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# **Fossil Fuel Combustion-Related Emissions Dominate Atmospheric** Ammonia Sources during Severe Haze Episodes: Evidence from <sup>15</sup>N-Stable Isotope in Size-Resolved Aerosol Ammonium

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# Supporting Information

ABSTRACT: The reduction of ammonia (NH<sub>3</sub>) emissions is urgently needed due to its role in aerosol nucleation and growth causing haze formation during its conversion into ammonium  $(NH_4^+)$ . However, the relative contributions of individual  $NH_3$ sources are unclear, and debate remains over whether agricultural emissions dominate atmospheric NH<sub>3</sub> in urban areas. Based on the chemical and isotopic measurements of size-resolved aerosols in urban Beijing, China, we find that the natural abundance of <sup>15</sup>N (expressed using  $\delta^{15}$ N values) of NH<sub>4</sub><sup>+</sup> in fine particles varies with the development of haze episodes, ranging from -37.1% to -21.7% during clean/dusty days (relative humidity: ~ 40%), to -13.1% to +5.8% during hazy days (relative humidity: 70-90%). After accounting for the isotope exchange between NH<sub>3</sub> gas and



aerosol NH<sub>4</sub><sup>+</sup>, the  $\delta^{15}$ N value of the initial NH<sub>3</sub> during hazy days is found to be -14.5% to -1.6%, which indicates fossil fuelbased emissions. These emissions contribute 90% of the total NH<sub>3</sub> during hazy days in urban Beijing. This work demonstrates the analysis of  $\delta^{15}$ N values of aerosol NH<sub>4</sub><sup>+</sup> to be a promising new tool for partitioning atmospheric NH<sub>3</sub> sources, providing policy makers with insights into NH<sub>3</sub> emissions and secondary aerosols for regulation in urban environments.

# 1. INTRODUCTION

Severe and persistent haze episodes in China, which are characterized by extremely high concentrations of particulate matter (PM), are of concern due to regional and global impacts PM has on human health, the environment and climate change.<sup>1,2</sup> The severe PM concentrations in China's urban centers are dominated by secondary aerosols, and their chemical composition is similar to the compositions typically observed in other urban areas.<sup>3</sup> Secondary aerosols can be categorized as either secondary organic aerosols (SOAs) or secondary inorganic aerosols (SIAs), and both of them are important sources of fine (<2.5  $\mu$ m diameter) particles.<sup>3</sup> In many urban areas of China, such as Beijing, a higher proportion of SIAs relative to SOAs has been observed during haze episodes, suggesting a greater importance of SIAs in haze pollution chemistry.<sup>4</sup> SIAs are mainly formed when the dominant alkaline gas in the lower atmosphere, ammonia

(NH<sub>3</sub>), reacts with acidic compounds such as sulfuric acid  $(H_2SO_4)$  and nitric acid  $(HNO_3)$  to form particulate ammonium  $(NH_4^+)$ .<sup>5</sup> In addition to acid gas to particle conversion, NH<sub>3</sub> can also play a role in aerosol nucleation enhancing SIAs formation and growth by neutralizing H<sub>2</sub>SO<sub>4</sub> droplets.<sup>2</sup> However, despite the importance of NH<sub>3</sub> in urban haze chemistry, this pollutant is currently not included in emission control policies in China or in other regions worldwide that also experience severe particulate pollution.<sup>6</sup> Besides, the relative emission strength of individual NH<sub>3</sub> sources remains unclear, and a debate continues over whether NH<sub>3</sub> transported from agricultural regions is the major

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contributor to atmospheric NH<sub>3</sub> in urban areas as opposed to local NH<sub>3</sub> sources. Thus, identifying NH<sub>3</sub> emission sources and quantifying the relative contributions of different sources to the NH<sub>3</sub> budget is important for management strategies designed to reduce the adverse impacts of atmospheric NH<sub>3</sub>.<sup>7</sup>

