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# Source appointment of nitrogen in PM<sub>2.5</sub> 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<sub>2.5</sub> 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<sub>2.5</sub> ( $-4.1\text{‰}$  to  $+13.5\text{‰}$ ,  $+2.8 \pm 6.4\text{‰}$ ) were distributed within the range of major anthropogenic sources (including  $\text{NH}_3$  and  $\text{NO}_2$  from coal combustion, vehicle exhausts and domestic wastes/sewage). At Menyuan site,  $\delta^{15}\text{N}$  values of PM<sub>2.5</sub> ( $+8.0\text{‰}$  to  $+27.9\text{‰}$ ,  $+18.5 \pm 5.8\text{‰}$ ) were significantly higher than that of potential sources (including  $\text{NH}_3$  and  $\text{NO}_2$  from biomass burning, animal wastes, soil N cycle, fertilizer application and dust N). High molar ratios of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  and/or  $\text{SO}_4^{2-}$  in PM<sub>2.5</sub> at the background site suggested that the equilibrium of  $\text{NH}_3 \leftrightarrow \text{NH}_4^+$  caused apparent  $^{15}\text{N}$  enrichments in ammonium. Results of the SIAR model showed that 39 and 32% of bulk N in PM<sub>2.5</sub> of Beijing site were contributed from N emissions of coal combustion and vehicle exhausts, respectively, whereas N in PM<sub>2.5</sub> at Menyuan site was derived mainly from N emissions of biomass burning (46%) and  $\text{NH}_3$  volatilization (34%). These results revealed that the stoichiometry between  $\text{NH}_3$  and acidic gases plays an important role in controlling the bulk  $\delta^{15}\text{N}$  signatures of PM<sub>2.5</sub> 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 ( $\text{NH}_4^+$ ) and readily reacts with available acids formed by  $\text{SO}_2$  and  $\text{NO}_2$ , 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 ( $\text{NO}_3^-$ )) and organic (as organic  $\text{NO}_3^-$ )

N aerosols (Berkemeier et al., 2016). Therefore, the source apportionment of N in PM<sub>2.5</sub> 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<sub>2.5</sub> 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  $\text{NO}_x$  and  $\text{NH}_3$  emissions in the atmosphere.

Sources	N species	$\delta^{15}\text{N}/\text{‰}$	References
Coal combustion	$\text{NO}_2$	$+19.8 \pm 5.2$	Felix et al. (2012)
Coal combustion	$\text{NH}_3$	$-8.9 \pm 4.1$	Freyer (1991), Felix et al. (2013)
Vehicle exhausts	$\text{NO}_2$	$-2.5 \pm 1.5$	Walters et al. (2015)
Vehicle exhausts	$\text{NH}_3$	$-3.4 \pm 1.7$	Felix et al. (2013)
Biomass burning	$\text{NO}_2$	$+12.5 \pm 3.1$	Hastings et al. (2009), Felix et al. (2012)
Biomass burning	$\text{NH}_3$	$+12.0$	Kawashima and Kurahashi (2011)
Microbial N cycle	$\text{NO}_2$	$-30.3 \pm 9.4$	Li and Wang (2008), Felix et al. (2013), Felix and Elliott (2014)
Animal wastes	$\text{NH}_3$	$-19.0 \pm 14.1$	Freyer (1978), Heaton (1987), Felix et al. (2013, 2014)
Fertilizer application	$\text{NH}_3$	$-26.8 \pm 15.4$	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,  $\text{NO}_2$  and/or  $\text{NH}_3$  from microbial N cycle, fertilization application and animal wastes are strongly  $^{15}\text{N}$ -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  $^{15}\text{N}$ -enriched. At urban site, most N sources of  $\text{PM}_{2.5}$  are anthropogenic. The  $\text{NH}_3$  from animal wastes (including sewages; Heaton, 1986), coal combustion and vehicle exhausts (Felix et al., 2013), as well as  $\text{NO}_2$  from vehicle exhausts (Walters et al., 2015) showed negative  $\delta^{15}\text{N}$  values, but  $\text{NO}_2$  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  $\text{NH}_3$  and  $\text{NH}_4^+$ , and much smaller in the case of  $\text{NO}_2$  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  $\text{NO}_2$  (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  $^{14}\text{N}$  in  $\text{NH}_3$  and  $^{15}\text{N}$  in  $\text{NH}_4^+$  of aerosols (Heaton et al., 1997; Fukuzaki and Hayasaka, 2009; Li et al., 2012). This explained generally higher  $\delta^{15}\text{N}$  values of  $\text{NH}_4^+$  in aerosols

