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Isotopic advances in understanding reactive nitrogen deposition and atmospheric processing

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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 (NO_x =nitric oxide (NO) + nitrogen dioxide (NO_2)), atmospheric nitrate (NO_3^-), nitric acid (HNO_3), and NH_x ammonia (NH_3), and ammonium (NH_4^+). This isotopic information provides new insight into the mechanisms of transformation and cycling of reactive N in the atmosphere and moreover help resolve the contribution of multiple NO_x and NH_3 emission sources to deposition across landscapes, regions, and continents. Here, we highlight the current state of knowledge regarding the isotopic ratios of NO_x and NH_3 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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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, 2003). Isotopic analysis of N in reactive N species – and simultaneous analysis of N and O in oxidized reactive N species (NO_y) – 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:

$$\delta(\text{‰}) = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000 \quad (\text{Equation 1})$$

where R is the ratio of heavy-to-light isotope (e.g., ¹⁵N/¹⁴N), R_{sample} is that ratio in a sample, and R_{standard} is that ratio in the international standard. The international standard for N is atmospheric N₂ (¹⁵N/¹⁴N = 0.0036782 (De Bièvre et al., 1996)). Oxygen has three stable isotopes (¹⁶O, ¹⁷O, ¹⁸O), and isotopic analysis of oxygen isotope ratios (¹⁷O/¹⁶O and ¹⁸O/¹⁶O) is placed on the scale of Vienna Standard Mean Ocean Water (VSMOW) scale (¹⁷O/¹⁶O = 0.0003799, ¹⁸O/¹⁶O = 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, changes in the heavy-to-light isotope rates (e.g., ¹⁵N/¹⁴N, ¹⁷O/¹⁶O and ¹⁸O/¹⁶O), known as isotopic fractionation. The degree of isotopic fractionation in kinetic processes can be quantified by a kinetic fractionation factor (α_k), which is defined by the instantaneous change in the isotope ratio of the reaction product (R_p) at a given substrate isotope ratio (R_s): α_k=R_p/R_s. As molecules containing heavier isotopes usually react more slowly than those containing lighter isotopes, a normal kinetic fractionation will enrich heavier isotopes in the reaction substrate than in the reaction product, resulting in an α_k<1. In reversible equilibrium reactions, isotope ratios of two species, A and B, at equilibrium can be related by an equilibrium fractionation factor, α_{eq}=R_B/R_A. By convention, isotopic fractionation can also be expressed in units of ‰ as isotope effect (ε): ε=(α-1)×1000.

While the vast majority of the isotope effects observed in nature, whether equilibrium or kinetic, depend in some way upon mass differences between the different isotopes (Kaye, 1987), one important exception is the ozone (O_3) formation reaction, in which a rare isotope effect leads to excess ^{17}O enrichment relative to what would be expected based on the ^{18}O enrichment (Thiemens, 2006). This mass-independent effect leads to a unique signature (excess ^{17}O , termed ^{17}O , quantified as $^{17}O = \delta^{17}O - (0.52 * \delta^{18}O)$) in atmospheric O_3 ($^{17}O-O_3$) that is not affected by mass-dependent isotopic fractionations (Michalski et al. 2003). Moreover, this mass-independent signal can be transferred to atmospheric NO_3^- in various degrees during NO_x oxidation reactions with O_3 , rendering measurement of $^{17}O-NO_3^-$ a robust tool to constrain photochemical formation pathways of atmospheric NO_3^- (Michalski et al., 2003; Alexander et al., 2009; Morin et al., 2011).

In the sections below, we highlight the current state of knowledge regarding: 1) the isotopic ratios of NO_x and NH_3 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.

1) Inventory of $\delta^{15}N-NO_x$ and $\delta^{15}N-NH_3$ source values

Use of N isotopes in atmospheric reactive N species as quantitative tracers of NO_x and NH_3 source contributions requires that different emission sources have relatively distinct and well-characterized $\delta^{15}N$ signatures. Globally, NO_x emissions from fossil fuel combustion via electricity generating units (EGU) and vehicles are the dominant NO_x source to the atmosphere (Figure 1).