The application of stable nitrogen (N) isotopes as a potential tracer of the origin of NH<sub>3</sub> has been proposed,<sup>7</sup> which might help constrain regional NH<sub>3</sub> budgets. N isotopic signatures in the U.S. revealed that the NH<sub>3</sub> emitted from volatilized livestock waste and fertilizer has relatively low  $\delta^{15}$ N values (-56% to -23%, relative to air N<sub>2</sub>) that could be used to differentiate it from NH<sub>3</sub> emitted from fossil fuel sources, which have higher  $\delta^{15}$ N values (-15% to +2%).<sup>7</sup> This approach was applied in Pittsburgh, an urban center in the U.S., and revealed high  $\delta^{15}$ N values (-8.5  $\pm$  7.2%) of NH<sub>3</sub>, which were suggested to mainly originate from fossil fuel combustionrelated emissions,<sup>8</sup> despite the fact that global emission inventories indicate that agricultural NH3 emissions are responsible for 80-93% of NH<sub>3</sub> emissions.<sup>9</sup> To date, atmospheric NH<sub>3</sub> from fossil fuel sources in China has not been accurately quantified, although nonagricultural sources of NH<sub>3</sub> in Beijing have been elucidated during the winter based on correlations between NH<sub>3</sub> and the traffic-related pollutants  $NO_x$  and  $CO.^{10,11}$  In large urban centers, such as Beijing, the high spatial variability of NH<sub>3</sub> concentrations, and the potential complexity of determining NH<sub>3</sub> source attribution in a system with a mixture of multiple sources, 10-12 makes closing the NH<sub>3</sub> budget a challenge. Therefore, quantitative estimates based on the  $\delta^{15}$ N technique and other top-down constraints are needed to further quantify the NH<sub>3</sub> sources in large cities.

Here, we present stable N isotopic composition results for NH4<sup>+</sup> that was sampled using a size-resolved aerosol sampler in urban Beijing during extreme haze episodes in early 2013. These haze pollution events were persistent, and they covered  $\sim 1.3$  million km<sup>2</sup> and affected  $\sim 800$  million people.<sup>13</sup> PM measurements in urban Beijing showed that the daily average concentrations of PM10 and PM25 exceeded the Chinese National Ambient Air Quality Standard (GB3095-2012, grade I) of 50 and 35  $\mu$ g m<sup>-3</sup> for 88% and 81% of the days, respectively, between January 1 and February 28, 2013, with record-breaking instantaneous concentrations of 995 and 772  $\mu$ g m<sup>-3</sup>, respectively, on January 12.<sup>14</sup> Five episodes with mean  $PM_{2.5}$  concentrations above 500 µg m<sup>-3</sup> occurred in January 2013.<sup>15</sup> These five episodes were cyclic with a period ranging from 4 to 7 days. Such strong haze cycles are regional in nature and are controlled by synoptic scale weather systems, specifically the passage of cold fronts, which induce inversion layers and stagnate air flow.<sup>16</sup> In this study, we focused on the samples collected during the period from January 24 to February 1, which represents an extreme haze pollution episode with a clear periodic cycle of 7 days.

The objective of this study was to identify the major sources of  $NH_3$  in urban regions during haze pollution based on the N isotope fractionation that occurs during the conversion of  $NH_3$  gas to  $NH_4^+$  in fine particles. To our knowledge, this study represents the first isotopic interpretation of size-resolved aerosol  $NH_4^+$  in China and is likely the first such interpretation in a highly urbanized environment in the world. The size-resolved isotopic data collected here are unique and may be useful for characterizing  $NH_3$  sources and N chemistry during haze formation. This information is critical for atmospheric chemistry and transport modeling and for the assessment of

haze mitigation policy options in the regions with severe NH<sub>3</sub>-related air pollution.

#### 2. MATERIALS AND METHODS

**2.1. Aerosol Sampling.** The PM sampling was performed on the roof of a building (15 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 ( $39^{\circ}58'$  N,  $116^{\circ}22'$  E).<sup>12</sup> The site is located in Yuandadu Park and is surrounded by a dense residential area (ca. 7500 persons km<sup>-2</sup>). 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<sup>-1</sup> 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-segregated aerosols were collected using a 9-stage impactor sampler (Anderson Series 20-800) at a flow rate of 28.3 L min<sup>-1</sup>. The 50% cutoff size bins of the sampler are >9.0, 9.0-5.8, 5.8-4.7, 4.7-3.3, 3.3-2.1, 2.1-1.1, 1.1-0.65, 0.65-0.43, and <0.43  $\mu$ m. The filter substrate was quartz fiber (Munktell, type MK360,  $\phi = 81$  mm). Each set of samples was continuously collected for 48 or 24 h, depending on the Air Pollution Prediction Index provided by the local government. Routine sampling was conducted for 48 h from 10:00 (local time) on Monday to 10:00 on Wednesday every week. Intensive sampling intervals of 24 h were also performed to capture the formation and dissipation processes of haze episodes. Procedural aerosol filter blanks were collected for each set of samples and appropriate corrections were applied. In total, 24 sets of size-resolved samples  $(24 \times 9 \text{ aerosol filters})$ plus 24 blank filters) were collected during the campaign and subjected to chemical analyses (Supporting Information (SI) Figure S1), and the initial general results have been reported elsewhere.

