REVIEW

A Review of the Techniques Used for Measurements of Nitrogen Isotopes in Atmospheric Aerosols

Xiaoqing Wang[1,2] · Jing Hu[3] · Weiguo Liu[2,3] · Junji Cao[1,2,4]

Abstract

This review of the methods used for measurements of stable nitrogen isotopes in gases and aerosol particles also summarizes some of the latest research on nitrate, ammonium, nitrogen oxides and ammonia in the atmosphere. The main methods used for the determination of N isotopes in nitrate and nitrogen oxides are one that makes use of denitrifying bacteria and a two-step chemical reduction method (cadmium + hydrazoic acid). A commonly used method for measuring nitrogen isotopes in ammonia and ammonium ion is a chemical conversion that uses sodium azide in an acetic acid buffer or hydroxylamine hydrochloride. A common characteristic of these methods is that nitrous oxide is the final analysis product, and the isotopes are determined by mass spectrometry. The precision of the analyses are typically very high (~0.25‰), and the methods require a small amount of sample, usually tens of nmols is sufficient. Some improvements to these methods and collection methods have been made in recent years, and these advances will facilitate research on nitrogen isotopes in the atmosphere.

Keywords Nitrate · Ammonium · Nitrogen oxides · Ammonia · Nitrogen isotope composition

1 Introduction

For decades, China has experienced frequent and all too often severe hazy weather, especially in the Beijing-Tianjin-Hebei region, the Pearl River Delta, the Yangtze River Delta and the areas in and around Chengdu and Chongqing (Sun 2016). Light extinction caused by aerosol particles dispersed in the atmosphere leads to reductions in atmospheric visibility that are characteristic of the most common types of hazy weather (He et al. 2013). Moreover, the emission sources for aerosols are numerous, and the composition of aerosols is complex, and these complicating factors have serious implications for the ecological environment, global climate, and human health (Chen and Xiao 2009; Shao et al. 2018; Zhao et al. 2019). As a result, atmospheric aerosols have become a hot topic for domestic research in China and throughout the world (He et al. 2013; Huang et al. 2014).

Advances in industrial desulfurization technology and the strict monitoring of sulfur dioxide (SO_2) in China have led to some improvements in air quality. However, increases in nitrogen oxide (NO_x) emissions caused by human activities (Wen 2015) have led to a gradual increase in nitrate (NO_3^-) concentrations. Ammonium (NH_4^+) is mainly produced by the conversion of ammonia gas (NH_3) in the troposphere, which is the third most abundant nitrogen-containing gas in the atmosphere after N_2 and N_2O, and together with NH_4^+, it is collectively referred to as NHx ($NH_3 + NH_4^+$) (Seinfeld et al. 1998; Walters and Hastings 2018). NO_3^- and NH_4^+ are important components of secondary inorganic aerosols (SNA), and they participate in various reactions that affect the global nitrogen cycle (Behera et al. 2013; Tang et al. 2006; Walters and Hastings 2018). Recent studies have shown that precursors of NO_3^- also can promote the formation of sulfates and in so doing aggravate atmospheric pollution (Cheng et al. 2016). Therefore, it is of great importance to understand the chemical formation of NO_3^- and NH_4^+ and how these substances are removed from the atmosphere.

✉ Junji Cao
  cao@loess.llqg.ac.cn

1   Key Laboratory of Aerosol Chemistry and Physics, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China

2   University of the Chinese Academy of Sciences, Beijing 100049, China

3   China State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China

4   Institute of Global Environment Change, Xi'an Jiaotong University, Xi'an 710049, China

Moreover, the sources and mechanisms leading to the formation of NO_3^- and NH_4^+ in urban aerosols are not yet fully understood, and the rapid increases in concentrations of NO_3^- during heavy pollution is also uncertain. Stable isotopes have become more widely used in studies of the sources, chemical formation and migration process of pollutants in recent years (Zhao et al. 2019), and the determination of the N and O isotopic composition of NO_3^- can be used to identify sources and investigate conversion processes (Xu et al. 2014; Zhao et al. 2019). The application of stable isotope techniques holds promise for tracing the movements of atmospheric NO_3^-, and similarly, N isotope measurements of NH_4^+ may provide insights into N sources and removal processes (Walters and Hastings 2018). Therefore, this paper reviews the existing research on N isotope analysis of NO_3^- and NH_4^+.

2 Analytical Techniques for Nitrogen Isotopes in Nitrate and Nitrogen Oxides

2.1 Nitrogen Isotopes and the Formation of Nitrogen Oxides

NO_3^- in the atmosphere mainly forms through reactions of NO_x and free radicals. It is generally agreed that during the daytime, the formation of NO_3^- is mainly driven by gas-phase reactions between NO_2 and OH radicals ($NO_2 + OH$) (Fig. 1) (Seinfeld and Pandis 2016; Tang et al. 2006). At night, HNO_3 mainly forms through reactions of N_2O_5 in the liquid phase ($N_2O_5 + H_2O$) (Fig. 2) (Jia et al. 2006). The factors that affect the formation of NO_3^- include not only temperature but also relative humidity (RH) and solar radiation intensity (Elliott et al. 2009). In addition, N_2O_5 at night also forms through multi-step reactions of NO_x involving O_3. The main sources for gaseous NO_x include emissions from soil microbes, biomass burning, thermal power plants and motor vehicle exhaust (Bao et al. 2015; Wang et al. 2014).
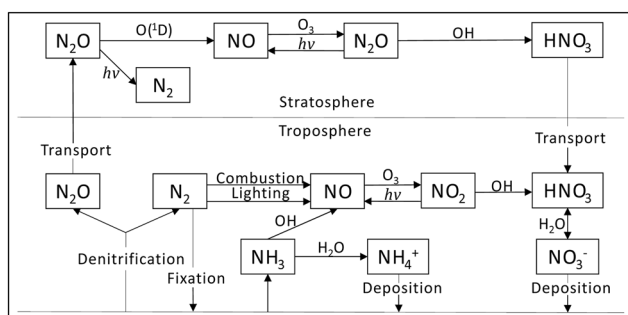
Fig. 1 Oxidation of NO_x to NO_3^- during the day (Seinfeld and Pandis 2016; Tang et al. 2006)
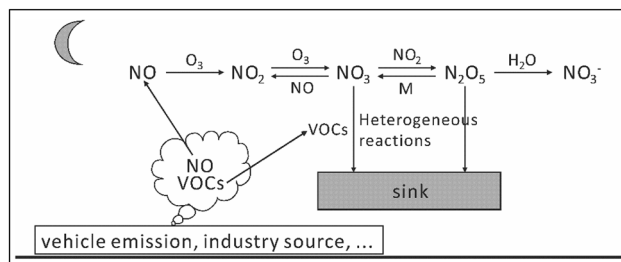
Fig. 2 Oxidation of NO_x to NO_3^- at night (Jia et al. 2006)

