Isotopic partitioning of nitrogen in PM$_{2.5}$ at Beijing and a background site of China

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Abstract.

Using isotope mixing model (IsoSource) and natural δ¹⁵N method, this study evaluated contributions of major sources to N of PM$_{2.5}$ at Beijing (collected during a severe haze episode of January 22$^{nd}$ – 30$^{th}$, 2013) and a background site (Menyuan, Qinghai province; collected from September to October of 2013) of China. At Beijing, δ¹⁵N values of PM$_{2.5}$ (-4.1 – +13.5‰; mean = +2.8 ± 6.4‰) distributed within the range reported for major anthropogenic sources (including NH$_3$ and NO$_2$ from coal combustion, vehicle exhausts and domestic wastes/sewage). However, δ¹⁵N values of PM$_{2.5}$ at the background site (+8.0 – +27.9‰; mean = +18.5 ± 5.8‰) were significantly higher than that of potential sources (including NH$_3$ and NO$_2$ from biomass burning, animal wastes, soil N cycle, fertilizer application, and organic N of soil dust). Evidences from molecular ratios of NH$_4^+$ to NO$_3^-$ and/or SO$_4^{2-}$ in PM$_{2.5}$, NH$_3$ to NO$_2$ and/or SO$_2$ in ambient atmosphere suggested that the equilibrium of NH$_3$↔NH$_4^+$ caused apparent $^{15}$N enrichment only in NH$_4^+$ of PM$_{2.5}$ at the background site due to more abundant NH$_3$ than SO$_2$ and NO$_2$. Therefore, a net $^{15}$N enrichment (33‰) was assumed for NH$_3$ sources of background PM$_{2.5}$ when fractional contributions were estimated by IsoSource model. Results showed that 41%, 30% and 14% of N in PM$_{2.5}$ of Beijing originated from coal combustion, vehicle exhausts and domestic wastes/sewage, respectively. Background PM$_{2.5}$ derived N mainly from biomass burning (58%), animal wastes (15%) and fertilizer application (9%). These results revealed the regulation of the stoichiometry between ammonia and acidic gases on δ¹⁵N signals in PM$_{2.5}$. Emissions of NO$_2$ from coal combustion and NH$_3$ from urban transportation should be strictly controlled to advert the risk of haze episodes in Beijing.
1 Introduction

Over the past two decades, increasing fine particulate matter (PM, such as PM$_{2.5}$ with an aerodynamic diameter less than 2.5μm) pollution events as well as haze days have been observed in many urbanized and populated areas of China (Zhang et al., 2013). Recent source-apportionment studies suggested that prior regulations should be planned on industrial and transport-related emissions (such as NH$_3$, NO$_2$, SO$_2$, etc) with major sources from combustions of fossil fuels (Guo et al., 2014; Huang et al., 2014). In parallel, studies showed substantial but uncharacterized contributions from non-fossil emissions, particularly from agricultural and biogenic sources in rural regions (Huang et al., 2014; Zhang et al., 2015). Deciphering origins of key components (such as nitrogen (N) and sulfur (S)) in PM$_{2.5}$ at Beijing and the background site are needed for a better evaluation of anthropogenic precursor emissions and efficient mitigation of PM pollution in China (Cheng et al., 2011; Fu et al., 2015).