**2.2. Chemical and Isotopic Analysis.** Chemical analysis was conducted on a  ${}^{1}/{}_{4}$  section of each quartz filter. Soluble ions in the filter samples were extracted in 25 mL of deionized water (Millipore, 18.2 M $\Omega$ ) in an ultrasonic bath for 30 min at room temperature. Each extraction solution was passed through a 0.22  $\mu$ m filter, and the solutes were analyzed using an ion chromatograph (Dionex, ICS-90) for the concentrations of Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>. The mean instrumental limits of detection (LOD) for all the ions were less than 5  $\mu$ g L<sup>-1</sup>, and the precision, at 2 mg L<sup>-1</sup>, was ±5%.

Ten sets of size-resolved samples were selected for N isotopic analysis, which was conducted at the Stable Isotope Ecology Laboratory in the Institute of Applied Ecology, CAS, following the method described by Liu et al.<sup>17</sup> These samples were selected based on the chemical data and the haze development period. In brief, the method is based on the filter extract was initially oxidized to nitrite (NO<sub>2</sub><sup>-</sup>) by hypobromite (BrO<sup>-</sup>), and NO<sub>2</sub><sup>-</sup> was then quantitatively converted into N<sub>2</sub>O by hydroxylamine (NH<sub>2</sub>OH) under strongly acidic conditions. The produced N<sub>2</sub>O 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<sub>2</sub>) as follows:



**Figure 1.** Size-resolved aerosol  $NH_4^+$  concentrations vs particulate matter and meteorological parameters. Meteorological conditions (temperature-T, relative humidity-RH, wind speed-WS and wind direction-WD) were recorded by an automatic meteorological observation instrument (Milos520, Vaisala, Finland). In addition, the mass concentrations of  $PM_1$ ,  $PM_{2.5}$  and  $PM_{10}$  were measured through a tapered element oscillating microbalance (TEOM,RP1400, Thermal, USA). The results shown in (a), (b) and (c) were derived from our previous report.<sup>14</sup>

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

Three international reference standards (IAEA N1, USGS25 and USGS26) were used for the calibration to air N<sub>2</sub>, the accepted international standard for N isotopes. The typical analysis size was 4 mL and produced 60 nmol N<sub>2</sub>O, with a  $\delta^{15}$ N standard deviation of less than 0.3‰ and often less than 0.1‰ based on replicates (n = 3-5).

**2.3.** Calculation of the  $\delta^{15}$ N Value of NH<sub>3</sub> Gas Based on  $\delta^{15}$ N Measurement of Aerosol NH<sub>4</sub><sup>+</sup>. The  $\delta^{15}$ N value of aerosol NH<sub>4</sub><sup>+</sup> ( $\delta^{15}$ N-NH<sub>4</sub><sup>+</sup>) cannot be directly used to trace NH<sub>3</sub> emissions in haze pollution in Beijing due to isotope exchange equilibrium between NH<sub>3</sub> gas and aqueous NH<sub>4</sub><sup>+</sup> in air. This exchange is written as  $^{15}$ NH<sub>3(g)</sub> + NH<sub>4</sub><sup>+</sup>(aq)  $\leftrightarrow$  NH<sub>3(g)</sub> +  $^{15}$ NH<sub>4</sub><sup>+</sup>(aq), and the experimental isotope enrichment factor,  $\varepsilon_{\text{NH<sub>4</sub>^+} - \text{NH<sub>3</sub>}} = 33\% o$ , agrees well with that predicted by theory.<sup>19</sup> (see SI text for details).

Briefly, at low  $NH_3:H_2SO_4$  stoichiometric ratios (either ammonium bisulfate or sulfate), the neutralization tends to be unidirectional at the onset and favors the reaction of the lighter isotope. In this case, the isotope effect is likely due to the different diffusion rates of isotopologues at the nonturbulent interface between the atmosphere and the aerosol surface at small distances ( $\mu$ m). For the N isotopologues of NH<sub>3</sub>, this enrichment factor is  $\sqrt{17/18} = 0.972$ . The formation of a hydrated H<sub>2</sub>SO<sub>4</sub> aerosol by SO<sub>2</sub> oxidation and the subsequent diffusion of NH<sub>3</sub> into the new aerosol can readily occur. In such a scenario, the initial  $\delta^{15}$ N value of NH<sub>4</sub><sup>+</sup> would be approximately -28%° relative to the ambient NH<sub>3</sub>. This assessment is in good agreement with the results of Heaton et al.,<sup>18</sup> who showed an instantaneous  $\delta^{15}$ N value of -20%° relative to reactant NH<sub>3</sub>. When the stoichiometric NH<sub>3</sub>:H<sub>2</sub>SO<sub>4</sub> ratio is reached or exceeded, isotope exchange equilibrium is rapidly achieved, yielding a difference between the  $\delta^{15}$ N value of NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub> of +33%°.

