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Isotopic evidence for enhanced fossil fuel sources of aerosol ammonium in the urban atmosphere[☆]

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ABSTRACT

The sources of aerosol ammonium (NH_4^+) are of interest because of the potential of NH_4^+ to impact the Earth's radiative balance, as well as human health and biological diversity. Isotopic source apportionment of aerosol NH_4^+ is challenging in the urban atmosphere, which has excess ammonia (NH_3) and where nitrogen isotopic fractionation commonly occurs. Based on year-round isotopic measurements in urban Beijing, we show the source dependence of the isotopic abundance of aerosol NH_4^+, with isotopically light (−33.8‰) and heavy (0 to +12.0‰) NH_4^+ associated with strong northerly winds and sustained southerly winds, respectively. On an annual basis, 37–52% of the initial NH_3 concentrations in urban Beijing arises from fossil fuel emissions, which are episodically enhanced by air mass stagnation preceding the passage of cold fronts. These results provide strong evidence for the contribution of non-agricultural sources to NH_3 in urban regions and suggest that priority should be given to controlling these emissions for haze regulation. This study presents a carefully executed application of existing stable nitrogen isotope measurement and mass-balance techniques to a very important problem: understanding source contributions to atmospheric NH_3 in Beijing. This question is crucial to informing environmental policy on reducing particulate matter concentrations, which are some of the highest in the world. However, the isotopic source attribution results presented here still involve a number of uncertain assumptions and they are limited by the incomplete set of chemical and isotopic measurements of gas NH_3 and aerosol NH_4^+. Further field work and lab experiments are required to adequately characterize endmember isotopic signatures and the subsequent isotopic fractionation process under different air pollution and meteorological conditions.

1. Introduction

Ammonia (NH_3) plays an important role in atmospheric chemistry, contributing to air quality problems and enhanced nitrogen deposition (Zhang et al., 2015). As a major alkaline gas, NH_3 can neutralize sulfuric acid (H_2SO_4) and nitric acid (HNO_3) to form particulate ammonium (NH_4^+) in the atmosphere. Consequently, NH_4^+, SO_4^{2-} and NO_3^- together currently account for approximately 20–40% of the fine particles during extreme haze episodes in China (Huang et al., 2014), with major implications for human health, the ecosystem and the climate. The relative contribution of NH_4^+ is expected to increase given that NH_3 emissions are generally unregulated in many regions worldwide (Li et al., 2016). This idea is supported by the significant increasing trends in NH_3 observed by satellites over the U.S. (2.61% yr^{-1}), the European Union (1.83%

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yr^{-1}), and China (2.27% yr^{-1}) between 2002 and 2013 (Warner et al., 2017). Further evidence has suggested that controlling NH_3 emissions may represent the critical step in mitigating severe haze in China (Wang et al., 2016). However, it will be difficult to identify the most effective strategies for reducing future NH_3 emissions without confirming and quantifying the major sources of NH_3 (Liu et al., 2008).

One approach that can help quantify the sources of ambient NH_3 concentrations is based on the stable isotopic composition of NH_3 ($\delta^{15}N$-NH_3) for various endmembers (Felix et al., 2013). However, isotope-based source apportionment of aerosol NH_4^+ is challenging because the $\delta^{15}N$ values of NH_4^+ may differ from the precursor NH_3 (Fukuzaki and Hayasaka, 2009; Kawashima and Kurahashi, 2011). The difference in isotopic signals between NH_x ($NH_x = NH_4^+$ and NH_3) depends on equilibrium isotopic enrichment factors and the distribution of NH_4^+/NH_3 (Heaton et al., 1997; Li et al., 2012; Savard et al., 2017). When NH_3 is in deficit (e.g., in the marine atmosphere), the aerosols collected are close to acidic, recycling and fractionation between NH_3 and NH_4^+ are unlikely, and hence, the $\delta^{15}N$ values of NH_4^+ reflect their NH_3 sources (Jickells et al., 2003). When NH_3 is in excess (e.g., in the continental atmosphere), however, the aerosols are well neutralized, and the $\delta^{15}N$ values of NH_4^+ tend to be higher than their precursor NH_3 due to isotopic fractionation. For the latter scenario, we proposed a method of quantitatively estimating the sources of NH_4^+ after accounting for nitrogen isotopic exchange between NH_3 and NH_4^+ (Pan et al., 2016). In that case study, the $\delta^{15}N$ value of the initial NH_3 during hazy days was found to range from −14.5‰ to −1.6‰ in urban Beijing, which indicated fossil fuel-based emissions (Pan et al., 2016). These emissions contributed up to 90% of the total NH_3 during the extreme haze events in early 2013. That study provides a starting point from which to refine the sources of urban NH_4^+. Without long-term observations covering different seasons, however, it is unclear whether fossil fuel emissions only dominated NH_3 sources during haze episodes that winter.

