Isotopic advances in understanding reactive nitrogen deposition and atmospheric processing

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HIGHLIGHTS
• Isotopes of reactive nitrogen species can aid in understanding emissions sources and chemical transformations that contribute to reactive nitrogen deposition.
• Methodological advances have ushered in an unprecedented examination of reactive nitrogen isotope chemistry.
• Here, we review advances in methods, applications, and gains in knowledge during the past decade.
• We conclude with promising opportunities for future research in the short, medium-, and long-term.

ABSTRACT
Recent advances in stable isotope measurements now allow for detailed investigations of the sources, transformations, and deposition of reactive nitrogen (N) species. Stable isotopes show promise as a complementary tool for apportioning emissions sources that contribute to deposition and also for developing a more robust understanding of the transformations that can influence these isotope ratios. Methodological advances have facilitated the unprecedented examination of the isotopic composition of reactive N species in the atmosphere and in precipitation including nitrogen oxides (NOx = nitric oxide (NO) + nitrogen dioxide (NO2)), atmospheric nitrate (NO3−), nitric acid (HNO3), ammonia (NH3), and ammonium (NH4+). This isotopic information provides new insight into the mechanisms of transformation and cycling of reactive N in the atmosphere and moreover helps resolve the contribution of multiple NOx and NH3 emission sources to deposition across landscapes, regions, and continents. Here, we highlight the current state of knowledge regarding the isotopic ratios of NOx and NH3 emission sources and chemical alterations of isotopic ratios during atmospheric transformations. We also highlight illustrative examples where isotopic approaches are used and review recent methodological advances. While these highlights are not an exhaustive review of the literature, we hope they provide a glimpse of the potential for these methods to help resolve knowledge gaps regarding total N deposition to Earth surfaces. We conclude with promising opportunities for future research in the short-, medium-, and long-term.

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1. Introduction
The abundance of stable isotopes in a chemical species depends not only on the natural abundance of isotopes available, but also on the
chemical and physical processes that created that species. Therefore, measuring isotopic ratios can yield invaluable information regarding the sources and (bio)geochemical cycling of the species beyond what concentration measurements alone can provide. A classic example is the measurement of oxygen (O) and hydrogen isotope ratios in glacial ice, which are correlated with local temperatures, to reconstruct temperatures over millennia (e.g. Petit et al., 1999). With recent technical and methodological improvements that allow for measurements of stable isotopes in trace species in the environment, a wealth of new applications has since opened up. Reactive nitrogen (N) cycling is one application to which isotopic approaches can now be applied, due to recent and ongoing development of methods for sampling and analyzing reactive N species including NO, NO2, NO3, NH3, and NH4. Anthropogenic reactive N is of interest because of its contributions to air quality, water quality, soil acidification and eutrophication (e.g., Galloway et al., 2003). Isotopic analysis of N in reactive N species – and simultaneous analysis of N and O in oxidized reactive N species (NOy) – can be a powerful tool for assessing their sources, transformation processes, and relative contributions to ecosystem nitrogen.

Given that isotopic differences between atmospheric N- and O-bearing compounds are minute, the isotopic composition is reported relative to an international standard and expressed as the deviation, in parts per thousand (‰), from that standard:

$$\delta(\%o) = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$$

(1)

where R is the ratio of heavy-to-light isotope (e.g., $^{15}\text{N}/^{14}\text{N}$), $R_{\text{sample}}$ is that ratio in a sample, and $R_{\text{standard}}$ is that ratio in the international standard. The international standard for N is atmospheric $N_2$ ($^{15}\text{N}/^{14}\text{N} = 0.0036782$ (De Bièvre et al., 1996)). Oxygen has three stable isotopes ($^{16}\text{O}$, $^{17}\text{O}$, $^{18}\text{O}$), and isotopic analysis of oxygen isotope ratios ($^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$) is placed on the scale of Vienna Standard Mean Ocean Water (VSMOW) scale ($^{17}\text{O}/^{16}\text{O} = 0.003799$, $^{18}\text{O}/^{16}\text{O} = 0.0020052$ (Li et al., 1988; Baertschi, 1976)).

Importantly, the mass differences between isotopically substituted N- and O-bearing compounds impact their partitioning rates between chemical species and phases, resulting in subtle, albeit measurable, differences between the different isotopes (Kaye, 1987). Given that isotopic differences between atmospheric N- and O-bearing compounds are minute, the isotopic composition is reported relative to an international standard and expressed as the deviation, in parts per thousand (‰), from that standard:

$$\delta(\%o) = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$$

In the sections below, we highlight the current state of knowledge regarding: 1) the isotopic ratios of NOx and NH3 emission sources; 2) transformations in the atmosphere that can influence the fidelity of isotope ratios; 3) illustrative examples where isotopic approaches are used; and 4) methodological advances that have facilitated this burst of new knowledge. These highlights are not an exhaustive review of the literature, yet we hope they provide a glimpse of recent exponential growth in knowledge and demonstrate the potential for these methods to help resolve knowledge gaps regarding total N deposition to Earth surfaces. We conclude with promising opportunities for future research in the short-, medium-, and long-term.

2. Inventory of $^{15}\text{N}$-NOx and $^{16}\text{O}$-NH3 source values

Use of N isotopes in atmospheric reactive N species as quantitative tracers of NOx and NH3 source contributions require that different emission sources have relatively distinct and well-characterized $^{15}\text{N}$ signatures. Globally, NOx emissions from fossil fuel combustion via electricity generating units (EGU) and vehicles are the dominant NOx source to the atmosphere (Fig. 1).