The  $\delta^{15}$ N-NH<sub>4</sub><sup>+</sup> values will depend not only on whether the system is at equilibrium but also on the pH of the deliquesced aerosols. For example, below a pH of 5, for even extreme tropospheric NH<sub>3</sub> mixing ratios, nearly all of the NH<sub>3</sub> will partition into the aqueous phase thus the  $\delta^{15}$ N of NH<sub>4</sub><sup>+</sup> values would reflect the  $\delta^{15}$ N values of the NH<sub>3</sub> sources.<sup>20</sup> In contrast, at a pH above 12, almost all of the N will occur as NH<sub>3</sub>, and the few NH<sub>4</sub><sup>+</sup> aerosols that exist will be +33% relative to the  $\delta^{15}$ N

values of the NH<sub>3</sub> sources. This effect can be quantified using an isotopic mass balance in a well-mixed closed system as follows:

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

where  $\delta_{\rm gas}$  and  $\delta_{\rm aerosol}$  are the isotopic composition of the initial atmospheric gas and final ion phase in aerosols, respectively, and *f* is the fraction of the initial gas converted to the ion phase. Thus,  $\delta_{\rm gas}$  can be calculated from this equation if  $\delta_{\rm aerosol}$  and *f* are available:

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

To obtain *f*, the concurrent measurement of  $NH_4^+$  and  $NH_3$  concentrations is needed. Although the daily aerosol  $NH_4^+$  concentrations were observed in the present study, daily observations of  $NH_3$  were unavailable. Thus, the WRF-CMAQ model with newly added heterogeneous reactions was applied to reproduce the heterogeneous chemistry and the meteorological anomaly in January 2013 during regional haze formation. The revised CMAQ with heterogeneous chemistry not only captures the magnitude and temporal variation in  $NH_4^{+,21}$  but also reproduces the general variations in  $NH_3$  from clean days to hazy days (SI Figure S2). The simulated concentrations of  $NH_4^+$  and  $NH_3$  were used to calculate *f*, enabling the evaluation of the initial  $\delta^{15}N-NH_3$  values, which were then used to estimate the  $NH_3$  emissions.

2.4. Isotope Mixing Model. The "IsoSources" isotopic mixing model was used to determine the fraction of total NH<sub>3</sub> that could be attributed to different NH<sub>3</sub> emission sources.<sup>22,23</sup> This model iteratively generates source isotopic mixtures with fractions that sum to 1. It compares each calculation against a known  $\delta^{15}$ N endmember value and retains only those signatures that satisfy the known value within some mass balance tolerance, as defined using a data set of feasible solutions. Although this model can only generate feasible solutions (SI Figure S3; presented here as the average probability), it nevertheless provides a systematic mode of constraining the attribution of N sources in an underdetermined system. We applied a mass-balance tolerance of 0.5% to our calculations, which is consistent with the analytical uncertainties in the combined N isotope abundance measurements.

In our case, the calculated mixtures reflected combinations of the  $\delta^{15}$ N values of three main contributors to NH<sub>3</sub> in the urban environment: agricultural sources, fossil fuel sources (coal combustion and vehicle exhaust) and NH<sub>3</sub> slip from power plants, with mean endmember  $\delta^{15}$ N values of  $-39.5\%_{o}$ ,  $-2.95\%_{o}$  and  $-12.95\%_{o}$ , respectively. The  $\delta^{15}$ N values assumed uniform distributions for each source range of  $\delta^{15}$ N-NH<sub>3</sub> values, as observed in a comprehensive inventory of  $\delta^{15}$ N-NH<sub>3</sub> values from major emission sources in the U.S.<sup>7</sup>

Fossil fuel-related NH<sub>3</sub> arises from two main sources: as a byproduct of three-way catalytic converters that are part of the exhaust system in most modern automobiles, and NH<sub>3</sub> derived from urea that is used in the selective catalytic reduction (SCR) technology operating in some diesel engines and industrial/ power generation plants. NH<sub>3</sub> is derived from air N<sub>2</sub> in the former sources and from commercial urea in the latter, both of which have  $\delta^{15}N \sim 0$ .<sup>24,25</sup> The process that generates NH<sub>3</sub> from both N sources likely produces NH<sub>3</sub> depleted in  $\delta^{15}N$ ,<sup>7</sup> similar to the depletion found in NO produced by catalytic reduction.<sup>26</sup> The amount of  $\delta^{15}N$  depletion is expected to

depend on the temperature of the catalyst and its reduction efficiency. Thus, the  $\delta^{15}$ N-NH<sub>3</sub> values from automobiles, diesels, or power plants are unlikely to be significantly different between China and the U.S. as the two countries use similar catalytic technology.

