



Source appointment of nitrogen in PM_{2.5} based on bulk $\delta^{15}\text{N}$ signatures and a Bayesian isotope mixing model

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ABSTRACT

Nitrogen isotope ($\delta^{15}\text{N}$) has been employed to differentiate major sources of atmospheric N. However, it remains a challenge to quantify contributions of multiple sources based on $\delta^{15}\text{N}$ values of the N mixture in atmospheric samples. This study measured $\delta^{15}\text{N}$ of bulk N in PM_{2.5} at an urban site of Beijing during a severe haze episode of 22–30 January 2013 and a background site of Qinghai, north-western China from 6 September to 15 October 2013, then applied a Bayesian isotope mixing model (SIAR, Stable Isotope Analysis in R) to analyse the N sources. At Beijing site, $\delta^{15}\text{N}$ values of PM_{2.5} (−4.1‰ to +13.5‰, $+2.8 \pm 6.4\%$) were distributed within the range of major anthropogenic sources (including NH₃ and NO₂ from coal combustion, vehicle exhausts and domestic wastes/sewage). At Menyuan site, $\delta^{15}\text{N}$ values of PM_{2.5} (+8.0‰ to +27.9‰, $+18.5 \pm 5.8\%$) were significantly higher than that of potential sources (including NH₃ and NO₂ from biomass burning, animal wastes, soil N cycle, fertilizer application and dust N). High molar ratios of NH₄⁺ to NO₃[−] and/or SO₄^{2−} in PM_{2.5} at the background site suggested that the equilibrium of NH₃ ↔ NH₄⁺ caused apparent ¹⁵N enrichments in ammonium. Results of the SIAR model showed that 39 and 32% of bulk N in PM_{2.5} of Beijing site were contributed from N emissions of coal combustion and vehicle exhausts, respectively, whereas N in PM_{2.5} at Menyuan site was derived mainly from N emissions of biomass burning (46%) and NH₃ volatilization (34%). These results revealed that the stoichiometry between NH₃ and acidic gases plays an important role in controlling the bulk $\delta^{15}\text{N}$ signatures of PM_{2.5} and emissions of reactive N from coal combustion and urban transportation should be strictly controlled to avert the risk of haze episodes in Beijing.

Keywords: nitrogen isotope, aerosol, air pollution, source apportionment, ammonium

1. Introduction

Urban air pollution is a globally challenging issue. Nitrogen (N) emissions play a key role in the formation of atmospheric particulates, especially secondary N-containing aerosols (Huang et al., 2014). Ammonia is the precursor of ammonium (NH₄⁺) and readily reacts with available acids formed by SO₂ and NO₂, and also it can be transformed to organic N or amines (Ge et al., 2011). Nitrogen oxides are major precursors of both inorganic (as nitrate ions (NO₃[−])) and organic (as organic NO₃[−])

N aerosols (Berkemeier et al., 2016). Therefore, the source apportionment of N in PM_{2.5} is always of significance for better understanding origins of particulates and haze pollution (Guo et al., 2014).

Stable isotopes of N (i.e. $\delta^{15}\text{N}$ values) have been used to trace major sources and processes of atmospheric N (Heaton, 1986; Michalski et al., 2004; Kendall et al., 2007; Pavuluri et al., 2010; Savarino et al., 2013). The analysis of bulk $\delta^{15}\text{N}$ in PM_{2.5} is a quick method compared to $\delta^{15}\text{N}$ measurements of inorganic and organic N components (Widory, 2007; Hegde et al., 2015; Bikkina et al., 2016), and it does also provide valuable information on $\delta^{15}\text{N}$ of dry N deposition (Yeatman et al., 2001a;

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Table 1. $\delta^{15}\text{N}$ values (mean \pm SD) reported for major NO_x and NH_3 emissions in the atmosphere.

Sources	N species	$\delta^{15}\text{N}/\text{‰}$	References
Coal combustion	NO_2	$+19.8 \pm 5.2$	Felix et al. (2012)
Coal combustion	NH_3	-8.9 ± 4.1	Freyer (1991), Felix et al. (2013)
Vehicle exhausts	NO_2	-2.5 ± 1.5	Walters et al. (2015)
Vehicle exhausts	NH_3	-3.4 ± 1.7	Felix et al. (2013)
Biomass burning	NO_2	$+12.5 \pm 3.1$	Hastings et al. (2009), Felix et al. (2012)
Biomass burning	NH_3	$+12.0$	Kawashima and Kurahashi (2011)
Microbial N cycle	NO_2	-30.3 ± 9.4	Li and Wang (2008), Felix et al. (2013), Felix and Elliott (2014)
Animal wastes	NH_3	-19.0 ± 14.1	Freyer (1978), Heaton (1987), Felix et al. (2013, 2014)
Fertilizer application	NH_3	-26.8 ± 15.4	Felix et al. (2013, 2014)

Heaton et al., 2004; Elliott et al., 2007, 2009). At a background site, the $\delta^{15}\text{N}$ of $\text{PM}_{2.5}$ allows us to examine the impacts of emissions from non-point sources' agricultural N emissions on the N chemistry of regional atmosphere, whereas at an urban site, it can imprint the anthropogenic N emissions.