Previous studies have shown that the normalized ratios of ^{14}N to ^{15}N isotopes ($\delta^{15}N$) of NO_x to its oxidation product, NO_3^-, can be used as a type of "fingerprint" to evaluate the contributions of NO_x from various sources to atmospheric nitrogen deposition (Elliott et al. 2007). The N isotope ratios for NO_x vary among sources, and therefore, the stable N isotope ratio for NO_3^- ($\delta^{15}N$-NO_3^-) can be used to trace its main sources. In addition, ^{15}N fractionation occurs during the oxidation of NO_x to NO_3^- (Walters and Michalski 2016), and therefore, N isotopes also can provide insights into NO_3^- formation (Walters and Michalski 2016; Zhang and Gao 2012; Zheng 2000). A limitation in the application of N isotope for source assessments is that the $\delta^{15}N$ values for NO_x from different sources can overlap to a degree, and the fractionation that occurs when NO_x is converted to NO_3^- can be another confounding effect. To maximize the usefulness of isotopic information, both N and O isotopes are often measured together in the stable isotope analysis of NO_3^- (Qin et al. 2019). This approach makes use of the fact that the oxygen isotope composition of O_3 and OH radicals are different ($\delta^{18}O$-O_3: $+90$ to $+120‰$ versus $\delta^{18}O$-OH: -89 to $-56‰$) (Johnston and Thiemens 1997; Michalski et al. 2012). Indeed, $\delta^{18}O$-NO_3^- can provide additional insights into the formation of NO_3^- because data for both O and N isotopes can compensate for the limitations in relying on NO_3^- nitrogen isotopes alone (Altieri et al. 2013; Wankel et al. 2009). Therefore, the use of isotope techniques can effectively investigate the sources for NO_3^- and the oxidation pathways for NO_x.

2.2 Methods for Measuring Nitrogen Isotopes in Nitrate

Quartz fiber filters are commonly used to collect aerosol NO_3^- particles, and then, ultrapure water is used to extract NO_3^- for subsequent analysis. The solution is then used for the N and O isotope determination of NO_3^- (Zhao et al. 2019). At present, the methods for determining the N isotopes in NO_3^- involve distillation, diffusion, graphite combustion, ion exchange resins, denitrifying bacteria, and chemical reduction (Qin et al. 2019; Zhao et al. 2019).

The operating principles for the distillation and diffusion methods are straightforward; that is, NO_3^- is reduced to NH_4^+ for the instrumental analysis. However, these two methods require relatively large sample sizes, and isotope fractionation is likely to occur during the procedures, resulting in large uncertainties in the results. More important, these techniques cannot be used to determine nitrogen and oxygen isotopes simultaneously, so their applications are limited (Liu et al. 2017; Xiao and Liu 2001b; Zhao et al. 2019). For the graphite combustion procedure, which has been improved several times, the NO_3^- sample and granular graphite are first placed in a glass/graphite carbon reaction tube, and then they are converted into N_2 and CO at a high pyrolysis temperature of 1400 °C. After purification, N and O isotopes can be simultaneously determined by mass spectrometry, and this method been automated (Kornexl et al. 1999; Qin et al. 2019). The ion exchange method uses an anion resin to adsorb and concentrate NO_3^- from aqueous solution, and HCl is then used to remove the adsorbed NO_3^-. After a series of purification steps, N and O isotopes can be determined by mass spectrometry (Qin et al. 2019; Silva et al. 2000). However, the pretreatment steps for the ion exchange method are cumbersome, require large sample quantities, and the cost of pretreatment is high because of the consumables used; therefore, this method is not often used (Liu et al. 2017; Xiao and Liu 2001b).

More recently, denitrifying bacteria and chemical reduction methods have developed for isotopic NO_3^- analyses with N_2O as the final product. These methods are not sensitive to atmospheric background, and they can be used for small samples (usually 10–60 nmol) (Casciotti et al. 2002; Mcilvin and Altabet 2005; Sigman et al. 2001). The molecular structure of N_2O is such that the $\delta^{15}N$ value for this compound is the average of the $\delta^{15}N$ for the two nitrogen atoms (Wang et al. 2015) as follows:

$$\delta^{15}N_{(N_2O)} = \frac{\delta^{15}N_{(^{15}N-N-O)} + \delta^{15}N_{(N-^{15}N-O)}}{2}. \tag{1}$$

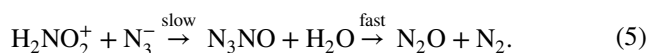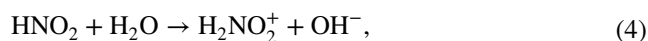The denitrifying bacteria method uses obligate denitrifying bacteria lacking N_2O reductase to reduce all NO_3^- to N_2O in the sample solution. Nitrogen and oxygen isotopes are then determined using a mass spectrometer (Casciotti et al. 2002; Sigman et al. 2001; Yang et al. 2014; Zhang et al. 2010). The denitrifying bacteria method is suitable for different types of samples, and it can be used to measure very low concentration (10–20 nmol N) samples (Liu et al. 2017; Sigman et al. 2001). Meanwhile, the precision of the final analytical results is very high (around 0.2‰) (Sigman et al. 2001). The drawbacks for the method are complex biological responses, poor universality, degradation of bacteria characteristics, and high maintenance costs, and therefore, it is not so commonly used (Wang et al. 2015; Zhao et al. 2019). A chemical reduction method

has been developed by Mcilvin and Altabet (2005), and it is based on two reduction steps. The first step is to reduce NO_3^- to NO_2^- over cadmium (Cd), and the second step is to use the sodium azide (NaN_3) prepared in an acidic buffer (commonly an acetic acid buffer) to quantitatively reduce NO_2^- to N_2O. After that, the ratios of N and O isotopes can be determined by isotope ratio mass spectrometry. The specific reaction equation is as follows (Wang et al. 2015):

