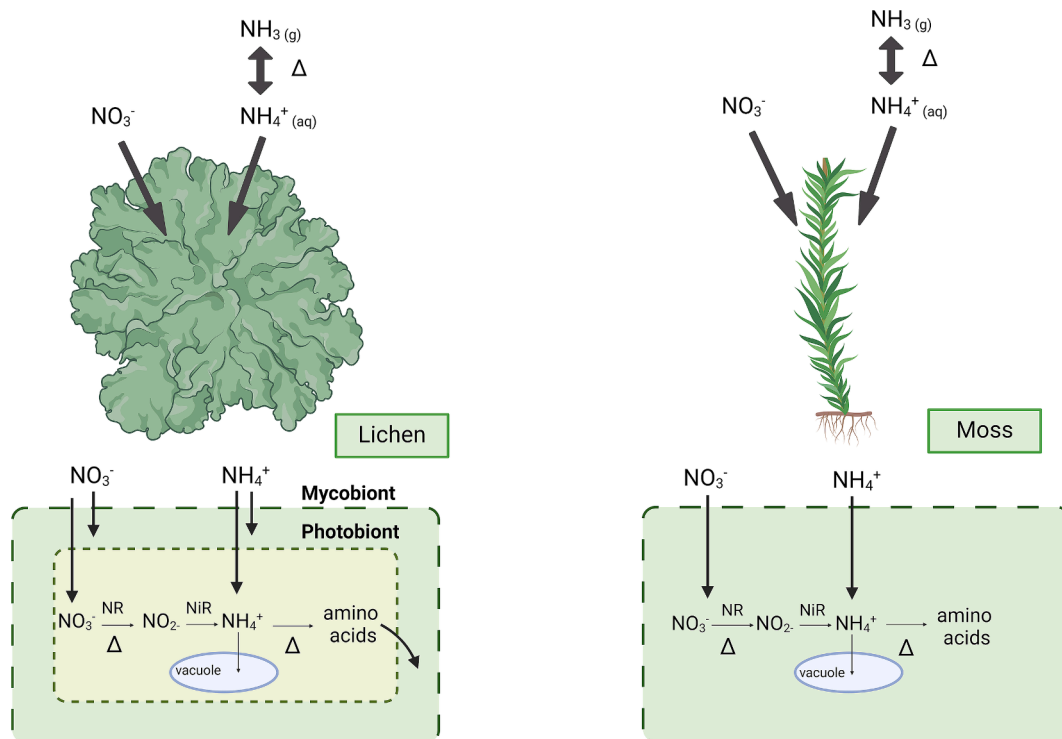


Fig. 2. N uptake and assimilation pathways for lichens (left) and mosses (right) including potential isotopic effects. NR = nitrate reductase; NiR = nitrite reductase. Δ signifies observed discrimination ($\Delta = \delta_{source} - \delta_{product}$). Figure created with BioRender.com.

predicts that $\Delta > 0$ will only occur if significant efflux of enriched N in N_{in} occurs, causing $F_{eff} > 0$ and $F_{assim} < F_{in}$. However, under most conditions N demand is high compared to N availability, so all N entering the cell will be assimilated, so $F_{in} = F_{assim}$ and observed discrimination will be 0 ‰. Discrimination has been observed in vascular plants under very high nutrient supply rates, allowing F_{in} to exceed F_{assim} , but any efflux of N in biomonitors will return to F_{out} , allowing it to be readsorbed, again resulting in $\Delta = 0$ ‰. $\Delta > 0$ ‰ would only be observed if N efflux evaporates off the surface or is washed away during a precipitation event. Thus, biomonitors act like a closed system, with biomonitor $\delta^{15}N$ reflecting the $\delta^{15}N$ of N sources.

Two factors that may cause differences between the $\delta^{15}N$ of N_{dep} and biomonitors are equilibrium reactions between gaseous and surface N, and preferential use of different N forms with contrasting $\delta^{15}N$. The observed discrimination of $NH_{3(g)}$ equilibrating with $NH_{4(aq)}^+$ can be > 30 ‰ (Kirshenbaum et al., 1947; Heaton et al., 1997) (Fig. 2). This has been observed under unique circumstances and will be discussed in Section 7.3, but it is not likely to be important in most studies. Different forms of available N often have distinct $\delta^{15}N$ (see Section 5). Preferential uptake can be misinterpreted as a product of fractionation during uptake when the $\delta^{15}N$ of the biomonitor is compared to that of bulk N_{dep} rather than individual sources. Mosses and lichens may prefer reduced N (Dahlman et al., 2002, 2004; Palmqvist and Dahlman, 2006; Liu et al., 2013), but preferential uptake is rare and only occurs under certain conditions such as with elevated N_{dep} since mosses and lichens efficiently uptake all N forms (Hauck, 2010).

7.3. Evidence of physiological isotopic effects from extreme environments

Isotopic effects attributed to physiological processes have been observed in several studies in extreme, N-limited environments (Tozer et al., 2005; Bokhorst et al., 2019). Tozer et al. (2005) found very low $\delta^{15}N$ (-20 ‰) in lithophytic and epiphytic lichens and proposed that the extremely low $\delta^{15}N$ were due to the additive discriminations from (1) fractionation associated with $NH_{3(g)}$ volatilization and (2) fractionation associated with diffusive $NH_{3(g)}$ uptake into the lichens. Alternatively, in an Antarctic ecosystem, discrepancies were observed between isotopically enriched mosses and lichens and their putative N source, isotopically depleted volatilized $NH_{3(g)}$ from penguin and seal guano (Erskine et al., 1998; Crittenden et al., 2015; Bokhorst et al., 2019). Crittenden et al. (2015) hypothesized that this was caused by deposition of enriched particulate matter on the biomonitor surfaces, although Bokhorst et al. (2019) posited that the chemical exchange reaction of $NH_{3(g)}$ equilibrating with $NH_{4(aq)}^+$ on the biomonitor surfaces was the mechanism (Fig. 2). Species-specific differences in $\delta^{15}N$ were observed in the field (Bokhorst and Convey, 2016), but not under experimental conditions (Bokhorst et al., 2019). They conclude that physiological factors, such as form preference, tissue pH, tissue N content, and N scavenging capability, may influence the $\delta^{15}N$ of biomonitors. Furthermore, how N is taken up and assimilated can also be potentially influenced by the amount and type of N_{dep} as well as climatic variables (Díaz-Álvarez et al., 2018; Liu et al., 2012a; Hoffman et al., 2019).

8. Applications of biomonitor $\delta^{15}N$

8.1. Spatial patterns: Can we identify emission sources?

8.1.1. Direct correlations

Direct correlations occur between moss and lichen $\delta^{15}N$ and proximity to known N emission sources (Pearson et al., 2000; Boltersdorf and Werner, 2013; Bermejo-Orduna et al., 2014; Pinho et al., 2017; Donovan et al., 2022) (Table 1). Higher moss and lichen $\delta^{15}N$ is observed closer to roadways and areas of high population density due to traffic and industrial NO_x emissions (Pearson et al., 2000; Gerdol et al., 2002; Bermejo-Orduna et al., 2014; Manninen, 2018; Donovan et al., 2022). Higher $\delta^{15}N$ in moss (Pearson et al., 2000; Gerdol et al., 2002) and lichen

(Purvis et al., 2005; Bermejo-Orduna et al., 2014) was linked to oxidized N from traffic emissions by analyzing known heavy metal markers such as Pb, Zn, and As. In turn, lower $\delta^{15}N$ are found closer to intensive agricultural areas because of the influence of agricultural NH_x emissions (Boltersdorf and Werner, 2014; Boltersdorf et al., 2014; Pinho et al., 2017; Hoffman et al., 2019). Lichen $\delta^{15}N$ varies according to the $\delta^{15}N$ of NH_3 providing evidence that lichen $\delta^{15}N$ reflects the $\delta^{15}N$ of atmospheric NH_3 (Munzi et al., 2019).

Accurate data on $\delta^{15}N$ of emission sources is still a crucial element for the interpretation of biomonitor $\delta^{15}N$. Newer industries such as oil sands mining in the Athabasca region of Alberta, CA are not as well-studied and do not have reported values for all distinct N emission sources including upgrader stacks and exhaust from diesel-powered mine fleets (Wieder et al., 2022). Though this paucity of data precludes conclusive source apportionment, several studies have shown epiphytic lichen $\delta^{15}N$ was correlated to proximity to oil sands operations (Proemse and Mayer, 2012; Wieder et al., 2022). While Proemse and Mayer (2012) found the $\delta^{15}N$ of an epiphytic lichen, *Evernia mesomorpha*, was higher with closer proximity to oil sands operations, Wieder et al. (2022) observed a decrease in lichen $\delta^{15}N$ with increasing proximity to oil sands operations, suggesting the influence of an oil sands emission source(s) with a more negative $\delta^{15}N$.

8.1.2. Correlation with $NH_x:NO_x$ ratio

Biomonitor $\delta^{15}N$ often exhibits a negative correlation with the ratio of $NH_x:NO_x$ in N_{dep} (Ellis et al., 2003; Asada et al., 2005; Liu et al., 2008; Xiao et al., 2010; Skudnik et al., 2014) (Fig. 3). This relationship is consistent across different areas of the globe (Xu et al., 2021) (Fig. 3). Xu et al. (2021) found a significant negative relationship between the ratio of $NH_x:NO_x$ in N_{dep} and lichen $\delta^{15}N$ for data from six separate studies ($R^2 = 0.49$; $p < 0.001$) (Fig. 3a). There are significant negative relationships between the ratio of $NH_x:NO_x$ in N_{dep} and moss $\delta^{15}N$ at the local and regional scale, but these are often distinct from one another, and global relationships are not apparent (Fig. 3b).

Lower biomonitor $\delta^{15}N$ associated with a higher $NH_x:NO_x$ indicates a greater contribution of NH_x emissions from agricultural activities (Bragazza et al., 2005; Xu et al., 2021; Du et al., 2022). This relationship allows assessment of N emission chemistries (Xu et al., 2021; Du et al., 2022) at local or regional scales and informs potential ecological effects. Biomonitor $\delta^{15}N$ can potentially be utilized to quantitatively reconstruct site-based $\delta^{15}N$ of NH_x and NO_x deposition (Xu et al., 2021); for example, Xu et al. (2021) determined lichen $\delta^{15}N$ lower than -7.8 ‰ indicated the dominance of ^{15}N -depleted NH_4^+ relative to ^{15}N -enriched NO_3^- in wet deposition (Xu et al., 2021) (Fig. 3a).