The bulk $\delta^{15}\text{N}$ in atmospheric particulates is mainly determined by the $\delta^{15}\text{N}$ of N precursors (Aggarwal et al., 2013; Hegde et al., 2015). Often, reported $\delta^{15}\text{N}$ values of typical inorganic N sources (Table 1) can be used in studies on sources and fates of atmospheric N (Elliott et al., 2007, 2009; Kendall et al., 2007; Kawashima and Kurahashi, 2011; Michalski et al., 2014). For $\text{PM}_{2.5}$, dust is a primary N source (Zhang, 2010; Huang et al., 2014). At background site, NO_2 and/or NH_3 from microbial N cycle, fertilization application and animal wastes are strongly ^{15}N -depleted (Elliott et al., 2007; Li and Wang, 2008; Felix et al., 2014), while N emissions from biomass burning (Kawashima and Kurahashi, 2011; Divers et al., 2014) are typically ^{15}N -enriched. At urban site, most N sources of $\text{PM}_{2.5}$ are anthropogenic. The NH_3 from animal wastes (including sewages; Heaton, 1986), coal combustion and vehicle exhausts (Felix et al., 2013), as well as NO_2 from vehicle exhausts (Walters et al., 2015) showed negative $\delta^{15}\text{N}$ values, but NO_2 from coal combustion had exclusively positive $\delta^{15}\text{N}$ values (Felix et al., 2012).

Besides, the bulk $\delta^{15}\text{N}$ in atmospheric particulates is influenced by the isotopic fractionations during gas (g) \leftrightarrow particle (p) exchange processes. However, isotope effects between N precursors and the aerosol N remain unclear, especially in field conditions. Isotope effects are assumed to be more significant between NH_3 and NH_4^+ , and much smaller in the case of NO_2 and aerosol N (Yeatman et al., 2001a; Kawashima and Kurahashi, 2011). This assumption was supported by small differences in mean $\delta^{15}\text{N}$ values between roadside NO_2 (5.7‰) and local aerosol N (6.8‰) (Ammann et al., 1999; Pearson et al., 2000). Although the kinetic isotope effect of $\text{NH}_3 \rightarrow \text{NH}_4^+$ reaction is small at the beginning, it becomes significant when $\text{NH}_3 \leftrightarrow \text{NH}_4^+$ equilibrium attains and causes a preferential enrichment of ^{14}N in NH_3 and ^{15}N in NH_4^+ of aerosols (Heaton et al., 1997; Fukuzaki and Hayasaka, 2009; Li et al., 2012). This explained generally higher $\delta^{15}\text{N}$ values of NH_4^+ in aerosols

than that in rain NH_4^+ and gaseous NH_3 (Yeatman et al., 2001a, 2001b; Jia and Chen 2010; Felix et al., 2013). In a hypothetical model by Heaton et al. (1997), the $\delta^{15}\text{N}$ of particulate NH_4^+ stabilized at values of 33‰ (an enrichment coefficient) higher than that of NH_3 when $\text{NH}_3 \leftrightarrow \text{NH}_4^+$ equilibrium was achieved at 25 °C. However, mechanisms for atmospheric $\text{NH}_3 \leftrightarrow \text{NH}_4^+$ equilibrium in the field circumstances are poorly understood, which is particularly important for interpreting the $\delta^{15}\text{N}$ variations of $\text{PM}_{2.5}$ at locations dominated by $\text{NH}_4^+\text{-N}$.

This study measured bulk $\delta^{15}\text{N}$ of $\text{PM}_{2.5}$ at an urban site (Chinese Research Academy of Environmental Sciences (CRAES), Beijing, northern China) and a national atmospheric background monitoring station (Menyuan, Qinghai province, northwestern China). Based on bulk $\delta^{15}\text{N}$ of $\text{PM}_{2.5}$ and major N sources, a Bayesian isotope mixing model (SIAR, Stable Isotope Analysis in R) (Parnell and Jackson, 2008) was used to estimate the proportions of different source contributions to N in $\text{PM}_{2.5}$ and to evaluate anthropogenic N emissions during the haze events in Beijing. As inorganic N in the atmosphere of both sites was dominated by $\text{NH}_4\text{-N}$, we hypothesized that ^{15}N enrichments in $\text{PM}_{2.5}$ relative to dominant sources were mainly derived from the $\text{NH}_3 \leftrightarrow \text{NH}_4^+$ equilibrium (assumed as 33‰) (Heaton et al., 1997; Li et al., 2012).

2. Materials and methods

2.1. Study sites

The sampling site in Beijing is located in the courtyard of CRAES (40°04' N, 116°42' E), at Lishuiqiao South of Beiyuan Road. Due to rapid urbanization and economic development, the vehicle exhausts and energy consumption are large in Beijing, resulting in deterioration of air quality. Atmospheric $\text{PM}_{2.5}$ in Beijing was characterized by high contributions of secondary components from anthropogenic origins (Sun et al., 2006). Secondary inorganic ions (such as SO_4^{2-} , NH_4^+ and NO_3^-) were the dominant contributors in $\text{PM}_{2.5}$ of Beijing (Zhang et al., 2013). During the sampling period (January 2013), Beijing suffered from the worst $\text{PM}_{2.5}$ pollutions

in history (<http://cleanairinitiative.org/portal/node/11599>), registering the highest PM_{2.5} hourly concentration of 886 µg/m³ (<http://www.nasa.gov/multimedia/imagegallery/image-feature2425.html>).

The background site is located on the Daban Mountain (37°36' N, 101°15' E) in Menyuan county, north-eastern of Qinghai province, which is one of the 14 National Background Stations established by the Chinese Ministry of Environmental Protection in 2012. It has a typical Plateau continental climate, with an altitude of 3295 m above sea level, lower than the average of the Tibetan Plateau (about 4000 m). The mean annual temperature and precipitation amount are 0.8 °C and 520 mm, respectively. Agricultural activity is not intensive locally, except in low-altitude areas far away from the Daban Mountain in Menyuan. The sampling period (6 September–15 October 2013) is within the harvesting period after an intensive fertilization and pronounced biomass burning. The mean hourly temperature was 6.5 °C (3–11 °C) during the study period. There is no fossil fuel emission locally, with limited road traffic on the national highway of G227.