than that in rain  $\text{NH}_4^+$  and gaseous  $\text{NH}_3$  (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  $\text{NH}_4^+$  stabilized at values of 33‰ (an enrichment coefficient) higher than that of  $\text{NH}_3$  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  $^{15}\text{N}$  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  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) 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<sub>2.5</sub> hourly concentration of 886 µg/m<sup>3</sup> (<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<sub>2.5</sub> 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<sub>2.5</sub> sample for bulk δ<sup>15</sup>N 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<sub>2.5</sub> 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<sub>2.5</sub> (mainly including NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and organic N) were measured using three punches (ca. 0.53 cm<sup>2</sup> 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 δ<sup>15</sup>N values of about 50 µg N in each PM<sub>2.5</sub> 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; δ<sup>15</sup>N = 0.4‰), USGS25 (Ammonium sulphate, δ<sup>15</sup>N = –30.4‰) and IAEA-NO-3 (Potassium nitrate; δ<sup>15</sup>N = +4.7‰) were used as standards for the calibration of δ<sup>15</sup>N values. The average standard deviation for replicate analyses of an individual sample was ±0.1‰. The δ<sup>15</sup>N in PM<sub>2.5</sub> 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 N<sub>2</sub>).

The concentrations of NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> in PM<sub>2.5</sub> 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<sub>2.5</sub> 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/m<sup>3</sup>. Gases such as SO<sub>2</sub>, NH<sub>3</sub> and HNO<sub>3</sub> 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<sub>2.5</sub> 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 NO<sub>2</sub> were measured using a NO–NO<sub>2</sub>–NO<sub>x</sub> 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<sub>2.5</sub> levels at Beijing varied from 43.0 to 433.6 µg/m<sup>3</sup> (mean = 264.3 ± 118.0 µg/m<sup>3</sup>) (Tables 1 and S2). Volumetric concentrations of elements and ions in PM<sub>2.5</sub> differed distinctly between the two study sites, thus N contents were presented in the unit of N mass in PM<sub>2.5</sub> mass for comparison. The bulk N and δ<sup>15</sup>N values of PM<sub>2.5</sub> 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 NH<sub>4</sub><sup>+</sup>-N, NO<sub>3</sub><sup>-</sup>-N and SO<sub>4</sub><sup>2-</sup>-S in PM<sub>2.5</sub> at Beijing averaged 7.4 ± 3.4%, 5.0 ± 3.0% and 5.5 ± 2.4%, respectively. The mean molar ratio of NH<sub>4</sub><sup>+</sup> to (NO<sub>3</sub><sup>-</sup> + 2 \* SO<sub>4</sub><sup>2-</sup>) was 0.8 (Table 2). Ambient concentrations of NO<sub>2</sub> (this study), NH<sub>3</sub> (during April of 2013) and SO<sub>2</sub> (during January of 2013) averaged 89.2 ± 21.2 µg/m<sup>3</sup>, 14.1 µg/m<sup>3</sup> and 22.9 µg/m<sup>3</sup> (He et al., 2014; Wei et al., 2015), respectively, showing a mean molar ratio of ambient NH<sub>3</sub> to (NO<sub>2</sub> + 2 \* SO<sub>2</sub>) of 0.3 (Table 2).