With these goals in mind, we conducted a long-term study of the isotopic composition of NH_4^+ in aerosols on a weekly basis in the urban atmosphere. In this study, we present a more extensive dataset including year-round records of the $\delta^{15}N$ value of NH_4^+ in fine-mode aerosols. We determine the sources of aerosol NH_4^+ based on backward trajectory analysis and an isotopic mixing model. This study provides evidence that fossil fuel-related sources contribute significantly to urban NH_x from a seasonal perspective. The results reported here emphasize that reduction of non-agricultural sources of NH_3 is urgently needed to mitigate haze pollution on the North China Plain. In addition, the methods developed here clarify the source apportionment of aerosol NH_4^+ under excess NH_3 conditions.

2. Materials and methods

2.1. Aerosol sampling and analytical protocols

The PM sampling was performed on the roof of a building (8 m height) at the State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC), Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (CAS) in urban Beijing (39°58′ N, 116°22′ E) (Pan et al., 2012). The site is located in Yuandadu Park and is surrounded by a dense residential area (ca. 7500 persons km^{-2}). The site is approximately 0.8 km north of the third Ring Road and 1.3 km south of the fourth Ring Road, with daily average traffic volumes of approximately 10 million day^{-1} for both ring roads. No major industrial emissions from coal combustion are present in urban Beijing, but residential coal burning during the cold observation period was expected due to home heating.

Size-resolved aerosol samples were collected weekly over the course of a year (between week 10 March 2013 and week 9 February 2014) in urban Beijing as part of the CARE-China project (Xin et al., 2015). A 48 h sampling interval was conducted using a cascade impactor (Anderson Series 20–800, Thermo Electron Corporation, USA) with cutoff points of 0.43, 0.65, 1.1, 2.1, 3.3, 4.7, 5.8, and 9.0 μm at a flow rate of 28.3 L min^{-1}. To collect the size-resolved particles, quartz fiber filters (Type MK 360, diameter in 81 mm, Munktell Filter, Sweden) were used as substrates. After sampling, the filters were sealed in a plastic box and stored at −20 °C to limit losses of volatile components. In total, 52 sets of size-resolved samples were collected during the campaign, and the initial general results have been reported elsewhere (Tian et al., 2016).

A quarter of each quartz filter was extracted using 25 ml of deionized water (Millipore, 18.2 MΩ) and an ultrasonic bath for 30 min. The extraction liquid was filtered and subsequently measured by ion chromatograph (Dionex, ICS-90, USA) for the concentrations of NH_4^+ and other water soluble ions (Tian et al., 2014). The mean instrumental limits of detection (LOD) for all the ions were less than 5 μg L^{-1}, and the precision, at 2 mg L^{-1}, was ±5%.

Considering that the size-resolved isotopic results of aerosol NH_4^+ exhibit few differences among the 2.1–1.1, 1.1–0.65, 0.65–0.43 and < 0.43 μm size bins (Pan et al., 2016), filter samples of aerosols < 2.1 μm were combined, and then extracted in 25 ml of deionized water for NH_4^+ isotopic analysis. Thus, the isotopic data reported here represent the aerosol fine mode.

A new chemical method was used to determine the ^{15}N natural abundance ($\delta^{15}N$) for NH_4^+ (Liu et al., 2014). In brief, the method is based on the isotopic analysis of nitrous oxide (N_2O). NH_4^+ in the filter extract was initially oxidized to nitrite (NO_2^-) by hypobromite (BrO^-), and NO_2^- was then quantitatively converted into N_2O by hydroxylamine (NH_2OH) under strongly acidic conditions. The produced N_2O was analyzed by a commercially available purge and cryogenic trap system coupled to an isotope ratio mass spectrometer (PT-IRMS, IsoPrime100, IsoPrime Ltd., UK). The $\delta^{15}N$ values are reported in parts per thousand relative to the standard (atmospheric N_2) as follows:

$$\delta^{15}N(‰) = \frac{(^{15}N/^{14}N)_{sample} - (^{15}N/^{14}N)_{standard}}{(^{15}N/^{14}N)_{standard}} \times 1000$$