2.2. Sample collection and chemical analyses

PM_{2.5} was collected using a pre-baked quartz filter (47 mm in diameter) and aerosol sampler (Leckel, MVS6, Germany) equipped with a size-segregating impactor. The operating air flow rate was 38.3 L/min. To collect sufficient PM_{2.5} sample for bulk δ¹⁵N analyses, sampling was conducted for every 47–71 h at Menyuan ($n = 14$) and for 23 h at Beijing ($n = 14$). Filter blanks were also collected following the same procedure. The PM_{2.5} mass on each filter was gravimetrically measured using microbalance (AWS-1, COMDE DERENDA, Germany, approved by European Standard) after being desiccated for at least 24 h under controlled temperature (20 ± 1 °C) and humidity (50 ± 5%). All filter samples were immediately stored at –20 °C prior to chemical analyses.

Concentrations of bulk N in PM_{2.5} (mainly including NH₄⁺, NO₃⁻ and organic N) were measured using three punches (ca. 0.53 cm² for each) of the filter in a vario MACRO cube (Elementar Analysensysteme GmbH, Germany) with an analytical precision of 0.02%. Based on N contents, bulk δ¹⁵N values of about 50 µg N in each PM_{2.5} sample were determined by a Thermo MAT 253 isotope ratio mass spectrometer (Thermo Scientific, Bremen, Germany) coupled with an elemental analyzer (Flash EA 2000). IAEA-N-1 (Ammonium sulphate; δ¹⁵N = 0.4‰), USGS25 (Ammonium sulphate, δ¹⁵N = –30.4‰) and IAEA-NO-3 (Potassium nitrate; δ¹⁵N = +4.7‰) were used as standards for the calibration of δ¹⁵N values. The average standard deviation for replicate analyses of an individual sample was ±0.1‰. The δ¹⁵N in PM_{2.5} was expressed in parts per thousand (per mille) by multiplying them by 1000:

$$\delta^{15}N = (R_{\text{sample}}/R_{\text{standard}}) - 1,$$

where $R = {}^{15}\text{N}/{}^{14}\text{N}$ for samples and standard (atmospheric N₂).

The concentrations of NO₃⁻, NH₄⁺ and SO₄²⁻ in PM_{2.5} were measured during the sampling period at both sites by an ambient ion monitor (AIM-IC system: Model URG 9000B, URG Corporation, USA). It draws air in through a PM_{2.5} sharp-cut cyclone at a volumetric flow controlled rate of 3 L/min to remove the larger particles from the air stream. The real-time instruments installed at both the stations have a detection limit of 0.05 µg/m³. Gases such as SO₂, NH₃ and HNO₃ are stripped from the air stream by passing through a liquid parallel plate denuder with continuously replenished solvent flowing across the surface. Then, the PM_{2.5} air stream is constrained into a supersaturated steam condensation coil and cyclone assembly and grown hygroscopically for collection. Enlarged particles are dissolved in water solutions for anion chromatographic analysis every hour following 60 min of ambient sampling. Concentrations of NO₂ were measured using a NO–NO₂–NO_x chemiluminescence analyzer (Model 42i, Thermo-Fisher Scientific). The instruments were operated and maintained properly to ensure data integrity. Scheduled quality control procedures included daily zero and span checks, weekly precision checks and data validations.

3. Results

The PM_{2.5} levels at Beijing varied from 43.0 to 433.6 µg/m³ (mean = 264.3 ± 118.0 µg/m³) (Tables 1 and S2). Volumetric concentrations of elements and ions in PM_{2.5} differed distinctly between the two study sites, thus N contents were presented in the unit of N mass in PM_{2.5} mass for comparison. The bulk N and δ¹⁵N values of PM_{2.5} at Beijing averaged 16.7 ± 4.6% (8.2% to 29.3%) and +2.8 ± 6.4‰ (–4.1‰ to +13.5‰), respectively (Tables 1 and S2; Fig. 1). The NH₄⁺-N, NO₃⁻-N and SO₄²⁻-S in PM_{2.5} at Beijing averaged 7.4 ± 3.4%, 5.0 ± 3.0% and 5.5 ± 2.4%, respectively. The mean molar ratio of NH₄⁺ to (NO₃⁻ + 2 * SO₄²⁻) was 0.8 (Table 2). Ambient concentrations of NO₂ (this study), NH₃ (during April of 2013) and SO₂ (during January of 2013) averaged 89.2 ± 21.2 µg/m³, 14.1 µg/m³ and 22.9 µg/m³ (He et al., 2014; Wei et al., 2015), respectively, showing a mean molar ratio of ambient NH₃ to (NO₂ + 2 * SO₂) of 0.3 (Table 2).

The filter-based average concentrations of PM_{2.5} at the background site (Menyuan, Qinghai province) varied from 7.0 to 17.8 µg/m³ (mean = 13.0 ± 3.2 µg/m³) (Tables 1 and S2), and (13.0 ± 4.8 µg/m³; 4.6–22.7 µg/m³) measured using an ambient monitor (AIM-IC system: Model URG 9000B, URG Corporation, USA). The bulk N concentrations and δ¹⁵N values of PM_{2.5} at the background site were 8.6 ± 5.6% and +18.5 ± 5.8‰ (+8.0‰ to +27.9‰), respectively (Tables 1 and S1; Fig. 1). Concentrations of NH₄⁺-N, NO₃⁻-N and SO₄²⁻-S in PM_{2.5} at Menyuan averaged 5.9 ± 1.8%, 1.9 ± 0.4% and 0.2 ± 0.0%, respectively (Table 2), showing a mean molar ratio of NH₄⁺ to (NO₃⁻ + 2 * SO₄²⁻) as 2.9 ± 1.0 (Table 2). Ambient concen-