8.2. Temporal changes in N_{dep} sources

8.2.1. Influence of the “ ^{15}N Haber-Bosch effect”

Herbaria collections can be used to reconstruct past and current patterns of N_{dep} (Peñuelas and Filella, 2001; Solga et al., 2006; Foan et al., 2010; Du et al., 2022). A decrease in $\delta^{15}N$ has been observed in biomonitors from the mid-late 1800s to the early 2000s (Saurer et al., 2004; Solga et al., 2006; Anderson, 2017) (Fig. 4). Solga et al. (2006) observed a significant decrease in moss $\delta^{15}N$ from the 1850s to 2000 in Germany. *Pleurozium schreberi* decreased from -3.7 to -5.2 ‰ and *Scleropodium purum* from -3.0 to -5.8 ‰ (Solga et al., 2006). The $\delta^{15}N$ of the lichen *Alectoria sarmentosa* collected across the western United States decreased from the late 1800s to early 2000s (Anderson, 2017) and suggests a greater contribution of NH_x emissions towards the end of the last century. This is supported by tree ring studies that show a decrease in $\delta^{15}N$ of tree rings from the late 1920s to about 1950 in Switzerland (Saurer et al., 2004) and from the 1960s to 1990s in the northeastern U.S. (Poulson et al., 1995), attributed to an intensification of agricultural production (Poulson et al., 1995; Saurer et al., 2004).

Trends observed for biomonitors (Solga et al., 2006; Anderson, 2017) are consistent with $\delta^{15}N$ - NO_3^- from Greenland ice cores (Hastings et al.,

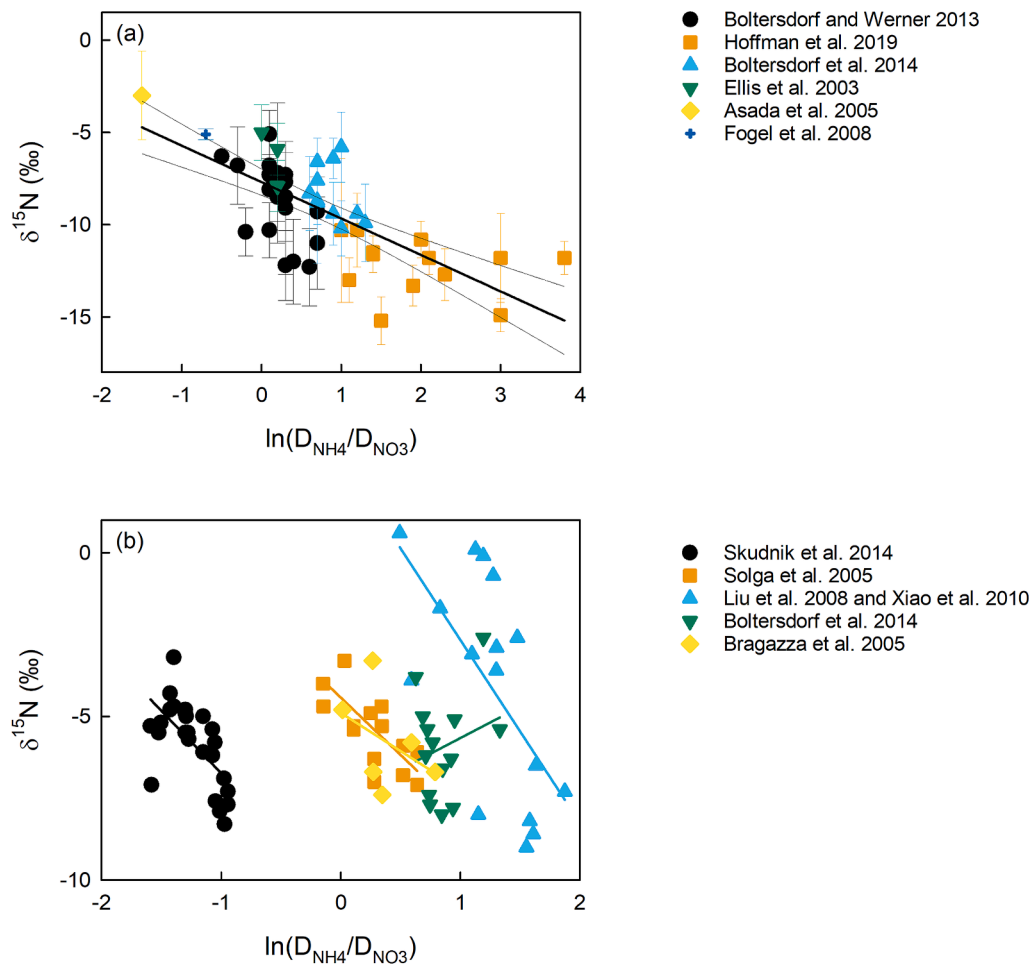


Fig. 3. (a) Relationship of lichen $\delta^{15}\text{N}$ to $\text{NH}_4^+:\text{NO}_3^-$ ratio in N deposition. Redrawn from Xu et al. (2021). (b) Relationship of moss $\delta^{15}\text{N}$ to $\text{NH}_4^+:\text{NO}_3^-$ ratio in N deposition. Redrawn from Du et al. (2022).

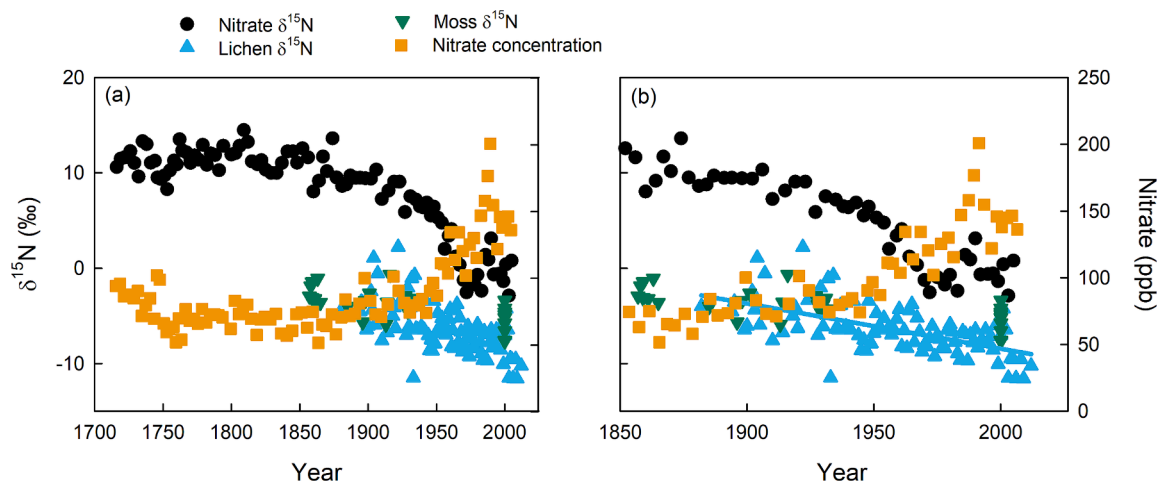


Fig. 4. (a) $\delta^{15}\text{N}$ of nitrate (‰) (black circles) and nitrate concentration (ppb) (orange squares) in a 100-m ice core from Summit, Greenland, spanning ~ 1718 to 2006 (from Hastings et al., 2009). $\delta^{15}\text{N}$ of moss (‰) (green upside-down triangles) (Solga et al., 2005) and lichen (blue triangles) (Anderson 2017) specimens from herbaria spanning ~ 1850 to 2010. (b) Zoomed-in view showing ice core, moss, and lichen data from 1850 to 2010 (note different x-axis scale). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2009) and remote lake sediments across the Northern Hemisphere (Holtgrieve et al., 2011) (Fig. 4). The $\delta^{15}\text{N}-\text{NO}_3^-$ in ice core and lake sediment records has decreased since the late 1800s due to increased anthropogenic N sources with lower $\delta^{15}\text{N}$ compared to preindustrial

sources (Hastings et al., 2009; Holtgrieve et al., 2011). Increasing NO_3^- from oil burning, which is associated with a more negative $\delta^{15}\text{N}-\text{NO}_3^-$ than biomass and coal burning, appears to be the main driver of this trend (Chellman et al., 2016). An increase in N soil emissions from

increased fertilizer use (Felix and Elliott, 2013) and atmospheric acidity caused by increased anthropogenic NO_x and SO_x emissions (Geng et al., 2014) could have also contributed to this decline. Modeled oceanic trends have also revealed a decrease in $\delta^{15}\text{N}$ of fixed N pools over time due to anthropogenic N sources, which Yang and Gruber (2016) coined the “ ^{15}N Haber-Bosch effect”. Though not solely responsible for global N cycle perturbations, the Haber-Bosch process has had an immense impact on N_f inputs since its advent in the early 1900s. The “ ^{15}N Haber-Bosch effect” can refer to the observed decline in $\delta^{15}\text{N}$ of total N_{dep} induced by anthropogenic N emissions, including both NO_x and NH_x emissions from industrial/vehicular and agricultural sources (Yang and Gruber, 2016).

Globally, historical trends in predominant N emission sources and deposition chemistry may vary due to differences in development stages of different countries as well as emission controls and policies. For instance, there is evidence that moss $\delta^{15}\text{N}$ has tended to be less negative in recent decades in China (Du et al., 2022), suggesting that NO_x emissions from industrial development and vehicle exhaust are still significant in this country. N_{dep} may still be dominated by traffic-related NO_x (Zhao et al., 2019). However, a shift from dominance of NO_3^- to NH_4^+ in N_{dep} was observed elsewhere with an associated decrease in moss $\delta^{15}\text{N}$ (Huang et al., 2021), similar to patterns observed in Europe and the United States (Fig. 4). Interestingly, they revealed that combustion-related NH_3 sources including vehicle exhaust, coal combustion, and biomass burning contributed more to the elevation of $\text{N}_{\text{dep}}\text{-NH}_4^+$ than volatilization NH_3 sources from wastes and fertilizers (Huang et al., 2021).