The filter-based average concentrations of PM<sub>2.5</sub> at the background site (Menyuan, Qinghai province) varied from 7.0 to 17.8 µg/m<sup>3</sup> (mean = 13.0 ± 3.2 µg/m<sup>3</sup>) (Tables 1 and S2), and (13.0 ± 4.8 µg/m<sup>3</sup>; 4.6–22.7 µg/m<sup>3</sup>) measured using an ambient monitor (AIM-IC system: Model URG 9000B, URG Corporation, USA). The bulk N concentrations and δ<sup>15</sup>N values of PM<sub>2.5</sub> 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 NH<sub>4</sub><sup>+</sup>-N, NO<sub>3</sub><sup>-</sup>-N and SO<sub>4</sub><sup>2-</sup>-S in PM<sub>2.5</sub> 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 NH<sub>4</sub><sup>+</sup> to (NO<sub>3</sub><sup>-</sup> + 2 \* SO<sub>4</sub><sup>2-</sup>) as 2.9 ± 1.0 (Table 2). Ambient concen-

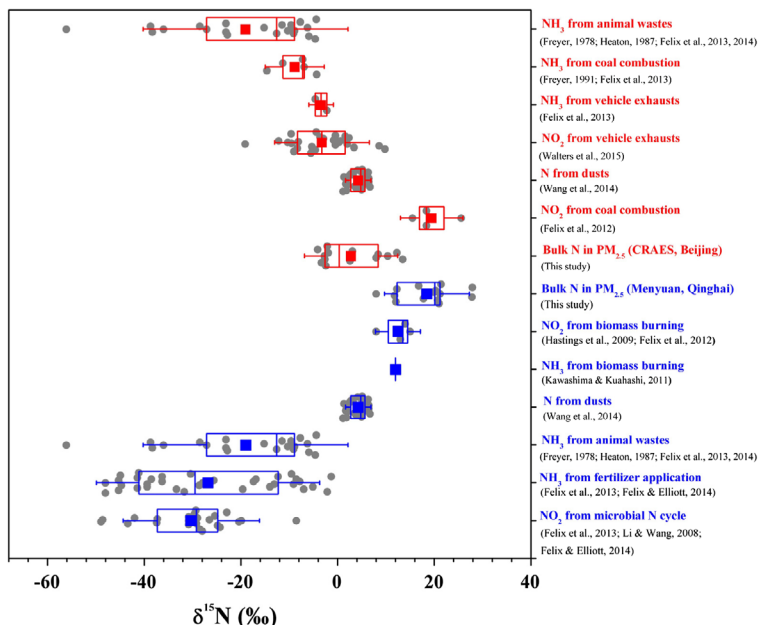


Fig. 1.  $\delta^{15}\text{N}$  values of bulk N in  $\text{PM}_{2.5}$  and dominant N sources assigned for  $\text{PM}_{2.5}$  at the Beijing CRAES site (in red) and the Menyuan site (in blue). The box encompasses the 25th–75th percentiles, whiskers are SD values. The line and square in each box mark 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  $\text{NO}_2$  averaged  $4.3 \pm 1.3 \mu\text{g}/\text{m}^3$  at the background site (Table 2). Ambient  $\text{NH}_3$  and  $\text{SO}_2$  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  $\text{NH}_3$  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:  $\text{NO}_2$  from coal combustion,
- S3:  $\text{NH}_3$  from coal combustion,
- S4:  $\text{NO}_2$  from vehicle exhausts,
- S5:  $\text{NH}_3$  from vehicle exhausts,
- S6:  $\text{NH}_3$  from animal wastes (mainly domestic wastes and sewages).

It should be explained that NO is the initial precursor for  $\text{NO}_x$  emission sources, but NO is quite reactive and readily oxidized to  $\text{NO}_2$  which is more often taken as the precursor of  $\text{NO}_3^-$  in the atmosphere. Thus,  $\text{NO}_2$  was used in this work uniformly and its  $\delta^{15}\text{N}$  values were assumed as those of corresponding  $\text{NO}_x$  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  $\text{NO}_2$  from microbial N cycle,  $\text{NH}_3$  emission from seawater ( $\delta^{15}\text{N} = -8\text{‰}$  to  $-5\text{‰}$  in Jickells et al., 2003) and lightning  $\text{NO}_x$  ( $\delta^{15}\text{N} = -0.5\text{‰}$  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  $\text{NO}_2$  and  $\text{NH}_3$  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 (NH<sub>4</sub><sup>+</sup>-N plus NO<sub>3</sub><sup>-</sup>-N), SO<sub>4</sub><sup>2-</sup>-S, bulk N, molecular ratios of NH<sub>4</sub><sup>+</sup> to NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> to SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup> to (NO<sub>3</sub><sup>-</sup> + SO<sub>4</sub><sup>2-</sup>) in PM<sub>2.5</sub> at Beijing (CRAES site) and a background site (Menyuan, Qinghai province) of China. Data of ambient NH<sub>3</sub> and SO<sub>2</sub> at Beijing site were cited from Carmichael et al. (2003), He et al. (2014), Wei et al. (2015). Data of NH<sub>3</sub> and SO<sub>2</sub> were cited from the background site of Waliguan in Qinghai Province (Carmichael et al., 2003).