Three international reference standards (IAEA N1, USGS25 and USGS26) were used for the calibration to air N_2, the accepted international standard for N isotopes. The typical analysis size was 4 ml and produced 60 nmol N_2O, with a $\delta^{15}N$ standard deviation of less than 0.3‰ and often less than 0.1‰ based on replicates (n = 3–5).

2.2. Prediction of $\delta^{15}N$-NH_3 gas from aerosol $\delta^{15}N$-NH_4^+

During the campaign, NH_4^+ was predominantly present in the fine fraction for all the samples, constituting 89% of the total NH_4^+. We calculated the acid status of the fine aerosols using the equivalent ratio of NH_4^+ to the sum of SO_4^{2-} and NO_3^- because these species represent the dominant cations and anions other than H^+. In almost all the fine aerosol samples, this ratio was close to unity, implying that the aerosols were effectively neutralized by NH_3. Nitrogen fractionation may occur under these conditions, with excess NH_3 remaining in the atmosphere. To circumvent this problem, the $\delta^{15}N$ values of the initial NH_3 were calculated using an isotopic mass-balance model in a well-mixed closed system, as follows:

$$\delta_{gas} = \delta_{aerosol} - \varepsilon_{aerosol-gas}(1 - f) \quad (1)$$

where δ_{gas} and $\delta_{aerosol}$ are the isotopic composition of the initial NH_3 gas and final aerosol NH_4^+, respectively, and *f* is the fraction of the initial NH_3 gas converted to the aerosol NH_4^+. The nitrogen equilibrium isotope fractionation factor between gas and aerosol (ε) increases with decreasing temperature (Savard, 2010; Savard et al., 2017). A series of experimental results (Li et al., 2012) are consistent with theoretical predictions and show that ε has a reciprocal relationship with temperature. Thus, a linear fitting relationship between $NH_{4(aq)}^+$–$NH_{3(g)}$ and temperature from Urey (1947) was employed here, as follows:

$$\varepsilon_{aerosol-gas}=12.4678*1000/T-7.6694 \tag{2}$$

where T is temperature in Kelvin. It is important to emphasize that this modeling yielded $\varepsilon_{NH_4^+-NH_3}$ values of +34‰ at 25 °C, which are largely identical to those determined experimentally (Heaton et al., 1997; Kirshenbaum et al., 1947).

To obtain *f*, the concurrent measurement of NH_4^+ and NH_3 concentrations is needed. In this study, the aerosol NH_4^+ concentrations were determined, but the corresponding NH_3 observations were unavailable. Thus, the WRF-CHEM model was applied to reproduce gas phase chemistry and aerosol evolution during the study period (see Supporting Information (SI) text for details). In general, the simulated concentrations of NH_3 captured the episodic nature of NH_3 in Beijing but failed to constrain the seasonal variations (SI Fig. S1). To address this concern, the simulated NH_3 concentrations were shaped on a monthly observation basis. The redistributed NH_3 data agree well with the available daily observations in August 2013, as shown in Fig. S1. Finally, the redistributed data were used to calculate the mean values of NH_3 on the different sampling days. This dataset, together with the observed NH_4^+ value, was used to calculate *f*, enabling estimation of the initial δ^{15}N-NH_3 values in equation (1).

2.3. Source apportionment of NH_3

Once the δ^{15}N-NH_3 values had been predicted, the IsoSources isotopic mixing model (http://www.epa.gov/eco-research/stable-isotope-mixing-models-estimating-source-proportions) was used to determine the fraction of total NH_3 that could be attributed to different NH_3 emission sources (Phillips et al., 2005). In our study, the calculated mixtures combined δ^{15}N values from three main sources of NH_3 in the urban environment (Felix et al., 2013): agricultural sources (volatilization from livestock waste and fertilizer [−56.1‰ to −23.1‰]), fossil fuel sources (coal combustion [−7 to +2‰] and vehicle exhaust [−4.6‰ to −2.2‰]), and NH_3 slip (from urea that is used in selective catalytic reduction technology used by operating industrial or power generation plants and in some diesel engines [−14.6‰ to −11.3‰]). These sources have mean endmember δ^{15}N values of −39.5‰, −2.95‰ and −12.95‰, respectively. These δ^{15}N values assume uniform distributions for each source range of δ^{15}N-NH_3 values, as observed in a comprehensive inventory of δ^{15}N-NH_3 values from major emissions sources in the U.S. (Felix et al., 2013). The δ^{15}N-NH_3 values from power plants, diesel engines, and automobiles are unlikely to differ significantly between the U.S. and China, given that the two countries use similar catalytic technology.