8.2.2. Changes in N_2 -fixation

Plant $\delta^{15}\text{N}$ has historically been used to estimate the amount of N_2 -fixation contributing to individual species as well as ecosystems. The same approach can also be used to assess changes in N_2 -fixation associated with the increased N_{dep} presented in Fig. 4. Cyanolichens such as *Lobaria oregana* are the dominant source of N input into coastal old-growth forests of the Pacific Northwest, USA, and rates of N input may exceed $16 \text{ kg N ha}^{-1} \text{ y}^{-1}$ (Antoine, 2004). The $\delta^{15}\text{N}$ of herbarium specimens demonstrate that the N derived from the atmosphere (% NDFA) is ca. 100 % in the early 1900s but decreased concurrent with industrialization and expansions of agriculture in this region (Fig. 5). The exact change in %NDFA has yet to be quantified because samples were not paired with non- N_2 -fixing lichens, but results are still informative and highlight the power of this approach.

9. Concluding Remarks and Future Perspectives

Biomonitoring can assess N emission sources and deposition chemistry at fine scales, ranging from a few meters to a few kilometers, that are more localized than those available from atmospheric models. They integrate factors such as elevation, topography, and meteorological conditions that can cause variation in atmospheric N_{dep} across the landscape (Lakatos et al., 2007; Williams et al., 2007). They also integrate N over time, capturing temporal variation in atmospheric N_{dep} (Williams et al., 2007). Biomonitoring can reflect the N fluxes being received by an ecosystem taking canopy processing into consideration. This can be an advantage, as it more accurately reflects the N inputs to a closed canopy system, but it can also be a disadvantage in that it is more difficult to ascertain contributions from anthropogenic N emission sources.

Mosses and lichens are effective biomonitors for assessing N_{dep} . Their $\delta^{15}\text{N}$ reflects N emission sources and deposition chemistry. The suitability of specific biomonitors may depend on a variety of local factors including geographic distribution and abundance. Future studies should consider potential species-specific differences in $\delta^{15}\text{N}$ such as that observed for lichens (Niepsch et al., 2023). A further consideration for mosses, noted in Section 6.2, is that diazotroph-associations could contribute to their N budget, but be difficult to identify during field

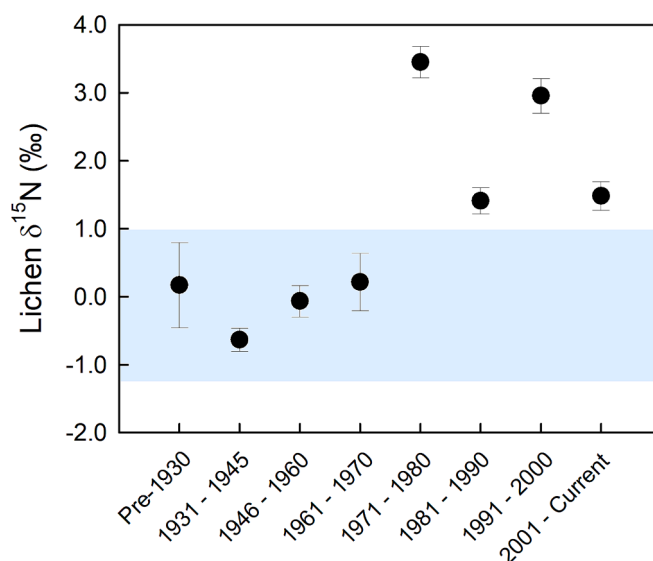


Fig. 5. Mean lichen $\delta^{15}\text{N} \pm \text{SE}$ for herbarium specimens within 8 distinct time periods (Evans, unpublished data). Increasing values across time represent a shift from N_2 -fixation towards fossil fuel emissions.

collections. Green algal lichens may be easier to target and better reflect anthropogenic N emission sources.

One of the future challenges of interpreting $\delta^{15}\text{N}$ in biomonitors is accounting for variability in $\delta^{15}\text{N}$ of N pollution sources. Just as emission control technologies have led to variation in $\delta^{15}\text{N}$ of NO_x emitted from EGUs and vehicles, advancement of NH_3 emission controls in livestock operations and manure management practices could also result in further variability in $\delta^{15}\text{N}\text{-NH}_3$ from agricultural activities. NH_3 emissions from vehicles are currently unregulated, but emission control strategies for this emerging N pollution source may also be developed and employed in the coming years, with possible impacts on $\delta^{15}\text{N}\text{-NH}_3$ from this source. With advancements in the ability to measure $\delta^{15}\text{N}$ of different N pollution sources (Elliott et al., 2019), maintaining an updated inventory of $\delta^{15}\text{N}$ for N pollution sources can be achieved and should be a priority as these values are necessary for source apportionment.

Additionally, further research is needed on how canopy processes and the physiology of biomonitor organisms influence the $\delta^{15}\text{N}$ of biomonitors. However, it should be re-emphasized that the $\delta^{15}\text{N}$ of biomonitors is acting as an integrator, reflecting the $\delta^{15}\text{N}$ of its N source(s) as well as processes that could alter $\delta^{15}\text{N}$ (Robinson, 2001; Williams et al., 2007). The $\delta^{15}\text{N}$ of biomonitors cannot be utilized as tracers of N emission sources; as was discussed in this review there are a variety of transformations and processes that may occur from N being emitted from a pollution source to then being assimilated into a biomonitor organism that may influence $\delta^{15}\text{N}$. However, $\delta^{15}\text{N}$ of biomonitors can still be useful in determining dominant sources of N emissions and forms of N_{dep} . Understanding prevailing emission sources and chemistries in an area is a requisite for effective air quality management and ecological risk assessment and mitigation. Studies that focus on the N concentration of biomonitors that provides insight on the level of N_{dep} loading are more common than those that measure N concentration and $\delta^{15}\text{N}$ (Du et al., 2022; Rai and Gupta, 2022). Further studies investigating the $\delta^{15}\text{N}$ of biomonitors, at all levels of spatio-temporal scales, are critical to further develop our knowledge on past and current patterns of N_{dep} and N_{dep} form, helping to assess major sources of N emissions and strategize for emission mitigation.

CRedit authorship contribution statement

Meaghan I. Petix: Writing – review & editing, Writing – original

draft, Visualization, Data curation, Conceptualization. **Michael D. Bell:** Writing – review & editing. **David G. Williams:** Writing – review & editing. **R. Dave Evans:** Writing – review & editing, Writing – original draft, Visualization, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was made possible by a grant from the National Park Service (Grant #P18AC00927) to RDE and funding from the Betty Higinbotham Trust and College of Arts & Sciences, Washington State University awarded to MIP.

Data availability

Data will be made available on request.