	Beijing (CRAES site)	Menyuan, Qinghai
PM <sub>2.5</sub> (μg/m <sup>3</sup> )	264.3 ± 118.0 (43.0–433.6)	13.0 ± 3.2 (7.0–17.8)
NH <sub>4</sub> <sup>+</sup> -N (%)	7.4 ± 3.4 (3.5–12.9)	5.9 ± 1.8 (3.1–9.4)
NO <sub>3</sub> <sup>-</sup> -N (%)	5.0 ± 3.0 (0.7–9.4)	1.9 ± 0.4 (1.2–2.6)
SO <sub>4</sub> <sup>2-</sup> -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 <sub>4</sub> <sup>+</sup> / <i>n</i> -NO <sub>3</sub> <sup>-</sup>	2.5 ± 2.5 (0.5–9.0)	3.3 ± 1.2 (1.2–4.9)
<i>n</i> -NH <sub>4</sub> <sup>+</sup> / <i>n</i> -SO <sub>4</sub> <sup>2-</sup>	3.5 ± 1.6 (1.2–6.3)	56.3 ± 14.3 (42.1–89.5)
<i>n</i> -NH <sub>4</sub> <sup>+</sup> / <i>n</i> -NO <sub>3</sub> <sup>-</sup> + <i>n</i> -SO <sub>4</sub> <sup>2-</sup>	1.1 ± 0.6 (0.4–2.9)	3.1 ± 1.1 (1.2–4.7)
<i>n</i> -NH <sub>4</sub> <sup>+</sup> / <i>n</i> -NO <sub>3</sub> <sup>-</sup> + 2* <i>n</i> -SO <sub>4</sub> <sup>2-</sup>	0.8 ± 0.4 (0.3–1.7)	2.9 ± 1.0 (1.1–4.5)
NH <sub>3</sub> (μg/m <sup>3</sup> )	14.1	4.8
NO <sub>2</sub> (μg/m <sup>3</sup> )	89.2 ± 21.2 (57.0–122.0)	4.3 ± 1.3 (2.6–6.7)
SO <sub>2</sub> (μg/m <sup>3</sup> )	22.9	0.3
<i>n</i> -NH <sub>3</sub> / <i>n</i> -NO <sub>2</sub>	0.4	3.0
<i>n</i> -NH <sub>3</sub> / <i>n</i> -SO <sub>2</sub>	2.3	60.2
<i>n</i> -NH <sub>3</sub> / <i>n</i> -NO <sub>2</sub> + <i>n</i> -SO <sub>2</sub>	0.4	2.9
<i>n</i> -NH <sub>3</sub> / <i>n</i> -NO <sub>2</sub> + 2* <i>n</i> -SO <sub>2</sub>	0.3	2.7