The first step of the reduction method occurs in a weakly alkaline environment, and Cd is used to reduce NO_3^- in the solution to NO_2^-:

$$NO_3^- + Cd + H_2O \rightarrow NO_2^- + Cd^{2+} + 2OH^-. \tag{2}$$
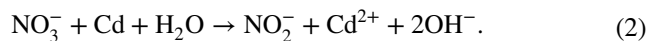
The second step of the reduction method is in a sodium azide-acetic acid buffer system, where N_3^- is used to reduce NO_2^- to N_2O gas:

$$NO_2^- + H^+ \rightarrow HNO_2, \tag{3}$$

$$HNO_2 + H_2O \rightarrow H_2NO_2^+ + OH^-, \tag{4}$$

$$H_2NO_2^+ + N_3^- \xrightarrow{slow} N_3NO + H_2O \xrightarrow{fast} N_2O + N_2. \tag{5}$$

The chemical reduction method has a wide range of applications and is operationally simple, highly sensitive, and relatively inexpensive, and it is now commonly used in China (Liu et al. 2017; Tu et al. 2016; Wang et al. 2015). However, a shortcoming of this method is that the azide reagent is toxic, requiring careful operation in a fume hood and appropriate safety measures in cleaning operations (Liu et al. 2017; Mcilvin and Altabet 2005).

2.3 Nitrogen Isotope Determination Methods for Nitrogen Oxides

The methods for determining N isotopes in NO_x are similar to those used for NO_3^-. The biggest difference between them is in the methods used for collection and pretreatment. For the collection of NO_x, a gas absorption bottle is typically used (Felix et al. 2012; Wang et al. 2015). After the end of sampling, the sealed gas absorption bottle, which contains a fixed volume of an absorption liquid, is shaken to oxidize the NO_x to NO_3^-, the later of which becomes dissolved in the absorbing liquid. The bottle is left for a sufficient amount of time to ensure that all NO_x is converted to NO_3^-. The reaction equation for the oxidation of NO_x to NO_3^- by H_2O_2 is as follows (Wang et al. 2015):

$$NO_2 + NO + 3H_2O_2 \xrightarrow{H^+} 2NO_3^- + 3H_2O. \tag{6}$$
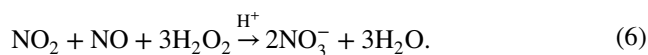
The methods used for the determination of NO_x nitrogen isotopes are the same as those previously described for NO_3^- nitrogen isotopes in Sect. 2.2.

2.4 Recent Research Progress

Tu et al. (2016) improved the chemical reduction methods (cadmium + hydrazoic acid) that were developed for determining N and O isotopes in NO_3^-. First, the sponge cadmium or activated cadmium was replaced with cadmium powder for the NO_3^- reduction step, and the reaction was carried out under ultrasound. Second, the amount of sodium azide in the acetic acid buffer was decreased to only 1% of the original method for the second reduction step; that reduced the amount of toxic reagents used. Third, sodium acetate was added to the buffer along with the sodium azide because that improved the performance of the buffer and decreased the oxygen isotope exchange with water during the NO_2^- reduction process (Liu et al. 2017).
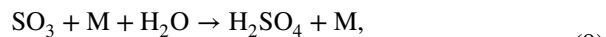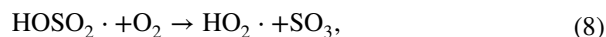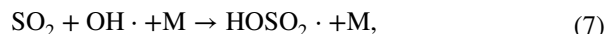
The types of cadmium powders used for the chemical reduction methods can affect the reaction systems and kinetics, pH, etc. (Tu et al. 2016; Wang et al. 2015). Zhao et al. (2019) studied the two-step chemical reduction methods under different conditions and optimized the scheme for accurate determination of N and O isotopes in NO_3^- aerosols. Their studies showed that when the concentration of Cl^- in the solution was ≥ 5 mol/L and pH 8, the cadmium powder was activated by HCl and that favored the reduction of NO_3^- to NO_2^-. And then, NO_2^- was reduced to N_2O with the sodium azide in an acetic acid buffer at a pH of 4.5–4.6, and isotopic determinations were performed with an isotope ratio mass spectrometer. The measurement accuracy for N isotopes determined by this method is ± 0.08%, and the corresponding accuracy for O isotopes is ± 0.24%.

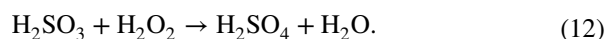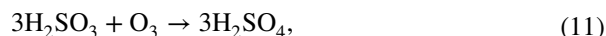## 3 Nitrogen isotope Analytical Techniques for Ammonium and Ammonia

3.1 Formation Mechanisms for Ammonium and Tracing the Reactions with Nitrogen Isotopes

Ammonium (NH_4^+) ions are formed by the reaction of gaseous NH_3 with acids in the atmosphere, mainly H_2SO_4 and HNO_3. Reaction products include ammonium hydrogen sulfate (NH_4HSO_4), ammonium sulfate ((NH_4)$_2SO_4$), and ammonium nitrate (NH_4NO_3), all of which are important aerosol particle components that can degrade atmospheric visibility (Liu 2017). H_2SO_4 and HNO_3 are most often formed through the oxidation of SO_2 and NO_2 in the atmosphere by OH radicals, O_3, H_2O_2, etc., and they further react with NH_3 to form NH_4HSO_4, (NH_4)$_2SO_4$ and NH_4NO_3 (Kong et al. 2014; Wang et al. 2012). The specific reaction equations are as follows (Seinfeld and Pandis 2016; Wang et al. 2009):
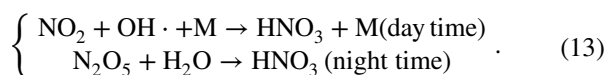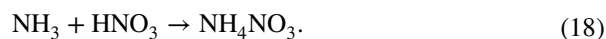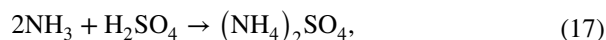
1. Formation of H_2SO_4:

$$SO_2 + OH \cdot + M \rightarrow HOSO_2 \cdot + M, \tag{7}$$

$$HOSO_2 \cdot + O_2 \rightarrow HO_2 \cdot + SO_3, \tag{8}$$

$$SO_3 + M + H_2O \rightarrow H_2SO_4 + M, \tag{9}$$
Or:

$$SO_2 + H_2O \Leftrightarrow H_2SO_3, \tag{10}$$

$$3H_2SO_3 + O_3 \rightarrow 3H_2SO_4, \tag{11}$$

$$H_2SO_3 + H_2O_2 \rightarrow H_2SO_4 + H_2O. \tag{12}$$

2. Formation of HNO_3:

$$\begin{cases} NO_2 + OH \cdot + M \rightarrow HNO_3 + M \text{(day time)} \\ N_2O_5 + H_2O \rightarrow HNO_3 \text{ (night time)} \end{cases}. \tag{13}$$