Nitrogen, a key component in aerosol formation and pollution, has been concerned in almost all source-apportionment studies of PM$_{2.5}$ (Zhang, 2010; Guo et al., 2014). The N in atmospheric PM, especially secondary particles, is mainly comprised of inorganic ions (i.e., nitrate (NO$_3^-$) and ammonium (NH$_4^+$)), with relatively lower fractions of non-soluble N (e.g., accounting for ~3% of TN in TSP at Jesu island) (Kundu et al., 2010). Nitrogen oxides (mainly NO$_2$) are major precursors during the formation of both secondary inorganic (as NO$_3^-$) and organic (as organic NO$_3^-$) aerosols (Huang et al., 2014). Ammonia (NH$_3$), the precursor of NH$_4^+$, readily reacts with available SO$_2$ and NO$_2$ to produce ammonium salts, which plays a key role in the formation of inorganic aerosols and fine particles (Guo et al., 2014). It should be noted that NH$_3$ can also be transformed to organic N or amines in the...
atmosphere. In other words, NO₂ and NH₃ precursors could not be transformed into corresponding inorganic ions completely (Ge et al., 2011ab). Moreover, contributions of NO₂ and NH₃ to counter ions vary among PM with different aerodynamic diameters. Hence it may not be straightforward to elucidate gaseous N sources using inorganic N analyses in PM₂.₅, or elucidate inorganic N in PM₂.₅ based on ambient NO₂ and NH₃ levels. Compared with the expensive and complex monitoring of gaseous and particulate N compounds, the natural abundance of N isotope (δ¹⁵N; the ¹⁵N/¹⁴N ratio expressed relative to atmospheric N₂) in PM₂.₅ can integrate all-involved N sources, as well as reflect potential δ¹⁵N changes of major N components during the formation of PM₂.₅ (Heaton, 1986; Michalski et al., 2004; Kendall et al., 2007; Elliott et al., 2007, 2009; Savarino et al., 2013). It calls for lower cost and less labor force than tedious isotopic analyses of inorganic and organic N components. Besides, δ¹⁵N of PM₂.₅ has an advantage of characterizing sources of major N pollutants and providing the δ¹⁵N information of dry N deposition for biogeochemistry studies (Yeatman et al., 2001; Heaton et al., 2004; Elliott et al., 2007, 2009). At remote sites, δ¹⁵N of PM₂.₅ can show influences of non-point sources (e.g., agricultural N emissions) on background atmospheric N chemistry. At polluted sites (e.g., during severe haze episodes in urban areas), δ¹⁵N of PM₂.₅ can provide direct evidences on sources and extents of anthropogenic N pollution. The δ¹⁵N variation of PM₂.₅ is controlled by δ¹⁵N values of initial gas precursors and gas (g) ↔ particle (p) isotope effects. It is ideal but difficult to measure δ¹⁵N values of each potential source at any given sites which might need a reasonably long period. Some N sources had actually small regional or global variability in δ¹⁵N values (Walters et al., 2015), but some others showed a wide but similar δ¹⁵N ranges at different locations (Hoering et al., 1957; Heaton, 1986, 1990; Ammann et al., 1999;
Pearson et al., 2000). Hence, the mean values of documented $\delta^{15}\text{N}$ values in precursors and precipitation were often used when constraining sources and fates of N in atmospheric and ecosystem processes (Kendall et al., 2007; Elliott et al., 2007, 2009; Kawashima et al., 2011; Michalski et al., 2014). At present, available studies have virtually covered $\delta^{15}\text{N}$ values of dominant natural and anthropogenic sources of PM$_{2.5}$ (Fig. 1) which were also stressed in emission inventory and source-apportionment studies (Felix et al., 2013; Divers et al., 2014). During the formation of primary and secondary aerosols, N (mainly as organic N) in soil dusts constitutes a primary and common N source (Zhang, 2010; Huang et al., 2014). At remote/background sites, if there was no substantial influence from the burning of agricultural biomass and fertilizer application (assumed as the main agricultural N sources in this study), the major N source for secondary inorganic aerosols is soil NO$_2$ emission, which is distinctly $^{15}\text{N}$-depleted due to the large $^{15}\text{N}$ discriminations during gaseous NO$_2$ losses of soil N cycle (Felix et al., 2014). PM$_{2.5}$ at background sites is expected to have low $\delta^{15}\text{N}$ values when atmospheric reactive N is substantially contributed from N emissions of agricultural fertilization and livestock, both of which are strongly $^{15}\text{N}$-depleted (Elliott et al., 2007; Felix et al., 2014). However, when the inorganic N is dominated by N emissions from biomass burning (the other major agricultural activity, especially in harvest seasons), the $\delta^{15}\text{N}$ values of PM$_{2.5}$ are expected to be positive because biomass burning emits N with $\delta^{15}\text{N}$ values distinctly higher than biogenic and other agricultural N sources (Kawashima et al., 2011; Divers et al., 2014). At urban sites, sources of N in PM$_{2.5}$ are largely anthropogenic. In summary, the $\delta^{15}\text{N}$ values are negative for NH$_3$ from urban wastes/sewage (Heaton et al., 1986), industries and vehicles (Felix et al., 2013), but are exclusively positive for NO$_2$ from coal-fired power plants (Felix et al., 2012). Vehicle exhaust NO$_2$, a major
source of NO\textsubscript{2} in the urban, had a wide $\delta^{15}\text{N}$ range ($-19.1 \pm +9.8\%$; a mass-weighted value: $-2.5 \pm 1.5\%$) (Walters et al., 2015) because of the kinetic isotope fractionations associated with the catalytic NO\textsubscript{2} reduction.

Besides sources, isotope effects the association of emitted N gases with atmospheric PM have long been poorly studied. In general, the net isotopic effects were assumed to be mainly derived from NH\textsubscript{3}, with very small gas-to-particle fractionation for nonvolatile NO\textsubscript{2} because its reaction and conversion is less limited by counter ions (Yeatman et al., 2001; Kawashima et al., 2011). The assumption was supported by small difference in mean $\delta^{15}\text{N}$ values between roadside NO\textsubscript{2} (5.7\%) and particulates (6.8\%) (Ammann et al., 1999; Pearson et al., 2000). For NH\textsubscript{3}, kinetic isotopic effect of NH\textsubscript{3}-to-NH\textsubscript{4}\textsuperscript{+} reaction was small at the whole time scale of PM formation, but NH\textsubscript{3}$\leftrightarrow$NH\textsubscript{4}\textsuperscript{+} equilibrium will cause $^{14}\text{N}$ to be preferentially associated with NH\textsubscript{3} and $^{15}\text{N}$ to be enriched in NH\textsubscript{4}\textsuperscript{+} of PM due to the stronger associative strength of $^{15}\text{N}$ than $^{14}\text{N}$ in NH\textsubscript{4}\textsuperscript{+} (Heaton et al., 1997; Fukuzaki et al., 2009; Li et al., 2012). This has been recognized as a major reason for generally higher $\delta^{15}\text{N}$-NH\textsubscript{4}\textsuperscript{+} in aerosols than that in rain NH\textsubscript{4}\textsuperscript{+} and precursor NH\textsubscript{3} (Yeatman et al., 2001a,b; Jia and Cheng 2010; Felix et al., 2013). In a hypothetical model proposed by Heaton et al (1997), the $\delta^{15}\text{N}$ of particulate NH\textsubscript{4}\textsuperscript{+} stabilized at values of 33\% higher than that of NH\textsubscript{3} at 25°C. However, chemical equilibrium mechanisms and isotopic effects for NH\textsubscript{3}$\leftrightarrow$NH\textsubscript{4}\textsuperscript{+} exchange in PM\textsubscript{2.5} and its environmental controls are still uncertain in the field circumstances. It is valuable to explore $\delta^{15}\text{N}$ characteristics of PM\textsubscript{2.5} and the mechanisms behind the $\delta^{15}\text{N}$ difference between PM\textsubscript{2.5} and precursor gases.