emissions influenced by post-emission processes and measured through controlled tests or simulation, e.g. the δ<sup>15</sup>N values of NH<sub>3</sub> near highway (−5.0‰ to +0.4‰ in Smirnov et al., 2012), NO<sub>2</sub> 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), NO<sub>2</sub> in tunnels (+15.0 ± 1.6‰ for NO<sub>2</sub>; +5.7 ± 2.8‰ for HNO<sub>3</sub>; Felix et al., 2014), NO<sub>2</sub> from vehicle engine (−13.0‰ to +3.7‰; Moore, 1977; Freyer, 1978, 1991; Heaton, 1990), NO<sub>2</sub> 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 δ<sup>15</sup>N 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 δ<sup>15</sup>N values of PM<sub>2.5</sub> at Beijing were distributed within those of major sources (Fig. 1), no substantial isotopic effect between N sources and bulk N of PM<sub>2.5</sub> at Beijing was assumed. In particular, as inorganic N of PM<sub>2.5</sub> was dominated by NH<sub>4</sub><sup>+</sup> (with a mean molar ratio of NH<sub>4</sub><sup>+</sup> to NO<sub>3</sub><sup>-</sup> of 2.5; Table 2), the isotope effect of NH<sub>3</sub> ↔ NH<sub>4</sub><sup>+</sup> equilibrium is considered

quite low in the PM<sub>2.5</sub> of Beijing. First, the low molar ratios of ambient NH<sub>3</sub> to (NO<sub>2</sub> + 2 \* SO<sub>2</sub>) as 0.3 (Table 2) reflected a relatively thorough neutralization of NH<sub>3</sub> by acidic gases, producing relatively more stable ammonium salts of NH<sub>4</sub>NO<sub>3</sub>, NH<sub>4</sub>HSO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Second, the molar ratios of NH<sub>4</sub><sup>+</sup> to (NO<sub>3</sub><sup>-</sup> + 2 \* SO<sub>4</sub><sup>2-</sup>) were calculated as 0.8 (Table 2), indicating a full fixation of NH<sub>4</sub><sup>+</sup> by existing NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> for PM<sub>2.5</sub> of Beijing. In the calculation, NH<sub>4</sub><sup>+</sup> is the actual molar concentrations of NH<sub>4</sub><sup>+</sup> in PM<sub>2.5</sub> while the (NO<sub>3</sub><sup>-</sup> + 2 \* SO<sub>4</sub><sup>2-</sup>) in PM<sub>2.5</sub> represents the concentrations of NH<sub>4</sub><sup>+</sup> that can be fixed by NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. More often, due to the high emissions of anthropogenic SO<sub>2</sub> and NO<sub>2</sub> in urban environments, NH<sub>3</sub>, after converting to NH<sub>4</sub><sup>+</sup>, reacts mainly with acids formed by SO<sub>2</sub> and NO<sub>2</sub>, with little opportunity of NH<sub>3</sub> losses from PM<sub>2.5</sub>; thus, no substantial <sup>15</sup>N enrichment in NH<sub>4</sub><sup>+</sup> of PM<sub>2.5</sub> (Yeaman et al., 2001a; Pavuluri et al., 2010; Kawashima and Kurahashi, 2011) is observed. Consequently, bulk δ<sup>15</sup>N values of PM<sub>2.5</sub> at Beijing were mainly controlled by the mixing of N sources with inappreciable isotopic effects.

#### 4.2. Major sources of N in PM<sub>2.5</sub> of Menyuan

According to the molar ratios of ambient NH<sub>3</sub> to NO<sub>2</sub> (ca. 3.0) or NH<sub>4</sub><sup>+</sup> to NO<sub>3</sub><sup>-</sup> (ca. 3.3) in PM<sub>2.5</sub> at Menyuan (Table 2), inorganic N in both ambient atmosphere and PM<sub>2.5</sub> were dominated by NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>, respectively. Moreover, δ<sup>15</sup>N values of PM<sub>2.5</sub> did not assemble those of dust N and/or natural N (mainly NO<sub>2</sub> from N cycle) emissions; instead, they were much higher than those of potential sources (Table 1, Fig. 1). More likely, agricultural and biogenic NH<sub>3</sub> sources should be important to bulk N of the background PM<sub>2.5</sub>. Hence, we assigned major N sources of PM<sub>2.5</sub> at the background site as follows:

- S7: N from dust,
- S8: NO<sub>2</sub> from biomass burning,
- S9: NH<sub>3</sub> from biomass burning,
- S10: NH<sub>3</sub> from animal wastes,
- S11: NH<sub>3</sub> from fertilizer application,
- S12: NO<sub>2</sub> from microbial N cycle.