Felix et al. (2012) collected EGU in-stack NOx and found that EGU $^{15}\text{N}$-NOx ranged from 9% to 26‰, significantly higher than that of other measured NOx emission sources (Felix et al., 2012) (Fig. 2a). NOx resulting from vehicle fossil fuel combustion has been reported to have $^{15}\text{N}$ values ranging from −13‰ to 9‰ and −21‰ to −2‰ for gasoline- and diesel-powered vehicles, respectively (Walters et al., 2015a, 2015b) (Fig. 2a). Although the $^{15}\text{N}$ ranges of vehicle-emitted NOx and NOx produced in biomass burning overlap to a large extent (Fibiger and Hastings, 2016), vehicular $^{15}\text{N}$-NOx measured either at tailpipes or in near-road environments is significantly higher than that of biogenic NOx emissions from agricultural soils that ranges from −60‰ to −20‰ (Li and Wang, 2008; Yu and Elliott, 2017) (Fig. 2a). The low $^{15}\text{N}$ values of soil-emitted NOx stem from large kinetic isotope effects associated with microbial NO production in soils that strongly discriminate against $^{15}\text{N}$ (Yu and Elliott, 2017). Correspondingly, as shown in Fig. 2, the $^{15}\text{N}$ values of NOx emitted from EGUs, vehicles, and soils are significantly different from each other, suggesting that $^{15}\text{N}$-NOx is a robust indicator for NOx source partitioning in relatively constrained environments (e.g., environments with a priori information on biomass burning and lightning) (Fig. 2a). Importantly, at the power plants studied in Felix et al. (2012), large differences exist in the $^{15}\text{N}$ of NOx emitted with and without selective catalytic reduction (SCR) technology (Fig. 2a), indicating that EGU $^{15}\text{N}$-
NO\textsubscript{x} is altered by kinetic isotope effects during the catalytic NO\textsubscript{x} reduction (Felix et al., 2012) (Fig. 3a). This has also been observed in δ\textsuperscript{15}N of NO\textsubscript{x} emitted from vehicles equipped with three-way catalytic converters (TWC) (Fig. 3a), rendering vehicular δ\textsuperscript{15}N-NO\textsubscript{x} dependent on vehicle operating conditions (e.g., cold versus warm engines) and NO\textsubscript{x} mitigation efficiency (Walters et al., 2015a, 2015b). Consequently, gradual implementation of emission control technologies (e.g., SCR and TWC) is expected to increase δ\textsuperscript{15}N-NO\textsubscript{x} of fuel combustion-related NO\textsubscript{x} emissions (Felix et al., 2012).

Global NH\textsubscript{3} emissions are dominated by agricultural activities, including livestock operations and fertilizer application (Fig. 1). The primary agricultural source, urea in livestock waste and fertilizers, is quickly hydrolyzed to NH\textsubscript{3}, which is then volatilized to the atmosphere. This is also the case with NH\textsubscript{4}\textsuperscript{+} in fertilizers and hydrolyzed human waste where both are subject to direct volatilization after application and dissociation to NH\textsubscript{3}. Hence, given the large equilibrium isotope effect associated with the aqueous NH\textsubscript{3}-NH\textsubscript{4}\textsuperscript{+} system (e.g., 45‰ at 296 K (Li et al., 2012)) and the kinetic isotope fractionations during NH\textsubscript{3} volatilization (e.g., −8 to −5‰ at 298 K (Deng et al., 2018)), field-observed δ\textsuperscript{15}N of NH\textsubscript{3} emitted from agricultural sources (i.e., −56 to −10‰) is significantly lower than that of other anthropogenic and natural NH\textsubscript{3} emission sources (Fig. 2b), allowing its potential use in tracing...
agricultural NH₃ emissions and their fate during atmospheric transformations. However, δ¹⁵N-NH₃ derived in controlled laboratory incubations of liquid manure spans a wider range (Fig. 2b) due to the strong temperature dependency of the equilibrium and kinetic isotope effects accompanying the NH₃ volatilization (Fig. 3b), suggesting that δ¹⁵N-NH₃ of the agricultural sources and human wastes may be subject to seasonal variations (Schulz et al., 2001).

Therefore, despite the indications that δ¹⁵N-NOₓ and δ¹⁵N-NH₃ can serve as robust tracers of NOₓ and NH₃ source contributions, further characterization of δ¹⁵N-NOₓ and δ¹⁵N-NH₃ is required to minimize uncertainty and to further understand mechanisms driving atmospheric δ¹⁵N-NOₓ and δ¹⁵N-NH₃ dynamics. Moreover, the current inventory of δ¹⁵N-NOₓ and δ¹⁵N-NH₃ source signatures is still limited, incomplete, and future efforts are needed to characterize diffuse, non-fossil fuel-based sources, especially lightning and natural soils for δ¹⁵N-NH₃. Therefore, despite the indications that δ¹⁵N-NOₓ and δ¹⁵N-NH₃ can serve as robust tracers of NOₓ and NH₃ source contributions, further characterization of δ¹⁵N-NOₓ and δ¹⁵N-NH₃ is required to minimize uncertainty and to further understand mechanisms driving atmospheric δ¹⁵N-NOₓ and δ¹⁵N-NH₃ dynamics. Moreover, the current inventory of δ¹⁵N-NOₓ and δ¹⁵N-NH₃ source signatures is still limited, incomplete, and future efforts are needed to characterize diffuse, non-fossil fuel-based sources, especially lightning and natural soils for δ¹⁵N-NH₃.

3. The role of atmospheric chemistry on isotopic signatures

Once released into the atmosphere, inorganic N gases such as NOₓ and NH₃ undergo a number of physical and chemical processes that can alter their isotopic composition and the composition of their reaction products (e.g., aqueous and solid NO₃⁻ and NH₄⁺). These processes may be equilibrium (reversible) reactions, such as the partitioning of NH₃ (NH₃ = NH₃ + NH₄⁺) between the gas, dissolved, and solid phases (reactions (1) to (3)).

\[ ^{15}NH_3(g) + ^{14}NH_3(aq) \leftrightarrow ^{14}NH_3(g) + ^{15}NH_3(aq) \quad \text{Reaction (1)} \]
\[ ^{15}NH_3(g) + ^{14}NH_4^+(aq) \leftrightarrow ^{14}NH_3(g) + ^{15}NH_4^+(aq) \quad \text{Reaction (2)} \]
\[ ^{15}NH_3(g) + ^{14}NH_4^+(aq) \leftrightarrow ^{15}NH_3(g) + ^{14}NH_4^+(aq) \quad \text{Reaction (3)} \]