Felix et al. (2012) collected EGU in-stack NO_x and found that EGU $\delta^{15}N-NO_x$ ranged from 9‰ to 26‰, significantly higher than that of other measured NO_x emission sources (Felix et al., 2012)(Figure 2a). NO_x resulting from vehicle fossil fuel combustion has been reported to have $\delta^{15}N$ values ranging from -13‰ to 9‰ and -21‰ to -2‰ for gasoline- and diesel-powered vehicles, respectively (Walters et al., 2015a, b) (Figure 2a). Although $\delta^{15}N$ ranges of vehicle-emitted NO_x and NO_x produced in biomass burning overlap to a large extent (Fibiger and Hastings, 2016), vehicular $\delta^{15}N-NO_x$ measured either at tailpipes or in near-road environments is significantly higher than that of biogenic NO_x emissions from agricultural soils ranging from -60‰ to -20‰ (Li and Wang, 2008; Yu and Elliott, 2017) (Figure 2a). The low $\delta^{15}N$ values of soil-emitted NO stem from large kinetic isotope effects associated with microbial NO production in soils that strongly discriminates against ^{15}N (Yu and Elliott, 2017). Correspondingly, as shown in Figure 2, the $\delta^{15}N$ values of NO_x emission from EGU, vehicles, and soils are significantly different from each other, suggesting that $\delta^{15}N-NO_x$ is a robust indicator for NO_x source partitioning in relatively constrained environments (e.g., environments with *a priori* information on biomass burning and lightning) (Figure 2a).

Importantly, at the power plants studied in Felix et al. (2012), large differences exist in the $\delta^{15}\text{N}$ of NO_x emitted with and without selective catalytic reduction (SCR) technology (Figure 2a), indicating that EGU $\delta^{15}\text{N}\text{-NO}_x$ is altered by kinetic isotope effects during the catalytic NO_x reduction (Felix et al., 2012)(Figure 3a). This has also been observed in $\delta^{15}\text{N}$ of NO_x emitted from vehicles equipped with three-way catalytic converters (TWC) (Figure 3a), rendering vehicular $\delta^{15}\text{N}\text{-NO}_x$ dependent on vehicle operating conditions (e.g., cold versus warm engines) and NO_x mitigation efficiency (Walters et al., 2015a, b). Consequently, gradual implementation of emission control technologies (e.g., SCR and TWC) is expected to increase $\delta^{15}\text{N}\text{-NO}_x$ of fuel combustion-related NO_x emissions (Felix et al., 2012).

Global NH_3 emissions are dominated by agricultural activities, including livestock operations and fertilizer application (Figure 1). The primary agricultural source, urea in livestock waste and fertilizers, is quickly hydrolyzed to NH_3 , which is then volatilized to the atmosphere. This is also the case with NH_4^+ in fertilizers and hydrolyzed human waste where both are subject to direct volatilization after application and dissociation to NH_3 . Hence, given the large equilibrium isotope effect associated with the aqueous $\text{NH}_3\text{-NH}_4^+$ system (e.g., 45‰ at 296 K (Li et al., 2012)) and the kinetic isotope fractionations during NH_3 volatilization (e.g., -8 to -5‰ at 298 K (Deng et al., 2018)), field-observed $\delta^{15}\text{N}$ of NH_3 emitted from the agricultural sources (i.e., -56‰ to -10‰) is significantly lower than that of other anthropogenic and natural NH_3 emission sources (Figure 2b), allowing its potential use in tracing agricultural NH_3 emissions and their fate during atmospheric transformations. However, $\delta^{15}\text{N}\text{-NH}_3$ derived in controlled laboratory incubations of liquid manure spans a wider range (Figure 2b) due to the strong temperature dependency of the equilibrium and kinetic isotope effects accompanying the NH_3 volatilization (Figure 3b), suggesting that $\delta^{15}\text{N}\text{-NH}_3$ of the agricultural sources and human wastes may be subject to seasonal variations (Schulz et al., 2001).

Therefore, despite the indications that $\delta^{15}\text{N}\text{-NO}_x$ and $\delta^{15}\text{N}\text{-NH}_3$ can serve as robust tracers of NO_x and NH_3 source contributions, further characterization of $\delta^{15}\text{N}\text{-NO}_x$ and $\delta^{15}\text{N}\text{-NH}_3$ is required to minimize uncertainty and to further understand mechanisms driving atmospheric $\delta^{15}\text{N}\text{-NO}_x$ and $\delta^{15}\text{N}\text{-NH}_3$ dynamics. Moreover, the current inventory of $\delta^{15}\text{N}\text{-NO}_x$ and $\delta^{15}\text{N}\text{-NH}_3$ 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 $\delta^{15}\text{N}\text{-NO}_x$ and biomass burning, natural soils, and marine sources for $\delta^{15}\text{N}\text{-NH}_3$.