References

- Altieri, K.E., Hastings, M.G., Peters, A.J., Oleynik, S., Sigman, D.M., 2014. Isotopic evidence for a marine ammonium source in rainwater at Bermuda. *Global Biogeochem. Cycles* 28, 1066–1080. <https://doi.org/10.1002/2014GB004809>.
- Anderson, S.M., 2017. *Atmospheric nitrogen deposition in the western United States: sources, sinks, and changes over time*. Washington State University. PhD Dissertation.
- Antoine, M.E., 2004. An ecophysiological approach to quantifying nitrogen fixation by *Lobaria oregana*. *Bryologist* 107, 82–87. [https://doi.org/10.1639/0007-2745\(2004\)107\[82:AEATQN\]2.0.CO;2](https://doi.org/10.1639/0007-2745(2004)107[82:AEATQN]2.0.CO;2).
- Asada, T., Warner, B.G., Aravena, R., 2005. Nitrogen isotope signature variability in plant species from open peatland. *Aquat. Bot.* 82, 297–307. <https://doi.org/10.1016/j.aquabot.2005.05.005>.
- Avila, A., Aguilera, L., Izquieta-Rojano, S., García-Gómez, H., Elustondo, D., Santamaría, J.M., Alonso, R., 2017. Quantitative study on nitrogen deposition and canopy retention in Mediterranean evergreen forests. *Environ. Sci. Pollut. Res.* 24, 26213–26226. <https://doi.org/10.1007/s11356-017-8861-4>.
- Bargagli, R., Sanchez-Hernandez, J.C., Martella, L., Monaci, F., 1998. Mercury, cadmium and lead accumulation in Antarctic mosses growing along nutrient and moisture gradients. *Polar Biol.* 19, 316–322. <https://doi.org/10.1007/s003000050252>.
- Barre, J.P.G., Deletraz, G., Sola-Larrañaga, C., Santamaría, J.M., Béral, S., Donard, O.F. X., Amouroux, D., 2018. Multi-element isotopic signature (C, N, Pb, Hg) in epiphytic lichens to discriminate atmospheric contamination as a function of land-use characteristics (Pyrénées-Atlantiques, SW France). *Environ. Pollut.* 243, 961–971. <https://doi.org/10.1016/j.envpol.2018.09.003>.
- Bates, J.W., 1992. Mineral nutrient acquisition and retention by bryophytes. *J. Bryol.* 17, 223–240. <https://doi.org/10.1179/jbr.1992.17.2.223>.
- Bermejo-Orduna, R., McBride, J.R., Shiraishi, K., Elustondo, D., Lasheras, E., Santamaría, J.M., 2014. Biomonitoring of traffic-related nitrogen pollution using *Letharia vulpina* (L.) Hue in the Sierra Nevada. *California. Sci. Total Environ.* 490, 205–212. <https://doi.org/10.1016/j.scitotenv.2014.04.119>.
- Bobbink, R., Hicks, K., Galloway, J., Spranger, T., Alkemade, R., Ashmore, M., Bustamante, M., Cinnerby, S., Davidson, E., Dentener, F., Emmett, B., Erismann, J.-W., Fenn, M., Gilliam, F., Nordin, A., Pardo, L., De Vries, W., 2010. Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis. *Ecol. Appl.* 20, 30–59. <https://doi.org/10.1890/08-1140.1>.
- Bokhorst, S., Convey, P., 2016. Impact of marine vertebrates on Antarctic terrestrial micro-arthropods. *Antarct. Sci.* 28, 175–186. <https://doi.org/10.1017/S0954102015000607>.
- Bokhorst, S., van Logtestijn, R., Convey, P., Aerts, R., 2019. Nitrogen isotope fractionation explains the ^{15}N enrichment of Antarctic cryptogams by volatilized ammonia from penguin and seal colonies. *Polar Res.* 38, 3355. <https://doi.org/10.33265/polar.v38.3355>.
- Boltersdorf, S.H., Pesch, R., Werner, W., 2014. Comparative use of lichens, mosses and tree bark to evaluate nitrogen deposition in Germany. *Environ. Pollut.* 189, 43–53. <https://doi.org/10.1016/j.envpol.2014.02.017>.
- Boltersdorf, S., Werner, W., 2013. Source attribution of agriculture-related deposition by using total nitrogen and $\delta^{15}\text{N}$ in epiphytic lichen tissue, bark and deposition water samples in Germany. *Isotopes Environ. Health Stud.* 49, 197–218. <https://doi.org/10.1080/10256016.2013.748051>.
- Boltersdorf, S.H., Werner, W., 2014. Lichens as a useful mapping tool?—an approach to assess atmospheric N loads in Germany by total N content and stable isotope signature. *Environ. Monit. Assess.* 186, 4767–4778. <https://doi.org/10.1007/s10661-014-3736-3>.
- Bortolazzi, A., Da Ros, L., Rodeghiero, M., Tognetti, R., Tonon, G., Ventura, M., 2021. The canopy layer, a biogeochemical actor in the forest N-cycle. *Sci. Total Environ.* 776, 146024. <https://doi.org/10.1016/j.scitotenv.2021.146024>.
- Bragazza, L., Limpens, J., Gerdol, R., Grosvernier, P., Hajek, M., Hajek, T., Hajkova, P., Hansen, I., Iacumin, P., Kutnar, L., Rydin, H., Tahvanainen, T., 2005. Nitrogen concentration and $\delta^{15}\text{N}$ signature of ombrotrophic *Sphagnum* mosses at different N deposition levels in Europe. *Glob. Change Biol.* 11, 106–114. <https://doi.org/10.1111/j.1365-2486.2004.00886.x>.
- Brown, D.H., 1982. Mineral Nutrition. In: Smith, A.J.E. (Ed.), *Bryophyte Ecology*. Springer, Netherlands, Dordrecht, pp. 383–444.
- Carlisle, A., Brown, A.H.F., White, E.J., 1966. The organic matter and nutrient elements in the precipitation beneath a sessile oak (*Quercus petraea*) canopy. *J. Ecol.* 54, 87–98. <https://doi.org/10.2307/2257660>.
- Carlisle, A., Brown, A.H.F., White, E.J., 1967. The nutrient content of tree stem flow and ground flora litter and leachates in a sessile oak (*Quercus petraea*) woodland. *J. Ecol.* 55, 615–627. <https://doi.org/10.2307/2258413>.
- Carroll, G.C., 1980. Forest canopies: complex and independent subsystems. In: Waring, R.H. (Ed.), *Forests: Fresh Perspectives from Ecosystem Analysis*. Oregon State University Press, Corvallis, Oregon, Presented at the Biology Colloquium, pp. 87–107.
- Carter, T.S., Clark, C.M., Fenn, M.E., Jovan, S., Perakis, S.S., Riddell, J., Schaberg, P.G., Greaver, T.L., Hastings, M.G., 2017. Mechanisms of nitrogen deposition effects on temperate forest lichens and trees. *Ecosphere* 8, e01717.
- Chang, Y., Liu, X., Deng, C., Dore, A.J., Zhuang, G., 2016. Source apportionment of atmospheric ammonia before, during, and after the 2014 APEC summit in Beijing using stable nitrogen isotope signatures. *Atmospheric Chem. Phys.* 16, 11635–11647. <https://doi.org/10.5194/acp-16-11635-2016>.
- Chellman, N.J., Hastings, M.G., McConnell, J.R., 2016. Increased nitrate and decreased $\delta^{15}\text{N}$ - NO_3^- in the Greenland Arctic after 1940 attributed to North American oil burning. *Cryosphere Discuss.* 1–22. <https://doi.org/10.5194/tc-2016-163>.
- Chen, F., Lao, Q., Jia, G., Chen, C., Zhu, Q., Zhou, X., 2019. Seasonal variations of nitrate dual isotopes in wet deposition in a tropical city in China. *Atmos. Environ.* 196, 1–9. <https://doi.org/10.1016/j.atmosenv.2018.09.061>.
- Ciečka, M.M., Górka, M., Trzyna, A., Modelska, M., Łubek, A., Widory, D., 2022. The multi isotope biogeochemistry (S, C, N and Pb) of *Hypogymnia physodes* lichens: air quality approach in the Świętokrzyski National Park. *Poland. Isot. Environ. Health Stud.* 58, 340–362. <https://doi.org/10.1080/10256016.2022.2110591>.
- Ciečka, M., Kossowska, M., Paneth, P., Górka, M., 2016. Carbon, nitrogen and sulphur concentration and $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ values in *Hypogymnia physodes* within the montane area - preliminary data. *Geosci. Res. C.* 24, 24–32. <https://doi.org/10.1515/georec-2016-0004>.
- Cipro, C.V.Z., Yogui, G.T., Bustamante, P., Taniguchi, S., Sericano, J.L., Montone, R.C., 2011. Organic pollutants and their correlation with stable isotopes in vegetation from King George Island, Antarctica. *Chemosphere* 85, 393–398. <https://doi.org/10.1016/j.chemosphere.2011.07.047>.
- Cocozza, C., Ravera, S., Cherubini, P., Lombardi, F., Marchetti, M., Tognetti, R., 2016. Integrated biomonitoring of airborne pollutants over space and time using tree rings, bark, leaves and epiphytic lichens. *Urban for. Urban Green.* 17, 177–191. <https://doi.org/10.1016/j.ufug.2016.04.008>.
- Cornell, S.E., 2011. Atmospheric nitrogen deposition: revisiting the question of the importance of the organic component. *Environ. Pollut.* 159, 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. *Atmos. Environ.* 37, 2173–2191. [https://doi.org/10.1016/S1352-2310\(03\)00133-X](https://doi.org/10.1016/S1352-2310(03)00133-X).
- Crittenden, P.D., Scrimgeour, C.M., Minnullina, G., Sutton, M.A., Tang, Y.S., Theobald, M.R., 2015. Lichen response to ammonia deposition defines the footprint of a penguin rookery. *Biogeochemistry* 122, 295–311. <https://doi.org/10.1007/s10533-014-0042-7>.
- Dahlman, L., Näsholm, T., Palmqvist, K., 2002. Growth, nitrogen uptake, and resource allocation in the two tripartite lichens *Nephroma arcticum* and *Peltigera aphthosa* during nitrogen stress. *New Phytol.* 153, 307–315. <https://doi.org/10.1046/j.0028-646X.2001.00321.x>.
- Dahlman, L., Persson, J., Palmqvist, K., Näsholm, T., 2004. Organic and inorganic nitrogen uptake in lichens. *Planta* 219, 459–467. <https://doi.org/10.1007/s00425-004-1247-0>.
- De Groot, P.A. (Ed.), 2004. *Handbook of stable isotope analytical techniques* (Vol. 1). Elsevier, Amsterdam.
- De Groot, P.A. (Ed.), 2009. *Handbook of stable isotope analytical techniques* (Vol. 2). Elsevier, Amsterdam.
- Deane-Coe, K.K., Sparks, J.P., 2016. Cyanobacteria associations in temperate forest bryophytes revealed by $\delta^{15}\text{N}$ analysis. *J. Torrey Bot. Soc.* 143, 50–57. <https://doi.org/10.3159/TORREY-D-15-00013>.
- DeFoort, M., Olsen, D., Willson, B., 2004. The effect of air-fuel ratio control strategies on nitrogen compound formation in three-way catalysts. *Int. J. Engine Res.* 5, 115–122. <https://doi.org/10.1243/146808704772914291>.
- Delgado, V., Eddera, A., Santamaría, J.M., 2013. Nitrogen and carbon contents and $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ signatures in six bryophyte species: assessment of long-term deposition changes (1980–2010) in Spanish beech forests. *Glob. Change Biol.* 19, 2221–2228. <https://doi.org/10.1111/gcb.12210>.
- Delwiche, C.C., Steyn, P.L., 1970. Nitrogen isotope fractionation in soils and microbial reactions. *Environ. Sci. Technol.* 4, 929–935. <https://doi.org/10.1021/es60046a004>.
- Díaz-Álvarez, E.A., de la Barrera, E., 2018. Characterization of nitrogen deposition in a megalopolis by means of atmospheric biomonitors. *Sci Rep* 8, 13569. <https://doi.org/10.1038/s41598-018-32000-5>.