The stoichiometry between ambient NH<sub>3</sub> and acidic gases (NO<sub>2</sub> + 2 \* SO<sub>2</sub>), NH<sub>4</sub><sup>+</sup> and (NO<sub>3</sub><sup>-</sup> + 2 \* SO<sub>4</sub><sup>2-</sup>) in PM<sub>2.5</sub> allowed us to further interpret different patterns of bulk δ<sup>15</sup>N values of PM<sub>2.5</sub> against those major sources (Figs. 1 and 2). At Menyuan, the molar ratios of ambient NH<sub>3</sub> to (NO<sub>2</sub> + 2 \* SO<sub>2</sub>) averaged 2.7 (Table 2), illustrating an incomplete neutralization of ambient NH<sub>3</sub> by NO<sub>2</sub> and SO<sub>2</sub>. Molar ratios of NH<sub>4</sub><sup>+</sup> to (NO<sub>3</sub><sup>-</sup> + 2 \* SO<sub>4</sub><sup>2-</sup>) in PM<sub>2.5</sub> (ca. 2.9; Table 2) also suggested that part of NH<sub>4</sub><sup>+</sup> existed as relatively less stable ammonium salts (e.g. NH<sub>4</sub>Cl). The diffusion of NH<sub>3</sub> back to the atmosphere during the reversible reaction and strong equilibrium between NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> caused significant <sup>15</sup>N enrichment in NH<sub>4</sub><sup>+</sup> of PM<sub>2.5</sub>, thus exhibiting much higher δ<sup>15</sup>N values of PM<sub>2.5</sub> than potential sources

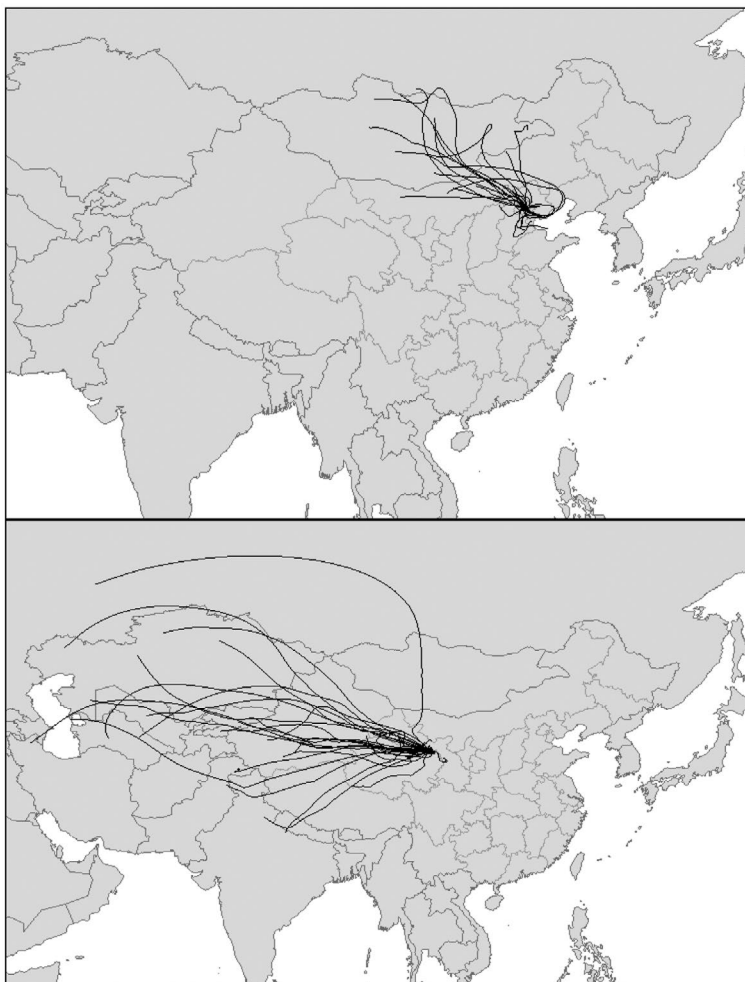


Fig. 2. Seventy-two-h air mass backward trajectories for all sampling dates at the Beijing CRAES site and the Menyuan site, based on NOAA HYSPLIT model back trajectories.