The IsoSources isotopic mixing model iteratively generates source isotopic mixtures with fractions that sum to 1. This model compares each calculation against a known δ^{15}N endmember value and retains only those signatures that satisfy the known value within some mass-balance tolerance, as defined using a dataset of feasible solutions. Although this model can only generate feasible solutions (presented in this study as the average probability), it nevertheless provides a systematic way to constrain the attribution of nitrogen sources in an underdetermined system. We applied a mass-balance tolerance of 0.5‰ to the calculations, which is consistent with the analytical uncertainties in the combined nitrogen isotope abundance measurements.

3. Results and discussion

3.1. Isotopic features of the fine-mode aerosol NH_4^+

The year-round isotopic results of fine-mode NH_4^+ are presented in Fig. 1. As shown, several samples with high δ^{15}N-NH_4^+ values were observed during the spring and summer, but no distinct seasonal pattern was found. The year-round δ^{15}N-NH_4^+ values have a wide range, from −33.8‰ to +12.0‰; these values are similar to those observed at coastal sites, with values of −40‰ to +15‰ (Yeatman et al., 2001). However, they are more depleted than the values of 4‰ to +32‰ observed in the marine atmosphere (Kundu et al., 2010). In general, the δ^{15}N-NH_4^+ values indicate a trend of increasing NH_4^+ concentration and decreasing relative humidity ($p > 0.05$) (Fig. S2). Additionally, the δ^{15}N-NH_4^+ values increased as visibility decreased (<10 km, p>0.05), indicating that aerosol NH_4^+ is preferentially enriched in ^{15}N; the ^{14}N thus remains in the atmosphere during haze pollution episodes.

Since the haze pollution in the target region varies with wind direction (Jia et al., 2008), we then classified the isotopic dataset into five categories based on air mass histories obtained using 3-day back trajectories from the NOAA HYSPLIT model. As noted in Fig. 1, the aerosol samples with the lowest δ^{15}N-NH_4^+ values (−33.8‰) originated from the north after at least 3 days of long-range transport over the Mongolian Plateau. Relatively low δ^{15}N-NH_4^+ values (−37‰ to −22‰) were also observed during both dusty and clear days with air masses originating from the northwest (NW), indicating regional transport (Pan et al., 2016). In contrast, high δ^{15}N-NH_4^+ values (0‰ to +12‰) corresponded to stagnant air masses with back trajectories indicating that they originated from the southeast (SE), having spent at least 2 days over the Beijing-Tianjin-Hebei region. This is an industrial region of the North China Plain, coinciding with a hotspot of potential aerosol NH_4^+ sources (Fig. S3). The remaining samples had moderate δ^{15}N-NH_4^+ values (−20‰–0‰) and were characterized by mixed air mass trajectories arriving at the observation site from the SE and NW. This mixed pattern of moderate δ^{15}N-NH_4^+ values reflected a mixture between the isotopically light NH_x from the NW and the isotopically heavy NH_x from the SE. These findings indicate that the isotopic abundance of aerosol NH_4^+ at the observation site is associated with potential source regions in the North China Plain, where severe air pollution frequently occurs.