These isotopic exchange reactions have been shown in both theoretical calculations (Urey, 1947; Walters et al., 2018b) and/or laboratory experiments (Kirshenbaum et al., 1947; Li et al., 2012) to favor the right-hand side of the equilibrium, resulting in higher δ¹⁵N/¹⁴N ratios in dissolved and solid NH₃ than in gaseous NH₃. Moreover, under non-equilibrium conditions such as unidirectional neutralization reactions between gaseous NH₃ and atmospheric acids (e.g., H₂SO₄, HNO₃, and HCl), partitioning of N isotopes between NH₃ and NH₄⁺ may be controlled by kinetic fractionations, giving rise to ¹⁵N-enriched dissolved and solid NH₄⁺ products (Pan et al., 2016). Consistent with theory and experiments, simultaneous observations of NH₃ with particle-bound NH₄⁺ in precipitation (Moore, 1977; Heaton, 1987; Savard et al., 2017) have found a significantly higher proportion of ¹⁵N in NH₄⁺, whether in the solid or aqueous phase, than in gas-phase NH₃. However, the range of observed values is large, is not the same for precipitation and particle phases, and both theory and observations predict a significant difference in the amount of isotopic fractionation in reactions (1) to (3) with ambient temperature (Urey, 1947; Savard et al., 2017; Walters et al., 2018b). Importantly, one potential mechanism driving the observed variability in δ¹⁵N of atmospheric NH₃ species may involve the large differences in kinetic and equilibrium isotope effects associated with multi-step NH₃ gas-to-particle conversion (Walters et al., 2018b). For example, while isotopic equilibrium between NH₃ and solid NH₄⁺ (i.e., reaction (3)) is predicted to have a large isotope effect (i.e., 31% at 298 K), a small isotope effect is calculated for equilibrium of NH₃ at the gas-liquid interface (i.e., reaction (1); 4% at 298 K) (Walters et al., 2018b). Consequently, differences in N isotopic composition between NH₃ and particle-bound NH₄⁺ may be highly dependent on atmospheric conditions (e.g., temperature and relative humidity) that determine the limiting step during the gas-to-particle conversion. These issues complicate the quantitative use of the ¹⁵N signature in NH₃ or NH₄⁺ for source attribution.

The atmospheric cycle of NOₓ is complex, with different processes taking place during the day and night (Calvert et al., 1985) (Fig. 4). During the day, photochemical cycling between NO and NO₂ is rapid, controlled by the oxidation of NO by either O₃ (reaction (4)) or peroxy radicals (HO₂/RO₂) (reaction (5)) to form NO₂ and the subsequent photolysis of NO₂ back to NO (reaction (6)).

\[ NO + O_3 \rightarrow NO_2 + O_2 \quad \text{Reaction (4)} \]
\[ NO + RO_2(RO_2) \rightarrow NO_2 + RO(RO) \quad \text{Reaction (5)} \]
\[ NO_2 + h\nu \rightarrow NO + O(\delta P) \quad \text{Reaction (6)} \]

Using ab initio calculations, Walters and Michalski (2016) revealed that the NO + O₃ reaction is associated with a kinetic N isotope effect of −7‰ (at 298 K), indicating that the produced NO₂ from reaction (4) has a δ¹⁵N value lower than NO and the total NOₓ. On the other hand, δ¹⁵N values of NO and NO₂ are also controlled by a N isotope exchange equilibrium between NO and NO₂ (reaction (7)), which has recently been experimentally confirmed to have a large isotope effect (37‰ at 298 K) (Walters et al., 2016).

\[ ^{15}NO + ^{14}NO_2 \rightarrow ^{15}NO_2 + ^{14}NO \quad \text{Reaction (7)} \]

As a result, when NO and NO₂ exist in comparable concentrations, δ¹⁵N is preferentially partitioned into NO₂ if the N isotopic equilibrium is achieved, leading to significantly higher δ¹⁵N-NO₂ relative to δ¹⁵N-NO and δ¹⁵N-NOₓ (Freyer et al., 1993; Walters et al., 2016). Thus, the

![Fig. 4. Chemistry leading to formation of atmospheric nitrate (black text and arrows) and corresponding N isotope exchange equilibrium (blue arrows and text) & Δ¹⁷O transfer from O₃ to NO₂ (red text). The calculated kinetic isotope effect for the NO + O₃ reaction (k(NO2/NO)) is also shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image-url)
N isotopic partitioning between NO and NO$_2$ will likely reflect the competition between photochemical NO-NO$_2$ cycling and isotopic equilibrium and is therefore highly dependent on atmospheric conditions (i.e., temperature, radiation, and oxidant availability) (Freyer et al., 1993; Walters et al., 2016). Unfortunately, kinetic isotope effects associated with reactions (5) and (6) have not been determined at this point (Walters et al., 2018a), therefore making it difficult to fully assess the conservation of $^{15}$N-NO$_x$ source signatures in NO$_2$ under varying atmospheric conditions.

The major sink for NO$_3$ in the atmosphere is oxidation to HNO$_3$ (Fig. 4), which occurs during the day through the reaction between NO$_3$ and photochemically-produced hydroxyl radicals (OH)

\[ \text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3 \]

and at night via heterogeneous hydrolysis of dinitrogen pentoxide (N$_2$O$_5$) (reactions (9)-(11)) or hydrogen abstraction from hydrocarbons by nitrate radical (NO$_3$) (reaction (12)).

\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \]

\[ \text{NO}_2 + \text{NO}_3 \rightarrow \text{N}_2\text{O}_5 \]

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 (aq) \]

\[ \text{NO}_3 + \text{hydrocarbons} \rightarrow \text{HNO}_3 + \text{products} \]

The equilibrium N isotope exchange between NO$_2$, NO$_x$, and N$_2$O$_5$, the substrates for the HNO$_3$ production in the above-mentioned formation pathways, was recently investigated using theoretical calculations by Walters and Michalski (2015). Based on these calculations, $^{15}$N-NO$_x$ and $^{15}$N-N$_2$O$_5$ are significantly lower and higher than $^{15}$N-NO$_2$, respectively, if N isotopic equilibrium is achieved (Fig. 4). These calculated equilibrium isotope effects have been recently applied to correct isotopic fractionations of NO$_x$ during HNO$_3$ production for source partitioning of particulate NO$_3$ deposition (Zong et al., 2017; Chang et al., 2018). While these recent attempts that couple isotopic measurement and modeling can provide new insights into the complex nature of the land-atmospheric cycling of NO$_x$, it is important to point out the simplicity inherent in this method. Particularly, the final steps in forming atmospheric NO$_3$ in the respective production pathways (reactions (8), (11), and (12)) are irreversible and may therefore be associated with kinetic isotope effects, which are currently unknown.