# 3. RESULTS

**3.1. Concentrations and Size Distributions of Aerosol**  $NH_4^+$ . During the extreme haze episode, distinct temporal variation was apparent in the size-resolved aerosol  $NH_4^+$  concentrations; the  $PM_1$ ,  $PM_{2.5}$  and  $PM_{10}$  concentrations; and the corresponding meteorological parameters (Figure 1). This episode was divided into three stages: the initial stage (clean days: January 24–25), the development stage (haze days: January 25–30) and the dissipation stage (haze days: January 30–February 1).

The NH<sub>4</sub><sup>+</sup> concentrations were low during the initial clean days (January 24–25), at which time the air mass originated from the NW and had a low relative humidity (RH) and high wind speed (WS) (Figures 1 and S4). The size distribution of the NH<sub>4</sub><sup>+</sup> concentrations showed a peak at 4.7–5.8  $\mu$ m, which may be indicative of soil dust.<sup>27</sup> In addition to a peak at 0.65–2.1  $\mu$ m, a minor peak at 4.7–5.8  $\mu$ m was found on the dusty day of February 28, with instantaneous PM<sub>10</sub> concentrations above 1000  $\mu$ g m<sup>-3</sup> (Figures 2 and S1).



Figure 2. Size distribution of aerosol NH4<sup>+</sup> during the study period.

During the haze development stage from January 25 to 30, the NH<sub>4</sub><sup>+</sup> concentrations increased significantly from 9.8 to 61.3  $\mu$ g m<sup>-3</sup> and preferentially accumulated in the aerosol size bin of 0.65–2.1  $\mu$ m (Figures 1-2). During this period, the wind was weak, the RH increased from 40% to 90%, and the air masses at heights of 1000–3000 and 100 m were from the NW and SE, respectively (SI Figure S4). Interestingly, the main NH<sub>4</sub><sup>+</sup> particle size shifted from the submicrometer size of 0.43–0.65  $\mu$ m on January 25–27 to 0.65–1.1  $\mu$ m on January 27–28 and to 1.1–2.1  $\mu$ m on January 28–30 (Figure 2). This size shift may have been due to gas-particle conversion and hygroscopic growth with the increase in RH.<sup>14</sup>

During the haze dissipation stage between January 30 and 31, the RH was stable between 80% and 90%, but the  $NH_4^+$  concentrations decreased from 61.3 to 53.1  $\mu$ g m<sup>-3</sup> (Figure 1). Unlike the pattern observed during the haze development



Figure 3. Variations in the  $\delta^{15}$ N values of aerosol NH<sub>4</sub><sup>+</sup> with size bins and the initial  $\delta^{15}$ N-NH<sub>3</sub> values in air against the NH<sub>3</sub> emission signatures of individual sources. The source signatures are obtained from a previous report.<sup>7</sup>

stage, NH<sub>4</sub><sup>+</sup> concentrations decreased in the fine mode (<2.1  $\mu$ m) but increased in the coarse mode between 2.1 and 4.7  $\mu$ m during the dissipation stage. This difference in particle NH<sub>4</sub><sup>+</sup> size distribution was likely caused by the enhanced RH that facilitated the hygroscopic growth of coarse particles (>2.1  $\mu$ m), causing the NH<sub>3</sub> to dissolve on the surface of wet particles. During January 31 to February 1, when the air mass shifted from the SE to the NW with increased WS, the NH<sub>4</sub><sup>+</sup> concentrations decreased to 15.8  $\mu$ g m<sup>-3</sup> and peaked at 1.1–2.1  $\mu$ m (Figures 1 and 2).

**3.2.** Isotopic Features of Size-Resolved  $NH_4^+$ . Figure 3 plots the  $\delta^{15}$ N-NH<sub>4</sub><sup>+</sup> values as a function of particle size during the observation period. Since the formation pathway of fine and coarse particles is different, the isotopic features of size-resolved NH<sub>4</sub><sup>+</sup> were discussed separately below.