2) The role of atmospheric chemistry on isotopic signatures

Once released into the atmosphere, inorganic N gases such as NO_x and NH_3 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 NO_3^- and NH_4^+). These processes may be equilibrium (reversible) reactions, such as the partitioning of NH_x ($\text{NH}_x = \text{NH}_3 + \text{NH}_4^+$) between the gas, dissolved, and solid phases (Reactions 1 to 3):

These isotopic exchange reactions have been shown in both theoretical calculations (Urey, 1947; Walters et al., accepted) and/or laboratory experiments (Kirshenbaum et al., 1947; Li et al., 2012) to favor the right-hand side of the equilibrium, resulting in higher $^{15}\text{N}/^{14}\text{N}$ ratios in dissolved and solid NH_x than in gaseous NH_3 . Moreover, under non-equilibrium conditions such as unidirectional neutralization reactions between gaseous NH_3 and atmospheric acids (e.g., H_2SO_4 , HNO_3 , and HCl), partitioning of N isotopes between NH_3 and NH_4^+ may be controlled by kinetic fractionations, giving rise to ^{15}N -enriched dissolved and solid NH_4^+ products (Pan et al., 2016). Consistent with theory and experiments, simultaneous observations of NH_3 with particle-bound NH_4^+ and/or NH_4^+ in precipitation (Moore, 1977; Heaton, 1987; Savard et al., 2017) have found a significantly higher proportion of ^{15}N in NH_4^+ , whether in the solid or aqueous phase, than in gas-phase NH_3 . 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., accepted). Importantly, one potential mechanism driving the observed variability in $\delta^{15}\text{N}$ of atmospheric NH_x species may involve the large differences in kinetic and equilibrium isotope effects associated with multi-step NH_3 gas-to-particle conversion (Walter et al., accepted). For example, while isotopic equilibrium between NH_3 and solid NH_4^+ (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 NH_3 at the gas-liquid interface (i.e., reaction 1; 4‰ at 298 K) (Walters et al., accepted). Consequently, N isotopic composition differences between NH_3 and particle-bound NH_4^+ 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 ^{15}N signature in NH_3 or NH_4^+ for source attribution.

The atmospheric cycle of NO_x is complex, with different processes taking place during the day and night (Hastings et al., 2003; Elliott et al., 2009) (Figure 4). During the day, photochemical cycling between NO and NO_2 is rapid, controlled by the oxidation of NO by either O_3 (Reaction 4) or peroxy radicals (HO_2/RO_2) (Reaction 5) to form NO_2 and the subsequent photolysis of NO_2 back to NO (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 NO_x. 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).

As a result, when NO and NO₂ exist in comparable concentrations, ¹⁵N is preferentially partitioned into NO₂ if the N isotopic equilibrium is achieved, leading to significantly higher δ¹⁵N-NO₂ relative to δ¹⁵N-NO and δ¹⁵N-NO_x (Freyer et al., 1993; Walters et al., 2016). Thus, the N isotopic partitioning between NO and NO₂ will likely reflect the competition between the photochemical NO-NO₂ cycling and the 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., 2018), therefore making it difficult to fully assess the conservation of δ¹⁵N-NO_x source signatures in NO₂ under varying atmospheric conditions.

The major sink for NO_x in the atmosphere is oxidation to HNO₃ (Figure 4), which occurs during the day through the reaction between NO₂ and photochemically-produced hydroxyl radicals (OH)

and at night via heterogeneous hydrolysis of dinitrogen pentoxide (N₂O₅) (Reactions 9–11) or hydrogen abstraction from hydrocarbons by nitrate radical (NO₃) (Reaction 12).

The equilibrium N isotope exchange between NO₂, NO₃, and N₂O₅, the substrates for the HNO₃ production in the above-mentioned formation pathways, was recently investigated using theoretical calculations by Walters and Michalski (2015). Based on these calculations, δ¹⁵N-NO₃ and δ¹⁵N-N₂O₅ are significantly lower and higher than δ¹⁵N-NO₂, respectively, if N isotopic equilibrium is achieved (Figure 4). These calculated equilibrium isotope effects