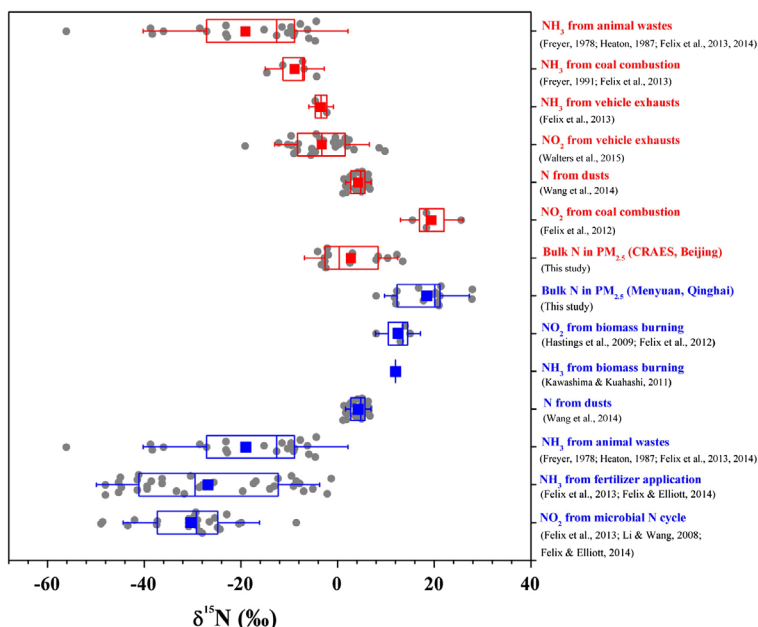


Fig. 1. $\delta^{15}\text{N}$ values of bulk N in $\text{PM}_{2.5}$ and dominant N sources assigned for $\text{PM}_{2.5}$ at the Beijing CRAES site (in red) and the Menyuan site (in blue). The box encompasses the 25th–75th percentiles, whiskers are SD values. The line and square in each box mark the median and arithmetic mean values, respectively. The number of jittered replicate $\delta^{15}\text{N}$ data (dots around the boxes) is 1–34. Mean and SD values of source $\delta^{15}\text{N}$ data were used in the SIAR model. $\delta^{15}\text{N}$ values of N from dust were assumed as those of surface soils (Wang et al., 2014) according to the air mass backward trajectories (Fig. 2).

trations of NO_2 averaged $4.3 \pm 1.3 \mu\text{g}/\text{m}^3$ at the background site (Table 2). Ambient NH_3 and SO_2 concentrations were not available at the Menyuan site ($37^\circ 36' \text{N}$, $101^\circ 15' \text{E}$; 3295 m); however, these concentrations were reported as $4.8 \mu\text{g}/\text{m}^3$ and $0.31 \mu\text{g}/\text{m}^3$, respectively, at Waliguan (a global baseline station, $36^\circ 30' \text{N}$, $100^\circ 10' \text{E}$, 3816 m), another background site in Qinghai (Carmichael et al., 2003). The estimated molar ratio of ambient NH_3 to $(\text{NO}_2 + 2 * \text{SO}_2)$ averaged 2.7 at the background site (Table 2).

4. Discussion

4.1. Major sources of N in $\text{PM}_{2.5}$ of Beijing

According to the source appointment of $\text{PM}_{2.5}$ at Beijing during the severe haze episode of January 2013 (Huang et al., 2014; Zhang et al., 2015), the following six dominant sources can be assigned for bulk N of $\text{PM}_{2.5}$.

- S1: N from dust,
- S2: NO_2 from coal combustion,
- S3: NH_3 from coal combustion,
- S4: NO_2 from vehicle exhausts,
- S5: NH_3 from vehicle exhausts,
- S6: NH_3 from animal wastes (mainly domestic wastes and sewages).

It should be explained that NO is the initial precursor for NO_x emission sources, but NO is quite reactive and readily oxidized to NO_2 which is more often taken as the precursor of NO_3^- in the atmosphere. Thus, NO_2 was used in this work uniformly and its $\delta^{15}\text{N}$ values were assumed as those of corresponding NO_x emissions.

In this study, agricultural and biogenic N emissions were not considered as the major sources of bulk N in $\text{PM}_{2.5}$ of Beijing for two main reasons. First, the urban site is located in the centre of Beijing city cluster in CRAES. During the severe haze events occurring in Beijing, several studies have shown that aerosols have been mainly influenced by anthropogenic sources. Second, as the sampling of Beijing $\text{PM}_{2.5}$ was conducted in the winter time, contributions of NO_2 from microbial N cycle, NH_3 emission from seawater ($\delta^{15}\text{N} = -8\text{‰}$ to -5‰ in Jickells et al., 2003) and lightning NO_x ($\delta^{15}\text{N} = -0.5\text{‰}$ to $+1.4\text{‰}$; Hoering, 1957) were quite small, with relatively lower contribution than anthropogenic N sources to the formation of near-surface $\text{PM}_{2.5}$, especially in urban circumstances.

To date, $\delta^{15}\text{N}$ values of various NO_2 and NH_3 emissions are unavailable in China. However, according to source $\delta^{15}\text{N}$ data compiled from previous studies (Table 1, Fig. 1), $\delta^{15}\text{N}$ values were distinctive between most typical sources, which have been broadly used in isotopic tracing or partitioning of atmospheric N deposition (e.g. Elliott et al., 2007, 2009; Kawashima and Kurahashi, 2011). In this study, we did not use $\delta^{15}\text{N}$ data of

Table 2. Mass concentrations of inorganic N (NH₄⁺-N plus NO₃⁻-N), SO₄²⁻-S, bulk N, molecular ratios of NH₄⁺ to NO₃⁻, NH₄⁺ to SO₄²⁻, NH₄⁺ to (NO₃⁻ + SO₄²⁻) in PM_{2.5} at Beijing (CRAES site) and a background site (Menyuan, Qinghai province) of China. Data of ambient NH₃ and SO₂ at Beijing site were cited from Carmichael et al. (2003), He et al. (2014), Wei et al. (2015). Data of NH₃ and SO₂ were cited from the background site of Waliguan in Qinghai Province (Carmichael et al., 2003).