For fine particles, we observed relatively low  $\delta^{15}$ N-NH<sub>4</sub><sup>+</sup> values on the clean days of January 24-25, with mean values of -26.6% (range: -31.9% to -21.7%). Because the air mass was from the NW during this period, this signature may indicate a regional transport of NH4+. This pattern is evident from another dusty day on February 28, with the comparable range of  $\delta^{15}$ N-NH<sub>4</sub><sup>+</sup> values (-37.1% to -26.2%) found in fine particles. The clean and dusty days are also characterized by low RH ( $\sim$ 40%), which could indicate that the particles are less deliquesced; thus the NH4<sup>+</sup> in transported particles is much slower to equilibrate with local NH3 sources because it is mostly in the solid phase. In contrast, the increase in RH and  $\mathrm{NH_4^{+}}$  concentrations during the haze development stage suggests that the equilibration of NH<sub>3</sub> with fine particle NH4<sup>+</sup> became favored under these conditions because the particles are deliquesced and liquid-gas exchange is expected to be rapid. This interpretation is supported by the increase in  $\delta^{15}$ N-NH<sub>4</sub><sup>+</sup> values from -2.7% on January 25-27 and to +1% on January 27-28. During the subsequent days, the  $\delta^{15}$ N-NH<sub>4</sub><sup>+</sup> value was stable at approximately -10%, although the NH<sub>4</sub><sup>+</sup> concentrations reached their peak on January 29–30 and then decreased from January 30-31 to January 31-February 1.

For coarse particles, the  $\delta^{15}$ N-NH<sub>4</sub><sup>+</sup> values showed an irregular pattern, which is also different from that of the fine mode. In general, the value of  $\delta^{15}$ N-NH<sub>4</sub><sup>+</sup> in the coarse mode (except for 2.1–4.7  $\mu$ m) on January 24–25 was higher than

that on January 25–28 but lower than that on January 28-February 1, which is in profound contrast to the temporal pattern of the NH<sub>4</sub><sup>+</sup> concentrations. During the January 28-February 1 period, however, the  $\delta^{15}$ N-NH<sub>4</sub><sup>+</sup> values in coarse particles (except for 4.7–5.8  $\mu$ m) tended to increase and showed values similar to those of fine particles.

In addition, the size distribution and isotopic features of  $NH_4^+$  on January 7–9 (hazy days) and February 28 (dusty day) from other pollution episodes exhibited similar patterns to the hazy days and clean days during January 24–February 1 (Figures 2 and 3). Moreover, prior to the arrival at Beijing during the sampling days, the air parcels during this study overlapped with the source regions of  $NH_4^+$  on an annual basis (SI Figure S5). The findings indicate that the results presented are representative and reproducible on a regular basis.

3.3. Tracing NH<sub>3</sub> Emissions Using the Calculated **Initial**  $\delta^{15}$ **N-NH**<sub>3</sub> **Values.** The  $\delta^{15}$ **N-NH**<sub>4</sub><sup>+</sup> values of fine particles observed in this study span a wide range from -37.1% to +5.8% (Figure 3). This range is similar to that reported at coastal sites, with values of -40% to +15%,<sup>28</sup> but is more depleted than the reported values of 4% to +32% in marine aerosols.<sup>29</sup> However, these  $\delta^{15}$ N values of NH<sub>4</sub><sup>+</sup> may differ from the isotopic composition of the precursor NH<sub>3</sub> due to isotopic fractionation during the conversion from NH<sub>3</sub> gas to aerosol NH<sub>4</sub><sup>+</sup>, highlighting the difficulties in tracing the sources of NH<sub>3</sub> using aerosol  $\delta^{15}$ N-NH<sub>4</sub><sup>+</sup> values. Currently, it is also difficult to perform source apportionment of NH<sub>4</sub><sup>+</sup> in different particle sizes due to the lack of size-resolved isotopic signatures of aerosol NH<sub>4</sub><sup>+</sup>. Fortunately, the difference in  $\delta^{15}$ N-NH<sub>4</sub><sup>+</sup> values among the different size bins in the fine mode was small for a given sampling day, indicating the similarity of their sources. Thus, the concentration-weighted mean of  $\delta^{15}$ N-NH<sub>4</sub><sup>+</sup> values for fine particles with sizes less than 2.1  $\mu$ m was used to calculate the initial  $\delta^{15}$ N-NH<sub>3</sub> values, after accounting for the isotope exchange between NH<sub>3</sub> gas and aerosol NH<sub>4</sub><sup>+</sup>.