These additional isotopic fractionations can potentially play an important role in controlling $^{15}$N-HNO$_3$ beyond the N isotopic equilibrium between NO$_2$, NO$_x$, and N$_2$O$_5$ (Walters and Michalski, 2016). For example, during reaction (11), the mechanism of the reaction can determine the amount and direction (i.e., whether the $^{14}$N or $^{15}$N reacts faster) of isotope fractionation (Kaye, 1987). If the reaction rate is limited only by the frequency of the N$_2$O$_5$ molecule colliding with the droplet or wet surface, then the $^{15}$N-containing molecule, which moves slightly slower than the lighter $^{14}$N-containing molecule, will collide less frequently and lead to a lower $^{15}$N value for the HNO$_3$ product than for the N$_2$O$_5$ reactant. On the other hand, if the reaction proceeds through an intermediate complex (a “transition state”) that is in equilibrium with the reactants, the apparent kinetic isotope effect associated with reaction (11) may be in the opposite direction, favoring HNO$_3$ with more $^{15}$N (i.e., higher $^{15}$N values). Therefore, due to the number and complexity of the NO$_x$ (NO + NO$_2$ + NO$_3$ + HNO$_3$ + N$_2$O$_5$ + particle NO$_3$ + organic nitrates) reactions taking place in the atmosphere, linking $^{15}$N values of deposited atmospheric NO$_3$ to that of emitted NO$_x$ is not trivial. In addition to the source $^{15}$N signatures, further experimental and field studies are required to determine empirical isotope effects during atmospheric oxidation of NO$_x$ to HNO$_3$ and to validate the calculated isotopic fractionation factors under a range of conditions.

Importantly, while $^{15}$N and $^{18}$O of atmospheric NO$_3$ can be significantly changed by equilibrium and kinetic isotope effects during atmospheric reactions, $^{17}$O of atmospheric NO$_3$ is a conservative tracer of photochemical NO$_3$ production from NO$_x$ due to its mass-independent nature (Michalski et al., 2003). As shown in Fig. 4, the $^{17}$O value of NO$_3$ is determined by: 1) the fraction of total NO$_3$ production that is a result of O$_3$ oxidation (f$_{O3}$, Fig. 4), which is subject to pronounced diel and seasonal variations (Morin et al., 2011), and 2) the $^{17}$O anomaly transferred from O$_3$ to NO$_2$ during reaction (2) ($\Delta^{17}$O-O$_2$, Fig. 4), which has been experimentally quantified to range between 39‰ and 45‰ (Savarino et al., 2008; Morin et al., 2011; Vicars and Savarino, 2014). This $\Delta^{17}$O-NO$_2$ signal is further transferred to atmospheric NO$_3$ along the three NO$_3$ formation pathways that involve O$_3$ to different extents and thus have distinct $\Delta^{17}$O transfer functions constrained by the oxygen mass balance (Fig. 4). Therefore, $\Delta^{17}$O-NO$_3$ can be potentially used as an independent constraint on the NO$_3$ formation pathways to help resolve the complex N isotopic fractionations during NO$_x$ oxidation to HNO$_3$ (Fig. 4). Future studies should explore the utility of coupled $\Delta^{17}$O-NO$_3$ and $^{15}$N-NO$_3$ analysis in source partitioning of deposited atmospheric NO$_3$.

$\Delta^{17}$O-NO$_3$ has another particularly important application in watershed-scale studies. Because $\Delta^{17}$O-NO$_3$ does not fractionate with any processes that normally complicate interpretation of dual isotope data (e.g., denitrification), $\Delta^{17}$O-NO$_3$ is a robust tracer for examining the relative proportions of atmospheric NO$_3$ in soils and streams. To date, only a few studies have applied $\Delta^{17}$O-NO$_3$ analysis at the watershed scale (Rose et al., 2015b and references therein). In southern California, $\Delta^{17}$O was used to trace the flux of atmospheric NO$_3^-$ into soil, ground-, and surface waters (Michalski et al., 2004). Based on $\Delta^{17}$O measurement, they concluded that 40% of NO$_3^-$ in rural streams was from atmospheric sources during peak storm flows. Moreover, they documented that relative to $^{15}$N-NO$_3$, $\Delta^{17}$O-NO$_3$ was a more sensitive and precise tracer that allows for exact quantification of atmospheric NO$_3^-$ contributions. Subsequent studies have used $\Delta^{17}$O to quantify NO$_3^-$ export from watersheds exhibiting various signs of N saturation (Rose et al., 2015a), contributions of atmospheric NO$_3^-$ to groundwater (Tsunogai et al., 2010), stormwater NO$_3^-$ runoff from arid urban watersheds (Rhiu et al., 2014), and watershed NO$_3^-$ sources in mixed land use systems (Tsunogai et al., 2016; Bourgeois et al., 2018). Additionally, when combined with $^{15}$N-NO$_3^-$, $\Delta^{17}$O-NO$_3$ shows promise as a complementary tool for estimating the role of denitrification in mediating NO$_3^-$ fluxes in soils and streams (Fang et al., 2015; Yu and Elliott, 2018).

4. Application studies of isotope distributions

Experimental, field, and modeling studies have furthered our understanding of the source apportionment, seasonality, and atmospheric cycling influences on the isotopic composition of reactive N species in both the atmosphere and in deposition. Spanning vast spatial scales, from micro-scale to regional-sized gradient studies, studies measuring gaseous, particulate, and wet deposition, bulk plant/moss/fungi/soil, lake core, or ice core $^{15}$N values have attempted to characterize isotope dynamics and their corresponding changes over space and time.

Microscale gradient studies provide insight into how $^{15}$N values of NO$_x$ and NH$_3$ compounds are deposited with distance away from direct emission sources. For example, Ammann et al. (1999) observed decreasing $^{15}$N values collected in spruce needles and soil along a ~1000 m gradient away from a highway and related $^{15}$N variations to the decreasing influence of mobile sourced NO$_2$. Similarly, Redling et al. (2013) presented isotopic evidence of NO$_x$ source mixing on gaseous NO$_x$ and HNO$_3$ isotopic dynamics along a ~500 m gradient downwind from a highway. Moreover, the researchers also traced the uptake of vehicle-sourced NO$_2$ into plant tissue using $^{15}$N of foliar Bentgrass as a biomonitor across the gradient (Redling et al., 2013). However, in two polluted ombrotrophic bogs in central Europe, Novak et al. (2016) found that $^{15}$N of living Sphagnum was higher than that
of atmospheric NO$_3^-$ and NH$_4^+$ deposition, suggesting that fixation of atmospheric N$_2$ is the major N source for living Spinifex. This indicates that the utility of plants in tracing atmospheric reactive N may be highly species-specific. $\delta^{15}$N-NH$_4^+$ values have also been observed along microscale gradients in agricultural fields and used to estimate sources of gaseous NH$_3$ (Felix et al., 2014). Microscale gradient studies are particularly beneficial because long-range transport processes can be constrained. Most importantly, microscale deposition studies of NO$_2$/NH$_3$ isotopes, using multiple ecosystem components (e.g. deposition, plants, soil, etc.), can provide a greater understanding of how deposition fluxes influence biota and thus have important implications for critical load studies.