	Beijing (CRAES site)	Menyuan, Qinghai
PM _{2.5} (μg/m ³)	264.3 ± 118.0 (43.0–433.6)	13.0 ± 3.2 (7.0–17.8)
NH ₄ ⁺ -N (%)	7.4 ± 3.4 (3.5–12.9)	5.9 ± 1.8 (3.1–9.4)
NO ₃ ⁻ -N (%)	5.0 ± 3.0 (0.7–9.4)	1.9 ± 0.4 (1.2–2.6)
SO ₄ ²⁻ -S (%)	5.5 ± 2.4 (2.4–8.3)	0.2 ± 0.0 (0.2–0.3)
Inorganic N (%)	12.4 ± 4.6 (5.1–22.2)	7.8 ± 1.7 (5.7–11.3)
Bulk N (%)	16.7 ± 4.6 (8.2–29.3)	8.6 ± 5.6 (1.4–18.7)
<i>n</i> -NH ₄ ⁺ / <i>n</i> -NO ₃ ⁻	2.5 ± 2.5 (0.5–9.0)	3.3 ± 1.2 (1.2–4.9)
<i>n</i> -NH ₄ ⁺ / <i>n</i> -SO ₄ ²⁻	3.5 ± 1.6 (1.2–6.3)	56.3 ± 14.3 (42.1–89.5)
<i>n</i> -NH ₄ ⁺ / <i>n</i> -NO ₃ ⁻ + <i>n</i> -SO ₄ ²⁻	1.1 ± 0.6 (0.4–2.9)	3.1 ± 1.1 (1.2–4.7)
<i>n</i> -NH ₄ ⁺ / <i>n</i> -NO ₃ ⁻ + 2* <i>n</i> -SO ₄ ²⁻	0.8 ± 0.4 (0.3–1.7)	2.9 ± 1.0 (1.1–4.5)
NH ₃ (μg/m ³)	14.1	4.8
NO ₂ (μg/m ³)	89.2 ± 21.2 (57.0–122.0)	4.3 ± 1.3 (2.6–6.7)
SO ₂ (μg/m ³)	22.9	0.3
<i>n</i> -NH ₃ / <i>n</i> -NO ₂	0.4	3.0
<i>n</i> -NH ₃ / <i>n</i> -SO ₂	2.3	60.2
<i>n</i> -NH ₃ / <i>n</i> -NO ₂ + <i>n</i> -SO ₂	0.4	2.9
<i>n</i> -NH ₃ / <i>n</i> -NO ₂ + 2* <i>n</i> -SO ₂	0.3	2.7

emissions influenced by post-emission processes and measured through controlled tests or simulation, e.g. the δ¹⁵N values of NH₃ near highway (−5.0‰ to +0.4‰ in Smirnov et al., 2012), NO₂ near highway (+2‰ to +10‰ in Moore, 1977; Ammann et al., 1999; Pearson et al., 2000; −13.3‰ to +0.4‰ in Smirnov et al., 2012), NO₂ in tunnels (+15.0 ± 1.6‰ for NO₂; +5.7 ± 2.8‰ for HNO₃; Felix et al., 2014), NO₂ from vehicle engine (−13.0‰ to +3.7‰; Moore, 1977; Freyer, 1978, 1991; Heaton, 1990), NO₂ from controlled experiments of diesel combustion (+3.9‰ to +5.4‰; Widory, 2007) and coal combustion (−5.3‰; Widory, 2007). According to the air mass backward trajectories (Fig. 2), the δ¹⁵N values of surface soils in northern China (+4.3 ± 1.8‰; Wang et al., 2014) were used as the value of N from dust in this study.

As bulk δ¹⁵N values of PM_{2.5} at Beijing were distributed within those of major sources (Fig. 1), no substantial isotopic effect between N sources and bulk N of PM_{2.5} at Beijing was assumed. In particular, as inorganic N of PM_{2.5} was dominated by NH₄⁺ (with a mean molar ratio of NH₄⁺ to NO₃⁻ of 2.5; Table 2), the isotope effect of NH₃ ↔ NH₄⁺ equilibrium is considered

quite low in the PM_{2.5} of Beijing. First, the low molar ratios of ambient NH₃ to (NO₂ + 2 * SO₂) as 0.3 (Table 2) reflected a relatively thorough neutralization of NH₃ by acidic gases, producing relatively more stable ammonium salts of NH₄NO₃, NH₄HSO₄ and (NH₄)₂SO₄. Second, the molar ratios of NH₄⁺ to (NO₃⁻ + 2 * SO₄²⁻) were calculated as 0.8 (Table 2), indicating a full fixation of NH₄⁺ by existing NO₃⁻ and SO₄²⁻ for PM_{2.5} of Beijing. In the calculation, NH₄⁺ is the actual molar concentrations of NH₄⁺ in PM_{2.5} while the (NO₃⁻ + 2 * SO₄²⁻) in PM_{2.5} represents the concentrations of NH₄⁺ that can be fixed by NO₃⁻ and SO₄²⁻. More often, due to the high emissions of anthropogenic SO₂ and NO₂ in urban environments, NH₃, after converting to NH₄⁺, reacts mainly with acids formed by SO₂ and NO₂, with little opportunity of NH₃ losses from PM_{2.5}; thus, no substantial ¹⁵N enrichment in NH₄⁺ of PM_{2.5} (Yeaman et al., 2001a; Pavuluri et al., 2010; Kawashima and Kurahashi, 2011) is observed. Consequently, bulk δ¹⁵N values of PM_{2.5} at Beijing were mainly controlled by the mixing of N sources with inappreciable isotopic effects.