have been recently applied to correct isotopic fractionations on NO_x during HNO_3 production for source partitioning of particulate NO_3^- deposition (Zong et al., 2017; Chang et al., 2018). While these new attempts adopting a coupled isotopic measurement and modeling approach provide new insights into the complex nature of the land-atmospheric cycling of NO_x , it is important to point out the simplicity inherent to 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 $\delta^{15}\text{N}$ - HNO_3 beyond the N isotopic equilibrium between NO_2 , NO_3 , and N_2O_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_2O_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 lower $\delta^{15}\text{N}$ value for the HNO_3 product than for the N_2O_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 $\delta^{15}\text{N}$ values). Therefore, due to the number and complexity of the NO_y ($= \text{NO} + \text{NO}_2 + \text{NO}_3 + \text{HNO}_3 + \text{N}_2\text{O}_5 + \text{HONO} + \text{particle NO}_3^- + \text{organic nitrates}$) reactions taking place in the atmosphere, linking the $\delta^{15}\text{N}$ of deposited atmospheric NO_3^- to that of emitted NO_x is not trivial. In addition to the source $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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 Figure 4, the ^{17}O value of NO_2 is determined by: 1) the fraction of total NO_2 production that is a result of O_3 oxidation (f_{O_3} , Figure 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 ($^{17}\text{O}\text{-O}_3^*$, Figure 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 $^{17}\text{O}\text{-NO}_2$ 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 ^{17}O transfer functions constrained by the oxygen mass balance (Figure 4). Therefore, $^{17}\text{O}\text{-NO}_3^-$ 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 (Figure 4). Future studies should explore the utility of coupled $^{17}\text{O}\text{-NO}_3^-$ and $\delta^{15}\text{N}\text{-NO}_3^-$ analysis in source partitioning of deposited atmospheric NO_3^- .

$^{17}\text{O}\text{-NO}_3^-$ has another particularly important application in watershed-scale studies. Because $^{17}\text{O}\text{-NO}_3^-$ does not fractionate with any processes that normally complicate interpretation of dual isotope data (e.g., denitrification), $^{17}\text{O}\text{-NO}_3^-$ 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 ^{17}O - NO_3^- analysis at the watershed scale (Rose et al., 2015b and references therein). In southern California, ^{17}O was used to trace the flux of atmospheric nitrate into soil-, ground-, and surface waters (Michalski et al., 2004). Based on ^{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 $\delta^{18}\text{O}$ - NO_3^- , ^{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 ^{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 (Rhia 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 $\delta^{15}\text{N}$ - NO_3^- , ^{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).

3) 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 on 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 $\delta^{15}\text{N}$ values have attempted to characterize isotope dynamics and their corresponding changes over space and time.

Microscale gradient studies provide insight into how $\delta^{15}\text{N}$ values of NO_y and NH_x compounds are deposited with distance away from direct emission sources. For example, Ammann et al. (1999) observed decreasing $\delta^{15}\text{N}$ values collected in spruce needles and soil along a ~ 1000 m gradient away from a highway and related $\delta^{15}\text{N}$ 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_2 and HNO_3 isotope dynamics along a ~ 500 m gradient downwind from a highway. Moreover, the researchers also traced the uptake of vehicle-source NO_2 into plant tissue using $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ 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 *Sphagnum*. This indicates that the utility of plants in tracing atmospheric reactive N may be highly species-specific. $\delta^{15}\text{N}$ - NH_3 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_y/NH_x 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_y/NH_x 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_3 , and dry and/or wet deposited forms of NO_y , NH_x , 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., 2018; 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 $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{15}\text{N}\text{-NH}_4^+$ 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 fractionation 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 $\delta^{15}\text{N}$ values in warm months generally reflect the importance of soil-derived biogenic emissions or lightning in some areas while cold month $\delta^{15}\text{N}$ values are more heavily influenced by fossil fuel combustion (electricity generation) (Elliott et al., 2007; Elliott et al., 2009; Hastings et al., 2003), although temperature dependence of isotopic equilibrium exchange between NO and NO_2 (Reaction 5) can also lead to more enriched $\delta^{15}\text{N}$ values during winter (Freyer, 1991; Freyer et al., 1993).

