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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 $\delta^{15}N$ method, this study evaluated contributions of major sources to N of $PM_{2.5}$ at Beijing (collected during a severe haze episode of January 22nd – 30th, 2013) and a background site (Menyuan, Qinghai province; collected from September to October of 2013) of China. At Beijing, $\delta^{15}N$ 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, $\delta^{15}N$ 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 $NH_3 \leftrightarrow NH_4^+$ 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 $\delta^{15}N$ 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.

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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

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atmosphere. In other words, NO_2 and NH_3 precursors could not be transformed into corresponding inorganic ions completely (Ge et al., 2011ab). Moreover, contributions of NO_2 and NH_3 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 $PM_{2.5}$, or elucidate inorganic N in $PM_{2.5}$ based on ambient NO_2 and NH_3 levels. Compared with the expensive and complex monitoring of gaseous and particulate N compounds, the natural abundance of N isotope ($\delta^{15}N$: the $^{15}N/^{14}N$ ratio expressed relative to atmospheric N_2) in $PM_{2.5}$ can integrate all-involved N sources, as well as reflect potential $\delta^{15}N$ changes of major N components during the formation of $PM_{2.5}$ (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, $\delta^{15}N$ of $PM_{2.5}$ has an advantage of characterizing sources of major N pollutants and providing the $\delta^{15}N$ information of dry N deposition for biogeochemistry studies (Yeatman et al., 2001; Heaton et al., 2004; Elliott et al., 2007, 2009). At remote sites, $\delta^{15}N$ of $PM_{2.5}$ 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), $\delta^{15}N$ of $PM_{2.5}$ can provide direct evidences on sources and extents of anthropogenic N pollution.

The $\delta^{15}N$ variation of $PM_{2.5}$ is controlled by $\delta^{15}N$ values of initial gas precursors and gas (g) ↔ particle (p) isotope effects. It is ideal but difficult to measure $\delta^{15}N$ 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 $\delta^{15}N$ values (Walters et al., 2015), but some others showed a wide but similar $\delta^{15}N$ ranges at different locations (Hoering et al., 1957; Heaton, 1986, 1990; Ammann et al., 1999;

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Pearson et al., 2000). Hence, the mean values of documented $\delta^{15}N$ 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 $\delta^{15}N$ 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}N-depleted due to the large ^{15}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 $\delta^{15}N$ values when atmospheric reactive N is substantially contributed from N emissions of agricultural fertilization and livestock, both of which are strongly ^{15}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 $\delta^{15}N$ values of $PM_{2.5}$ are expected to be positive because biomass burning emits N with $\delta^{15}N$ 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 $\delta^{15}N$ 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

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source of NO_2 in the urban, had a wide $\delta^{15}N$ range (-19.1 – +9.8‰; a mass-weighted value: -2.5 ± 1.5‰) (Walters et al., 2015) because of the kinetic isotope fractionations associated with the catalytic NO_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_3, with very small gas-to-particle fractionation for nonvolatile NO_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 $\delta^{15}N$ values between roadside NO_2 (5.7‰) and particulates (6.8‰) (Ammann et al., 1999; Pearson et al., 2000). For NH_3, kinetic isotopic effect of NH_3-to-NH_4^+ reaction was small at the whole time scale of PM formation, but $NH_3 \leftrightarrow NH_4^+$ equilibrium will cause ^{14}N to be preferentially associated with NH_3 and ^{15}N to be enriched in NH_4^+ of PM due to the stronger associative strength of ^{15}N than ^{14}N in NH_4^+ (Heaton et al., 1997; Fukuzaki et al., 2009; Li et al., 2012). This has been recognized as a major reason for generally higher $\delta^{15}N$-NH_4^+ in aerosols than that in rain NH_4^+ and precursor NH_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 $\delta^{15}N$ of particulate NH_4^+ stabilized at values of 33‰ higher than that of NH_3 at 25 ℃. However, chemical equilibrium mechanisms and isotopic effects for $NH_3 \leftrightarrow NH_4^+$ exchange in $PM_{2.5}$ and its environmental controls are still uncertain in the field circumstances. It is valuable to explore $\delta^{15}N$ characteristics of $PM_{2.5}$ and the mechanisms behind the $\delta^{15}N$ difference between $PM_{2.5}$ and precursor gases.