3.2. Identification of major sources of aerosol NH_4^+

We argue above that the aerosols collected here are nearly neutralized by excess NH_3 and that isotopic fractionation between NH_3 and NH_4^+ may thus occur. We therefore suggest that the δ^{15}N-NH_4^+ values in Fig. 1 cannot be linked directly to their source signatures. To address this problem, the initial δ^{15}N-NH_3 values were estimated based on the δ^{15}N-NH_4^+ values after accounting for nitrogen isotopic exchange between NH_3 gas and aerosol NH_4^+. As shown in Fig. 2, the initial δ^{15}N-NH_3 values were all lower than those of the respective NH_4^+, reflecting the larger degree of modification of the original δ^{15}N values of NH_3 gas due to equilibrium isotopic fractionation (Heaton et al., 1997). Similar to the aerosol NH_4^+, the δ^{15}N values of NH_3 gas also varied with the air mass trajectories. Over the course of the year, the initial δ^{15}N-NH_3 values of 31 samples were consistent with those of volatized NH_3 from an agricultural fertilizer and livestock waste source (−56‰ to −23‰)

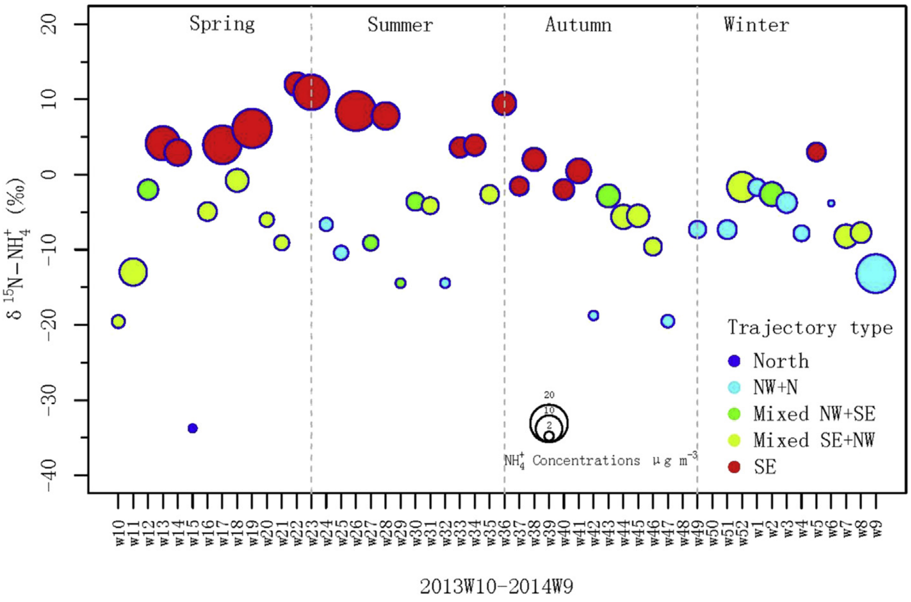

Fig. 1. Year-round isotopic values (Y-axis) and concentrations (pie chart sizes, legend provided as circles) of fine-mode NH_4^+ measured in urban Beijing between March (week 10) 2013 and February (week 9) 2014. The isotopic dataset was classified into five categories (pie colors) based on air mass histories arriving at the observation site (North = air mass trajectories from the north [natural emissions], NW + N = air mass trajectories from the northwest and north [agricultural and soil emissions], Mixed NW + SE or SE + NW = mixed air mass trajectories from the northwest and southeast [mixed emissions], and SE = air mass trajectories from the southeast [agricultural and industrial emissions]). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