3. Formation of NH_4^+:

$$NH_3 + H_2SO_4 \rightarrow NH_4HSO_4, \tag{14}$$

$$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4, \tag{15}$$

$$NH_3 + NH_4HSO_4 \rightarrow (NH_4)_2SO_4, \tag{16}$$

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4, \tag{17}$$

$$NH_3 + HNO_3 \rightarrow NH_4NO_3. \tag{18}$$
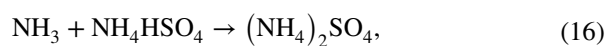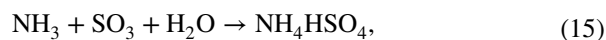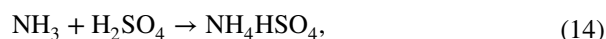
H_2SO_4 has a lower saturation vapor pressure than HNO_3, and therefore, H_2SO_4 will preferentially react with NH_3 to form NH_4HSO_4 and (NH_4)$_2SO_4$ (Baek and Aneja 2004; Liu 2017). That is, when the concentration of NH_3 is low, it will preferentially react with H_2SO_4 to form NH_4HSO_4 and (NH_4)$_2SO_4$, but when NH_3 is in abundance, the excess NH_3 will react with HNO_3 to form NH_4NO_3. The main factors affecting the formation of NH_4^+ are the concentrations of NH_3, SO_2, NO_x and other precursors, temperature, relative humidity (RH), solar light intensity and weather conditions (Hu 2015; Liu 2017). In particular, the main factors affecting the reversible reaction between NH_3 and HNO_3 that forms NH_4NO_3, are the concentration of NH_3, and temperature (Hueglin et al. 2005). In addition, NH_3 is the main precursor of NH_4^+, and it can be oxidized by OH radicals to form NO_x, which in turn is involved in the formation of NO_3^- in a related nitrogen cycle (as shown in Fig. 1) (Seinfeld and Pandis 2016; Tang et al. 2006).

The source of NH_3 in different regions is generally different. In agricultural areas, NH_3 is mainly derived from animal husbandry and the use of fertilizers (Zbieranowski and Aherne 2013). In urban areas, NH_3 has many sources, including industrial sources, vehicle exhaust, external area transmission, solid waste, sewage, and human feces (Dentener and Crutzen 1994; Dong et al. 2010; Gu et al. 2012). In the suburbs, NH_3 is mainly derived from natural emissions such as microbial activities and animal wastes (Sutton et al. 2009). The nitrogen isotope composition of NH_3 ($\delta^{15}N$-NH_3) emitted from different emission sources is generally different (Fig. 3), and the nitrogen isotope composition of NH_4^+ ($\delta^{15}N$-NH_4^+) produced is also different. Therefore, the nitrogen isotope composition of NH_4^+ in atmospheric aerosols can effectively trace its source and formation and transformation processes (Felix et al. 2013).

Previous studies have used a wide variety of collection techniques for measuring the nitrogen isotope composition of NH_3 emission sources ($\delta^{15}N$-NH_3), and it has been found that there can be large variations in $\delta^{15}N$ from a single NH_3 emission source. There also can be considerable overlap in the $\delta^{15}N$ values for different NH_3 emission sources (Chang et al. 2016; Felix et al. 2013; Freyer 1978; Heaton 1987; Hristov et al. 2009; Savard et al. 2017; Smirnoff et al. 2012; Walters and Hastings 2018). This suggests that there needs to be better information on nitrogen isotopes for that major NH_3 sources, and the development of a representative database will require extensive field sampling with many actual measurements (Zong et al. 2017). Another complicating factor is that some processes involving NH_3 can cause isotope fraction: one example of this is the evaporation of NH_3 which can lead to increases in $\delta^{15}N$ in the sample.

In addition, when NH_3 is converted to NH_4^+, equilibrium fractionation of the N isotopes occurs (Freyer 1978; Savard et al. 2017), and that affects the isotopic composition of NH_4^+ and NH_3. The specific reaction equation is as follows (Urey 1947):

$$^{15}NH_3 + {}^{14}NH^{4+} \rightleftharpoons {}^{14}NH_3 + {}^{15}NH^{4+}. \tag{19}$$
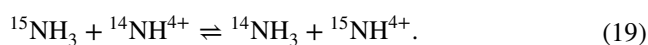
The equilibrium constant (K) or isotope fractionation coefficient (α) for the above formula is 1.034 ± 0.002 at 298.1 K (Urey 1947), and therefore

$$K_{298.1\ K} = \alpha_{298.1\ K} = \frac{{}^{15}NH^{4+}/{}^{14}NH^{4+}}{{}^{15}NH_3/{}^{14}NH_3} = 1.034 \pm 0.002. \tag{20}$$

This shows that conversions between NH_3 and NH_4^+ should favor the partitioning of ^{15}N into NH_4^+, and the net result would be higher $\delta^{15}N$ values for NH_4^+ compared with NH_3 (Urey 1947). Therefore, the determination of $\delta^{15}N$ for NH_x provides information on the heterogeneous conversion of NH_3 into new particles, and that has implications for the relative importance of kinetics versus equilibrium control in the formation of NH_4^+. As the $\delta^{15}N$ of NH_3 may change during the formation of new particles, the form of NH_x must be considered in field sampling and laboratory measurements, and the source of the emissions should also be determined to minimize the effects of chemical and physical processes and to obtain meaningful data for the $\delta^{15}N$ in NH_4^+ and NH_3 (Walters and Hastings 2018).

3.2 Nitrogen Isotope Determination Methods for Ammonium Ion

Quartz fiber filters are generally used for the collection of aerosol NH_4^+, and ultrapure water is then used to extract the NH_4^+ from the particles, and the solution is then used for the nitrogen and oxygen isotope determinations of NH_4^+.(Huang et al. 2018; Xiang et al. 2019). The methods currently used for determining NH_4^+ nitrogen isotopes ($\delta^{15}N$-NH_4^+) can be divided into two categories: Duma and chemical conversion methods (Liu et al. 2017). The Duma methods are traditional, mainly including distillation, diffusion, ion exchange, etc. These methods usually convert the NH_4^+ extracted from the sample into N_2 by combustion and oxidation, and then the N isotopes of the NH_4^+ are determined by isotope ratio mass spectrometry (IRMS) (Liu et al. 2017; Wen et al. 2016; Xiang et al. 2019).