This study measured $\delta^{15}N$ ratios of $PM_{2.5}$ at Beijing (CRAES site) and a national atmospheric background monitoring station (Menyuan, Qinghai province, northwestern China). Based on the $\delta^{15}N$ values of observed $PM_{2.5}$ samples and

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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

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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 16800km^2), 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

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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 ℃ and the precipitation is 426 – 860 mm. The mean hourly temperature was 6.5 ℃ (3 – 11 ℃) 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 $\delta^{15}N$ signals, for testing our hypothesis and partitioning method stated in introduction. Each $PM_{2.5}$ sample was collected by a pre-baked quartz filter (diameter = 47 mm, sampling area ≈ 13.2 cm^2) 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 $\delta^{15}N$ of $PM_{2.5}$ 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

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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 DERENDA, Germany, approved by European Standard) with controlled temperature (20 ℃±1 ℃) 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 ℃ 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 $\delta^{15}N$ 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; $\delta^{15}N$ = 0.4‰), USGS25 (Ammonium Sulfate, $\delta^{15}N$ = -30.4‰), IAEA-NO-3 (Potassium Nitrate; $\delta^{15}N$ = +4.7‰) were measured as standards for the calibration of $\delta^{15}N$ values. The average standard deviations for replicate analyses of an individual sample was ±0.1‰. TN concentrations, $\delta^{15}N$ values are reported as the average of three replicated measurements per sample. The natural abundance of ^{15}N ($\delta^{15}N$) in $PM_{2.5}$ was expressed in parts per thousand (per mille) by multiplying them by 1000:

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

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

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0.05 μg/m^3. 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. Gases (e.g., SO_2, NH_3, and HNO_3) 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 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_2 were measured using a NO-NO_2-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

At the Beijing site (CRAES), the mean $PM_{2.5}$ level reached 264.3 ±118.0 μg/m^3 (43.0 – 433.6 μg/m^3) 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 $PM_{2.5}$ differed distinctly between the two studying sites, thus they were presented as mass concentrations of $PM_{2.5}$ for comparison. The mass concentrations and $\delta^{15}N$ values of TN in $PM_{2.5}$ 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_4^+-N, NO_3^--N and SO_4^{2-}-S in $PM_{2.5}$ mass averaged 7.4 ± 3.4%, 5.0 ±3.0%, 5.5 ±2.4%, respectively at Beijing site, showing mean molecular ratios of NH_4^+ to NO_3^-, NH_4^+ to SO_4^{2-}, NH_4^+ to (NO_3^- + SO_4^{2-}), NH_4^+ to (NO_3^- +

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273 1/2*SO_4^{2-}) as 2.5, 3.5, 1.1, 1.4, respectively (Table 1). Ambient concentrations of NO_2
274 averaged 89.2 ±21.2 μg/m^3 at Beijing (Table 1). Mean concentrations of ambient
275 NH_3 (during April of 2013) and SO_2 (during January of 2013) were reported as 14.1
276 and 22.9 μg/m^3, respectively (He et al., 2014; Wei et al., 2015). Using these data,
277 mean molecular ratios of NH_3 to NO_2, NH_3 to SO_2, NH_3 to (NO_2 + SO_2), NH_3 to (NO_2
278 + 1/2*SO_2) were 0.4, 2.3, 0.4, 0.4, respectively (Table 1).

279 At the background site (Menyuan, Qinghai province), the filter-based
280 concentrations of atmospheric $PM_{2.5}$ averaged 13.0 ±3.2 μg/m^3 (7.0 – 17.8 μg/m^3)
281 during the studying period (September 6th – October 15th, 2013) (Tables 1 and S1),
282 which was almost the same as that (13.0 ±4.8 μg/m^3; 4.6 – 22.7 μg/m^3) based on an
283 ambient monitor (AIM-IC system: Model URG 9000B, URG Corporation, USA). The
284 mass concentrations and $\delta^{15}N$ values of TN in $PM_{2.5}$ at the background site averaged
285 8.6 ±5.6% and +18.5 ±5.8‰ (+8.0 – +27.9‰) (Tables 1 and S1; Fig. 1).
286 Concentrations of NH_4^+-N, NO_3^--N and SO_4^{2-}-S in the mass of $PM_{2.5}$ at Menyuan
287 averaged 5.9 ±1.8%, 1.9 ±0.4%, 0.2 ±0.0%, respectively (Table 1), showing mean
288 molecular ratios of NH_4^+/NO_3^-, NH_4^+/SO_4^{2-}, $NH_4^+/(NO_3^- + SO_4^{2-})$, $NH_4^+/(NO_3^- +$
289 1/2*SO_4^{2-}) as 3.3, 56.3, 3.1, 3.2, respectively (Table 1). Ambient concentrations of
290 NO_2 averaged 4.3 ± 1.3 μg/m^3 at the background site (Table 1). Ambient NH_3 and
291 SO_2 concentrations were not available at the Menyuan site (37°36′ N, 101°15′ E;
292 3295m), but the other background site in the same province (Waliguan, Qinghai;
293 36 °30′ N, 100 °10′ E, 3816m; a global baseline station) showed mean atmospheric
294 NH_3 and SO_2 concentrations as 4.8 μg/m^3 and 0.31 μg/m^3 (Carmichael et al., 2003),
295 showing mean molecular ratios of NH_3 to NO_2, NH_3 to SO_2, NH_3 to (NO_2 + SO_2),
296 NH_3 to (NO_2 + 1/2*SO_2) as 3.0, 60.2, 2.9, 2.9, respectively (Table 1).