This study measured $\delta^{15}\text{N}$ ratios of PM\textsubscript{2.5} at Beijing (CRAES site) and a national atmospheric background monitoring station (Menyuan, Qinghai province, northwestern China). Based on the $\delta^{15}\text{N}$ values of observed PM\textsubscript{2.5} samples and
potential N sources, a stable isotopic mixing model (IsoSource; Phillips et al., 2003) was used to calculate fractional contributions of major sources to TN in PM$_{2.5}$. The main objective of this paper is to explore an isotopic regime for differentiating specific sources of N in atmospheric PM$_{2.5}$. As inorganic N in the atmosphere was dominated by NH$_4$-N at both sites, we hypothesized that significant $^{15}$N enrichment in PM$_{2.5}$ relative to potential sources was mainly derived from the isotopic effect of NH$_3$$\leftrightarrow$NH$_4^+$ equilibrium (assumed as 33‰) (Heaton et al., 1997; Li et al., 2012). At the monitoring site of Beijing, NH$_3$ could not neutralize abundant SO$_2$ and NO$_2$, with an efficient conversion to ammonium salts, little opportunity to volatilize thus no substantial isotopic effect from NH$_3$$\leftrightarrow$NH$_4^+$ equilibrium (Garten et al., 1992; Yeatman et al., 2001; Kawashima et al., 2011). Therefore, $\delta^{15}$N values of PM$_{2.5}$ in Beijing are expected to fall in the $\delta^{15}$N range of verified N sources (Huang et al., 2014; Zhang et al., 2013; Zhang et al., 2015). At the background site, much lower acid gases (especially SO$_2$) relative to ambient NH$_3$ could not allow an efficient and quick conversion of NH$_3$ to ammonium salts. As a result, substantial $^{15}$N enrichment associated NH$_3$$\leftrightarrow$NH$_4^+$ equilibrium occurred for NH$_4^+$ in PM$_{2.5}$ and $\delta^{15}$N values of PM$_{2.5}$ are expected to be significantly higher than potential sources.

2 Materials and Methods

2.1 Study sites

The Beijing site (40°04' N, 116°42' E) was settled in the courtyard of Chinese Research Academy of Environmental Sciences (CRAES), at Lishuiqiao South of Beiyuan Road (surrounded by residential areas, without direct industrial emission sources nearby). As located on the northern edge of the North China Plain, the four
seasons of Beijing are characterized by variable meteorological conditions: spring by high-speed winds and low rainfall, summer by high temperature and frequent rain usually accounting for 75% of annual rainfall, autumn by sunny days and northwest winds, and winter by cold and dry air. Due to the urbanization and rapid economic development, there’s a huge increase in energy consumption and vehicle quantities, resulted in deterioration of air quality. Air quality monitoring reports of 74 key cities/regions revealed that nearly 70% of urban areas in China could not meet the Ambient Air Quality Standards (GB3095-2012) (http://www.cnemc.cn/publish/106/news/news_34605.html). As the capital of China, a developed megacity in Beijing-Tianjin-Hebei city cluster, Beijing is the foci, not only because of its dense population (more than 20 million inhabitants distributed over 16800km²), but also the ubiquitous air pollution that Beijing has been facing for years. Previous studies showed that atmospheric PM$_{2.5}$ in Beijing were characterized by multiple components and sources, both inorganic to organic constituents, from anthropogenic to natural origins, from primary to secondary components (Duan et al., 2006; Sun et al., 2006; Song et al., 2007). Studies have also proved that secondary inorganic ions (such as SO$_4^{2-}$, NH$_4^{+}$ and NO$_3^{-}$) were the dominant contributors in PM$_{2.5}$ of Beijing (Han et al., 2008; Zhang et al., 2013). During the sampling period of urban site (January 2013), Beijing suffered from the worst PM$_{2.5}$ pollutions in history (http://cleanairinitiative.org/portal/node/11599), registering the highest PM$_{2.5}$ hourly concentration of 886 μg/m$^3$ (http://www.nasa.gov/multimedia/imagegallery/image feature2425.html).

The background site (37°36’N, 101°15’E) of this study was located on the Daban Mountain in Menyuan county, northeastern of Qinghai province, which is one of 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 3295m above sea level, a little bit lower than the average of the Tibetan Plateau (about 4000m). The mean annual temperature is -1 – -2°C and the precipitation is 426 – 860 mm. The mean hourly temperature was 6.5°C (3 – 11°C) during the studying period (September 6th – October 15th, 2013). The sampling period belongs to the harvest time after intensive fertilization and pronounced biomass burning. The sampling site is relatively pristine with most areas covered by typical Tibetan Plateau plants. The distance from this site to Xining, the capital City of Qinghai province, is approximately 160 km. There is no locally fossil emission except a national road G227 with few traffic vehicles. Agricultural activity is not intensive locally, except in low-altitude areas far away from the Daban Mountain in Menyuan. Indeed, Menyuan station is an ideal site for monitoring background aerosol and detecting influences of N emissions from human activities (especially biomass burning) on regional atmospheric N chemistry.