- Díaz-Álvarez, E.A., Lindig-Cisneros, R., de la Barrera, E., 2018. Biomonitoring of atmospheric nitrogen deposition: potential uses and limitations. *Conserv. Physiol.* 6, coy011. <https://doi.org/10.1093/conphys/coy011>.
- Donovan, M., Norman, A.-L., Reid, M.L., 2022. Local vehicles add nitrogen to moss biomonitoring in a low-traffic protected wilderness area as revealed by a long-term isotopic study. *J. Nat. Conserv.* 70, 126292. <https://doi.org/10.1016/j.jnc.2022.126292>.
- Dörter, M., Karadeniz, H., Saklangıç, U., Yenisoğlu-Karakaş, S., 2020. The use of passive lichen biomonitoring in combination with positive matrix factor analysis and stable isotopic ratios to assess the metal pollution sources in throughfall deposition of Bolu plain, Turkey. *Ecol. Indic.* 113, 106212. <https://doi.org/10.1016/j.ecolind.2020.106212>.
- Du, E., 2016. Rise and fall of nitrogen deposition in the United States. *Proc. Natl. Acad. Sci.* 113, E3594–E3595. <https://doi.org/10.1073/pnas.1607543113>.
- Du, E., de Vries, W., Galloway, J.N., Hu, X., Fang, J., 2014. Changes in wet nitrogen deposition in the United States between 1985 and 2012. *Environ. Res. Lett.* 9, 095004. <https://doi.org/10.1088/1748-9326/9/9/095004>.
- Du, C., Guo, Q., Zhang, J., 2022. A review on moss nitrogen and isotope signatures evidence for atmospheric nitrogen deposition. *Sci. Total Environ.* 806, 150765. <https://doi.org/10.1016/j.scitotenv.2021.150765>.
- Elliott, E.M., Kendall, C., Wankel, S.D., Burns, D.A., Boyer, E.W., Harlin, K., Bain, D.J., Butler, T.J., 2007. Nitrogen isotopes as indicators of NO_x source contributions to atmospheric nitrate deposition across the Midwestern and Northeastern United States. *Environ. Sci. Technol.* 41 (22), 7661–7667. <https://doi.org/10.1021/es070898t>.
- Elliott, E.M., Yu, Z., Cole, A.S., Coughlin, J.G., 2019. Isotopic advances in understanding reactive nitrogen deposition and atmospheric processing. *Sci. Total Environ.* 662, 393–403. <https://doi.org/10.1016/j.scitotenv.2018.12.177>.
- Ellis, C.J., Crittenden, P.D., Scrimgeour, C.M., Ashcroft, C., 2003. The natural abundance of ¹⁵N in mat-forming lichens. *Oecologia* 136, 115–123. <https://doi.org/10.1007/s00442-003-1201-z>.
- Erskine, P.D., Bergstrom, D.M., Schmidt, S., Stewart, G.R., Tweedie, C.E., Shaw, J.D., 1998. Subantarctic Macquarie Island - a model ecosystem for studying animal-derived nitrogen sources using ¹⁵N natural abundance. *Oecologia* 117, 187–193. <https://doi.org/10.1007/s004420050647>.
- Evans, R.D., 2001. Physiological mechanisms influencing plant nitrogen isotope composition. *Trends Plant Sci.* 6, 121–126. [https://doi.org/10.1016/S1360-1385\(01\)01889-1](https://doi.org/10.1016/S1360-1385(01)01889-1).
- Evans, R.D., 2007. Soil nitrogen isotope composition. In: Michener, R., Lajtha, K. (Eds.), *Stable Isotopes in Ecology and Environmental Science*. Blackwell Publishing, Malden, MA, pp. 83–98.
- Felix, J.D., Elliott, E.M., Gish, T.J., McConnell, L.L., Shaw, S.L., 2013. Characterizing the isotopic composition of atmospheric ammonia emission sources using passive samplers and a combined oxidation-bacterial denitrifier approach: improved method for isotope characterization of ammonia in air. *Rapid Commun. Mass Spectrom.* 27, 2239–2246. <https://doi.org/10.1002/rcm.6679>.
- Felix, J.D., Elliott, E.M., 2013. The agricultural history of human-nitrogen interactions as recorded in ice core δ¹⁵N-NO₃⁻. *Geophys. Res. Lett.* 40, 1642–1646. <https://doi.org/10.1002/grl.50209>.
- Felix, J.D., Elliott, E.M., Shaw, S.L., 2012. Nitrogen isotopic composition of coal-fired power plant NO_x: influence of emission controls and implications for global emission inventories. *Environ. Sci. Technol.* 46, 3528–3535. <https://doi.org/10.1021/es203355v>.
- Felix, J.D., Elliott, E.M., Gish, T., Maghirang, R., Cambal, L., Clougherty, J., 2014. Examining the transport of ammonia emissions across landscapes using nitrogen isotope ratios. *Atmos. Environ.* 95, 563–570. <https://doi.org/10.1016/j.atmosenv.2014.06.061>.
- Felix, J.D., Elliott, E.M., Gay, D.A., 2017. Spatial and temporal patterns of nitrogen isotopic composition of ammonia at U.S. ammonia monitoring network sites. *Atmos. Environ.* 150, 434–442. <https://doi.org/10.1016/j.atmosenv.2016.11.039>.
- Fenn, M.E., Baron, J.S., Allen, E.B., Rueth, H.M., Nydick, K.R., Geiser, L., Bowman, W.D., Sickman, J.O., Meixner, T., Johnson, D.W., Neitlich, P., 2003a. Ecological effects of nitrogen deposition in the western United States. *Bioscience* 53, 404–420. [https://doi.org/10.1641/0006-3568\(2003\)053\[0404:EEONDI\]2.0.CO;2](https://doi.org/10.1641/0006-3568(2003)053[0404:EEONDI]2.0.CO;2).
- Fenn, M.E., Haeuber, R., Tonnesen, G.S., Baron, J.S., Grossman-Clarke, S., Hope, D., Jaffe, D.A., Copeland, S., Geiser, L., Rueth, H.M., Sickman, J.O., 2003b. Nitrogen emissions, deposition, and monitoring in the western United States. *Bioscience* 53, 391–403. [https://doi.org/10.1641/0006-3568\(2003\)053\[0391:NEDAMI\]2.0.CO;2](https://doi.org/10.1641/0006-3568(2003)053[0391:NEDAMI]2.0.CO;2).
- Fenn, M.E., Ross, C.S., Schilling, S.L., Baccus, W.D., Larrabee, M.A., Lofgren, R.A., 2013. Atmospheric deposition of nitrogen and sulfur and preferential canopy consumption of nitrate in forests of the Pacific Northwest USA. *For. Ecol. Manag.* 302, 240–253. <https://doi.org/10.1016/j.foreco.2013.03.042>.
- Fibiger, D.L., Hastings, M.G., 2016. First measurements of the nitrogen isotopic composition of NO_x from biomass burning. *Environ. Sci. Technol.* 50, 11569–11574. <https://doi.org/10.1021/acs.est.6b03510>.
- Foan, L., Sablayrolles, C., Elustondo, D., Lasheras, E., González, L., Ederia, A., Simon, V., Santamaría, J.M., 2010. Reconstructing historical trends of polycyclic aromatic hydrocarbon deposition in a remote area of Spain using herbarium moss material. *Atmos. Environ.* 44, 3207–3214. <https://doi.org/10.1016/j.atmosenv.2010.05.019>.
- Fogel, M.L., Wooller, M.J., Cheeseman, J., Smallwood, B.J., Roberts, Q., Romero, I., Meyers, M.J., 2008. Unusually negative nitrogen isotopic compositions (δ¹⁵N) of mangroves and lichens in an oligotrophic, microbially-influenced ecosystem. *Biogeochemistry* 5, 1693–1704. <https://doi.org/10.1519/bg-5-1693-2008>.
- Frank, D.A., Evans, R.D., Tracy, B.F., 2004. The role of ammonia volatilization in controlling the natural ¹⁵N abundance of a grazed grassland. *Biogeochemistry* 68, 169–178. <https://doi.org/10.1023/B:BIOG.0000025736.19381.91>.