Ecosystem, regional, and national scale gradient studies of NO$_2$/NH$_3$ isotopes in the atmosphere and in deposition have recently emerged in the literature and have facilitated a greater understanding of the seasonality, atmospheric processes, and emission source influences on reactive N isotopes. Isotopes of ambient forms of NO$_x$ and/or NH$_x$, and dry and/or wet deposited forms of NO$_3^-$, NH$_4^+$, and/or secondary aerosols, have been well studied on regional scales and ecosystem localities around the globe (Widory, 2007; Elliott et al., 2007; Elliott et al., 2009; Zhang et al., 2008; Chang et al., 2016; Wankel et al., 2010; Savard et al., 2017; Savard et al., 2018; Kawashima and Kurahashi, 2011; Jia and Chen, 2010; Hastings et al., 2003; Felix et al., 2015; Felix et al., 2017; Walters et al., 2018a; Liu et al., 2017; Pan et al., 2016; Pavuluri et al., 2010; Ti et al., 2018; Zong et al., 2017; Novak et al., 2018). Seasonal $\delta^{15}$N-NO$_3^-$ and $\delta^{15}$N-NH$_4^+$ values are generally lower in summer months and higher in winter months due to the combined influence of source changes, seasonal fluctuations in reaction chemistry, and fractionalization factors that are temperature dependent (Beyn et al., 2015; Beyn et al., 2014; Freyer, 1991; Elliott et al., 2007; Elliott et al., 2009), however exceptions to this general trend have also been observed (Pan et al., 2018). Lower $\delta^{15}$N values in warm months generally reflect the importance of soil-derived biogenic emissions or lightning in some areas while cold month $\delta^{15}$N values are more heavily influenced by fossil fuel combustion (electricity generation) (Elliott et al., 2007; Elliott et al., 2009; Hastings et al., 2003), although the temperature dependence of isotopic equilibrium exchange between NO and NO$_2$ (reaction (5)) can also lead to more enriched $\delta^{15}$N values during winter (Freyer, 1991; Freyer et al., 1993).

In the rapidly expanding literature dedicated to $\delta^{15}$N in atmospheric N and deposition, there is an active discussion regarding the relative influence of source signature and atmospheric processing as primary drivers for environmental $\delta^{15}$N values. Recent studies demonstrate that $\delta^{15}$N-NO$_x$ source signatures remain intact under conditions of high ozone concentration relative to NO$_x$ concentration (i.e., $\delta^{15}$N close to 1) (Walters et al., 2018a). Some regional field transect studies and paleo-studies have concluded that emission sources are the primary driver of $\delta^{15}$N-NO$_3^-$ and/or $\delta^{15}$N-NH$_4^+$ variations using back trajectory analyses (Beyn et al., 2014; Beyn et al., 2015; Fang et al., 2011; Wankel et al., 2010), emission sector comparisons (Elliott et al., 2007; Elliott et al., 2009; Zhang et al., 2015), NH$_4^+$/NO$_3^-$ ratios (Beyn et al., 2014; Lee et al., 2012; Zhao et al., 2009; Jia and Chen, 2010), or mixing models (Proeme et al., 2013; Felix et al., 2013; Felix et al., 2015; Felix et al., 2017; Chang et al., 2016; Liu et al., 2017; Pan et al., 2016; Zong et al., 2017; Ti et al., 2018; Chang et al., 2018). On the other hand, other studies highlight atmospheric processes (NO$_x$ cycling, halogen chemistry, gas-particle phase partitioning, seasonal cycling, and peroxyacyl nitrate (PAN) formation) as the dominant driver of $\delta^{15}$N-NO$_3^-$ and/or $\delta^{15}$N-NH$_4^+$ variations in marine boundary layer aerosol sampling (Morin et al., 2009; Vicars et al., 2013; Gobel et al., 2013; Savarino et al., 2013), stationary sampling with back trajectory analysis (Wankel et al., 2010; Altieri et al., 2013; Buda and Dewalle, 2009; Savard et al., 2017; Pavuluri et al., 2010), and historical ice core $\delta^{15}$N-NO$_3^-$ studies (Geng et al., 2014). The most probable explanation for the large variations reported for deposition NO$_3^-$ and NH$_4^+$ isotopes in environmental systems is a combination of source and isotopic effects.

Future efforts should aim to quantify potential isotopic effects on source signatures by supplementing traditional isotope sampling with multi-parameter sampling (e.g., NO$_x$, HNO$_3$, NH$_x$, sulfur oxides, particulate matter, trace metals, PAN, volatile organic compounds, amongst others) and chemical transport modeling (e.g., CMAQ, GEO-CHEM) to quantify reaction rates and interactions between meteorological conditions, emissions, and isotope effects. These types of analyses would further the community’s understanding of atmospheric reactive N reactions and their resulting deposited forms.

One additional way to observe isotope variations across time and space is by conducting spatial analyses to generate isoscapes (West et al., 2009 and references therein) where isoscapes are spatially explicit predictions of isotope ratios generated in a geographical information system (GIS) using modeling tools such as inverse distance weighting. A previous study used isoscapes to characterize spatio-temporal variations in $\delta^{15}$N-NO$_x$ in wet deposition in the northeastern U.S. and was able to predict emission source contributions (Elliott et al., 2007). Isoscapes have been used to predict spatial variations in $\delta^{15}$N-NO$_x$ values in the U.S. based on primary vehicle emissions and commute time (Walters et al., 2015a) and measured in the northeastern U.S. using in-situ $\delta^{15}$N-NO$_x$ sampling methods (Miller et al., 2017). Indeed, as more field sampling campaigns are conducted, isoscapes employed in conjunction with atmospheric processing models (e.g. CMAQ, GEOS-Chem) can implicitly integrate variations in $\delta^{15}$N source signatures and isotopic fractionations over large spatial and temporal scales and are therefore expected to provide invaluable empirical information about the complex land-atmosphere interactions of NO$_x$ and NH$_x$.