Figure 3 also shows the calculated results of the initial  $\delta^{15}$ N-NH<sub>3</sub> value against various NH<sub>3</sub> emission signatures. For clean days, the initial  $\delta^{15}$ N-NH<sub>3</sub> value was  $-48\%_o$ , which is close to the value of NH<sub>3</sub> from agricultural sources. During the remaining haze days, the initial  $\delta^{15}$ N-NH<sub>3</sub> value was estimated to be approximately  $-10\%_o$  (range:  $-1.6\%_o$  to  $-14.5\%_o$ ), which differs from the values of agricultural sources but falls

within the range of  $NH_3$  related to fossil fuel sources (e.g., vehicles, power plants and coal combustion).<sup>7</sup> This result is the first isotopic evidence showing that fossil fuel combustion, rather than agricultural sources, might be the major source of  $NH_3$  in urban Beijing.

Interestingly, on hazy days, the initial  $\delta^{15}$ N-NH<sub>3</sub> value fell within the range for vehicle exhaust and power plant slip sources and was comparable to that of aerosol  $\delta^{15}$ N-NH<sub>4</sub><sup>+</sup> (Figure 3, right). However, on clean days, the difference between aerosol  $\delta^{15}$ N-NH<sub>4</sub><sup>+</sup> and initial  $\delta^{15}$ N-NH<sub>3</sub> for the agricultural emissions is substantially larger than that for the other two sources. The lower degree of modification of the original  $\delta^{15}$ N value of NH<sub>3</sub> gas for these two sources compared with that for agricultural emissions results from the lower gas/ aerosol phase distribution of N (hence, higher f) in the air during haze periods. This effect is expected because the concentration of  $NH_3$  is significantly lower than that of  $NH_4^+$  during cold seasons.<sup>11</sup> This is especially true under conditions with lower temperature and higher humidity, which favor the conversion of gaseous NH<sub>3</sub> to particulate NH<sub>4</sub><sup>+,6</sup> In contrast, NH<sub>3</sub> gas is usually higher than particulate NH<sub>4</sub><sup>+</sup> under warm weather conditions (SI Figure S2-b). In addition, the equilibrium fractionation factor may be greater when temperatures decrease,<sup>30</sup> and this should considered when comparing aerosol  $\delta^{15}$ N-NH<sub>4</sub><sup>+</sup> values to gas  $\delta^{15}$ N-NH<sub>3</sub> values under various conditions.

To further quantify the contribution of  $NH_3$  sources to the initial air concentrations of  $NH_3$ , the isotope model "IsoSources" was run. The source apportionment results shown in Figure 4 indicate that 84% and 16% of ambient



**Figure 4.** Contributions of individual emissions to the atmospheric concentrations of  $NH_3$  in urban Beijing during the haze episode. Infeasible solutions included days on January 24–25 and January 27–28 when modeled initial isotopic values exceed the maximum or are less than the minimum of the source signature described in sect. 3.3 in this study. Alternatively, the lowest  $(-56\%_0)$  and the highest  $(+2\%_0)$  boundaries of the source signatures summarized for agricultural emissions and fossil fuel combustion were accounted for the aformentioned 2 days, respectively.

 $NH_3$  during the clean days of January 24–25 can be attributed to agricultural emissions and nonagricultural sources, respectively. The reverse was true during hazy days, when nonagricultural sources dominated the ambient  $NH_3$ , with a mean contribution of approximately 90%. During the haze development stage, the contribution from fossil fuels increased from 34% (January 25–26) to 59% (January 26–27) and to 81% (January 27–28), whereas the contribution of NH<sub>3</sub> slip (power plants) decreased from 48% (January 25–26) to 34% (January 26–27) and to 18% (January 27–28). However, the percent contributions of fossil fuels and NH<sub>3</sub> slip to each sampling day were comparable during January 28- February 1 (Figure 4). These results suggest that fossil fuel combustion can be a substantial contributor to ambient NH<sub>3</sub> in urban environments during haze pollution, whereas that from agricultural sources can be minor.

#### 4. DISCUSSION

Previous studies showed that the major aerosol compounds, such as nitrate, sulfate, and carbon, in the extreme haze events in early 2013 in China were due to fossil fuel combustion and biomass burning, <sup>1,4,13</sup> but the source of aerosol  $\rm NH_4^+$  was not quantified. This study presents the first isotopic evidence that fossil fuel emissions and  $\rm NH_3$  slip from power plants are more important than agricultural sources during haze pollution periods in urban Beijing. In contrast, agricultural sources are the major sources of  $\rm NH_3$  in the air during clean days when the WS is higher and the air transport is from the SW of Beijing.