- Freyer, H.D., 1978. Preliminary ¹⁵N studies on atmospheric nitrogenous trace gases. *Pure Appl. Geophys.* 116, 393–404. <https://doi.org/10.1007/BF01636894>.
- Gaio-Oliveira, G., Branquinho, C., Máguas, C., Martins-Loução, M.A., 2001. The concentration of nitrogen in nitrophilous and non-nitrophilous lichen species. *Symbiosis* 31, 187–199.
- Galloway, J.N., Aber, J.D., Erisman, J.W., Seitzinger, S.P., Howarth, R.W., Cowling, E.B., Cosby, B.J., 2003. The nitrogen cascade. *Bioscience* 53, 341–356. [https://doi.org/10.1641/0006-3568\(2003\)053\[0341:TNC\]2.0.CO;2](https://doi.org/10.1641/0006-3568(2003)053[0341:TNC]2.0.CO;2).
- Geiser, L., 2004. *Monitoring Air Quality Using Lichens on National Forests of the Pacific Northwest: Methods and Strategy*. USDA-Forest Service Pacific Northwest Region Technical Paper R6-NR-AQ-TP-1-04, 134 pp.
- Geiser, L.H., Jovan, S.E., Glavich, D.A., Porter, M.K., 2010. Lichen-based critical loads for atmospheric nitrogen deposition in Western Oregon and Washington Forests. *USA. Environ. Pollut.* 158, 2412–2421. <https://doi.org/10.1016/j.envpol.2010.04.001>.
- Geiser, L.H., Root, H., Smith, R.J., Jovan, S.E., St Clair, L., Dillman, K.L., 2021. Lichen-based critical loads for deposition of nitrogen and sulfur in US forests. *Environ. Pollut.* 291, 118187. <https://doi.org/10.1016/j.envpol.2021.118187>.
- Geng, L., Alexander, B., Cole-Dai, J., Steig, E.J., Savarino, J., Sofen, E.D., Schauer, A.J., 2014. Nitrogen isotopes in ice core nitrate linked to anthropogenic atmospheric acidity change. *Proc. Natl. Acad. Sci.* 111, 5808–5812. <https://doi.org/10.1073/pnas.1319441111>.
- Gerdol, R., Bragazza, L., Marchesini, R., Medici, A., Pedrini, P., Benedetti, S., Bovolenta, A., Coppi, S., 2002. Use of moss (*Tortula muralis* Hedw.) for monitoring organic and inorganic air pollution in urban and rural sites in Northern Italy. *Atmos. Environ.* 36, 4069–4075. [https://doi.org/10.1016/S1352-2310\(02\)00298-4](https://doi.org/10.1016/S1352-2310(02)00298-4).
- 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. *Environ. Pollut.* 244, 560–574. <https://doi.org/10.1016/j.envpol.2018.09.135>.
- Glime, J.M., 2007. Bryophyte ecology. Ebook sponsored by Michigan Technological University and the International Association of Bryologists. <https://digitalcommons.mtu.edu/bryophyte-ecology/> (accessed 1 February 2023).
- Greaver, T., McDow, S., Phelan, J., Kaylor, S.D., Herrick, J.D., Jovan, S., 2023. Synthesis of lichen response to gaseous nitrogen: ammonia versus nitrogen dioxide. *Atmos. Environ.* 292, 119396. <https://doi.org/10.1016/j.atmosenv.2022.119396>.
- Guerrieri, M.R., Siegwolf, R.T.W., Saurer, M., Jäggi, M., Cherubini, P., Ripullone, F., Borghetti, M., 2009. Impact of different nitrogen emission sources on tree physiology as assessed by a triple stable isotope approach. *Atmos. Environ.* 43, 410–418. <https://doi.org/10.1016/j.atmosenv.2008.08.042>.
- Guerrieri, R., Vangelova, E.L., Michalski, G., Heaton, T.H.E., Mencuccini, M., 2015. Isotopic evidence for the occurrence of biological nitrification and nitrogen deposition processing in forest canopies. *Glob. Change Biol.* 21, 4613–4626. <https://doi.org/10.1111/gcb.13018>.
- Guerrieri, R., Lecha, L., Mattana, S., Cáliz, J., Casamayor, E.O., Barceló, A., Michalski, G., Peñuelas, J., Avila, A., Mencuccini, M., 2020. Partitioning between atmospheric deposition and canopy microbial nitrification into throughfall nitrate fluxes in a Mediterranean forest. *J. Ecol.* 108, 626–640. <https://doi.org/10.1111/1365-2745.13288>.
- Guerrieri, R., Templer, P., Magnani, F., 2021. Canopy exchange and modification of nitrogen fluxes in forest ecosystems. *Curr. for. Rep.* 7, 115–137. <https://doi.org/10.1007/s40725-021-00141-y>.
- Hastings, M.G., Jarvis, J.C., Steig, E.J., 2009. Anthropogenic impacts on nitrogen isotopes of ice-core nitrate. *Science* 324, 1288. <https://doi.org/10.1126/science.1170510>.
- Hauck, M., 2010. Ammonium and nitrate tolerance in lichens. *Environ. Pollut.* 158, 1127–1133. <https://doi.org/10.1016/j.envpol.2009.12.036>.
- Heaton, T.H.E., Spiro, B., Robertson, S.M.C., 1997. Potential canopy influences on the isotopic composition of nitrogen and sulphur in atmospheric deposition. *Oecologia* 109, 600–607. <https://doi.org/10.1007/s004420050122>.
- Hoering, T., 1957. The isotopic composition of the ammonia and the nitrate ion in rain. *Geochim. et Cosmochim. Acta* 12, 97–102. [https://doi.org/10.1016/0016-7037\(57\)90021-2](https://doi.org/10.1016/0016-7037(57)90021-2).
- Hoffman, A.S., Albeke, S.E., McMurray, J.A., Evans, R.D., Williams, D.G., 2019. Nitrogen deposition sources and patterns in the Greater Yellowstone Ecosystem determined from ion exchange resin collectors, lichens, and isotopes. *Sci. Total Environ.* 683, 709–718. <https://doi.org/10.1016/j.scitotenv.2019.05.323>.
- Hogan, C.M., Proemse, B.C., Barmuta, L.A., 2017. Isotopic fingerprinting of atmospheric nitrogen and sulfur using lichens (*Cladia retipora*) in Tasmania, Australia. *Appl. Geochem.* 84, 126–132. <https://doi.org/10.1016/j.apgeochem.2017.06.007>.
- Holtgrieve, G.W., Schindler, D.E., Hobbs, W.O., Leavitt, P.R., Ward, E.J., Bunting, L., Chen, G., Finney, B.P., Gregory-Eaves, I., Holmgren, S., Lisi, M.J., Lisi, P.J., Nydick, K., Rogers, L.A., Saros, J.E., Selbie, D.T., Shapley, M.D., Walsh, P.B., Wolfe, A.P., 2011. A coherent signature of anthropogenic nitrogen deposition to remote watersheds of the northern hemisphere. *Science* 334, 1545–1548. <https://doi.org/10.1126/science.1212267>.
- Houle, D., Marty, C., Duchesne, L., 2015. Response of canopy nitrogen uptake to a rapid decrease in bulk nitrate deposition in two eastern Canadian boreal forests. *Oecologia* 177, 29–37. <https://doi.org/10.1007/s00442-014-3118-0>.
- Hristov, A.N., Zaman, S., Vander Pol, M., Ndegwa, P., Campbell, L., Silva, S., 2009. Nitrogen losses from dairy manure estimated through nitrogen mass balance and chemical markers. *J. Environ. Qual.* 38, 2438–2448. <https://doi.org/10.2134/jeq2009.0057>.
- Huang, S., Elliott, E.M., Felix, J.D., Pan, Y., Liu, D., Li, S., Li, Z., Zhu, F., Zhang, N., Fu, P., Fang, Y., 2019. Seasonal pattern of ammonium ¹⁵N natural abundance in precipitation at a rural forested site and implications for NH₃ source partitioning. *Environ. Pollut.* 247, 541–549. <https://doi.org/10.1016/j.envpol.2019.01.023>.