5. Advances in field and laboratory methodologies

Analytical advances in characterizing small quantities of reactive N in the late 1990s (Chang et al., 1999) and early 2000s (Silva et al., 2000) have facilitated exponential growth in studies of atmospheric reactive N. One such analytical advance is the use of denaturing bacteria to analyze nanomolar quantities of NO$_x$ for $\delta^{15}$N (Sigman et al., 2001), $\delta^{18}$O (Casciotti et al., 2002), and $\Delta^{17}$O (Kaiser et al., 2004). Other recent methods chemically convert NO$_x$ and nitrite (NO$_2^-$) to nitrous oxide using either sodium azide (Mcilvin and Altabet, 2005) or hydroxylamine (Liu et al., 2014). Highly sensitive NH$_x$ isotope analyses have also been facilitated by these advanced methods – whereby hypobromite is used to oxidize NH$_4^+$ to NO$_3^-$ which is then converted to nitrous oxide using hydroxylamine (Liu et al., 2014), acetic acid (Zhang et al., 2007) or denaturing bacteria (Felix et al., 2013). Together, these methodological advances established a new foundation for subsequent method development and application studies.

5.1. Gaseous NO, NO$_2$, HNO$_3$, and NH$_3$

Gas phase reactive N compounds can be characterized using either active or passive sampling approaches (Fig. 2). Active sampling employs a pump to pass high volumes of air over a specialized filter or into solution. Alternatively, passive sampling approaches employ diffusive devices that expose specialized filters to ambient gases over longer-time scales (weeks to months). Passive samplers are advantageous in remote areas as they do not require power, integrate deposition over long-time scales, are relatively inexpensive, and are not labor intensive. Active sampling has the advantages of collecting larger samples in less time, simultaneous collection of multiple gases and particulates, and the possibility of selecting for certain conditions such as wind direction from a nearby source (e.g. Smirnov et al., 2012). Experiments to determine possible isotopic fractionation during active or passive sampling are limited. One study of Nylasorb filters for passive collection of HNO$_3$ determined that there was no systematic bias in $\delta^{15}$N or $\delta^{18}$O between the exposed and collected HNO$_3$ (Bell et al., 2014). A recent study of active NH$_3$ sampling using honeycomb denuders determined that collection efficiencies > 95% were necessary to avoid fractionation during
sampling (Walters and Hastings, 2018). The temperature dependence of the relative isotopic composition of particulate NO$_3^-$ and HNO$_3$ on actively sampled filter packs was not consistent with significant fractionation due to NH$_4$NO$_3$ volatilization (Elliott et al., 2009; Savard et al., 2017). However, controlled experiments on these and other sampling systems are recommended in order to quantify or rule out potential fractionation due to sampling methods.

The isotopic characterization of NO and NO$_2$ (NO + NO$_2$ = NO$_x$) has experienced a resurgence in interest since originally examined as early as 1967 (Moore, 1977), with a particular focus on characterizing fossil fuel NO$_x$. Starting in 1990, Heaton collected tailpipe and smokestack NO$_x$ emissions in a solution of sodium hydroxide and hydrogen peroxide (Heaton, 1990). Felix et al. (2012) modified an EPA stack sampling method (US EPA Method 7, Determination of Nitrogen Oxide Emissions from Stationary Sources) and compared the efficacy of sulfuric acid, sodium hydroxide, and triethanolamine (TEA) collection solutions for isotopic analysis of stack gases from coal-fired power plants in the U.S. (Felix et al., 2012), Walters et al. (2015a, 2015b) used the same EPA Method 7 to sample a series of vehicle tailpipe emissions (Walters et al., 2015a) as well as lawn equipment, buses, semi-trucks, and gas furnaces (Walters et al., 2015b). An alkaline permanganate solution has also been used to capture NO$_x$ as NO$_3^-$ for isotopic analysis (Fibiger et al., 2014) and was recently applied to on-road vehicle NO$_x$ signatures in the U.S. (Miller et al., 2017), although this collection solution is subject to a high blank that makes it inappropriate for some field applications. Ambient NO and NO$_x$ have also been collected for $^{15}$N analysis using passive samplers (Smirnoff et al., 2012; Dahal and Hastings, 2016) or actively-sampled cartridges (Savard et al., 2017) that use proprietary sampling media (Maxxam Analytics). When NO$_2$ is collected as NO$_3^-$ in solution for $^{34}$S analysis, it has been noted that an additional fractionation factor (e.g., 25–30%) must be applied to account for the reduction of NO$_3^-$ to NO$_2$ during bacterial processing if NO$_3^-$ isotopic references materials are used to calibrate $^{15}$N-NO$_3^-$ values (Casciotti et al., 2007; Dahal and Hastings, 2016; Coughlin et al., 2017).

Soil NO emissions that emanate from soils as byproducts of nitrification and denitrification reactions, are more difficult to characterize due to their transient nature and low concentrations. Li and Wang (2008) first characterized soil NO emissions in laboratory conditions where agricultural soils were fertilized and NO fluxes measured in a dynamic chamber. NO was oxidized to NO$_2$, using chromate (CrO$_4^2-$) and the resulting NO$_2$ was captured using a tubular denuder coated in potassium hydroxide and guaiacol (Li and Wang, 2008). In a series of field chamber experiments, Homyak et al. (2016) used a $^{15}$N tracer and passive NO$_x$ filters in arid conditions where vegetation cover and soil moisture were manipulated to collect soil NO emissions (Homyak et al., 2016). More recently, Yu and Elliott (2017) established a method to characterize soil NO emissions using a dynamic flux chamber where soil NO is oxidized to NO$_2$ in excess O$_3$, and resulting NO$_2$ is collected in a solution of TEA (Yu and Elliott, 2017).

NO$_x$ for isotopic analysis has been captured using passive diffusion samplers that contain a quartz filter impregnated with TEA (Redling et al., 2013; Felix and Elliott, 2014; Dahal and Hastings, 2016). A recent study using control laboratory experiments determined precision and accuracy of passive NO$_x$ filters as a collection medium for isotopic analysis of $^{15}$N and $^{34}$S across varying environmental conditions (Coughlin et al., 2017). Another recent study collected $^{35}$S and $^{32}$O of NO$_x$ using an active sampling denuder assembly coated with a potassium hydroxide solution, guaiacol, and methanol solution (Walters et al., 2018a).