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299 4.1 Major sources and isotopic effect

300 Natural ^{15}N isotope method can examine contributions of multiple N sources to a
301 given mixture pool, but a reasonable judgment of dominant sources is critical. At
302 Beijing site, six dominant N sources were assigned for TN in $PM_{2.5}$ samples collected
303 during the severe haze episode of January 2013:
304 S0: TN in soil dust,
305 S1: NO_2 from coal combustion,
306 S2: NH_3 from coal combustion,
307 S3: NO_2 from vehicle exhausts,
308 S4: NH_3 from vehicle exhausts,
309 S5: NH_3 from domestic wastes/sewage.
310 These putative origins have also been recognized to be responsible for PM pollution
311 during the severe haze episode of January 2013 (Zhang et al., 2013, 2015; Huang et
312 al., 2014). The mean $\delta^{15}N$ of soils (+6.0‰) was assumed as that of soil dust (Wang et
313 al., 2014), because the sampling time and sites of soil fit the air mass backward
314 trajectories of our studying sites (Fig. 2). So far, $\delta^{15}N$ values of NO_2 and NH_3
315 emissions are unavailable in many countries, but they were distinctive among most
316 typical sources and N species (Table S2, Fig. 1). Representative $\delta^{15}N$ values reported
317 for NO_2 and NH_3 emissions were adopted in our partitioning method (Table S2). But
318 we did not consider precursor $\delta^{15}N$ data which was influenced by post-emission
319 processes (e.g., roadside and tunnel because they can mix with other sources), and
320 measured through controlled tests or simulation. For examples, we did not use the
321 $\delta^{15}N$ data of NH_3 near highway (-5.0 – +0.4‰ in Smirnoff et al., 2012), NO_2 near

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322 highway (+2 – +10‰ in Moore et al., 1977, Ammann et al., 1999, Pearson et al., 2000;
323 -13.3 – +0.4‰ in Smirnoff et al., 2012), NO_2 in tunnels (+15.0 ±1.6‰ for NO_2; +5.7
324 ±2.8‰ for HNO_3 in Felix et al., 2014), NO_2 from vehicle engine (-13.0 – +3.7‰ in
325 Moore, 1977; Heaton, 1990; Freyer, 1978a,b, 1991), NO_2 from controlled
326 experiments of diesel combustion (+3.9 – +5.4‰ in Widory, 2007) and coal
327 combustion (-5.3‰ in Widory, 2007). Besides, the agricultural and biogenic N
328 emissions (mainly biomass burning, fertilizer application, animal wastes) were not
329 considered as sources of the urban $PM_{2.5}$ samples three reasons. First, these emissions
330 (mainly NH_3 if any) are less dispersible and long-distance transported. Second, the
331 CRAES site is located in the center of Beijing city cluster. Third, there was a severe
332 haze pollution event during our sampling time (January, 2013) (Huang et al., 2014).
333 We assumed a negligible contribution from NH_3 emission from seawater ($\delta^{15}N$ = -8 –
334 -5‰ in Jickells et al., 2003) and lightening NO_2 ($\delta^{15}N$ = -0.5 – +1.4‰ (Hoering et al.,
335 1957) because aerosols in inland urban environments derive almost all N from
336 land-based sources thus have a greater anthropogenic imprint. The lightening NO_2 can
337 be quickly scavenged by precipitation during the rain events, with little diffusion and
338 contribution to N in near-surface particulates.