### 2.2 Sample collection and chemical analyses

Sampling was conducted in the autumn of background and in the winter of Beijing, aiming at obtaining typical δ¹⁵N signals, for testing our hypothesis and partitioning method stated in introduction. Each PM₂.₅ sample was collected by a pre-baked quartz filter (diameter = 47 mm, sampling area ≈ 13.2 cm²) using an aerosol sampler (Leckel, MVS6, Germany) equipped with a size-segregating impactor. The operating flow rate was 38.3 L/min. Analyzing N and δ¹⁵N of PM₂.₅ at background sites require filter sampling with the duration ranging from days to weeks. The sampling time of individual samples were 47 – 71 hours for samples at the Menyuan site (n = 14) and 23 hours for CRAES site (n = 14), respectively. Filter blanks were assessed in the
same manner as the sampling procedure. The PM$_{2.5}$ mass on each filter was gravimetrically measured by the automatic weighting system (AWS-1, COMDE-225 DERENDA, Germany, approved by European Standard) with controlled temperature (20°C±1°C) and humidity (50±5%) after equilibrated for at least 24 hours, the equipped electro-balance in AWS-1 was WZA26-CW (Sartorius, Germany) with a sensitivity of 0.001mg. All filter samples collected were stored at -20°C prior to further analysis. Total N (TN) of PM$_{2.5}$ was measured using three punches (with an area of 0.53 cm$^2$ for each punch) of the filter in a vario MACRO cube (Elementar Analysensysteme GmbH, Germany) with an analytical precision of 0.02%. Based on N contents, the δ$^{15}$N value of about 50 μg N in each PM$_{2.5}$ sample was determined by a Thermo MAT 253 isotope ratio mass spectrometer (Thermo Scientific, Bremen, Germany) connected with an elemental analyzer (Flash EA 2000). IAEA-N-1 (Ammonium Sulfate; δ$^{15}$N = 0.4‰), USGS25 (Ammonium Sulfate, δ$^{15}$N = -30.4‰), IAEA-NO-3 (Potassium Nitrate; δ$^{15}$N = +4.7‰) were measured as standards for the calibration of δ$^{15}$N values. The average standard deviations for replicate analyses of an individual sample was ±0.1‰. TN concentrations, δ$^{15}$N values are reported as the average of three replicated measurements per sample. The natural abundance of $^{15}$N ($δ^{15}$N) in PM$_{2.5}$ was expressed in parts per thousand (per mille) by multiplying them by 1000:

$$δ^{15}N = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} \right) - 1,$$

where $R = ^{15}$N/$^{14}$N for samples and standard (atmospheric N$_2$).

The concentrations of NO$_3^-$, NH$_4^+$, SO$_4^{2-}$ 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). The real-time instruments installed at both stations have good performance for above water-soluble ions, with a detection limit as
0.05 μg/m³. 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. Gases (e.g., 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 are 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 minutes 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

At the Beijing site (CRAES), the mean PM<sub>2.5</sub> level reached 264.3 ± 118.0 μg/m³ (43.0 – 433.6 μg/m³) over the studying haze episode in January 2013, which was 20 times higher than that at the background site (Tables 1 and S1). Volumetric concentrations of elements and ions in PM<sub>2.5</sub> differed distinctly between the two studying sites, thus they were presented as mass concentrations of PM<sub>2.5</sub> for comparison. The mass concentrations and δ<sup>15</sup>N values of TN in PM<sub>2.5</sub> at Beijing site averaged 16.7 ± 4.6% (8.2 – 29.3%) and +2.8 ± 6.4% (-4.1 – +13.5‰), 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> mass averaged 7.4 ± 3.4%, 5.0 ± 3.0%, 5.5 ± 2.4%, respectively at Beijing site, showing mean 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>) and NH<sub>4</sub><sup>+</sup> to (NO<sub>3</sub><sup>-</sup> +
1/2*SO4^2-) as 2.5, 3.5, 1.1, 1.4, respectively (Table 1). Ambient concentrations of NO2 averaged 89.2 ± 21.2 μg/m^3 at Beijing (Table 1). Mean concentrations of ambient NH3 (during April of 2013) and SO2 (during January of 2013) were reported as 14.1 and 22.9 μg/m^3, respectively (He et al., 2014; Wei et al., 2015). Using these data, mean molecular ratios of NH3 to NO2, NH3 to SO2, NH3 to (NO2 + SO2), NH3 to (NO2 + 1/2*SO2) were 0.4, 2.3, 0.4, 0.4, respectively (Table 1).

At the background site (Menyuan, Qinghai province), the filter-based concentrations of atmospheric PM2.5 averaged 13.0 ± 3.2 μg/m^3 (7.0 – 17.8 μg/m^3) during the studying period (September 6th – October 15th, 2013) (Tables 1 and S1), which was almost the same as that (13.0 ± 4.8 μg/m^3; 4.6 – 22.7 μg/m^3) based on an ambient monitor (AIM-IC system: Model URG 9000B, URG Corporation, USA). The mass concentrations and δ15N values of TN in PM2.5 at the background site averaged 8.6 ± 5.6% and +18.5 ± 5.8‰ (+8.0 – +27.9‰) (Tables 1 and S1; Fig. 1).

Concentrations of NH4^+-N, NO3^-N and SO4^2- in the mass of PM2.5 at Menyuan averaged 5.9 ± 1.8%, 1.9 ± 0.4%, 0.2 ± 0.0%, respectively (Table 1), showing mean molecular ratios of NH4+/NO3^-, NH4+/SO4^2-, NH4+/((NO3^- + SO4^2-) / 2), NH4+/((NO3^- + 1/2*SO4^2-) as 3.3, 56.3, 3.1, 3.2, respectively (Table 1). Ambient concentrations of NO2 averaged 4.3 ± 1.3 μg/m^3 at the background site (Table 1). Ambient NH3 and SO2 concentrations were not available at the Menyuan site (37°36’ N, 101°15’ E; 3295m), but the other background site in the same province (Waliguan, Qinghai; 36°30’ N, 100°10’ E, 3816m; a global baseline station) showed mean atmospheric NH3 and SO2 concentrations as 4.8 μg/m^3 and 0.31 μg/m^3 (Carmichael et al., 2003), showing mean molecular ratios of NH3 to NO2, NH3 to SO2, NH3 to (NO2 + SO2), NH3 to (NO2 + 1/2*SO2) as 3.0, 60.2, 2.9, 2.9, respectively (Table 1).
4 Discussions

4.1 Major sources and isotopic effect

Natural $^{15}$N isotope method can examine contributions of multiple N sources to a given mixture pool, but a reasonable judgment of dominant sources is critical. At Beijing site, six dominant N sources were assigned for TN in PM$_{2.5}$ samples collected during the severe haze episode of January 2013:

S0: TN in soil dust,
S1: NO$_2$ from coal combustion,
S2: NH$_3$ from coal combustion,
S3: NO$_2$ from vehicle exhausts,
S4: NH$_3$ from vehicle exhausts,
S5: NH$_3$ from domestic wastes/sewage.