Gaseous HNO$_3$ has been characterized isotopically using both active and passive sampling approaches. Archived HNO$_3$ from eight CASTNET sites, where HNO$_3$ is collected on a nylon filters as air is drawn through a three-stage filter pack for a 1-week period, was analyzed for $^{15}$N and $^{18}$O (Elliott et al., 2009). Nylon filters were also used to collect HNO$_3$ downwind of specific source types using a wind sector-specific active sampling system for $^{15}$N, $^{31}$O and $^{17}$O analysis (Savard et al., 2017). Passive collection of HNO$_3$ over several weeks to a month-long period, employs a Teflon pre-filter (2 mm pore size) and nylon collection medium (Elliott et al., 2009; Redling et al., 2013; Felix and Elliott, 2014; Bell et al., 2014).

Gaseous NH$_3$ can be collected for isotopic analysis on an acidified (phosphorous or citric acid) filter using a diffusive membrane pre-filter (Felix et al., 2013; Chang et al., 2016; Smirnoff et al., 2012). Rather than the high mass requirements and other complications with filter combustion, Smirnoff et al. (2012) and Felix et al. (2013) adapted an approach to oxidize NH$_3$ collected on acid-coated filters to NO$_2^+$ using a bromate solution (Zhang et al., 2007). These studies coupled oxidized NH$_3$ to the denitrifier method and thus allowed for the isotopic analysis of nanomolar quantities of NH$_3$ (Felix et al., 2013) or to the sodium azide conversion for larger samples (Smirnoff et al., 2012). This analytical approach was then applied to field settings to: (1) characterize NH$_3$ emission sources (Felix et al., 2013) and partitioning to particulate NH$_4^+$ downwind of sources (Savard et al., 2017), (2) examine the fate of NH$_3$ emissions across field and landscape scales (Felix et al., 2014), and (3) determine variability across large regions (Felix et al., 2017). A similar oxidation approach was used by Chang et al. (2016) to examine local and regional sources of NH$_3$ that contribute to PM$_{2.5}$ formation in Beijing, China (Chang et al., 2016).

5.2. Precipitation, bulk deposition and throughfall

Reactive N in wet deposition, including rain, snow, and fog, can be characterized using several collection approaches. National monitoring networks, such as the National Atmospheric Deposition Program’s (NADP) National Trends Network (NTN), employ wet deposition-only collectors that are exposed to the atmosphere solely during precipitation events over a one-week period (i.e., each sample integrates wet deposition over a one-week period). Elliott et al. (2007) used archived NTN rainwater to examine spatio-temporal variations in $^{15}$N of NO$_3^-$ in wet deposition across the Northeastern U.S. Finer time resolved samples have also been used to examine changing NO$_3^-$ sources to rainwater during Hurricane Irene (Felix et al., 2015) or individual rain events (Buda and Dewalle, 2009). Bulk collectors are continuously exposed to the atmosphere and are thus considered to collect both wet and a portion of dry deposition (e.g., Zhang et al., 2008). Similarly, resin collectors that have long been used to passively measure reactive N fluxes have more recently been used as a medium for collection of bulk and throughfall NO$_3^-$ deposition for isotopic analysis (Templer and Weathers, 2011; Templar et al., 2015). The $^{13}$N values of NH$_4^+$ and NO$_3^-$ in wet deposition-only collectors were measured along with co-located particulate and gaseous species downwind of several sources in Alberta, Canada (Savard et al., 2017).

5.3. Particulates and aerosols containing NO$_3^-$ or NH$_4^+$

Aerosol NO$_3^-$ isotopes have been used in a similar fashion as wet NO$_3^-$ deposition isotopes to examine emission sources and atmospheric cycling (Elliott et al., 2009; Wankel et al., 2010). In particular, particulate NO$_3^-$ exhibits similar seasonal trends compared to wet NO$_3^-$ isotopes wherein $^{15}$N values are higher in colder months due to relative proportion of O atoms from isotopically enriched O$_2$ to NO$_3^-$ formation (Wankel et al., 2010). Particulate NO$_3^-$ $^{15}$N values were strongly correlated with surrounding power plant NO$_x$ emission densities at eight CASTNET sites in Ohio, Pennsylvania, and New York (Elliott et al., 2009). Moreover, monthly variability in $^{15}$N of particulate NO$_3^-$ aerosols at these same sites strongly mirrored monthly changes in emission densities surrounding individual sites (Elliott et al., 2009).

An analysis of $^{15}$N values of size segregated NO$_3^-$ and NH$_4^+$ aerosols from coastal sites in the United Kingdom yielded a strong dependence on geographical origin of air masses and found marine and terrestrial NH$_3$ sources were isotopically distinct (Yeatman et al., 2001).
More recently, Pan et al. have used $\delta^{15}$N values of size-resolved NH$_4^+$ aerosols to determine fossil fuel emissions of NH$_3$ were the dominant (90%) source of haze-forming NH$_3$ in Beijing, China (Pan et al., 2016; Pan et al., 2018). To distinguish between coarse and fine-mode aerosols, samples were collected using a 9-stage impactor and quartz fiber filters.

Lin et al., 2016 examined fine mode (<1 μm diameter) $\delta^{15}$N of NH$_4^+$ aerosols over the remote Atlantic Ocean using a high volume sampler with a cascade impactor and Whatman 41 filters (Lin et al., 2016). They concluded that NH$_4^+$ aerosols from remote high latitudes had lower $\delta^{15}$N values relative to higher concentration NH$_4^+$ aerosols collected in temperate and tropical latitudes (Lin et al., 2016).

Savard et al. (2017) analyzed $\delta^{15}$N of particulate NH$_4^+$ and NO$_3^-$ downwind of different anthropogenic sources in Alberta, Canada, actively collected on open-face Teflon filters similar to CASTNET filter packs. Isotopic signatures in both particulate species overlapped for different source types, and the role of temperature-dependent isotope partitioning between the gas and particle phases was evident, particularly for NH$_4^+$ and NH$_3$.