For the distillation method, the filter extract is heat-distilled in an alkaline environment to convert NH_4^+ into NH_3, which is then absorbed by an acidic liquid (most often H_2SO_4) (Freyer 1978; Heaton 1987; Velinsky et al. 1989). Then the Dumas combustion method is used to convert NH_4^+ into N_2 for the measurements of nitrogen isotopes (Liu et al. 2017; Wen et al. 2016). Although this method has a high nitrogen recovery rate, it is prone to cross-contamination of ^{15}N. The diffusion method for NH_4^+ nitrogen isotope measurements is similar to the distillation method, but for the diffusion method, the
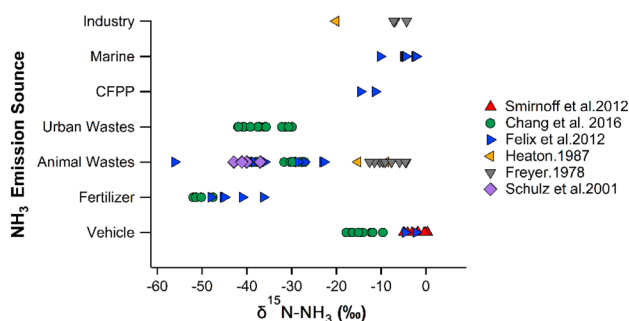
**Fig. 3** Previously reported $\delta^{15}N$-NH_3 values of NH_3 source emissions (Chang et al. 2016; Felix et al. 2013; Freyer 1978; Heaton 1987; Schulz et al. 2001; Smirnoff et al. 2012)

separated NH_3 is absorbed into a solution using a filter device (Holmes et al. 1998). The diffusion method is less prone to cross-contamination, but the absorption time is long (Zeng et al. 2013). The ion exchange method for NH_4^+ nitrogen isotopes uses a resin to adsorb NH_4^+, and after loading, the adsorbed ions are removed with a suitable eluent (Xiao and Liu 2001a, 2002). Unfortunately, the adsorption of NH_4^+ in this method is susceptible to artifacts from strong ions (Hu and Liu 2013). In addition, all of the Duma methods use N_2 for the IRMS analysis making them susceptible to interferences from the atmospheric N_2 background. As a result, these methods are not suitable for the determination of low concentration samples.

Zhang et al. (2007) developed a new analytical technique for low-concentration samples (< 0.5 μM) in which NH_4^+ is chemically converted to N_2O prior to mass spectrometry. The first step for the procedure is to add a low concentration of BrO^- solution to the original acidic absorption solution. The NH_4^+ is oxidized to NO_2^- which in turn is converted into N_2O for N isotope determinations with the use of sodium azide in an acetic acid buffer or hydroxylamine hydrochloride (Liu et al. 2014; Zhang et al. 2007). However, as noted above, hydrazoic acid is highly toxic, and it is also volatile, so it must be handled carefully in a fume hood. In comparison, hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) solutions are less volatile and less toxic. Indeed, Liu et al. (2014) used hydroxylamine hydrochloride to reduce the NO_2^- which is from the first step to N_2O and then determined the N isotopes in NH_4^+. This recently developed conversion method does not require the use of toxic reagents, and it also has the advantage of being simple operationally. The precision of the final results is also very high ($\sim 0.3‰$), and as a result, it has recently received much attention. The specific reaction equations are as follows:

1. In an alkaline environment, BrO^- oxidizes NH_4^+ to NO_2^- (Zhang et al. 2007):

$$BrO^- + NH_4^+ \rightarrow NO_2^- + 3H_2O + 3Br. \quad (21)$$
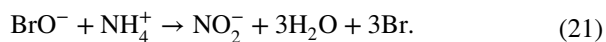
2. In an acidic environment, hydroxylamine hydrochloride reduces the NO_2^- to N_2O (Bothner-By and Friedman 1952; Liu et al. 2014):

$$NH_2OH + HNO_2 \rightarrow N_2O + 2H_2O. \quad (22)$$
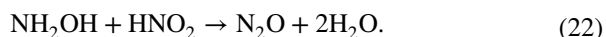
It is worth noting that when using chemical reagents (sodium azide in an acetic acid buffer or hydroxylamine hydrochloride) to reduce NO_2^- to N_2O, it is necessary to add sodium arsenite solution to remove excess BrO^- reagent before adding the next chemical reagent. Otherwise, the remaining BrO^- will react with the next reducing agent, causing an interference (Liu et al. 2017).

3.3 Determination Nitrogen Isotopes in Ammonia

Passive samplers are commonly used for collecting dry N deposits because the samplers are inexpensive, easy to use, and do not require power. The passive samplers commonly used for NH_3 sampling include those made by Ogawa and ALPHA (adapted low-cost passive high absorption)—these have been used many times to collect and measure NH_3 (Felix et al. 2013). For passive NH_3 sampling, polyamide fiber filters are typically impregnated with citric acid and then used to collect the samples. Compared with other acids, such as phosphoric acid or oxalic acid, the NH_4^+ concentration gap of citric acid is lower, and that makes it more suitable for high time-resolution measurements (Felix et al. 2012, 2013; Walters and Hastings 2018).

After a suitable sampling period, the NH_3 on the filter from the passive sampler is extracted with ultrapure water. Aliquots of the extract can then be used to determine the nitrogen isotope composition of NH_3 ($\delta^{15}N-NH_3$) by the same methods as described above for NH_4^+. In addition, as there are no interferences from NO_3^- or NO_2^- in the passively collected NH_3 sample, the NH_3 nitrogen isotope composition can be determined by the denitrifying bacteria method (Felix et al. 2013).