4.2. Major sources of N in PM_{2.5} of Menyuan

According to the molar ratios of ambient NH₃ to NO₂ (ca. 3.0) or NH₄⁺ to NO₃⁻ (ca. 3.3) in PM_{2.5} at Menyuan (Table 2), inorganic N in both ambient atmosphere and PM_{2.5} were dominated by NH₃ and NH₄⁺, respectively. Moreover, δ¹⁵N values of PM_{2.5} did not assemble those of dust N and/or natural N (mainly NO₂ from N cycle) emissions; instead, they were much higher than those of potential sources (Table 1, Fig. 1). More likely, agricultural and biogenic NH₃ sources should be important to bulk N of the background PM_{2.5}. Hence, we assigned major N sources of PM_{2.5} at the background site as follows:

- S7: N from dust,
- S8: NO₂ from biomass burning,
- S9: NH₃ from biomass burning,
- S10: NH₃ from animal wastes,
- S11: NH₃ from fertilizer application,
- S12: NO₂ from microbial N cycle.

The stoichiometry between ambient NH₃ and acidic gases (NO₂ + 2 * SO₂), NH₄⁺ and (NO₃⁻ + 2 * SO₄²⁻) in PM_{2.5} allowed us to further interpret different patterns of bulk δ¹⁵N values of PM_{2.5} against those major sources (Figs. 1 and 2). At Menyuan, the molar ratios of ambient NH₃ to (NO₂ + 2 * SO₂) averaged 2.7 (Table 2), illustrating an incomplete neutralization of ambient NH₃ by NO₂ and SO₂. Molar ratios of NH₄⁺ to (NO₃⁻ + 2 * SO₄²⁻) in PM_{2.5} (ca. 2.9; Table 2) also suggested that part of NH₄⁺ existed as relatively less stable ammonium salts (e.g. NH₄Cl). The diffusion of NH₃ back to the atmosphere during the reversible reaction and strong equilibrium between NH₃ and NH₄⁺ caused significant ¹⁵N enrichment in NH₄⁺ of PM_{2.5}, thus exhibiting much higher δ¹⁵N values of PM_{2.5} than potential sources

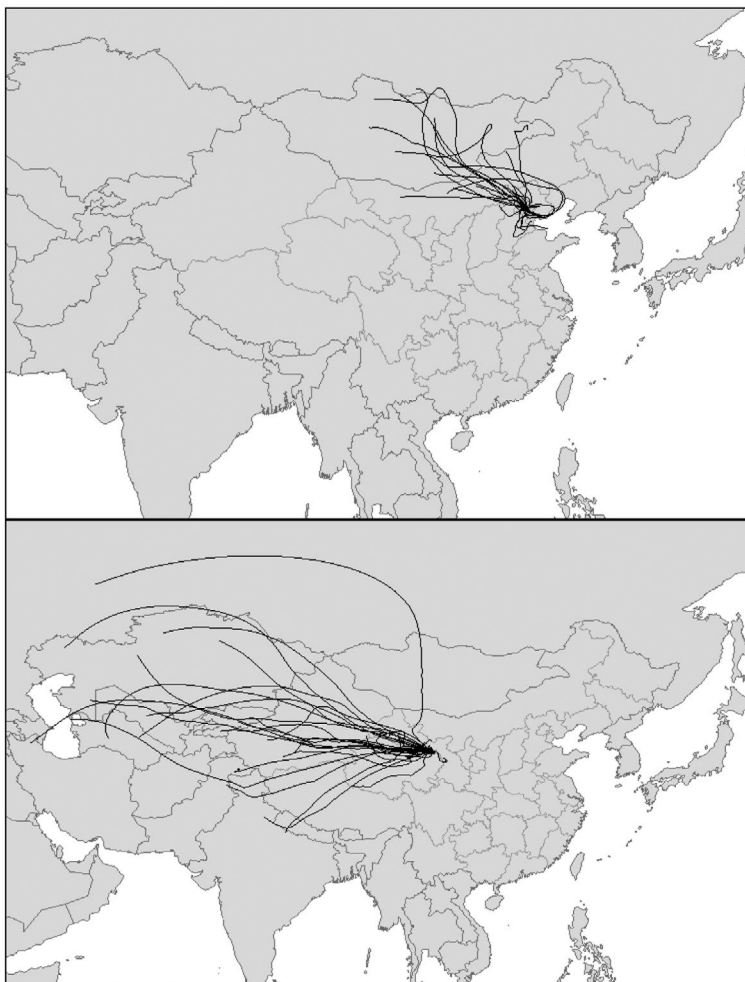


Fig. 2. Seventy-two-h air mass backward trajectories for all sampling dates at the Beijing CRAES site and the Menyuan site, based on NOAA HYSPLIT model back trajectories.

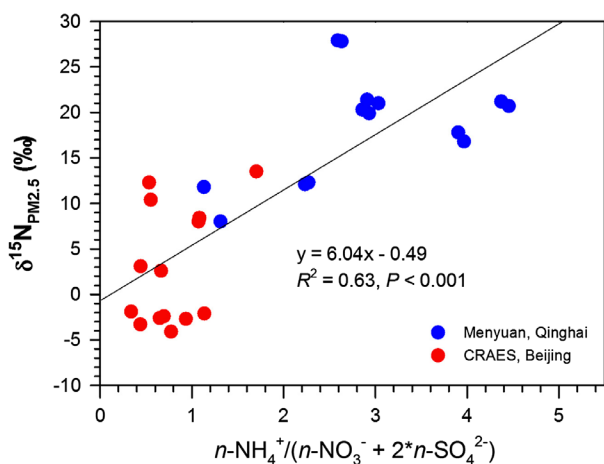


Fig. 3. Correlations between $\delta^{15}\text{N}$ values of $\text{PM}_{2.5}$ and molecular ratios of NH_4^+ to $(\text{NO}_3^- + 2 * \text{SO}_4^{2-})$ (expressed as $n\text{-NH}_4^+ / (n\text{-NO}_3^- + 2 * n\text{-SO}_4^{2-})$) in $\text{PM}_{2.5}$ at Beijing CRAES site and Menyuan site. The regression line was drawn on data of both sites.