339 At the Menyuan background site, potential sources of N in $PM_{2.5}$ include:
340 S0: TN in soil dust,
341 S6: NO_2 from biomass burning,
342 S7: NH_3 from biomass burning,
343 S8: NO_2 from animal wastes,
344 S9: NH_3 from animal wastes,
345 S10: NO_2 from soil N cycle,
346 S11: NH_3 from fertilizer application.

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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_4NO_3, NH_4HSO_4 and $(NH_4)_2SO_4$. 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

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suggested that part of ammonium existed as relative unstable salts (e.g., NH_4Cl). Most likely, the reversible reaction and a strong equilibrium between NH_3 and NH_4^+ occurred, the diffusion of NH_3 back to the atmosphere caused significant ^{15}N enrichment in $NH_4^+$of $PM_{2.5}$. As a result, $\delta^{15}N$ values of $PM_{2.5}$ were higher than potential sources at the background site of Qinghai (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 $\delta^{15}N$ values and $NH_4^+/(NO_3^- + 1/2*SO_4^{2-})$ ratios in $PM_{2.5}$ (Fig. 3). Therefore, $\delta^{15}N$ values of $PM_{2.5}$ 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 NH_3 (g) ↔ NH_4^+ (p) equilibrium (ε_{eq} = 33‰ in Heaton et al., 1997) should be added to NH_3 sources before inputting into IsoSource for calculations (details down in Section 4.2).

4.2 Fractional contributions of major sources to N in $PM_{2.5}$

The proportional contributions (f, %) of major sources to N in $PM_{2.5}$ are calculated using the IsoSource model (Phillips et al., 2003). For urban $PM_{2.5}$,

$\delta^{15}N_{PM2.5(Beijing)} = \delta^{15}N_{S0} \times f_{S0} + \delta^{15}N_{S1} \times f_{S1} + \delta^{15}N_{S2} \times f_{S2} + \delta^{15}N_{S3} \times f_{S3} + \delta^{15}N_{S4} \times f_{S4} + \delta^{15}N_{S5} \times f_{S5}$ (Equation 1).

For background $PM_{2.5}$,

$\delta^{15}N_{PM2.5(Background)} = \delta^{15}N_{S0} \times f_{S0} + \delta^{15}N_{S6} \times f_{S6} + (\delta^{15}N_{S7} + \varepsilon_{eq}) \times f_{S7} + \delta^{15}N_{S8} \times f_{S8} + (\delta^{15}N_{S9} + \varepsilon_{eq}) \times f_{S9} + \delta^{15}N_{S10} \times f_{S10} + (\delta^{15}N_{S11} + \varepsilon_{eq}) \times f_{S11}$ (Equation 2), where ε_{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: $f_{S0} + f_{S1} + f_{S2} + f_{S3} + f_{S4} + f_{S5} = 1$ for urban $PM_{2.5}$; In Equation 2: $f_{S0} + f_{S6} + f_{S7} + f_{S8} + f_{S9} + f_{S10} + f_{S11} = 1$ for background $PM_{2.5}$). It

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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 factional 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 ($f_{NO2(Beijing)}$ = 41 ±19%) than that at the background site ($f_{NO2(Menyuan)}$ = 30 ±8%) (Table 2). The mean ratio of f_{NH3} to f_{NO2} 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^+/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^+/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

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421 inorganic and organic aerosols (Huang et al., 2014). Secondly, the gas-to-particle
422 reaction rates differ between NO_2 and NH_3, the distributions of N ions or compounds
423 differ among particles with different aerodynamic diameters, between NO_2 and NH_3.
424 Thirdly, the abundance of SO_2 can make the ratios of NO_3^- to NH_4^+ difficult to follow
425 those of ambient NO_2 to NH_3. The concentrations of NO_3^- and NH_4^+ in particles can
426 be more sensitive to changes in SO_2 than in its own precursor emissions (Lei and
427 Wuebbles, 2013; He et al., 2014).