6. Future research

While the first studies of atmospheric reactive N isotopes occurred as early as the 1950s (Hoering, 1957), and the identification of isotope source signatures as early as the 1970s (Moore, 1974), the past decade has been marked by an explosion of research on atmospheric reactive N isotopes. While much has been observed, modeled, and quantified during this past decade of research, further research is required to more fully apply isotopes to understanding atmospheric reactive N chemistry and deposition. While existing studies demonstrate that isotopic ratios of atmospheric N have great promise to aid in source apportionment, the field needs further refinement before incorporation into regulatory contexts or frameworks.

Much of the needed future research will involve decoupling atmospheric chemical processing effects on atmospheric reactive N isotopes from N isotope signatures from emission sources. This will require two major components. First, a more robust inventory of emission source signatures for NO$_x$ and NH$_3$ is required. While a handful of studies now exist that document ranges in isotope ratios for major emission sources, source signatures have not been explored extensively for all sources using modern measurement techniques (e.g., lightning). Moreover, observations that focus on mechanisms driving variations in source signatures (e.g., effects of catalytic reduction technologies on vehicular $\delta^{15}$N-NO$_x$ and $\delta^{15}$N-NH$_3$) as a function of soil and environmental conditions) are extremely limited. We consider this research need to be a high priority that could be met in the short-term.

Secondly, further empirical experimental and field research is needed to characterize isotope effects (i.e., fractionations) that can occur in the atmosphere or during sampling that can alter the fidelity of isotopic source signatures and the composition of ambient and/or deposited NO$_x$ and NH$_3$. Because NO$_x$ and NH$_3$ cycling can complicate the interpretation of source apportionment to field-collected NO$_x$ and NH$_3$, empirical validation of recently modeled fractionation effects is imperative. Laboratory and field studies are needed to address the effects of field and climatic conditions, geographic scale, and atmospheric processes on resulting isotopic compositions of wet and dry deposited forms of NO$_x$ and NH$_3$. Controlled experiments employing active and passive sampling systems are recommended to quantify or rule out potential fractionation due to sampling methods.

Additional gradient studies, microscale to national-scale, should use all the most current methods available (i.e. NO$_x$ and NH$_3$ sampling, back trajectory analyses, mixing models, fractionation factors, measurement of NO$_x$/O$_3$ or NH$_4^+$/NO$_3^-$ ratios, as well as other gaseous compounds). By using a combination of these tools, a more complete understanding will emerge of wet and dry deposited isotope variations in time and space. There is a particular need to document high-resolution temporal changes in the isotopic composition of reactive N deposition and how these fine-scale changes are related to changing meteorological conditions, air masses, emission sources, or chemical transformations. Highly sensitive isotopic methods make these types of observations possible for the first time. Manifestation of these spatio-temporal patterns as isoswaps will be an important interface between isotope geochemists, atmospheric chemists, modelers, ecologists, resource managers, and policy analysts and regulators. For this reason, we consider this overall research need to be a high priority that could be met in the short-term.

Additionally, there are other key toolsets that can be utilized to further the scientific community’s understanding of atmospheric reactive N reactions and their resulting influence on the environment. While future efforts should aim to quantify potential isotope effects on emission source signatures by supplementing traditional isotope sampling with multi-parameter sampling (e.g., NO, NO$_x$, and HNO$_3$ concentrations), chemical transport modeling (e.g., CMAQ, GEOS-CHEM) can also be used in conjunction with sampling to quantify reaction rates and interactions between meteorological conditions, emissions, and isotope effects. As the understanding of the isotopic chemistry of atmospheric reactive N evolves, isotopic ratios can be extremely useful for chemical transport models. For example, isotopic methods could be used to empirically validate the relative contributions of hard-to-quantify emission sources such as lightning and diffuse soil NO emissions. Additionally, isotopes can be used as tracers within atmospheric chemistry models to provide empirical validation of chemical reactions, furthering the understanding of atmospheric reactions that are currently unknown. They can also play a significant role in the development of accurate “transfer ratios” used by models to quantify deposition fluxes to landscapes and the subsequent impact of that deposition to surface water N loads (U.S. EPA, 2011). We consider this overall research need to be a medium priority that could be met in the mid-term.

While $\Delta^{17}$O-NO$_3^-$ is a robust tracer of photochemical NO$_3^-$ production in the atmosphere, there is also tremendous potential for the application of $\Delta^{15}$O-NO$_3^-$ to understand the impact of atmospheric NO$_3^-$ deposition on ecosystems, including streams and rivers. To date, only a handful of studies have used this approach. Given that $\Delta^{17}$O is a conservative tracer, it can be used to quantify atmospheric NO$_3^-$ contributions to water bodies, as well as quantify the effects of mass-dependent processes like denitrification. Expansion of this approach to quantify the relative proportion of atmospheric NO$_3^-$ in streams and rivers beyond existing studies would help refine our general understanding of reactive N dynamics in watersheds and ecosystems. There are several groups pursuing this technique (e.g. Rose et al., 2015a; Michalski et al., 2004; Fang et al., 2015; Tsunogai et al., 2016; Bourgeois et al., 2018) that may be points of key research opportunities for parties interested in applying this technique to samples collected as part of national monitoring networks (government/academic collaborations). There is great potential for the use of this technique by environmental program managers to determine sources of nitrogen contamination to water bodies, for example, discerning a runoff or atmospheric reactive N deposition source. This information, on ecosystem to ecoregion scales, would provide highly desirable information to key decision-makers for determining appropriate standards (e.g., secondary NO$_3^-$ NAAQS) in protecting environmental health. We consider this future research to be a medium priority that can be met in the short-term.

Lastly, the aforementioned future research would benefit from a clearer recognition of the importance of atmospheric deposition within the field of “atmospheric chemistry”. In particular, agency funding is often siloed into disciplinary categories. While atmospheric deposition clearly plays a role in individual disciplines (e.g., ecosystem studies, hydrological sciences, atmospheric chemistry, etc.), research involving atmospheric deposition is often not clearly identified by funding organizations. It is certainly the case that cross-coordination is required across different disciplines to address the opportunities and questions outlined in this future research section. For example, isotope geochemists, field monitoring researchers, global modelers, and others will be...
required to collaborate to answer some of the larger questions pertaining to atmospheric N compound dynamics. Resolving potential funding venues for atmospheric deposition research is an immediate need and one that could be addressed in the short-term through conversations and collaborations between academic researchers and scientists at funding agencies.

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