- Huang, H., Song, W., Liu, X.-Y., 2021. Significant contributions of combustion-related NH_3 and non-fossil fuel NO_x to elevation of nitrogen deposition in southwestern China over past five decades. *Glob. Change Biol.* 27, 4392–4402. <https://doi.org/10.1111/gcb.15736>.
- Hurtado, P., Prieto, M., Martínez-Vilalta, J., Giordani, P., Aragón, G., López-Angulo, J., Košuthová, A., Merinero, S., Díaz-Peña, E.M., Rosas, T., Benesperi, R., Bianchi, E., Grube, M., Mayrhofer, H., Nascimbene, J., Wedin, M., Westberg, M., Martínez, I., 2020. Disentangling functional trait variation and covariation in epiphytic lichens along a continent-wide latitudinal gradient. *Proc. r. Soc. b: Biol. Sci.* 287, 20192862. <https://doi.org/10.1098/rspb.2019.2862>.
- Institute of Clean Air Companies (ICAC), 2009. Selective catalytic reduction (SCR) control of NO_x emissions from fossil fuel-fired electric power plants. Report prepared by NOx Control Technical Division, Institute of Clean Air Companies Inc, Washington, D.C., pp. 1–32.
- Jovan, S., Fenn, M.E., Buhler, M., Bytnerowicz, A., Kovasi, A., Hutten, M., DiMeglio, E., Schweizer, D., 2021. Challenges characterizing N deposition to high elevation protected areas: A case study integrating instrument, simulated, and lichen inventory datasets for the Devils Postpile National Monument and surrounding region, USA. *Ecol. Indic.* 122, 107311. <https://doi.org/10.1016/j.ecolind.2020.107311>.
- Kirshenbaum, I., Smith, J.S., Crowell, T., Graff, J., McKee, R., 1947. Separation of the nitrogen isotopes by the exchange reaction between ammonia and solutions of ammonium nitrate. *J. Chem. Phys.* 15, 440–446. <https://doi.org/10.1063/1.1746562>.
- Klopatek, J.M., Barry, M.J., Johnson, D.W., 2006. Potential canopy interception of nitrogen in the Pacific Northwest. *USA. for. Ecol. Manag.* 234, 344–354. <https://doi.org/10.1016/j.foreco.2006.07.019>.
- Lakatos, M., Hartard, B., Máguas, C., 2007. The stable isotopes $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of lichens can be used as tracers of microenvironmental carbon and water sources. In: Dawson, T.E., Siegwolf, R. (Eds.), *Stable Isotopes as Indicators of Ecological Change*. Elsevier Academic Press, San Diego, pp. 77–92.
- Lee, Y.I., Lim, H.S., Yoon, H.I., 2009. Carbon and nitrogen isotope composition of vegetation on King George Island, maritime Antarctic. *Polar Biol.* 32, 1607–1615. <https://doi.org/10.1007/s00300-009-0659-5>.
- Li, Y., Schichtel, B.A., Walker, J.T., Schwede, D.B., Chen, X., Lehmann, C.M.B., Puchalski, M.A., Gay, D.A., Collett, J.L., 2016. Increasing importance of deposition of reduced nitrogen in the United States. *Proc. Natl. Acad. Sci.* 113, 5874–5879. <https://doi.org/10.1073/pnas.1525736113>.
- Li, D., Wang, X., 2008. Nitrogen isotopic signature of soil-released nitric oxide (NO) after fertilizer application. *Atmos. Environ.* 42, 4747–4754. <https://doi.org/10.1016/j.atmosenv.2008.01.042>.
- Lindo, Z., Whiteley, J.A., 2011. Old trees contribute bio-available nitrogen through canopy bryophytes. *Plant Soil* 342, 141–148. <https://doi.org/10.1007/s11104-010-0678-6>.
- Liu, X., Koba, K., Makabe, A., Li, X., Yoh, M., Liu, C., 2013. Ammonium first: natural mosses prefer atmospheric ammonium but vary utilization of dissolved organic nitrogen depending on habitat and nitrogen deposition. *New Phytol.* 199, 407–419. <https://doi.org/10.1111/nph.12284>.
- Liu, X., Wu, D., Song, X., Dong, Y., Chen, C., Song, W., Liu, C., Koba, K., 2020. A non-steady state model based on dual nitrogen and oxygen isotopes to constrain moss nitrate uptake and reduction. *J. Geophys. Res. Biogeosciences* 125, e2019JG005498. <https://doi.org/10.1029/2019JG005498>.
- Liu, X.-Y., Xiao, H.-Y., Liu, C.-Q., Li, Y.-Y., Xiao, H.-W., 2008. Tissue N content and ^{15}N natural abundance in epilithic mosses for indicating atmospheric N deposition in the Guiyang area, SW China. *Appl. Geochem.* 23, 2708–2715. <https://doi.org/10.1016/j.apgeochem.2008.06.002>.
- Liu, X.-Y., Koba, K., Liu, C.-Q., Li, X.-D., Yoh, M., 2012a. Pitfalls and new mechanisms in moss isotope biomonitoring of atmospheric nitrogen deposition. *Environ. Sci. Technol.* 46, 12557–12566. <https://doi.org/10.1021/es300779h>.
- Liu, X.-Y., Koba, K., Yoh, M., Liu, C.-Q., 2012b. Nitrogen and oxygen isotope effects of tissue nitrate associated with nitrate acquisition and utilisation in the moss *Hypnum plumaeforme*. *Funct. Plant Biol.* 39, 598–608. <https://doi.org/10.1071/FP12014>.
- Manninen, S., 2018. Deriving nitrogen critical levels and loads based on the responses of acidophytic lichen communities on boreal urban *Pinus sylvestris* trunks. *Sci. Total Environ.* 613–614, 751–762. <https://doi.org/10.1016/j.scitotenv.2017.09.150>.
- Mariotti, A., Germon, J.C., Hubert, P., Kaiser, P., Letolle, R., Tardieu, A., Tardieu, X., 1981. Experimental determination of nitrogen kinetic isotope fractionation: some principles; illustration for the denitrification and nitrification processes. *Plant Soil* 62, 413–430.
- Merced, A., Renzaglia, K.S., 2017. Structure, function and evolution of stomata from a bryological perspective. *Bryophyte Divers. Evol.* 39, 7–20. <https://doi.org/10.11646/bde.39.1.4>.
- Millbank, J.W., 1982. The assessment of nitrogen fixation and throughput by lichens. III. Losses of nitrogenous compounds by *Peltigera membranacea*, *P. polydactyla* and *Lobaria pulmonaria* in simulated rainfall episodes. *New Phytol.* 92, 229–234. <https://doi.org/10.1111/j.1469-8137.1982.tb03380.x>.
- Munzi, S., Cruz, C., Maia, R., Máguas, C., Perestrello-Ramos, M.M., Branquinho, C., 2017. Intra and inter-specific variations in chitin in lichens along a N-deposition gradient. *Environ. Sci. Pollut. Res.* 24, 28065–28071. <https://doi.org/10.1007/s11356-017-0378-3>.
- Munzi, S., Branquinho, C., Cruz, C., Máguas, C., Leith, I.D., Sheppard, L.J., Sutton, M.A., 2019. $\delta^{15}\text{N}$ of lichens reflects the isotopic signature of ammonia source. *Sci. Total Environ.* 653, 698–704. <https://doi.org/10.1016/j.scitotenv.2018.11.010>.
- Munzi, S., Branquinho, C., Cruz, C., Máguas, C., Leith, I., Sheppard, L., Sutton, M., 2016. Is lichen $\delta^{15}\text{N}$ an indicator of nitrogen pollution and a surrogate of nitrogen atmospheric composition? Evidence from manipulative experiments. In: *Proceedings of the 2016 International Nitrogen Initiative Conference, "Solutions to Improve Nitrogen use Efficiency for the World"*, 4–8 December 2016, Melbourne, Australia.
- 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, 301–314. <https://doi.org/10.1007/s10533-022-00966-0>.
- Mustajärvi, K., Merilä, P., Derome, J., Lindroos, A.-J., Helmisaari, H.-S., Nöjd, P., Ukonmaanaho, L., 2008. Fluxes of dissolved organic and inorganic nitrogen in relation to stand characteristics and latitude in Scots pine and Norway spruce stands in Finland. *Boreal Environ. Res.* 13, 3–21.
- NADP, 2023. National Atmospheric Deposition Program (NADP). <https://nadp.slh.wisc.edu/> (accessed 6 June 2023).
- Nash, T.H. (Ed.), 1996. *Lichen Biology*. Cambridge University Press, Cambridge.
- 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: Boyer, E.W., Howarth, R.W. (Eds.), *The Nitrogen Cycle at Regional to Global Scales*. Springer, Netherlands, Dordrecht, pp. 99–136. https://doi.org/10.1007/978-94-017-3405-9_3.
- Nielsen, T.F., Larsen, J.R., Michelsen, A., Bruun, H.H., 2017. Are herbarium mosses reliable indicators of historical nitrogen deposition? *Environ. Pollut.* 231, 1201–1207. <https://doi.org/10.1016/j.envpol.2017.04.020>.
- Niepsch, D., Clarke, L.J., Tzoulas, K., Cavan, G., 2021. Distinguishing atmospheric nitrogen compounds (nitrate and ammonium) in lichen biomonitoring studies. *Environ. Sci.: Processes Impacts* 23, 2021–2036. <https://doi.org/10.1039/D1EM00274K>.
- Niepsch, D., Clarke, L.J., Newton, J., Tzoulas, K., Cavan, G., 2023. High spatial resolution assessment of air quality in urban centres using lichen carbon, nitrogen and sulfur contents and stable-isotope-ratio signatures. *Environ. Sci. Pollut. Res.* 30, 58731–58754. <https://doi.org/10.1007/s11356-023-26652-8>.
- Palmqvist, K., Dahlman, L., 2006. Responses of the green algal foliose lichen *Platismatia glauca* to increased nitrogen supply. *New Phytol.* 171, 343–356. <https://doi.org/10.1111/j.1469-8137.2006.01754.x>.
- Pardo, L.H., Fenn, M.E., Goodale, C.L., Geiser, L.H., Driscoll, C.T., Allen, E.B., Baron, J.S., Bobbink, R., Bowman, W.D., Clark, C.M., Emmett, B., Gilliam, F.S., Greaver, T.L., Hall, S.J., Lilleskov, E.A., Liu, L., Lynch, J.A., Nadelhoffer, K.J., Perakis, S.S., Robin-Abbott, M.J., Stoddard, J.L., Weathers, K.C., Dennis, R.L., 2011. Effects of nitrogen deposition and empirical nitrogen critical loads for ecoregions of the United States. *Ecol. Appl.* 21, 3049–3082. <https://doi.org/10.1890/10-2341.1>.
- Pearson, J., Wells, D.M., Seller, K.J., Bennett, A., Soares, A., Woodall, J., Ingrouille, M.J., 2000. Traffic exposure increases natural ^{15}N and heavy metal concentrations in mosses. *New Phytol.* 147, 317–326. <https://doi.org/10.1046/j.1469-8137.2000.00702.x>.
- Peñuelas, J., Filella, I., 2001. Herbaria century record of increasing eutrophication in Spanish terrestrial ecosystems. *Glob. Change Biol.* 7, 427–433. <https://doi.org/10.1046/j.1365-2486.2001.00421.x>.
- Piirainen, S., Finér, L., Starr, M., 1998. Canopy and soil retention of nitrogen deposition in a mixed boreal forest in Eastern Finland. *Water, Air, Soil Pollut.* 105, 165–174. <https://doi.org/10.1023/A:1005052030998>.
- Pike, L.H., 1978. The importance of epiphytic lichens in mineral cycling. *Bryologist* 81, 247–257. <https://doi.org/10.2307/3242186>.
- Pinho, P., Barros, C., Augusto, S., Pereira, M.J., Máguas, C., Branquinho, C., 2017. Using nitrogen concentration and isotopic composition in lichens to spatially assess the relative contribution of atmospheric nitrogen sources in complex landscapes. *Environ. Pollut.* 230, 632–638. <https://doi.org/10.1016/j.envpol.2017.06.102>.
- Poulson, S.R., Chamberlain, C.P., Friedland, A.J., 1995. Nitrogen isotope variation of tree rings as a potential indicator of environmental change. *Chem. Geol.* 125, 307–315. [https://doi.org/10.1016/0009-2541\(95\)00097-6](https://doi.org/10.1016/0009-2541(95)00097-6).
- Proemse, B.C., Mayer, B., 2012. Tracing industrial nitrogen and sulfur emissions in the Athabasca Oil Sands Region using stable isotopes. In: Percy, K.E. (Ed.), *Alberta Oil Sands: Energy, Industry and the Environment*. Elsevier Science, Oxford, UK, pp. 243–266. <https://doi.org/10.1016/B978-0-08-097760-7.00011-1>.
- Purvis, O.W., Chimonides, P.J., Jeffries, T.E., Jones, G.C., Read, H., Spiro, B., 2005. Investigating biogeochemical signatures in the lichen *Parmelia sulcata* at Burnham Beeches, Buckinghamshire, England. *Lichenologist* 37, 329–344. <https://doi.org/10.1017/S0024282905015288>.
- Rai, H., Gupta, R.K., 2022. Chapter 13 - Lichenized fungi, a primary bioindicator/biomonitor for bio-mitigation of excessive ambient air nitrogen deposition worldwide. In: Samuel, J., Kumar, A., Singh, J. (Eds.), *Relationship between Microbes and the Environment for Sustainable Ecosystem Services*, Volume 1. Elsevier, Amsterdam, pp. 267–301. <https://doi.org/10.1016/B978-0-323-89938-3.00013-X>.
- Raven, J.A., Griffiths, H., Smith, E.C., Vaughn, K.C., 1998. New perspectives in the biophysics and physiology of bryophytes. In: Bates, J.W., Ashton, N.W., Duckett, J.G. (Eds.), *Bryology for the Twenty-First Century*. Maney Publishing and the British Bryological Society, London, pp. 261–275.
- Robinson, D., 2001. $\delta^{15}\text{N}$ as an integrator of the nitrogen cycle. *Trends Ecol. Evol.* 16, 153–162. [https://doi.org/10.1016/S0169-5347\(00\)02098-X](https://doi.org/10.1016/S0169-5347(00)02098-X).
- Root, H.T., Geiser, L.H., Fenn, M.E., Jovan, S., Hutten, M.A., Ahuja, S., Dillman, K., Schirokauer, D., Berryman, S., McMurray, J.A., 2013. A simple tool for estimating throughfall nitrogen deposition in forests of western North America using lichens. *For. Ecol. Manag.* 306, 1–8. <https://doi.org/10.1016/j.foreco.2013.06.028>.
- Root, H.T., Geiser, L.H., Jovan, S., Neitlich, P., 2015. Epiphytic macrolichen indication of air quality and climate in interior forested mountains of the Pacific Northwest. *USA. Ecol. Indic.* 53, 95–105. <https://doi.org/10.1016/j.ecolind.2015.01.029>.
- Rousk, K., 2022. Biotic and abiotic controls of nitrogen fixation in cyanobacteria-moss associations. *New Phytol.* 235, 1330–1335. <https://doi.org/10.1111/nph.18264>.