In the rapidly expanding literature dedicated to $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ values. Recent studies demonstrate that $\delta^{15}\text{N}\text{-NO}_2$ source signatures remain intact under conditions of high ozone concentration relative to NO_x concentration (i.e., f_{NO_2} close to 1) (Walters et al., 2018). Some regional field transect studies and paleo-studies have concluded that emission sources are the primary driver of $\delta^{15}\text{N}\text{-NO}_3^-$ and/or $\delta^{15}\text{N}\text{-NH}_4^+$ 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; Zhan et al., 2015), $\text{NH}_4^+/\text{NO}_3^-$ ratios (Beyn et al., 2014; Lee et al., 2012; Zhao et al., 2009; Jia and Chen 2010), or using mixing models (Proemse et al., 2013; Felix et al., 2013; Felix et al., 2015; Felix et al., 2016; 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 $\delta^{15}\text{N}\text{-NO}_3^-$ and/or $\delta^{15}\text{N}\text{-NH}_4^+$ 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 $\delta^{15}\text{N}\text{-NO}_3^-$ 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 isotope effects. Future efforts should aim to quantify potential isotope effects on source signatures by supplementing traditional isotope sampling with multi-parameter sampling (e.g., NO_y , 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 $\delta^{15}\text{N-NO}_3^-$ 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 $\delta^{15}\text{N-NO}_x$ 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 $\delta^{15}\text{N-NO}_x$ 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 $\delta^{15}\text{N}$ 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_y and NH_x .

4) 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 denitrifying bacteria to analyze nanomolar quantities of NO_3^- for $\delta^{15}\text{N}$ (Sigman et al., 2001), $\delta^{18}\text{O}$ (Casciotti et al., 2002), and ^{17}O (Kaiser et al., 2004). Other recent methods chemically convert nitrate and nitrite to nitrous oxide using either sodium azide (McIlvin and Altabet, 2005) or hydroxylamine (Liu et al., 2014). Highly sensitive ammonium isotope analyses have also been facilitated by these advanced methods – whereby hypobromite is used to oxidize ammonium to nitrite which is then converted to nitrous oxide using hydroxylamine (Liu et al., 2014), acetic acid (Zhang et al., 2007) or denitrifying bacteria (Felix et al., 2013). Together, these methods advances established a new foundation for subsequent method development and application studies.

Gaseous nitric oxide, nitrogen dioxide, nitric acid, and ammonia—Gas phase reactive N compounds can be characterized using either active or passive sampling approaches (Figure 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 (two weeks to six 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 particles, 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 ^{15}N or ^{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 et al., 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 ammonium nitrate 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 nitric oxide (NO) and NO_x ($\text{NO} + \text{NO}_2 = \text{NO}_x$) 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. (2015) 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_2 and/or NO_x have also been collected for ^{15}N analysis using passive samplers (Smirnov et al., 2012; Dahal and Hastings, 2016) or experimental actively-sampled cartridges (Savard et al., 2017) based on proprietary sampling media (Maxxam Analytics). When NO_2 isotopes have been collected for ^{15}N analysis and analyzed as nitrite in solution, it has been noted that an additional fractionation factor ($\sim +27.5\%$) must be applied when using the denitrifier method to account for an additional oxidation to NO_3^- during bacterial processing (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 soil were fertilized and NO fluxes measured in a dynamic chamber. NO was oxidized to NO_2 using chromate (CrO_3) 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 NO₂ in excess O₃, and resulting NO₂ is collected in a solution of TEA (Yu and Elliott, 2017).

Nitrogen dioxide (NO₂) 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 NO₂ filters as a collection medium for isotopic analysis of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ across varying environmental conditions (Coughlin et al., 2017). Another recent study collected $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO₂ using an active sampling denuder assembly coated with a potassium hydroxide solution, guaiacol, and methanol solution (Walters et al., 2018).

Gaseous HNO₃ has been characterized isotopically using both active and passive sampling approaches. Archived HNO₃ from eight CASTNET sites, where HNO₃ is collected on a nylon filters as air is drawn through a three-stage filter pack for a 1-week period, was analyzed for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ (Elliott et al., 2009). Nylon filters were also used to collect HNO₃ downwind of specific source types using a wind sector-specific active sampling system for $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and ^{17}O analysis (Savard et al., 2017). Passive collection of HNO₃, 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 NH₃ 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; Smirnov et al., 2012). Rather than the high mass requirements and other complications with filter combustion, Smirnov et al. (2012) and Felix et al. (2013) adapted an approach to oxidize NH₃ collected on acid-coated filters to nitrite using a bromate solution (Zhang et al., 2007). These studies coupled oxidized NH₃ to the denitrifier method and thus allowed for the isotopic analysis of nanomolar quantities of NH₃ (Felix et al., 2013) or to the sodium azide conversion for larger samples (Smirnov et al., 2012). This analytical approach was then applied to field settings to: (1) characterize NH₃ emission sources (Felix et al., 2013) and partitioning to particulate NH₄⁺ downwind of sources (Savard et al., 2017), (2) examine the fate of NH₃ emissions across field and landscape scales (Felix et al., 2014), and (2) 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 NH₃ that contribute to PM_{2.5} formation in Beijing, China (Chang et al., 2016).