428 On average, 86% of N in $PM_{2.5}$ at Beijing site was anthropogenic, in which 71%
429 was derived from fossil fuel combustion and NO_2 from coal burning was the biggest
430 contributor (26%) (Table 2). Regarding to fossil-derived N sources, coal combustion
431 contributed more N (41%) than traffic emissions (30%), NO_2 contributed more N
432 (41%) than NH_3 (30%) (Table 2). Coal combustion and traffic emissions had the same
433 contribution (15% to TN) in fossil-derived NH_3, NH_3 and NO_2 had the same
434 contribution (15% to TN) in vehicle-derived N (Table 2). These results demonstrated
435 that fossil fuel-based NH_3 emissions substantially contributed to $PM_{2.5}$ N pollution in
436 densely populated urban areas. In particular, vehicles equipped with three-way
437 catalytic converters, electrical generating units and units with selective catalytic
438 reduction or selective non-catalytic NO_2 reduction technologies should be significant
439 'fuel NH_3' sources (Cape et al., 2004; Kirchner et al., 2005). Our results
440 unambiguously illustrate that regulatory controls of NO_2 emissions from coal burning
441 (nearby industrial facilities) and NH_3 from urban transportation is important to advert
442 the risk of severe haze episodes in Beijing. It should be noted that 29% of N in urban
443 $PM_{2.5}$ was from non-fossil N sources (domestic wastes/sewage and soil dust) (Table 2).
444 Before this, non-fossil contribution to $PM_{2.5}$ mass was shown as ~15% (only primary
445 and secondary organic aerosols were considered) in Beijing during the severe haze

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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; Crutzen and Andreae, 1990). A burning experiment by Lobert et al (1990) also 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 $NH_3 \leftrightarrow NH_4^+$ 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,

471 $PM_{2.5}$ of Beijing derived N mainly came from coal combustion (41%), vehicle
472 exhausts (30%) and domestic wastes/sewage (14%), while background $PM_{2.5}$ derived
473 N mainly came from biomass burning (58%), animal wastes (15%) and fertilizer
474 application (9%). Regulatory controls of NO_2 emissions from coal burning and NH_3
475 from urban transportation is still an important and effective step to reduce the risk of
476 the formation of severe haze episodes in Chinese cities. However, emissions of N
477 from biomass burning in broad rural areas should be stressed to meet a rigorous
478 reduction of reactive N emissions in China.
479

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488

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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).

	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)
IN (%)	12.4 ±4.6 (5.1–22.2)	7.8 ±1.7 (5.7–11.3)
TN (%)	16.7 ±4.6 (8.2 –29.3)	8.6 ±5.6 (1.4–18.7)
n-NH_4^+/n-NO_3^-	2.5 ±2.5 (0.5–9.0)	3.3 ±1.2 (1.2–4.9)
n-NH_4^+/n-SO_4^{2-}	3.5 ±1.6 (1.2–6.3)	56.3 ±14.3 (42.1–89.5)
n-NH_4^+/n-(NO_3^- + SO_4^{2-})	1.1 ±0.6 (0.4–2.9)	3.1 ±1.1 (1.2–4.7)
n-NH_4^+/n-(NO_3^- + 1/2*SO_4^{2-})	1.4 ±1.0 (0.5–4.3)	3.2 ±1.2 (1.2–4.8)
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
n-NH_3/n-NO_2	0.4	3.0
n-NH_3/n-SO_2	2.3	60.2
n-NH_3/n-(NO_2 + SO_2)	0.4	2.9
n-NH_3/n-(NO_2 + 1/2*SO_2)	0.4	2.9

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688 **Table 2.** Fractional contributions (*f*, %) of dominant N precursors and anthropogenic
689 N sources to N in $PM_{2.5}$ at Beijing (CRAES site) and a background site (Menyuan,
690 Qinghai province) of China.

Site	Precursor		f_{NH3}/f_{NO2}	Anthropogenic source			
	f_{NH3}	f_{NO2}		$f_{industrial}$	$f_{traffic}$	$f_{agricultural}$	$f_{biomass\text{-}burning}$
Beijing	44 ±20	41 ±19	1.5 ±1.1	41 ±18	30 ±12		
Menyuan	61 ±11	27 ±8	2.3 ±1.1			82 ±7	58 ±9