4 Research Progress for the Determination of Stable Isotopes in Ammonia and Ammonium

The currently used NH_3 collection methods have not yet been fully verified relative to the characterization of $\delta^{15}N-NH_3$, but Walters and Hastings (2018) have discussed the suitability of an established collection device for that purpose. The device uses a honeycomb denuder (HCD) that is acid-coated (2% citric acid (w/v) + 1% glycerol (w/v) in a 80:20 methanol to water solution) and housed in Chem-Comb Speciation Cartridge (CCSC) (Koutrakis et al. 1993, 1988; Walters and Hastings 2018). The polytetrafluoroethylene (PTFE) coating inlet on the device can have a NH_3 transmission efficiency $> 97.3\%$, and a circular reservoir on the $PM_{2.5}$ impactor is covered with PTFE to prevent particle bounce and to limit the absorption of NH_3. In practice, two HCDs are used in series, and they are separated by a PTFE spacer: the first HCD is used to capture NH_3 from the sample airstream, and the second is used as a control to check for possible NH_3 breakthrough. The subsequent chemical treatment for N isotope determinations is carried out using the chemical conversion method with sodium azide in an acetic acid buffer (Zhang et al. 2007).

Walters et al. evaluated the reagent blanks, matrix effects, collection efficiency, selectivity, operative capacity, the stability of reaction products, field utility, and isotope bias for

this device (Perrino et al. 1990), and they concluded that the method is suitable for the determination of $\delta^{15}N$-NH_3. The acid-coated HCD collection device for $\delta^{15}N$-NH_3 analysis and the subsequent chemical treatment lead to extremely high accuracy, with a precision of $\pm 1.6‰$ (2σ; $n = 75$). The device has an operational capacity (collection efficiency > 95%) of 400 μg of collected NH_3 at a concentration of ≤ 207 ppbv. In addition, this method is also applicable to studies of the natural atmosphere, and the resolution of $\delta^{15}N$-NH_3 is ~ 1 h (Walters and Hastings 2018). This sampler represents the first laboratory-proven $\delta^{15}N$-NH_3 device that has high time resolution and excellent $\delta^{15}N$-NH_3 accuracy, and it may well become the sampler of choice for the air quality studies needed to improve our understanding of NH_3 sources and sedimentation processes.

If a filter suitable for collecting $PM_{2.5}$ is used, the HCD device could simultaneously measure $\delta^{15}N$-NH_3 and $\delta^{15}N$-NH_4^+, making it useful for studying NH_x. In addition, the combined denuder-filter collection technique may be extended to isotope analysis of other gaseous compounds such as sulfur dioxide (SO_2), nitric acid (HNO_3), and nitrogen dioxide (NO_2) because, with a suitable HCD coating, the device may be used to collect different gases. For example, NH_3 can be collected with the use of an acidic coating on the HCD, and acid gases such as HNO_3 or SO_2 can be collected by a carbonate coating on the HCD.

5 Conclusions

Due to the frequent haze events in China, there has been increasing interest and concern over the behavior of atmospheric NO_3^- and NH_4^+. Analysis of the stable N isotopes of atmospheric NO_3^- and NH_4^+ could provide a powerful tool to identify NO_x or NH_3 sources. Combined with some models, the contribution of different sources can be qualitatively and quantitatively assessed by isotope techniques. With this tool, it is possible to control and reduce the emission of nitrogen-containing pollutants from the emission sources. Therefore, it is necessary to review the techniques used for measurements of N isotopes in atmospheric aerosols. However, there also can be considerable overlap in the $\delta^{15}N$ values for different emission sources. This suggests that there should be further exploration of N isotopes of major emission sources.

Compliance with Ethical Standards

Conflict of interest Editor(s) are expected to inform the Publisher of any interests that may influence, or may be perceived to influence, their decisions as Editor(s) of the Journal. Financial and non-financial interests (including, but not limited to personal relationships, professional interests or personal beliefs) should be disclosed. Please note that the declaration of these interests does not disqualify the Editor(s) from the role as Editor(s) of the Journal. We would expect Editor(s) to respect the confidentiality of the peer review and editorial process. Although Editor(s) may publish in the journal for which they are Editor(s), they are expected to ensure that a (senior) member of the Editorial Board is assigned to assume responsibility for overseeing peer review and making decisions regarding acceptance or rejection of any manuscript submitted and/or co-authored by the Editor(s). Where Editor(s) have a conflict of interest regarding a specific manuscript, a (senior) member of the Editorial Board should be assigned to assume responsibility for overseeing peer review and decisions making on that manuscript. Editor(s) are expected to ensure that Editorial Board members are not involved with the peer review or decision-making process on any manuscript on which they are an author or on any manuscript where they may have a conflict of interest or potential conflict of interest. Editor(s) submitting to the Journal any manuscript on which they are authors are expected to comply with the Journal's editorial policies for authors on disclosures of potential conflicts of interests.

References

Altieri KE, Hastings MG, Gobel AR, Peters AJ, Sigman DM (2013) Isotopic composition of rainwater nitrate at Bermuda: the influence of air mass source and chemistry in the marine boundary layer. J Geophys Res Atmos 118(11):304

Baek BH, Aneja VP (2004) Measurement and analysis of the relationship between ammonia, acid gases, and fine particles in eastern North Carolina. J Air Waste Manag Assoc 54:623–633

Bao JZ, Yu ZY, Ma WS, Wang XF (2015) Monitoring of the main components in NO_x in traffic intersection of Yangzhou city and their health risk. J Yangzhou Polytech Coll 19:49–53

Behera SN, Sharma M, Aneja VP, Balasubramanian R (2013) Ammonia in the atmosphere: a review on emission sources, atmospheric chemistry and deposition on terrestrial bodies. Environ Sci Pollut Res 20:8092–8131

Bothner-By A, Friedman L (1952) The reaction of nitrous acid with hydroxylamine. J Chem Phys 20:459–462

Casciotti KL, Sigman DM, Hastings MG, Böhlke JK, Hilkert A (2002) Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. Anal Chem 74:4905–4912

Chang Y, Liu X, Deng C, Dore AJ, Zhuang G (2016) Source apportionment of atmospheric ammonia before, during, and after the 2014 APEC summit in Beijing using stable nitrogen isotope signatures. Atmos Chem Phys 16:11635–11647

Chen YZ, Xiao HY (2009) Classification of atmospheric aerosol and its hazards to human health. JiangXi Sci 27:912–915

Cheng YF, Zheng GJ, Wei C et al (2016) Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China. Sci Adv 2:e1601530

Dentener FJ, Crutzen PJ (1994) A three-dimensional model of the global ammonia cycle. J Atmos Chem 19:331–369

Dong WX, Xing J, Wang SX (2010) Temporal and spatial distribution of anthropogenic ammonia emissions in China: 1994–2006. Environ Sci 31:1457–1463