(Fig. 1). The regulation of acidic gases-to- NH_3 stoichiometry on the reaction and isotopic effect between NH_3 and NH_4^+ was supported by a positive correlation between $\delta^{15}\text{N}$ values and $\text{NH}_4^+ / (\text{NO}_3^- + 2 * \text{SO}_4^{2-})$ ratios in $\text{PM}_{2.5}$ (Fig. 3). Accordingly, a net isotopic effect of $\text{NH}_3(g) \leftrightarrow \text{NH}_4^+(p)$ at equilibrium (ϵ_{eq}) (33‰; Heaton et al., 1997) was considered in the SIAR model for the background $\text{PM}_{2.5}$ (details down in Section 4.2). However, it should be noted that isotope effects for the atmospheric $\text{NH}_3(g) \leftrightarrow \text{NH}_4^+(p)$ equilibrium in the field circumstances remain unclear. The value of 33‰ is the only empirical one for ^{15}N enrichment in particulate NH_4^+ (Heaton et al., 1997). Experimental studies have been conducted on the isotope fractionations of NH_3 volatilization (e.g. Li et al., 2012), but it is uncertain what factors can be used to make corrections of the isotope effects for background $\text{PM}_{2.5}$. Further studies are strongly needed to verify the relationships between the isotope effects and the ratio of $\text{NH}_3(g)$ to $\text{NH}_4^+(p)$, which may be a feasible factor to make a correction of the isotope effects.

Table 3. Fractional contributions (F , %) of dominant N precursors and sources to bulk N in PM_{2.5} at Beijing (CRAES site) and a background site (Menyuan, Qinghai province) of China. Values (mean \pm SD; $n = 10^4$) were calculated based on the output of the SIAR model.

	Beijing (CRAES site)	Menyuan, Qinghai
F_{NH_3}	40 \pm 10	64 \pm 11
F_{NO_2}	41 \pm 11	22 \pm 10
$F_{\text{NH}_3}/F_{\text{NO}_2}$	1.1 \pm 6.3	4.4 \pm 5.6
F_{fossil}	71 \pm 12	
$F_{\text{non-fossil}}$	29 \pm 12	
$F_{\text{coal combustion}}$	39 \pm 10	
$F_{\text{vehicle exhausts}}$	32 \pm 12	
$F_{\text{NH}_3 \text{ volatilization}}$		34 \pm 12
$F_{\text{biomass burning}}$		46 \pm 10

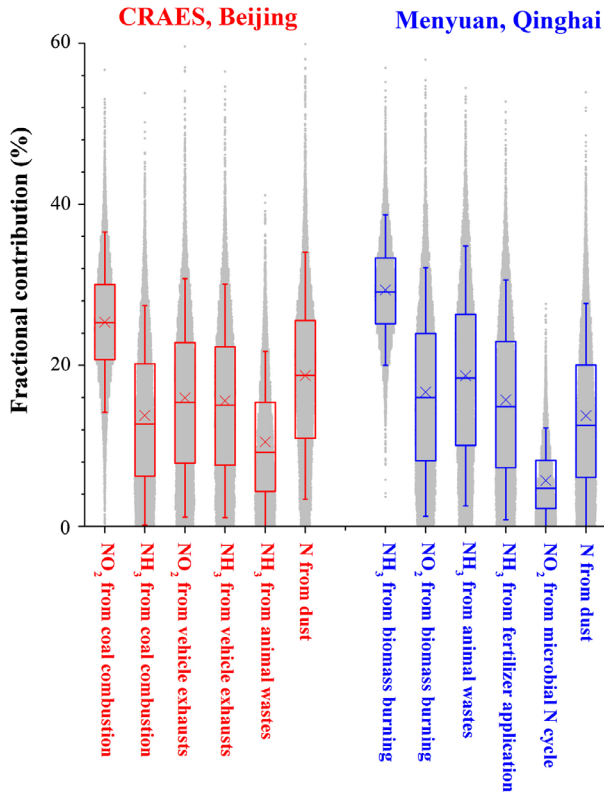


Fig. 4. Fractional contributions of dominant N sources to bulk N in PM_{2.5} at the Beijing CRAES site and the Menyuan site. Dots around the boxes ($n = 10^4$) show the percentages estimated by the SIAR model. The box encompasses the 25th–75th percentiles, whiskers are the 5th and 95th percentiles. The line and cross in each box mark the median and arithmetic mean values, respectively.

4.3. Using the SIAR model to partition bulk N in PM_{2.5}

The proportional contributions (F , %) of major sources to N in PM_{2.5} are estimated using the SIAR model. This model uses a Bayesian framework to establish a logical prior distribution based on Dirichlet distribution (Evans et al., 2000), and then to determine the probability distribution for the contribution of

each source to the mixture (Parnell and Jackson, 2008). It can substantially incorporate the uncertainties associated with multiple sources, fractionations and isotope signatures (Moore and Semmens, 2008; Davis et al., 2015). In our estimations, uncertainties should be evaluated for the $\delta^{15}\text{N}$ variabilities of bulk N in PM_{2.5} and N sources, isotopic effect of the $\text{NH}_3(\text{g}) \leftrightarrow \text{NH}_4^+(\text{p})$ equilibrium.