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709 **Figure captions**

710 **Fig. 1.** $\delta^{15}N$ values of $PM_{2.5}$ and potentially dominant N sources at Beijing (CRAES
711 site) (red) and a background site (Menyuan, Qinghai province) (blue) of China,
712 respectively. The solid and doted lines within the boxes mark the arithmetic mean and
713 median values, respectively. Source $\delta^{15}N$ data (detailed in Table S2) were cited from
714 Moore, 1974, 1977; Heaton, 1986; Heaton, 1990; Freyer, 1991; Kiga et al., 2000;
715 Laffray et al., 2000; Heaton et al., 2004; Li & Wang, 2008; Elliott et al., 2009;
716 Hastings et al., 2009; Kawashima & Kurahashi, 2011; Middlecamp & Elliot, 2011;
717 Felix et al., 2012, 2013, 2014; Felix & Elliott, 2014; Walters et al., 2015. The $\delta^{15}N$ of
718 TN in soil (Wang et al., 2014) was assumed as TN of soil dust according to the air
719 mass backward trajectories (Fig. 2).

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

723 **Fig. 3** Correlation between $\delta^{15}N$ values of $PM_{2.5}$ and molecular ratios of NH_4^+ to
724 $(NO_3^- + 1/2*SO_4^{2-})$ $(n\text{-}NH_4^+/n\text{-}(NO_3^- + 1/2*SO_4^{2-}))$ in $PM_{2.5}$ at Beijing (CRAES site)
725 and a background site (Menyuan, Qinghai province) of China.

726 **Fig. 4.** Fractional contributions (*f*, %) of dominant N sources to N in $PM_{2.5}$ at Beijing
727 (CRAES site) (red) and a background site (Menyuan, Qinghai province) (blue) of
728 China, respectively. The solid and dotted lines within the boxes mark the median and
729 the mean values. The mean percentage calculated by the IsoSource model was taken
730 as the fractional contribution of each source to TN of each $PM_{2.5}$ sample.

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733 **Figure 1**

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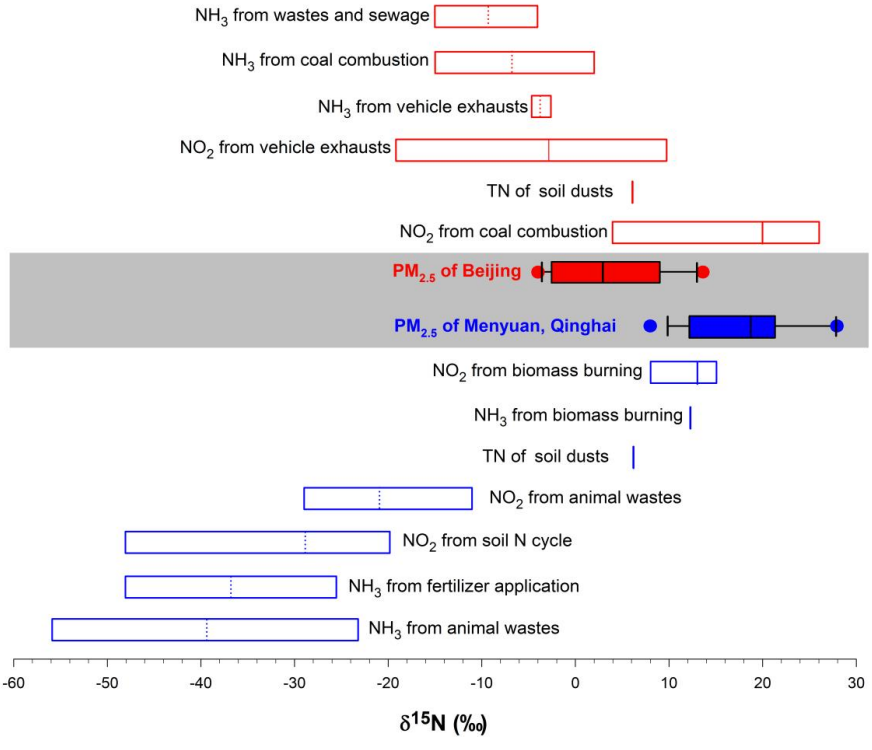

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745 **Figure 2**

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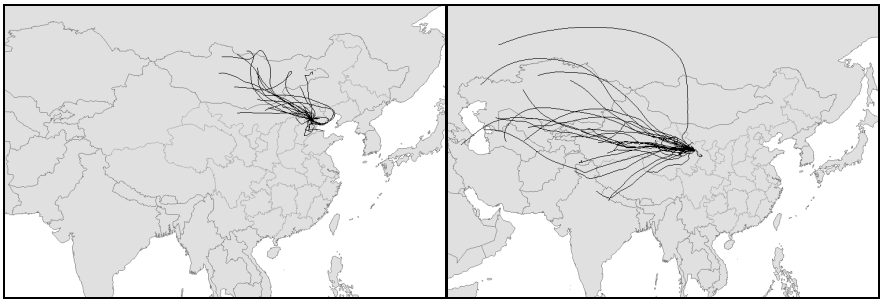