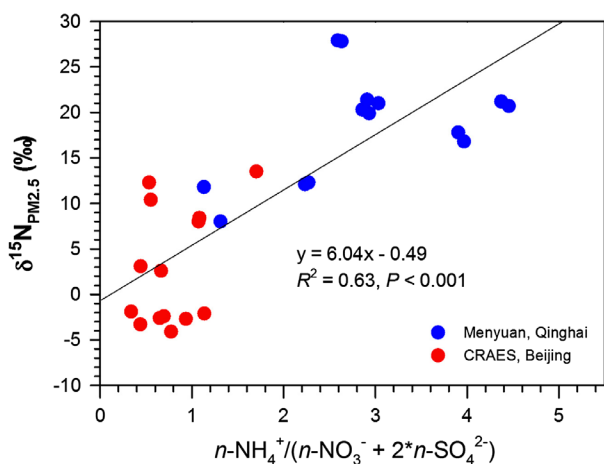


Fig. 3. Correlations between  $\delta^{15}\text{N}$  values of  $\text{PM}_{2.5}$  and molecular ratios of  $\text{NH}_4^+$  to  $(\text{NO}_3^- + 2 * \text{SO}_4^{2-})$  (expressed as  $n\text{-NH}_4^+ / (n\text{-NO}_3^- + 2 * n\text{-SO}_4^{2-})$ ) in  $\text{PM}_{2.5}$  at Beijing CRAES site and Menyuan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

(Fig. 1). The regulation of acidic gases-to- $\text{NH}_3$  stoichiometry on the reaction and isotopic effect between  $\text{NH}_3$  and  $\text{NH}_4^+$  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 ( $\epsilon_{\text{eq}}$ ) (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  $^{15}\text{N}$  enrichment in particulate  $\text{NH}_4^+$  (Heaton et al., 1997). Experimental studies have been conducted on the isotope fractionations of  $\text{NH}_3$  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<sub>2.5</sub> 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
$F_{\text{NH}_3}$	40 $\pm$ 10	64 $\pm$ 11
$F_{\text{NO}_2}$	41 $\pm$ 11	22 $\pm$ 10
$F_{\text{NH}_3}/F_{\text{NO}_2}$	1.1 $\pm$ 6.3	4.4 $\pm$ 5.6
$F_{\text{fossil}}$	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

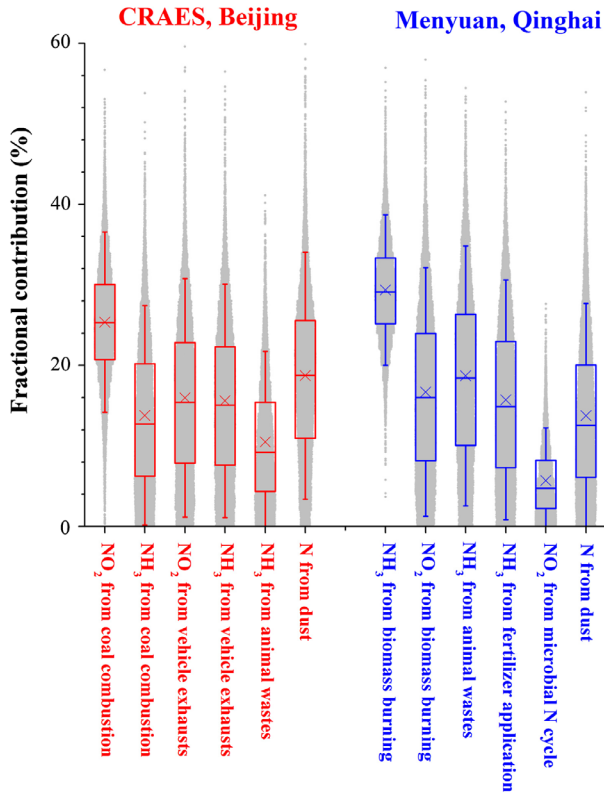


Fig. 4. Fractional contributions of dominant N sources to bulk N in PM<sub>2.5</sub> at the Beijing CRAES site and the Menyuan site. Dots around the boxes ( $n = 10^4$ ) show the percentages estimated by the SIAR model. The box encompasses the 25th–75th percentiles, whiskers are the 5th and 95th percentiles. 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<sub>2.5</sub>