- Rousk, K., Jones, D.L., DeLuca, T.H., 2013. Moss-cyanobacteria associations as biogenic sources of nitrogen in boreal forest ecosystems. *Front. Microbiol.* 4. <https://doi.org/10.3389/fmicb.2013.00150>.
- 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. *Atmos. Environ.* 32, 2453–2465. [https://doi.org/10.1016/S1352-2310\(98\)00044-2](https://doi.org/10.1016/S1352-2310(98)00044-2).
- Russow, R., Veste, M., Littmann, T., 2004. Using the natural ^{15}N abundance to assess the main nitrogen inputs into the sand dune area of the north-western Negev Desert (Israel). *Isotopes Environ. Health Stud.* 40, 57–67.
- Saurer, M., Cherubini, P., Ammann, M., De Cinti, B., Siegwolf, R., 2004. First detection of nitrogen from NO_x in tree rings: a $^{15}\text{N}/^{14}\text{N}$ study near a motorway. *Atmos. Environ.* 38, 2779–2787. <https://doi.org/10.1016/j.atmosenv.2004.02.037>.
- Saurer, M., Siegwolf, R., 2007. Human impacts on tree-ring growth reconstructed from stable isotopes. In: Dawson, T.E., Siegwolf, R. (Eds.), *Stable Isotopes as Indicators of Ecological Change*. Elsevier Academic Press, San Diego, pp. 49–62.
- Savard, M.M., Bégin, C., Smirnov, A., Marion, J., Rioux-Paquette, E., 2009. Tree-ring nitrogen isotopes reflect anthropogenic NO_x emissions and climatic effects. *Environ. Sci. Technol.* 43, 604–609. <https://doi.org/10.1021/es802437k>.
- Schulz, H., Gehre, M., Hofmann, D., Jung, K., 2001. Nitrogen isotope ratios in pine bark as an indicator of N emissions from anthropogenic sources. *Environ. Monit. Assess.* 69, 283–297.
- Schwarz, M.T., Bischoff, S., Blaser, S., Boch, S., Schmitt, B., Thieme, L., Fischer, M., Michalzik, B., Schulze, E.-D., Siemens, J., Wilcke, W., 2014. More efficient aboveground nitrogen use in more diverse Central European forest canopies. *For. Ecol. Manag.* 313, 274–282. <https://doi.org/10.1016/j.foreco.2013.11.021>.
- Shearer, G., Kohl, D.H., 1993. Natural abundance of ^{15}N : fractional contribution of two sources to a common sink and use of isotope discrimination. In: Knowles, R., Blackburn, T.H. (Eds.), *Nitrogen Isotope Techniques*. Elsevier Academic Press, San Diego, pp. 89–125. <https://doi.org/10.1016/B978-0-08-092407-6.50009-2>.
- Simonova, G.V., Kalashnikova, D.A., Melkov, V.N., 2018. Air quality biomonitoring with epiphytic lichens and mosses. In: 24th International Symposium on Atmospheric and Ocean Optics: Atmospheric Physics. Presented at the 24th International Symposium on Atmospheric and Ocean Optics: Atmospheric Physics, pp. 1202–1210. <https://doi.org/10.1117/12.2504559>.
- Skudnik, M., Jeran, Z., Batić, F., Simončić, P., Lojen, S., Kastelec, D., 2014. Influence of canopy drip on the indicative N, S and $\delta^{15}\text{N}$ content in moss *Hypnum cupressiforme*. *Environ. Pollut.* 190, 27–35. <https://doi.org/10.1016/j.envpol.2014.03.016>.
- Smith, D.C., 1960. Studies in the physiology of lichens: absorption and utilization of some simple organic nitrogen compounds by *Peltigera polydactyla*. *Ann. Bot.* 4 (2), 172–185. <https://doi.org/10.1093/oxfordjournals.aob.a083693>.
- Solga, A., Burkhardt, J., Zechmeister, H.G., Frahm, J.-P., 2005. Nitrogen content, ^{15}N natural abundance and biomass of the two pleurocarpous mosses *Pleurozium schreberi* (Brid.) Mitt. and *Scleropodium purum* (Hedw.) Limpr. in relation to atmospheric nitrogen deposition. *Environ. Pollut.* 134, 465–473. <https://doi.org/10.1016/j.envpol.2004.09.008>.
- Solga, A., Eichert, T., Frahm, J.-P., 2006. Historical alteration in the nitrogen concentration and ^{15}N natural abundance of mosses in Germany: indication for regionally varying changes in atmospheric nitrogen deposition within the last 140 years. *Atmos. Environ.* 40, 8044–8055. <https://doi.org/10.1016/j.atmosenv.2006.03.024>.
- Sollins, P., Grier, C.C., McCorison, F.M., Cromack, K., Fogel, R., Fredriksen, R.L., 1980. The internal element cycles of an old-growth Douglas-fir ecosystem in western Oregon. *Ecol. Monogr.* 50, 261–285. <https://doi.org/10.2307/2937252>.
- Srivastava, R.K., Hall, R.E., Khan, S., Culligan, K., Lani, B.W., 2005. Nitrogen oxides emission control options for coal-fired electric utility boilers. *J. Air Waste Manag. Assoc.* 55, 1367–1388. <https://doi.org/10.1080/10473289.2005.10464736>.
- Stuart, J.E.M., Holland-Moritz, H., Jean, M., Miller, S.N., Ponciano, J.M., McDaniel, S.F., Mack, M.C., 2021. The relationship of C and N stable isotopes to high-latitude moss-associated N_2 fixation. *Oecologia* 197, 283–295. <https://doi.org/10.1007/s00442-021-05005-7>.
- Templer, P.H., Pinder, R.W., Goodale, C.L., 2012. Effects of nitrogen deposition on greenhouse-gas fluxes for forests and grasslands of North America. *Front. Ecol. Environ.* 10, 547–553. <https://doi.org/10.1890/120055>.
- Templer, P.H., Weathers, K.C., Lindsey, A., Lenoir, K., Scott, L., 2015. Atmospheric inputs and nitrogen saturation status in and adjacent to Class I wilderness areas of the northeastern US. *Oecologia* 177, 5–15. <https://doi.org/10.1007/s00442-014-3121-5>.
- Tozer, W.C., Hackell, D., Miers, D.B., Silvester, W.B., 2005. Extreme isotopic depletion of nitrogen in New Zealand lithophytes and epiphytes: the result of diffusive uptake of atmospheric ammonia? *Oecologia* 144, 628–635. <https://doi.org/10.1007/s00442-005-0098-0>.
- Turetsky, M.R., 2003. The role of bryophytes in carbon and nitrogen cycling. *Bryologist* 106, 395–409. <https://doi.org/10.1639/05>.
- USFS (United States Forest Service), 2011. Phase 3 Field Guide – Lichen Communities, Version 5.1. United States Forest Service. <https://www.fia.fs.fed.us/library/field-guides/methods-proc/index.php> (accessed February 1, 2024).
- Vanguelova, E.L., Benham, S., Pitman, R., Moffat, A.J., Broadmeadow, M., Nisbet, T., Durrant, D., Barsoum, N., Wilkinson, M., Bocheau, F., Hutchings, T., Broadmeadow, S., Crow, P., Taylor, P., Durrant Houston, T., 2010. Chemical fluxes in time through forest ecosystems in the UK – soil response to pollution recovery. *Environ. Pollut.* 158, 1857–1869. <https://doi.org/10.1016/j.envpol.2009.10.044>.
- 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. *Atmos. Environ.* 60, 573–582. <https://doi.org/10.1016/j.atmosenv.2012.06.059>.
- Walters, W.W., Michalski, G., 2015. Theoretical calculation of nitrogen isotope equilibrium exchange fractionation factors for various NO_y molecules. *Geochim. Cosmochim. Acta* 164, 284–297. <https://doi.org/10.1016/j.gca.2015.05.029>.
- Walters, W.W., Goodwin, S.R., Michalski, G., 2015a. Nitrogen stable isotope composition ($\delta^{15}\text{N}$) of vehicle-emitted NO_x . *Environ. Sci. Technol.* 49, 2278–2285. <https://doi.org/10.1021/es505580v>.
- Walters, W.W., Michalski, G., 2016. *Ab initio* study of nitrogen and position-specific oxygen kinetic isotope effects in the $\text{NO} + \text{O}_3$ reaction. *J. Chem. Phys.* 145, 224311. <https://doi.org/10.1063/1.4968562>.
- Walters, W.W., Tharp, B.D., Fang, H., Kozak, B.J., Michalski, G., 2015b. Nitrogen isotope composition of thermally produced NO_x from various fossil-fuel combustion sources. *Environ. Sci. Technol.* 49, 11363–11371. <https://doi.org/10.1021/acs.est.5b02769>.
- Walters, W.W., Simonini, D.S., Michalski, G., 2016. Nitrogen isotope exchange between NO and NO_2 and its implications for $\delta^{15}\text{N}$ variations in tropospheric NO_x and atmospheric nitrate. *Geophys. Res. Lett.* 43, 440–448. <https://doi.org/10.1002/2015GL066438>.
- Wang, Y., Lett, S., Rousk, K., 2022. Too much of a good thing? Inorganic nitrogen (N) inhibits moss-associated N_2 fixation but organic N can promote it. *Biogeochemistry* 159, 179–191. <https://doi.org/10.1007/s10533-022-00920-0>.
- Wieder, R.K., Vile, M.A., Vitt, D.H., Scott, K.D., Xu, B., Quinn, J.C., Albright, C.M., 2022. Can plant or lichen natural abundance ^{15}N ratios indicate the influence of oil sands N emissions on bogs? *J. Hydrol. Reg. Stud.* 40, 101030. <https://doi.org/10.1016/j.ejrh.2022.101030>.
- Williams, D.G., Evans, R.D., West, J.B., Ehleringer, J.R., 2007. Applications of stable isotope measurements for early-warning detection of ecological change. In: Dawson, T.E., Siegwolf, R. (Eds.), *Stable Isotopes as Indicators of Ecological Change*. Elsevier Academic Press, San Diego, pp. 383–398.
- Wilson, D., Stock, W.D., Hedderson, T., 2009. Historical nitrogen content of bryophyte tissue as an indicator of increased nitrogen deposition in the Cape Metropolitan Area, South Africa. *Environ. Pollut.* 157, 938–945. <https://doi.org/10.1016/j.envpol.2008.10.021>.
- Xiao, H.-Y., Tang, C.-G., Xiao, H.-W., Liu, X.-Y., Liu, C.-Q., 2010. Stable sulphur and nitrogen isotopes of the moss *Haplodcladium microphyllum* at urban, rural and forested sites. *Atmos. Environ.* 44, 4312–4317. <https://doi.org/10.1016/j.atmosenv.2010.05.023>.
- Xu, S.-Y., Huang, H., Song, W., Liu, X.-Y., 2021. Lichen nitrogen concentrations and isotopes for indicating nitrogen deposition levels and source changes. *Sci. Total Environ.* 787, 147616. <https://doi.org/10.1016/j.scitotenv.2021.147616>.
- Yang, S., Gruber, N., 2016. The anthropogenic perturbation of the marine nitrogen cycle by atmospheric deposition: nitrogen cycle feedbacks and the ^{15}N Haber-Bosch effect: atmospheric N deposition and the N cycle. *Glob. Biogeochem. Cycles* 30, 1418–1440. <https://doi.org/10.1002/2016GB005421>.
- Yu, Z., Elliott, E.M., 2017. Novel method for nitrogen isotopic analysis of soil-emitted nitric oxide. *Environ. Sci. Technol.* 51, 6268–6278. <https://doi.org/10.1021/acs.est.7b00592>.
- Yu, L., Zheng, T., Hao, Y., Zheng, X., 2021. Determination of the nitrogen isotope enrichment factor associated with ammonification and nitrification in unsaturated soil at different temperatures. *Environ. Res.* 202, 111670. <https://doi.org/10.1016/j.envres.2021.111670>.
- Zechmeister, H.G., Richter, A., Smidt, S., Hohenwallner, D., Roder, I., Maringer, S., Wanek, W., 2008. Total nitrogen content and $\delta^{15}\text{N}$ signatures in moss tissue: indicative value for nitrogen deposition patterns and source allocation on a nationwide scale. *Environ. Sci. Technol.* 42, 8661–8667. <https://doi.org/10.1021/es801865d>.
- Zhao, J., Zhang, Z., Zhu, G., Zheng, N., Xiao, H., Tian, J., Zhou, Y., Guan, H., Xiao, H., 2019. The $\delta^{15}\text{N}$ values of epilithic mosses indicating the changes of nitrogen sources in Guiyang (SW China) from 2006 to 2016–2017. *Sci. Total Environ.* 696, 133988. <https://doi.org/10.1016/j.scitotenv.2019.133988>.