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766 **Figure 3**

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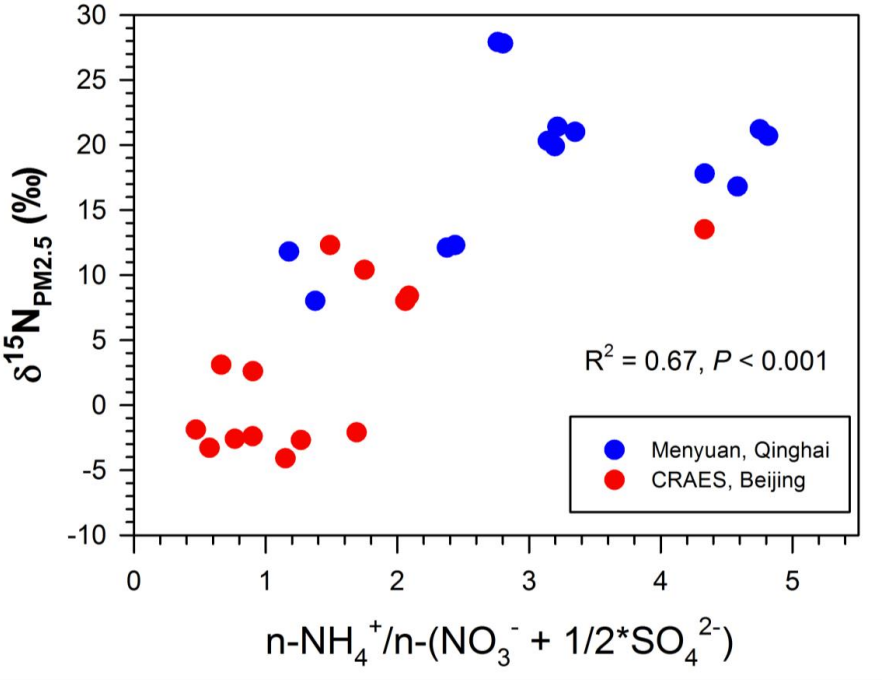

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780 **Figure 4**

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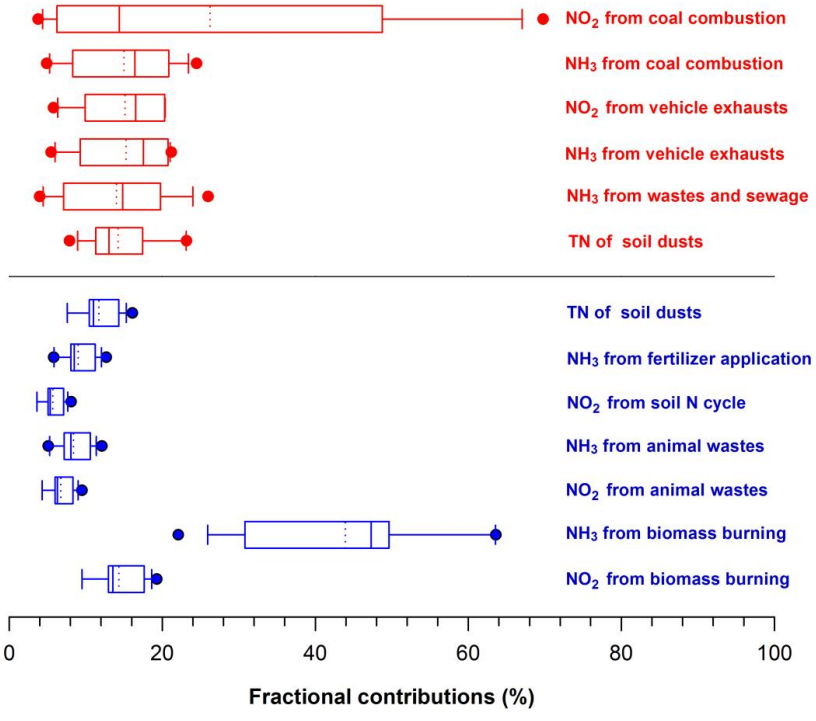

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