These putative origins have also been recognized to be responsible for PM pollution during the severe haze episode of January 2013 (Zhang et al., 2013, 2015; Huang et al., 2014). The mean $\delta^{15}$N of soils (+6.0‰) was assumed as that of soil dust (Wang et al., 2014), because the sampling time and sites of soil fit the air mass backward trajectories of our studying sites (Fig. 2). So far, $\delta^{15}$N values of NO$_2$ and NH$_3$ emissions are unavailable in many countries, but they were distinctive among most typical sources and N species (Table S2, Fig. 1). Representative $\delta^{15}$N values reported for NO$_2$ and NH$_3$ emissions were adopted in our partitioning method (Table S2). But we did not consider precursor $\delta^{15}$N data which was influenced by post-emission processes (e.g., roadside and tunnel because they can mix with other sources), and measured through controlled tests or simulation. For examples, we did not use the $\delta^{15}$N data of NH$_3$ near highway (-5.0 – +0.4‰ in Smirnoff et al., 2012), NO$_2$ near
highway (+2 – +10‰ in Moore et al., 1977, Ammann et al., 1999, Pearson et al., 2000; -13.3 – +0.4‰ in Smirnoff et al., 2012), NO₂ in tunnels (+15.0 ± 1.6‰ for NO₂; +5.7 ± 2.8‰ for HNO₃ in Felix et al., 2014), NO₂ from vehicle engine (-13.0 – +3.7‰ in Moore, 1977; Heaton, 1990; Freyer, 1978a,b, 1991), NO₂ from controlled experiments of diesel combustion (+3.9 – +5.4‰ in Widory, 2007) and coal combustion (-5.3‰ in Widory, 2007). Besides, the agricultural and biogenic N emissions (mainly biomass burning, fertilizer application, animal wastes) were not considered as sources of the urban PM₂.5 samples three reasons. First, these emissions (mainly NH₃ if any) are less dispersible and long-distance transported. Second, the CRAES site is located in the center of Beijing city cluster. Third, there was a severe haze pollution event during our sampling time (January, 2013) (Huang et al., 2014). We assumed a negligible contribution from NH₃ emission from seawater (δ¹⁵N = -8 – -5‰ in Jickells et al., 2003) and lightening NO₂ (δ¹⁵N = -0.5 – +1.4‰ (Hoering et al., 1957) because aerosols in inland urban environments derive almost all N from land-based sources thus have a greater anthropogenic imprint. The lightening NO₂ can be quickly scavenged by precipitation during the rain events, with little diffusion and contribution to N in near-surface particulates.

At the Menyuan background site, potential sources of N in PM₂.5 include:

S0: TN in soil dust,
S6: NO₂ from biomass burning,
S7: NH₃ from biomass burning,
S8: NO₂ from animal wastes,
S9: NH₃ from animal wastes,
S10: NO₂ from soil N cycle,
S11: NH₃ from fertilizer application.
We inferred a significant contribution from agricultural N (especially NH$_3$) emissions to the background PM$_{2.5}$ due to two reasons. First, the N of background PM$_{2.5}$ was dominated by NH$_4^+$-N (Table 1). Second, $\delta^{15}$N values of PM$_{2.5}$ should assemble or lower than that of soil N and NO$_2$ if no influence from agricultural NH$_3$ sources. However, the observed $\delta^{15}$N values of PM$_{2.5}$ at the background site fall in a range much higher than isotopic values of potential sources and most anthropogenic sources (Table S2, Fig. 1). Due to the dominance of NH$_4$-N in PM$_{2.5}$ and NH$_3$ in ambient atmosphere (Table 1), the $^{15}$N enrichment in PM$_{2.5}$ at the background site was mainly attributed to a significant isotope fractionation during the equilibrium between NH$_3$ and NH$_4^+$ (33‰; Heaton et al., 1997).

Here we provide possible reasons and mechanisms to explain why $\delta^{15}$N values of PM$_{2.5}$ assembled those of recognized sources at Beijing site, but were higher than potential sources at the background site of Qinghai (Fig. 1). At the CRAES site of Beijing, molecular ratios of ambient NH$_3$ to (NO$_2$ + SO$_2$) or to (NO$_2$ + 1/2*SO$_2$) (<1; Table 1) reflected a more thorough neutralization of NH$_3$ by acidic gases, producing relatively more stable ammonium salts of NH$_4$NO$_3$, NH$_4$HSO$_4$ and (NH$_4$)$_2$SO$_4$.

Molecular ratios of NH$_4^+$ to (NO$_3^-$ + SO$_4^{2-}$) or to (NO$_3^-$ + 1/2*SO$_4^{2-}$) in PM$_{2.5}$ (close to 1:1; Table 1) also verified that NH$_3$ reacts mainly with SO$_2$ and NO$_2$. Consequently, the equilibrium between NH$_3$ and NH$_4^+$ was weak or did not cause significant isotope fractionation for NH$_4^+$ of PM$_{2.5}$ and $\delta^{15}$N values of PM$_{2.5}$ distributed within those of recognized sources at Beijing site (Fig. 1).