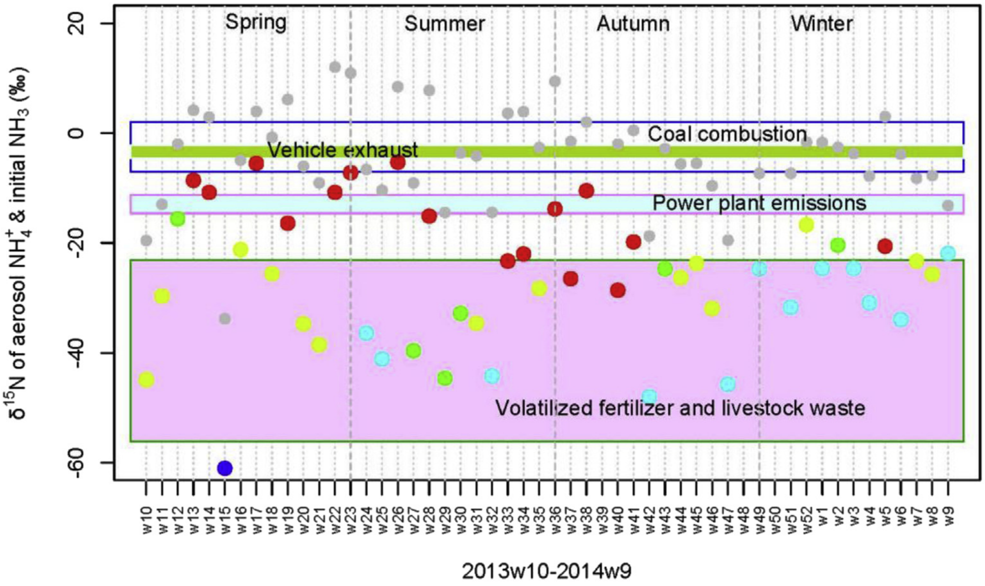

Fig. 2. Year-round isotopic values (Y-axis) of fine-mode NH_4^+ (gray pie charts) measured and initial NH3 (colored pie charts) estimated in this study against the NH3 emission signatures of individual sources (rectangles; see note) (Felix et al., 2013). The air mass trajectory type of weekly samples is indicated by colors (with the pie charts shown in Fig. 1). The difference in values between δ^{15}N-NH_3 and δ^{15}N-NH_4^+ represents the degree of modification of the original δ^{15}N values of NH_3 gas due to equilibrium isotopic fractionation. The sampling period is between March (week 10) 2013 and February (week 9) 2014. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

(Felix et al., 2013). The initial δ^{15}N-NH_3 values of the remaining samples ranged from −22‰ to −5.3‰, indicating a fossil fuel emission source (−15‰ to +2‰) (Felix et al., 2013).

Source attribution of initial NH_3 on a per sample basis was performed based on the results of the IsoSource model (Fig. 3). On an annual basis, agricultural emissions accounted for 55% (48%–63%) of the initial NH_3 in urban Beijing, indicating that fossil fuel-related sources such as vehicular exhaust (Sun et al., 2017), coal combustion (Meng et al., 2017) and NH_3 slip from power plants with SCR (Felix et al., 2013) comprised a large portion of the NH_3. The contribution of fossil fuel emissions was enhanced during spring and summer when the southerly winds prevailed with the seasonal monsoon change. This result may explain why high δ^{15}N-NH_4^+ values corresponded to stagnant air masses with air trajectories from the SE.

As expected, under conditions with polluted flow from the SE, 73% (35%–95%) of the initial NH_3 could be attributed to fossil fuel emissions. In contrast, under conditions with the clean north and

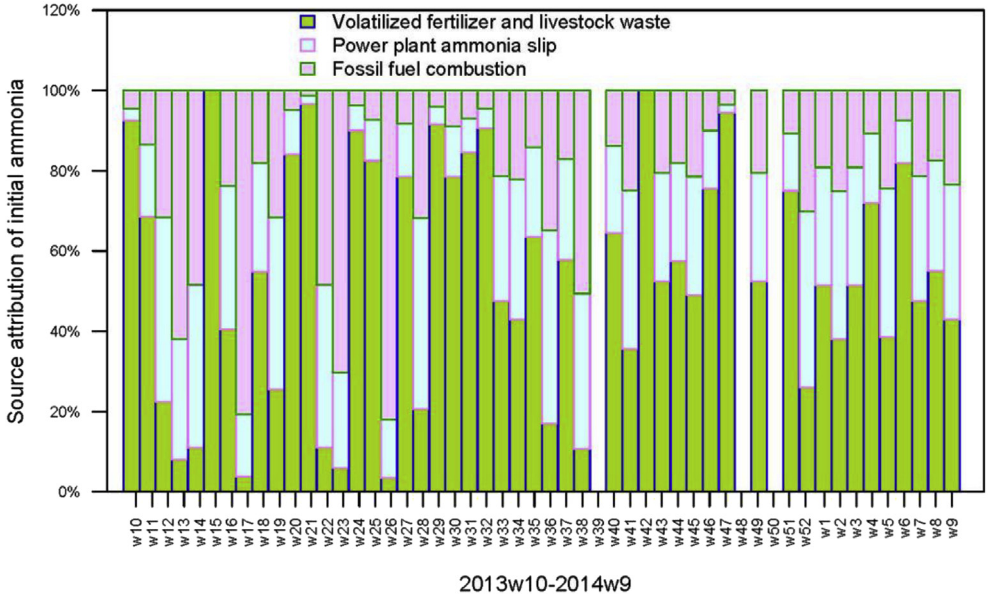

Fig. 3. Contributions of individual emissions to atmospheric NH_3 concentrations in urban Beijing over the course of a year between March (week 10) 2013 and February (week 9) 2014.