Elliott EM, Kendall C, Wankel SD et al (2007) Nitrogen isotopes as indicators of NO_x source contributions to atmospheric nitrate deposition across the midwestern and northeastern United States. Environ Sci Technol 41:7661–7667

Elliott EM, Kendall C, Boyer EW, Burns DA, Lear GG, Golden HE (2009) Dual nitrate isotopes in dry deposition: utility for

partitioning NO$_x$ source contributions to landscape nitrogen deposition. J Geophys Res Biogeosci 114:425–453

Felix JD, Elliott EM, Shaw SL (2012) Nitrogen isotopic composition of coal-fired power plant NO$_x$: influence of emission controls and implications for global emission inventories. Environ Sci Technol 46(6):3528–3535

Felix JD, Elliott EM, Gish TJ, Mcconnell LL, Shaw SL (2013) Characterizing the isotopic composition of atmospheric ammonia emission sources using passive samplers and a combined oxidation-bacterial denitrifier approach. Rapid Commun Mass Spectrom 27:2239–2246

Freyer HD (1978) Seasonal trends of NH_4^+ and NO_3^- nitrogen isotope composition in rain collected at Jülich, Germany. Tellus 30:83–92

Gu YG, Wang BG, Yang J, Zhong SF (2012) Study on sources and emission factors of ammonia from municipal wastewater treatment plants. Environ Chem 31(5):708–713

He H, Wang XM, Wang YS, Wang ZF, Liu JG, Chen YF (2013) Formation mechanism and control strategies of haze in China. Bull Chin Acad Sci 3:54–62

Heaton THE (1987) $^{15}N/^{14}N$ ratios of nitrate and ammonium in rain at Pretoria, South Africa. Atmos Environ 21:843–852

Holmes RM, Mcclelland JW, Sigman DM, Fry B, Peterson BJ (1998) Measuring $\delta^{15}N$–NH_4^+ in marine, estuarine and fresh waters: an adaptation of the ammonia diffusion method for samples with low ammonium concentrations. Mar Chem 60:235–243

Hristov AN, Zaman S, Vander Pol M, Ndegwa P, Campbell L, Silva S (2009) Nitrogen losses from dairy manure estimated through nitrogen mass balance and chemical markers. J Environ Qual 38:2438–2448

Hu QJ (2015) The study of ammonia, ammonium salt and aminium salt in the atmosphere. Doctoral dissertation, Ocean University of China

Hu J, Liu WG (2013) Determination of nitrogen isotopes in low concentration ammonium nitrogen samples by ion exchange chromatography. Rock Miner Anal 32(3):495–501

Huang RJ, Yl Z, Bozzetti C et al (2014) High secondary aerosol contribution to particulate pollution during haze events in China. Nature 514:218–222

Huang H, He BJ, Xiong ZY et al (2018) Distribution and conversion mechanism of ammonium in $PM_{2.5}$ and gaseous precursors in Nanchang. J Earth Environ 9:34–47

Hueglin C, Gehrig R, Baltensperger U, Gysel M, Monn C, Vonmont H (2005) Chemical characterisation of $PM_{2.5}$, PM_{10} and coarse particles at urban, near-city and rural sites in Switzerland. Atmos Environ 39:637–651

Jia L, Ge MF, Xu YF, Du L, Zhuang GS, Wang DX (2006) Advances in atmospheric ozone chemistry. Progr Chem 18:1565–1574

Johnston JC, Thiemens MH (1997) The isotopic composition of tropospheric ozone in three environments. J Geophys Res Atmos 102:25395–25404

Kong LD, Yang YW, Zhang SQ et al (2014) Observations of linear dependence between sulfate and nitrate in atmospheric particles. J Geophys Res Atmos 119:341–361

Kornexl BE, Gehre M, Hofling R, Werner RA (1999) On-line $\delta^{18}O$ measurement of organic and inorganic substances. Rapid Commun Mass Spectrom 13:1685–1693

Koutrakis P, Wolfson JM, Spengler JD (1988) An improved method for measuring aerosol strong acidity: results from a nine-month study in St Louis, Missouri and Kingston, Tennessee. Atmos Environ 22:157–162

Koutrakis P, Sioutas C, Ferguson ST, Wolfson JM, Mulik JD, Burton RM (1993) Development and evaluation of a glass honeycomb denuder/filter pack system to collect atmospheric gases and particles. Environ Sci Technol 27:2497–2501

Liu X (2017) Formation mechanism and efficiency of rainfall removal of ammonium in $PM_{2.5}$. Master dissertation, Nanchang University

Liu DW, Fang YT, Tu Y, Pan YP (2014) Chemical method for nitrogen isotopic analysis of ammonium at natural abundance. Anal Chem 86:3787–3792

Liu DW, Tu Y, Fang YT (2017) Isotope analysis of ammonium and nitrate: A review on measured methods and their application. Chin J Appl Ecol 28:2353–2360

Mcilvin MR, Altabet MA (2005) Chemical conversion of nitrate and nitrite to nitrous oxide for nitrogen and oxygen isotopic analysis in freshwater and seawater. Anal Chem 77:5589–5595

Michalski G, Bhattacharya SK, Mase DF (2012) Oxygen isotope dynamics of atmospheric nitrate and its precursor molecules. In: Handbook of environmental isotope geochemistry, pp 613–635

Perrino C, Santis FD, Febo A (1990) Criteria for the choice of a denuder sampling technique devoted to the measurement of atmospheric nirous and nitric acids. Atmos Environ Part A Gen Top 24:617–626

Qin R, Shi GT, Chen ZL (2019) Advances in research on stable nitrogen and oxygen isotopes in atmospheric nitrate. Adv Earth Sci 34:124–139

Savard MM, Cole A, Smirnoff A, Vet R (2017) $\delta^{15}N$ values of atmospheric N species simultaneously collected using sector-based samplers distant from sources—isotopic inheritance and fractionation. Atmos Environ 162:11–22

Schulz H, Gehre M, Hofmann D, Jung K (2001) Nitrogen isotope ratios in pine bark as an indicator of N emissions from anthropogenic sources. Environ Monit Assess 69:283–297

Seinfeld JH, Pandis SN (2016) Atmospheric chemistry and physics: from air pollution to climate change. Wiley, Hoboken

Seinfeld JH, Pandis SN, Noone K (1998) From air pollution to climate change. Atmos Chem Phys 40:26–26