Differently, molecular ratios of atmospheric NH$_3$ to (NO$_2$ + SO$_2$) or to (NO$_2$ + 1/2*SO$_2$) were high as 2.9 at the background site (Menyuan, Qinghai) (Table 1), illustrating an incomplete neutralization of NH$_3$ by NO$_2$ and SO$_2$. Molecular ratios of NH$_4^+$ to (NO$_3^-$ + SO$_4^{2-}$) or to (NO$_3^-$ + 1/2*SO$_4^{2-}$) in PM$_{2.5}$ (close to 3; Table 1) also
suggested that part of ammonium existed as relative unstable salts (e.g., NH₄Cl). Most likely, the reversible reaction and a strong equilibrium between NH₃ and NH₄⁺ occurred, the diffusion of NH₃ back to the atmosphere caused significant ¹⁵N enrichment in NH₄⁺of PM₂.₅. As a result, δ¹⁵N values of PM₂.₅ were higher than potential sources at the background site of Qinghai (Fig. 1). The regulation of acidic gases-to-NH₃ stoichiometry on the reaction and isotopic effect between NH₃ and NH₄⁺ was supported by a positive correlation between δ¹⁵N values and NH₄⁺/(NO₃⁻ + 1/2*SO₄²⁻) ratios in PM₂.₅ (Fig. 3). Therefore, δ¹⁵N values of PM₂.₅ in Beijing site reflected a mixing of major sources with no appreciable isotopic effects, thus support direct isotope estimation by IsoSource. However, a net isotope effect of NH₃ (g) ↔ NH₄⁺ (p) equilibrium (εₑ𝑞 = 33‰ in Heaton et al., 1997) should be added to NH₃ sources before inputting into IsoSource for calculations (details down in Section 4.2).

### 4.2 Fractional contributions of major sources to N in PM₂.₅

The proportional contributions (f, %) of major sources to N in PM₂.₅ are calculated using the IsoSource model (Phillips et al., 2003). For urban PM₂.₅,

\[
\delta^{15}N_{PM2.5(Beijing)} = \delta^{15}N_{SO4} \times f_{SO4} + \delta^{15}N_{NO3} \times f_{NO3} + \delta^{15}N_{NH4} \times f_{NH4} + \delta^{15}N_{CO2} \times f_{CO2} + \delta^{15}N_{PM2.5} \times f_{PM2.5} (Equation 1).
\]

For background PM₂.₅,

\[
\delta^{15}N_{PM2.5(Background)} = \delta^{15}N_{SO4} \times f_{SO4} + \delta^{15}N_{NO3} \times f_{NO3} + (\delta^{15}N_{NH4} + \epsilon_{eq}) \times f_{NH4} + \delta^{15}N_{PM2.5} \times f_{PM2.5} + \delta^{15}N_{other} \times f_{other} (Equation 2),
\]

where \(\epsilon_{eq}\) is 33‰ (Heaton et al., 1997). The IsoSource model iteratively generates source isotopic mixtures of which the proportions (f) sum to 1 (in Equation 1: \(f_{SO4} + f_{NO3} + f_{NH4} + f_{CO2} + f_{PM2.5} = 1\) for urban PM₂.₅; In Equation 2: \(f_{SO4} + f_{NO3} + f_{NH4} + f_{CO2} + f_{PM2.5} + f_{other} = 1\) for background PM₂.₅). It
compares each calculation against a known mixture ($\delta^{15}$N of PM$_{2.5}$ samples; Table S1) and retains only those mixtures that satisfy the known $\delta^{15}$N value within some mass balance tolerance. This model provides a systematic mode of constraining the attribution of N sources in an underdetermined system. In our case, the calculated mixtures reflected combinations of precursor $\delta^{15}$N values of dominant sources (Table S2) and N in collected PM$_{2.5}$ samples. We applied a mass balance tolerance of 0.02. The mean values of output percentages from the model are adopted for the fractional contribution of each source to TN in each PM$_{2.5}$ replicate sample. Then the range and mean values of all replicate samples are presented for each source at Beijing or background site (Fig. 4).

There was no difference in the fractional contributions of N from soil dusts between Beijing (14 ± 5%) and background (12 ± 3%) PM$_{2.5}$ samples (Fig. 4). This reflected a fundamental nucleus of soil dust for the formation of PM$_{2.5}$ (He et al., 2014). During the haze episode of January 2013 in Beijing, low fractions of the primary aerosol constituents (e.g., mineral dusts, black carbon) and high fractions of N from secondary processes have been demonstrated (Huang et al., 2014). Our estimation showed that NO$_2$ contributed more N to PM$_{2.5}$ at Beijing site ($f_{\text{NO}_2(\text{Beijing})} = 41 \pm 19$%) than that at the background site ($f_{\text{NO}_2(\text{Menyuan})} = 30 \pm 8$%) (Table 2). The mean ratio of $f_{\text{NH}_3}$ to $f_{\text{NO}_2}$ in N of PM$_{2.5}$ was generally higher at the background site (2.3 ± 1.1) than that at Beijing site (1.5 ± 1.1) (Table 2), which generally followed the pattern of NH$_4^+/\text{NO}_3^-$ ratios in PM$_{2.5}$ (Table 1). In fact, the contributing ratios of precursors can neither be exactly verified by the ratios of NH$_4^+/\text{NO}_3^-$ in PM$_{2.5}$, nor by the ratios of gaseous NH$_3$/NO$_2^-$ in the atmosphere. Firstly, NO$_2$ and NH$_3$ precursors can substantially react with organic compounds to form organic N compounds. The severe haze pollution event in January 2013 of Beijing was driven by both secondary
inorganic and organic aerosols (Huang et al., 2014). Secondly, the gas-to-particle reaction rates differ between NO$_2$ and NH$_3$, the distributions of N ions or compounds differ among particles with different aerodynamic diameters, between NO$_2$ and NH$_3$. Thirdly, the abundance of SO$_2$ can make the ratios of NO$_3^-$ to NH$_4^+$ difficult to follow those of ambient NO$_2$ to NH$_3$. The concentrations of NO$_3^-$ and NH$_4^+$ in particles can be more sensitive to changes in SO$_2$ than in its own precursor emissions (Lei and Wuebbles, 2013; He et al., 2014).