By defining a set of N mixture measurements on J isotopes with K source contributors, the mixing model can be expressed as follows (Parnell et al., 2010):

$$\begin{aligned}
 X_{ij} &= \sum_{k=1}^K F_k(S_{jk} + c_{jk}) + \varepsilon_{ij} \\
 S_{ij} &\sim N(\mu_{jk}, \omega_{jk}^2) \\
 c_{ij} &\sim N(\lambda_{jk}, \tau_{jk}^2) \\
 \varepsilon_{ij} &\sim N(0, \sigma_j^2)
 \end{aligned}$$

where all F values sum to 1 (unity), X_{ij} is the isotope value j of the mixture i , in which $i = 1, 2, 3, \dots, N$ and $j = 1, 2, 3, \dots, J$; S_{jk} is the source value k on isotope j ($k = 1, 2, 3, \dots, K$) and is normally distributed with mean μ^{jk} and standard deviation ω^{jk} ; F^k is the proportion of source k estimated by the SIAR model; c^{jk} is the fractionation factor for isotope j on source k and is normally distributed with mean λ^{jk} and standard deviation τ^{jk} ; and ε^{ij} is the residual error representing the additional unquantified variation between individual mixtures and is normally distributed with mean 0 and standard deviation σ^j . A detailed description of this model can be found in Moore and Semmens (2008), Jackson et al. (2009) and Parnell et al. (2010). To estimate the contributions of N sources in the PM_{2.5} samples at two study sites ($n = 14$ for each), one isotope ($j = 1$) ($\delta^{15}\text{N}$ of bulk N) and six potential N sources (as discussed in Sections 4.1 and 4.2: S1–S6 for Beijing and S7–S12 for Menyuan) (Fig. 1) are utilized. $\delta^{15}\text{N}$ values of replicate PM_{2.5} samples at each study site were analysed in the SIAR model as one group.

Our estimation showed that the contribution of NO_2 (F_{NO_2}) reached $41 \pm 11\%$ in bulk N of PM_{2.5} in Beijing, which was much higher than F_{NO_2} at the background site ($22 \pm 10\%$) (Table 3). The mean ratios of F_{NH_3} to F_{NO_2} were about 1.6 and 4.4 for PM_{2.5} at Beijing and at the background site, respectively (Table 3), which generally followed the molar ratios of NH_4^+ to NO_3^- in PM_{2.5} (Table 2). Aqueous phase reaction experiments have shown that atmospheric NO_2 and NH_3 potentially react with organic compounds to form organic N (Ge et al., 2011; Pavuluri et al., 2015), which might contribute to the high secondary organic aerosols during the study haze event in Beijing (Huang et al., 2014).

In Beijing, anthropogenic N in PM_{2.5} averaged 81% of its bulk N and was mainly derived from N emissions of fossil fuel combustions, with the highest contribution (ca. 25%) from NO_2 of coal combustion (Table 3; Fig. 4). The N emissions from coal combustion showed higher contributions (ca. 39%) than traffic emissions (ca. 32%), fossil-derived NO_2 contributed

more N (ca. 39%) than fossil-derived NH_3 (ca. 30%) (Table 3; Fig. 4). Comparable contributions (ca. 14–16%) were observed between NH_3 from coal combustion and NH_3 from traffic emissions, between NH_3 and NO_2 from vehicle exhausts (Fig. 4). Accordingly, fossil-derived NH_3 emissions substantially contributed to urban $\text{PM}_{2.5}$ pollution; regulatory controls of N emissions from coal combustion and urban transportation are important to avert the risk of severe haze episodes in Beijing.

The N in $\text{PM}_{2.5}$ at the background site was mainly contributed by N emissions from biomass burning ($46 \pm 10\%$) and NH_3 volatilization ($34 \pm 12\%$) (Table 3). The contribution of NH_3 from biomass burning ($29 \pm 6\%$) was comparable with the total contributions of NH_3 from animal wastes and fertilizer application (ca. 35%) (Table 3). Biomass burning contributed less N as NO_2 ($17 \pm 10\%$) than as NH_3 ($29 \pm 6\%$) to N of $\text{PM}_{2.5}$ at the background site (Table 3). Higher production of NH_3 than NO_2 from biomass burning has been documented previously (Crutzen and Andreae, 1990). A burning experiment by Lobert et al. (1990) showed higher emission ratios of NH_3 (ca. 3.8%) than that of SO_2 (ca. 0.3%) during biomass burning. The emission factors of NH_3 were ca. 2–5 times higher than that of SO_2 from various types of biomass burning (Andreae and Merlet, 2001).

5. Remarks

This study attempted to quantify major sources of N in $\text{PM}_{2.5}$ based on bulk $\delta^{15}\text{N}$ analysis using a Bayesian isotope mixing model. The isotopic effect of $\text{NH}_3 \leftrightarrow \text{NH}_4^+$ equilibrium was recognized under the condition of lower acid gases relative to ambient NH_3 , which was a main reason for higher bulk $\delta^{15}\text{N}$ of $\text{PM}_{2.5}$ than potential sources at the background site. Based on the estimations of SIAR model, $\text{PM}_{2.5}$ of Beijing derived N mainly from coal combustion and vehicle exhausts, while background $\text{PM}_{2.5}$ derived N mainly from biomass burning and NH_3 volatilization. Regulatory controls of N emissions from coal burning and urban transportation are important and effective steps to reduce the risk of severe haze episodes in Beijing. However, emissions of N from non-fossil emissions (particularly biomass burning) in broad rural areas should be stressed to meet a rigorous reduction of reactive N emissions in China.

Although $\delta^{15}\text{N}$ interpretation using the SIAR model provided proportional contributions of major sources to bulk N in $\text{PM}_{2.5}$, further investigations are needed to validate the assumptions and boundary conditions in this work. Particularly, $\delta^{15}\text{N}$ analyses of gaseous N emissions should be implemented for reducing the uncertainties of source $\delta^{15}\text{N}$ values. So far, isotopic studies on gaseous N emissions from typical anthropogenic and natural emissions are still sparse globally, especially in China. Isotope effects revealed in conversions between NO and NO_2 , NO_x and NO_3^- (Monse et al., 1969; Walters and Michalski, 2015), NH_3 and NH_4^+ (Heaton et al., 1997) and the regulatory mechanisms

behind the kinetic and equilibrium isotope effects should be explored and properly considered in future studies.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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