NW flow, the initial NH_3 in urban Beijing mainly originated from agricultural sources (75% on average). In addition, when the SE/SW stagnant flow was mixed with clean air flow from the NW, elevated NH_3 was attributed to agricultural emissions (64% on average). This source pattern varied with the haze development stages (Pan et al., 2016), which are controlled by synoptic cycles, especially the passage of cold fronts (Jia et al., 2008). These results provide strong evidence for the contribution of non-agricultural sources in the SE to the NH_3 in urban regions and suggest that controlling these emissions should be a priority for haze regulation.

4. Conclusions

This study presents measurements of the stable nitrogen isotopic composition of ambient NH_4^+ in Beijing, China. Fine particulate matter was sampled and isotopically-analyzed over a full year, which itself is a unique contribution in this field. The results were compared across days with different wind advection patterns, which generally reflected different sources (agricultural versus industrial pollution), as well as to prior characterizations of NH_3 source signatures.

Nitrogen isotopic fractionation occurred under conditions characterized by excess NH_3, in which case NH_4^+ isotopic values could not be used to identify the sources of NH_3. After accounting for nitrogen isotopic exchange between NH_3 gas and aerosol NH_4^+, the year-round results reported here provide strong evidence that fossil fuel-related emissions are an important source of aerosol NH_4^+ in the urban atmosphere. This result directly challenges the prevailing belief that controlling agricultural emissions represents the most effective method to mitigate haze pollution in China. Instead, this result supports the establishment of a new isotopically based conceptual framework to quantify the relative contributions of industrial versus agricultural NH_3 emissions. This study also suggests the importance of quantifying the impact of non-agricultural NH_3 sources on aerosol formation on an urban to regional scale and on nitrogen deposition in downwind ecosystems.

This study highlights the dependence of isotopic results on air mass history. Under conditions with winds from the south, NH_3 originating from regional NH_3 slip from power plants, coal combustion and vehicular emissions was enhanced. Controlling these emissions in the target region should be prioritized to disrupt the sulfate formation process during severe haze episodes (Wang et al., 2016). The $\delta^{15}N$ values of initial NH_3 calculated here represents a mixture of NH_3 and NH_4^+ with local to regional origins, which is an acknowledged limitation of this study. Future modeling studies should focus on defining the source regions of NH_3 based on an updated NH_3 emission inventory and an understanding of the regional transport and deposition of NH_x under different meteorological conditions.

The results of this study also represent a carefully executed application of existing stable nitrogen isotope measurement and mass balance techniques to a very important problem: understanding source contributions to atmospheric NH_3 in urban Beijing. This question is crucial to informing environmental policy that aims to reduce ambient particulate matter concentrations, which are some of the highest in the world. Predicting $\delta^{15}N$-NH_3 from $\delta^{15}N$-NH_4^+ using equations (1) and (2) represents a novel approach for the source apportionment of aerosol NH_4^+. This method of predicting $\delta^{15}N$-NH_3 was previously published (Pan et al., 2016) and further considered temperature effects on the nitrogen isotopic fractionation factor in this study. The isotopic source attribution results involve a number of assumptions and are limited by the incomplete set of NH_3 measurements available. There are several drawbacks associated with model-reproduced NH_3 concentrations and thus the NH_4^+ to NH_3 ratios used in equation (1). Future technique enhancement is also necessary to consider other possible fractionation scenarios such as dissociation (Yeatman et al., 2001). Concurrent chemical and isotopic measurements of gas NH_3 and aerosol NH_4^+ of selected sources and at receptor sites will help reduce the uncertainties in source attribution based on equations (1) and (2), the endmember signatures and the isotopic mixing model.

Author contributions

Y.P. and Y.W. conceived and designed the project; Y.P. and S.T. conducted the field work; S.T. and D.L. performed the laboratory experiments; M.G. and J.G. performed the modeling experiments and validation; Y.P., Y.F., X.Z. and G.M. analyzed the data; and Y.P. wrote the paper with comments from the coauthors.

Notes

The authors declare no competing financial interest.

Data availability

All data sets related to this paper can be requested by contacting the principal investigator, Yuepeng Pan (panyuepeng@mail.iap.ac.cn).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.03.038.

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