Shao LY, Wang WH, Xing JP, Li WJ, Niu HY, Hou C, Yang SS (2018) Physicochemical characteristics and effects of airborne particles: research progress and prospects. Earth Sci 43(5):333–350

Sigman DM, Casciotti KL, Andreani M, Barford C, Galanter MB, Bohlke JK (2001) A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. Anal Chem 73:4145–4153

Silva SR, Kendall C, Wilkison DH, Ziegler AC, Chang CC, Avanzino RJ (2000) A new method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen isotope ratios. J Hydrol 228:22–36

Smirnoff A, Savard MM, Vet R, Simard MC (2012) Nitrogen and triple oxygen isotopes in near-road air samples using chemical conversion and thermal decomposition. Rapid Commun Mass Spectrom 26:2791–2804

Sun K (2016) Formation mechanism and aerosol radiative effect of a severe haze episode in the Yangtze River Delta, China. Doctoral dissertation, Nanjing University

Sutton MA, Nemitz E, Theobald MR, Milford C, Dorsey JR, Gallagher MW (2009) Dynamics of ammonia exchange with cut grassland: strategy and implementation of the GRAMINAE Integrated Experiment. Biogeosciences 6:309–331

Tang XY, Zhang YH, Shao M (2006) Atmospheric environmental chemistry. Beijing

Tu Y, Fang YT, Liu D, Pan Y (2016) Modifications to the azide method for nitrate isotope analysis. Rapid Commun Mass Spectrom Rcm 30:1213–1222

Urey HC (1947) The thermodynamic properties of isotopic substances. J Chem Soc. https://doi.org/10.1039/jr9470000562

Velinsky DJ, Pennock JR, Sharp JH, Cifuentes LA, Fogel ML (1989) Determination of the isotopic composition of ammonium-nitrogen at the natural abundance level from estuarine waters. Mar Chem 26:351–361

Walters WW, Hastings MG (2018) Collection of ammonia for high time-resolved nitrogen isotopic characterization utilizing an acid-coated honeycomb denuder. Anal Chem 90:8051–8057

Walters WW, Michalski G (2016) Theoretical calculation of oxygen equilibrium isotope fractionation factors involving various NOy molecules, ·OH, and H$_2$O and its implications for isotope variations in atmospheric nitrate. Geochim Cosmochim Acta 191:89–101

Wang XF, Zhang YP, Chen H, Yang X, Chen JM, Geng FH (2009) Particulate nitrate formation in a highly polluted urban area: a case study by single-particle mass spectrometry in Shanghai. Environ Sci Technol 43:3061–3066

Wang XF, Wang WX, Yang LX, Gao XM, Nie W (2012) The secondary formation of inorganic aerosols in the droplet mode through heterogeneous aqueous reactions under haze conditions. Atmos Environ 63:68–76

Wang J, Zhao LJ, Yu JS (2014) Study on NO$_2$ and SO$_2$ sources and pollutant transmission in Xiamen city. Sci Technol West China 13(3):7–9

Wang X, Cao YC, Han Y, Tang HZ, Wang RH, Sun XL, Sun YF (2015) Determination of nitrogen oxygen isotope ratio of nitrate in water by chemical conversion method. Acta Pedol Sin 52(3):558–566

Wankel SD, Kendall C, Paytan A (2009) Using nitrate dual isotopic composition (δ^{15}N and δ^{18}O) as a tool for exploring sources and cycling of nitrate in an estuarine system: Elkhorn Slough, California. J Geophys Res Biogeosci 114:315–327

Wen L (2015) Formation machanism of particulate nitrate during haze period in Shandong. Masters dissertation, ShanDong University

Wen T, Cao YC, Zhang PY, Zhang JB (2016) A review of studies on ^{15}N stable isotopes of ammonium and nitrate by micro-diffusion method. Soils 48:634–640

Xiang YK, Cao F, Yang XY, Zhai XL, Zhang YL (2019) Hypobromite oxidation combined with hydroxylamine hydrochloride reduction method for analyzing ammonium nitrogen isotope in atmospheric samples. Chin J Appl Ecol 30:1847–1853

Xiao HY, Liu CQ (2001a) A fast method to prepare water samples for ^{15}N analysis. Sci China 44:105–107

Xiao HY, Liu CQ (2001b) Research status and development of pretreatment methods for nitrogen isotope analysis of water samples. Rock Miner Anal 20:125–130

Xiao HY, Liu CQ (2002) Discussion on a method for preparation nitrate in water samples for δ^{15}N analysis. Rock Miner Anal 21:105–108

Xu ZW, Zhang XY, Yu GR, Sun XM, Wen XF (2014) Review of dual stable isotope technique for nitrate source identification in surface and groundwater in China. Huanjing Kexue 35:3230–3238

Yang JY, Hsu SC, Dai MH, Hsiao SY, Kao SJ (2014) Isotopic composition of water-soluble nitrate in bulk atmospheric deposition at Dongsha Island: sources and implications of external N supply to the northern South China Sea. Biogeosciences 11:1833–1846

Zbieranowski AL, Aherne J (2013) Ambient concentrations of atmospheric ammonia, nitrogen dioxide and nitric acid in an intensive agricultural region. Atmos Environ 70:289–299

Zeng M, Yu LF, Zhang Y, Zhang ZW (2013) Determination of ammonium and nitrate nitrogen δ^{15}N in natural waters. Environ Chem 8:1486–1490

Zhang HF, Gao S (2012) Geochemistry, Beijing

Zhang L, Altabet MA, Wu T, Hadas O (2007) Sensitive measurement of NH$_4$$^{+15}$N/^{14}N (δ^{15}NH$_4$$^+$) at natural abundance levels in fresh and saltwaters. Anal Chem 79:5297–5303

Zhang CY, Zhang JX, Ma LN, Zhang S, Yin MY, Li ZH (2010) Study on nitrate nitrogen and oxygen isotope denitrification bacteria test. Adv Earth Sci 25(4):360–364

Zhao ZY, Cao F, Zhang WQ, Zhai XY, Fang Y, Fan MY, Zhang YL (2019) Determination of stable nitrogen and oxygen isotope ratios in atmospheric aerosol nitrates. Chin J Anal Chem 47:122–130

Zheng YF (2000) Stable isotope geochemistry. Beijing

Zong Z, Wang XP, Tian CG et al (2017) First assessment of NO$_x$ sources at a regional background site in North China using isotopic analysis linked with modeling. Environ Sci Technol 51:5923–5931