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 depositiononly 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 $\delta^{15}\text{N}$ of NO₃⁻ in wet deposition across the Northeastern U.S. Finer time resolved samples have also been used to examine changing NO₃⁻ 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 nitrate deposition for isotopic analysis (Templer and Weathers, 2011; Templer et al., 2015). The $\delta^{15}\text{N}$ 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).

Particulates and aerosols containing nitrate or ammonium—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 $\delta^{18}\text{O}$ values are higher in colder months due to relative proportion of O atoms from isotopically enriched O_3 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 $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ 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 ($< 1 \mu\text{m}$ diameter) $\delta^{15}\text{N}$ 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 the remote high latitudes had lower $\delta^{15}\text{N}$ values relative to higher concentration NH_4^+ aerosols collected in temperate and tropical latitudes (Lin et al., 2016).

Savard et al. (2017) analyzed $\delta^{15}\text{N}$ 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 .

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 emission sources 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 $\delta^{15}\text{N}\text{-NO}_x$ and $\delta^{15}\text{N}\text{-NH}_3$, $\delta^{15}\text{N}$ of soil-emitted NO and 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_y and NH_x . Because NO_y and NH_x cycling can complicate the interpretation of source apportionments to field-collected NO_y and NH_x , 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_y and NH_x . 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_y and NH_x sampling, back trajectory analyses, mixing models, fractionation factors, NO_x/O_3 or $\text{NH}_4^+/\text{NO}_3^-$ information, as well as a multitude of other gaseous compounds). By using a combination of these toolsets, 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 isotopes of reactive N deposition and chemistry 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 isoscapes 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, NO₂, and HNO₃ 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 (CTMs). 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 “transference ratios” used by models to quantify deposition fluxes to landscapes and the subsequent impact of that deposition to surface water N loads. We consider this overall research need to be a medium priority that could be met in the mid-term.

While ¹⁷O-NO₃⁻ is a robust tracer of photochemical NO₃⁻ production in the atmosphere, there is also tremendous potential for the application of ¹⁷O-NO₃⁻ to understand the impact of atmospheric NO₃⁻ deposition on ecosystems, including streams and rivers. To date, only a handful of studies have used this approach. Given that ¹⁷O is a conservative tracer, it can be used to quantify atmospheric nitrate 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 nitrate 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, 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 the technique to samples collected in 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 in 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 NO₂ 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 remaining 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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Figure 1.
Global sources of NO_x and NH_3 for the 1990s (IPCC, 2013).

Figure 2.

$\delta^{15}\text{N-NO}_x$ (a) and $\delta^{15}\text{N-NH}_3$ (b) values by emission sources. Letters on the y-axis indicate significant difference between $\delta^{15}\text{N}$ values of different sources determined by one-way ANOVA and Bonferroni post hoc test. Dashed horizontal lines classify individual emission sources into source categories shown in Figure 1.

Figure 3.

(a) $\delta^{15}\text{N-NO}_x$ of fuel combustion sources as a function of emitted NO_x concentration or collected NO_3^- concentration controlled by NO_x reduction technologies. Data are adapted from Felix et al. (2012), Walters et al. (2015a), and Walters et al. (2015b). Shaded area denotes range of $\delta^{15}\text{N-NO}_x$ measured on road, in traffic tunnels, and in roadside environments (see Figure 2a). (b) Instantaneous $\delta^{15}\text{N-NH}_3$ as a function of cumulative NH_3 volatilization from liquid manure under two different incubation temperatures. Data are adapted from Schultz et al. (2001). Shaded area denotes range of $\delta^{15}\text{N-NH}_3$ measured in livestock farms (see Figure 2b).

Figure 4.

Chemistry leading to formation of atmospheric nitrate (black text and arrows) and corresponding N isotope exchange equilibrium (blue arrows and text) and ^{17}O transfer from O_3 to nitrate (red text). Calculated kinetic isotope effect for the $\text{NO} + \text{O}_3$ reaction ($\epsilon_k(\text{NO}_2/\text{NO})$) is also shown.