On average, 86% of N in PM$_{2.5}$ at Beijing site was anthropogenic, in which 71% was derived from fossil fuel combustion and NO$_2$ from coal burning was the biggest contributor (26%) (Table 2). Regarding to fossil-derived N sources, coal combustion contributed more N (41%) than traffic emissions (30%), NO$_2$ contributed more N (41%) than NH$_3$ (30%) (Table 2). Coal combustion and traffic emissions had the same contribution (15% to TN) in fossil-derived NH$_3$, NH$_3$ and NO$_2$ had the same contribution (15% to TN) in vehicle-derived N (Table 2). These results demonstrated that fossil fuel-based NH$_3$ emissions substantially contributed to PM$_{2.5}$ N pollution in densely populated urban areas. In particular, vehicles equipped with three-way catalytic converters, electrical generating units and units with selective catalytic reduction or selective non-catalytic NO$_2$ reduction technologies should be significant ‘fuel NH$_3$’ sources (Cape et al., 2004; Kirchner et al., 2005). Our results unambiguously illustrate that regulatory controls of NO$_2$ emissions from coal burning (nearby industrial facilities) and NH$_3$ from urban transportation is important to advert the risk of severe haze episodes in Beijing. It should be noted that 29% of N in urban PM$_{2.5}$ was from non-fossil N sources (domestic wastes/wwage and soil dust) (Table 2). Before this, non-fossil contribution to PM$_{2.5}$ mass was shown as ∼15% (only primary and secondary organic aerosols were considered) in Beijing during the severe haze
event of January 2013 (Huang et al., 2014). However, higher non-fossil contribution
(35% of PM$_{2.5}$ mass) was observed at five cities of the Yangtze River Delta, China
(Cheng et al., 2011). At the background site, N in PM$_{2.5}$ was not dominated by natural
and biogenic N emissions, but by agricultural N sources (82 ± 7%; Table 2). In total,
NH$_3$ from animal wastes/excreta and fertilizer accounted for only 17%, but biomass
burning had the highest contribution (58%) in N of PM$_{2.5}$ at the background site
(Table 2). Moreover, biomass burning contributed more N as NH$_3$ (44%) than as NO$_2$
(14%) to N of PM$_{2.5}$ at the background site (Table 2). Higher production of NH$_3$ than
NO$_2$ from biomass burning have been documented previously (Hegg et al., 1988;
showed that the emission ratio of NH$_3$ (3.8%) was higher than that of SO$_2$ (0.3%)
during biomass burning. Andreae and Merlet (2001) further clarified that the emission
factors of NH$_3$ were 2 – 5 times higher than that of SO$_2$ from various types of biomass
burning. Our results revealed an important contribution of biomass-burning NH$_3$ to
the formation of secondary PM$_{2.5}$ at rural and background sites.

5 Conclusions

This paper provides a natural isotope method to quantify contributions of major
source precursors to N in atmospheric particulates based on TN of PM$_{2.5}$ at Beijing
and a background site. Significant $^{15}$N enrichment in PM$_{2.5}$ relative to potential
sources was observed at the background site, not at Beijing site. Combined with
evidences from the chemistry of local PM$_{2.5}$ and precursors, a significant isotopic
effect of NH$_3$↔NH$_4^+$ equilibrium was recognized under the condition of lower acid
gases (especially SO$_2$) relative to ambient NH$_3$, which should be considered into the
fractional estimation of NH$_3$ in TN of PM$_{2.5}$. Based on calculating results of IsoSource,
PM$_{2.5}$ of Beijing derived N mainly came from coal combustion (41%), vehicle exhausts (30%) and domestic wastes/sewage (14%), while background PM$_{2.5}$ derived N mainly came from biomass burning (58%), animal wastes (15%) and fertilizer application (9%). Regulatory controls of NO$_2$ emissions from coal burning and NH$_3$ from urban transportation is still an important and effective step to reduce the risk of the formation of severe haze episodes in Chinese cities. However, emissions of N from biomass burning in broad rural areas should be stressed to meet a rigorous reduction of reactive N emissions in China.