The proportional contributions ( $F$ , %) of major sources to N in PM<sub>2.5</sub> 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 δ<sup>15</sup>N variabilities of bulk N in PM<sub>2.5</sub> and N sources, isotopic effect of the NH<sub>3</sub> (g)  $\leftrightarrow$  NH<sub>4</sub><sup>+</sup> (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  $\mu^{jk}$  and standard deviation  $\omega^{jk}$ ;  $F^k$  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  $\lambda^{jk}$  and standard deviation  $\tau^{jk}$ ; and  $\varepsilon^{ij}$  is the residual error representing the additional unquantified variation between individual mixtures and is normally distributed with mean 0 and standard deviation  $\sigma^j$ . 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<sub>2.5</sub> samples at two study sites ( $n = 14$  for each), one isotope ( $j = 1$ ) (δ<sup>15</sup>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. δ<sup>15</sup>N values of replicate PM<sub>2.5</sub> samples at each study site were analysed in the SIAR model as one group.

Our estimation showed that the contribution of NO<sub>2</sub> ( $F_{\text{NO}_2}$ ) reached 41  $\pm$  11% in bulk N of PM<sub>2.5</sub> in Beijing, which was much higher than  $F_{\text{NO}_2}$  at the background site (22  $\pm$  10%) (Table 3). The mean ratios of  $F_{\text{NH}_3}$  to  $F_{\text{NO}_2}$  were about 1.6 and 4.4 for PM<sub>2.5</sub> at Beijing and at the background site, respectively (Table 3), which generally followed the molar ratios of NH<sub>4</sub><sup>+</sup> to NO<sub>3</sub><sup>-</sup> in PM<sub>2.5</sub> (Table 2). Aqueous phase reaction experiments have shown that atmospheric NO<sub>2</sub> and NH<sub>3</sub> 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<sub>2.5</sub> 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<sub>2</sub> 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<sub>2</sub> contributed



more N (ca. 39%) than fossil-derived  $\text{NH}_3$  (ca. 30%) (Table 3; Fig. 4). Comparable contributions (ca. 14–16%) were observed between  $\text{NH}_3$  from coal combustion and  $\text{NH}_3$  from traffic emissions, between  $\text{NH}_3$  and  $\text{NO}_2$  from vehicle exhausts (Fig. 4). Accordingly, fossil-derived  $\text{NH}_3$  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  $\text{NH}_3$  volatilization ( $34 \pm 12\%$ ) (Table 3). The contribution of  $\text{NH}_3$  from biomass burning ( $29 \pm 6\%$ ) was comparable with the total contributions of  $\text{NH}_3$  from animal wastes and fertilizer application (ca. 35%) (Table 3). Biomass burning contributed less N as  $\text{NO}_2$  ( $17 \pm 10\%$ ) than as  $\text{NH}_3$  ( $29 \pm 6\%$ ) to N of  $\text{PM}_{2.5}$  at the background site (Table 3). Higher production of  $\text{NH}_3$  than  $\text{NO}_2$  from biomass burning has been documented previously (Crutzen and Andreae, 1990). A burning experiment by Lobert et al. (1990) showed higher emission ratios of  $\text{NH}_3$  (ca. 3.8%) than that of  $\text{SO}_2$  (ca. 0.3%) during biomass burning. The emission factors of  $\text{NH}_3$  were ca. 2–5 times higher than that of  $\text{SO}_2$  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  $\text{NH}_3$ , 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  $\text{NH}_3$  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  $\text{NO}$  and  $\text{NO}_2$ ,  $\text{NO}_x$  and  $\text{NO}_3^-$  (Monse et al., 1969; Walters and Michalski, 2015),  $\text{NH}_3$  and  $\text{NH}_4^+$  (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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