The present interpretation is reasonable because agricultural and fossil fuel emissions are usually associated with rural and urban areas, respectively. During haze periods, the atmospheric transport velocity was  $50-100 \text{ km d}^{-1}$ , as estimated both from the measured surface WS (Figure 1) and by a back-trajectory analysis (SI Figure S4). Under such stagnant weather conditions, local emissions from fossil combustion are expected to be important. In contrast, during clean days, strong winds brought cleaner air from agricultural areas to Beijing. Hence, the ambient NH<sub>3</sub> that formed NH<sub>4</sub><sup>+</sup> aerosols during haze periods in Beijing was sourced at the local, urban scale rather than at the regional scale.

In urban environments, vehicles equipped with three-way catalytic converters can be an important  $NH_3$  source.<sup>31</sup> Previous estimates indicate that in 2005 the total emission of  $NH_3$  from traffic sources was 1.8 kt  $NH_3$ –N yr<sup>-1</sup>, which is half of the amount from agricultural sources in Beijing.<sup>10</sup> The total number of vehicles registered in Beijing, however, has increased by 10% per year, suggesting that the emission of  $NH_3$  by traffic in Beijing during 2013 may have become comparable to that of agricultural emissions.

In addition to being emitted form automobiles, NH3 is emitted as "fuel NH<sub>3</sub>" from electrical generating units (EGUs) and as "NH<sub>3</sub> slip" from EGUs equipped with SCR and selective noncatalytic NO<sub>x</sub> reduction (SNCR) technologies.<sup>8</sup> According to a recent report from China's Ministry of Environmental Protection, 25 coal-fired power utilities in Beijing have installed NO<sub>x</sub> removal systems. Of these utilities, 16 are controlled through an SCR system (with a total capacity of approximately 3400 MW), and the remaining utilities (with a total capacity of approximately 2000 MW) combine SCR and SNCR. Although it is currently difficult to determine the NH<sub>3</sub> emissions from these sources in Beijing, the emissions are expected to be enormous due to the electricity demand and the fact that extra coal is consumed for residential heating in the winter. A recent finding in Shanghai also highlights the importance of industrial NH<sub>3</sub> emissions, rather than those from vehicles.<sup>6</sup>

The above fossil fuel-based  $NH_3$  emissions are important in urban areas where the abundant acidic compounds (HNO<sub>3</sub> and  $H_2SO_4$ ) can react with  $NH_3$  to form fine particles, promoting serious haze pollution. Evidence can be found in the positive

relationship between  $NH_4^+$  and other fossil fuel-related species  $(SO_4^{2-}, NO_3^-, OC, SO_2, NO_x \text{ and } CO)$  in this study (SI Figure S6) and elsewhere.<sup>10,11</sup> Although  $NH_3$  is currently not included in emission control policies in China and is also unregulated in most other regions, the abatement of  $NH_3$  emissions has become an increasing concern to air quality managers, especially during periods of haze pollution.

The results reported here provide the first real isotopic evidence for fossil fuel sources of aerosol NH<sub>4</sub><sup>+</sup> during extreme haze episodes in urban Beijing. The use of stable isotopes of  $NH_4^+$  provides a powerful method to evaluate the relative contribution of fossil fuel-related and agricultural sources, allowing for better targeting of NH<sub>3</sub> reduction. Other nonagricultural area sources of NH<sub>3</sub> emissions include oceans, human waste, vegetation and soils,<sup>32</sup> which are unlikely major contributors during the winter at this location. Additional emissions from biomass/biofuel burning could also contribute, but intense biomass burning was not found based on moderate resolution imaging spectroradiometer (MODIS) fire/hotspot observation (SI Figure S7). We did not include indoor biofuel burning in this study due to the paucity of signature data, a point that should be considered in the interpretation of our results. Other potential limitations in this study include the assumptions that the  $\delta^{15}$ N values of the endmembers in China are similar to those in the U.S. and that the parameters used in N fractionation were well constrained. To further reduce the uncertainty in the calculation of initial  $\delta^{15}$ N-NH<sub>3</sub> values, additional field and laboratory experiments are required to adequately characterize the endmember signatures and the subsequent fractionation process under different air pollution and meteorological conditions.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b00634.

Figures S1–S7 illustrate haze pollution events, modeling validation, source apportionment, potential source regions, backward trajectory, various component correlations and fire/hotspot archive, and text details the N fractionation process, with accompanying references (PDF)

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#### **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; Q.Z. and B.Z. performed the modeling experiments; 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.

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