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<table>
<thead>
<tr>
<th></th>
<th>Beijing (CRAES site)</th>
<th>Menyuan, Qinghai</th>
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</thead>
<tbody>
<tr>
<td>PM$_{2.5}$ (μg/m$^3$)</td>
<td>264.3±118.0 (43.0–433.6)</td>
<td>13.0±3.2 (7.0–17.8)</td>
</tr>
<tr>
<td>NH$_4^+$-N (%)</td>
<td>7.4±3.4 (3.5–12.9)</td>
<td>5.9±1.8 (3.1–9.4)</td>
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<tr>
<td>NO$_3^-$-N (%)</td>
<td>5.0±3.0 (0.7–9.4)</td>
<td>1.9±0.4 (1.2–2.6)</td>
</tr>
<tr>
<td>SO$_4^{2-}$-S (%)</td>
<td>5.5±2.4 (2.4–8.3)</td>
<td>0.2±0.0 (0.2–0.3)</td>
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<tr>
<td>IN (%)</td>
<td>12.4±4.6 (5.1–22.2)</td>
<td>7.8±1.7 (5.7–11.3)</td>
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<tr>
<td>TN (%)</td>
<td>16.7±4.6 (8.2–29.3)</td>
<td>8.6±5.6 (1.4–18.7)</td>
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<tr>
<td>n-NH$_4^+/n$-NO$_3^-$</td>
<td>2.5±2.5 (0.5–9.0)</td>
<td>3.3±1.2 (1.2–4.9)</td>
</tr>
<tr>
<td>n-NH$_4^+/n$-SO$_2^{2-}$</td>
<td>3.5±1.6 (1.2–6.3)</td>
<td>56.3±14.3 (42.1–89.5)</td>
</tr>
<tr>
<td>n-NH$_4^+/n$-(NO$_3^-$ + SO$_2^{2-}$)</td>
<td>1.1±0.6 (0.4–2.9)</td>
<td>3.1±1.1 (1.2–4.7)</td>
</tr>
<tr>
<td>n-NH$_4^+/n$-(NO$_3^-$ + 1/2*SO$_2^{2-}$)</td>
<td>1.4±1.0 (0.5–4.3)</td>
<td>3.2±1.2 (1.2–4.8)</td>
</tr>
<tr>
<td>NH$_3$ (μg/m$^3$)</td>
<td>14.1</td>
<td>4.8</td>
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<tr>
<td>NO$_2$ (μg/m$^3$)</td>
<td>89.2±21.2 (57.0–122.0)</td>
<td>4.3±1.3 (2.6–6.7)</td>
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<td>SO$_2$ (μg/m$^3$)</td>
<td>22.9</td>
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<tr>
<td>n-NH$_3$/n-NO$_2$</td>
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<td>3.0</td>
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<tr>
<td>n-NH$_3$/n-SO$_2$</td>
<td>2.3</td>
<td>60.2</td>
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<td>n-NH$_3$/n-(NO$_2$ + SO$_2$)</td>
<td>0.4</td>
<td>2.9</td>
</tr>
<tr>
<td>n-NH$_3$/n-(NO$_2$ + 1/2*SO$_2$)</td>
<td>0.4</td>
<td>2.9</td>
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Table 1. Mass concentrations of inorganic N (IN, mainly including NH$_4^+$-N, NO$_3^-$-N), SO$_4^{2-}$-S, total N (TN), molecular ratios of NH$_4^+$ to NO$_3^-$, NH$_4^+$ to SO$_4^{2-}$, NH$_4^+$ to (NO$_3^-$ + SO$_4^{2-}$) in PM$_{2.5}$ at Beijing (CRAES site) and a background site (Menyuan, Qinghai province) of China. Data of ambient NH$_3$ and SO$_2$ at Beijing site were cited from Carmichael et al (2003), He et al (2014), Wei et al (2015). Data of NH$_3$ and SO$_2$ were cited from the background site of Waliguan in Qinghai Province (Carmichael et al., 2003).
Table 2. Fractional contributions (f, %) of dominant N precursors and anthropogenic N sources to N in PM$_{2.5}$ at Beijing (CRAES site) and a background site (Menyuan, Qinghai province) of China.

<table>
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<tr>
<th>Site</th>
<th>Precursor</th>
<th>$f_{\text{NH}_3}$</th>
<th>$f_{\text{NO}_2}$</th>
<th>Anthropogenic source</th>
<th>$f_{\text{Ind}}$</th>
<th>$f_{\text{Traffic}}$</th>
<th>$f_{\text{Agriculture}}$</th>
<th>$f_{\text{Biomass-burning}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beijing</td>
<td></td>
<td>44±20</td>
<td>41±19</td>
<td>1.5±1.1</td>
<td>41±18</td>
<td>30±12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Menyuan</td>
<td></td>
<td>61±11</td>
<td>27±8</td>
<td>2.3±1.1</td>
<td>82±7</td>
<td>58±9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure captions

**Fig. 1.** δ¹⁵N values of PM₂.₅ and potentially dominant N sources at Beijing (CRAES site) (red) and a background site (Menyuan, Qinghai province) (blue) of China, respectively. The solid and dotted lines within the boxes mark the arithmetic mean and median values, respectively. Source δ¹⁵N data (detailed in Table S2) were cited from Moore, 1974, 1977; Heaton, 1986; Heaton, 1990; Freyer, 1991; Kiga et al., 2000; Laffray et al., 2000; Heaton et al., 2004; Li & Wang, 2008; Elliott et al., 2009; Hastings et al., 2009; Kawashima & Kurahashi, 2011; Middlecamp & Elliot, 2011; Felix et al., 2012, 2013, 2014; Felix & Elliott, 2014; Walters et al., 2015. The δ¹⁵N of TN in soil (Wang et al., 2014) was assumed as TN of soil dust according to the air mass backward trajectories (Fig. 2).

**Fig. 2.** 72-hour air mass backward trajectories for all sampling dates at Beijing and a background site (Menyuan, Qinghai Province) of China, based on NOAA HYSPLIT model back trajectories.

**Fig. 3** Correlation between δ¹⁵N values of PM₂.₅ and molecular ratios of NH₄⁺ to (NO₃⁻ + 1/2²SO₄²⁻) (n-NH₄⁺/n-(NO₃⁻ + 1/2²SO₄²⁻)) in PM₂.₅ at Beijing (CRAES site) and a background site (Menyuan, Qinghai province) of China.

**Fig. 4.** Fractional contributions (f, %) of dominant N sources to N in PM₂.₅ at Beijing (CRAES site) (red) and a background site (Menyuan, Qinghai province) (blue) of China, respectively. The solid and dotted lines within the boxes mark the median and the mean values. The mean percentage calculated by the IsoSource model was taken as the fractional contribution of each source to TN of each PM₂.₅ sample.
Figure 1
Figure 2
Figure 3

![Diagram showing a scatter plot with blue and red markers. The plot compares $\delta^{15}$N$_{\text{PM2.5}}$ (in %) against n-NH$_4^+$/n-(NO$_3^-$ + 1/2SO$_4^{2-}$). The figure includes the text $R^2 = 0.67$, $P < 0.001$. The markers represent data from Menyuan, Qinghai (blue) and CRAES, Beijing (red).]
Figure 4