



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



Yuepeng Pan^{a,*}, Shili Tian^a, Dongwei Liu^b, Yunting Fang^{b,**}, Xiaying Zhu^c, Meng Gao^d, Jian Gao^e, Greg Michalski^f, Yuesi Wang^a

^a State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC), Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

^b CAS Key Laboratory of Forest Ecology and Management, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang, Liaoning 110164, China

^c National Climate Center, China Meteorological Administration, Beijing 100081, China

^d John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, United States

^e State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

^f Department of Chemistry, Department of Earth, Atmospheric, and Planetary Sciences, Purdue University, 560 Oval Drive, West Lafayette, IN 47907, United States

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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 $+12.0\text{‰}$) 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.

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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. ($2.61\% \text{ yr}^{-1}$), the European Union (1.83%

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* Corresponding author.

** Corresponding author.

E-mail addresses: panyuepeng@mail.iap.ac.cn (Y. Pan), fangyt@iae.ac.cn (Y. Fang).

yr⁻¹), and China (2.27% yr⁻¹) between 2002 and 2013 (Warner et al., 2017). Further evidence has suggested that controlling NH₃ 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 NH₃ emissions without confirming and quantifying the major sources of NH₃ (Liu et al., 2008).

One approach that can help quantify the sources of ambient NH₃ concentrations is based on the stable isotopic composition of NH₃ (δ¹⁵N-NH₃) for various endmembers (Felix et al., 2013). However, isotope-based source apportionment of aerosol NH₄⁺ is challenging because the δ¹⁵N values of NH₄⁺ may differ from the precursor NH₃ (Fukuzaki and Hayasaka, 2009; Kawashima and Kurahashi, 2011). The difference in isotopic signals between NH_x (NH_x = NH₄⁺ and NH₃) depends on equilibrium isotopic enrichment factors and the distribution of NH₄⁺/NH₃ (Heaton et al., 1997; Li et al., 2012; Savard et al., 2017). When NH₃ is in deficit (e.g., in the marine atmosphere), the aerosols collected are close to acidic, recycling and fractionation between NH₃ and NH₄⁺ are unlikely, and hence, the δ¹⁵N values of NH₄⁺ reflect their NH₃ sources (Jickells et al., 2003). When NH₃ is in excess (e.g., in the continental atmosphere), however, the aerosols are well neutralized, and the δ¹⁵N values of NH₄⁺ tend to be higher than their precursor NH₃ due to isotopic fractionation. For the latter scenario, we proposed a method of quantitatively estimating the sources of NH₄⁺ after accounting for nitrogen isotopic exchange between NH₃ and NH₄⁺ (Pan et al., 2016). In that case study, the δ¹⁵N value of the initial NH₃ 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 NH₃ during the extreme haze events in early 2013. That study provides a starting point from which to refine the sources of urban NH₄⁺. Without long-term observations covering different seasons, however, it is unclear whether fossil fuel emissions only dominated NH₃ sources during haze episodes that winter.

With these goals in mind, we conducted a long-term study of the isotopic composition of NH₄⁺ 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 δ¹⁵N value of NH₄⁺ in fine-mode aerosols. We determine the sources of aerosol NH₄⁺ 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 NH₃ is urgently needed to mitigate haze pollution on the North China Plain. In addition, the methods developed here clarify the source apportionment of aerosol NH₄⁺ under excess NH₃ 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 NH₄⁺ 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 NH₄⁺ 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 NH₄⁺ isotopic analysis. Thus, the isotopic data reported here represent the aerosol fine mode.

A new chemical method was used to determine the ¹⁵N natural abundance (δ¹⁵N) for NH₄⁺ (Liu et al., 2014). In brief, the method is based on the isotopic analysis of nitrous oxide (N₂O). NH₄⁺ in the filter extract was initially oxidized to nitrite (NO₂⁻) by hypobromite (BrO⁻), and NO₂⁻ was then quantitatively converted into N₂O by hydroxylamine (NH₂OH) under strongly acidic conditions. The produced N₂O 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 δ¹⁵N values are reported in parts per thousand relative to the standard (atmospheric N₂) as follows:

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

Three international reference standards (IAEA N1, USGS25 and USGS26) were used for the calibration to air N₂, the accepted international standard for N isotopes. The typical analysis size was 4 ml and produced 60 nmol N₂O, with a δ¹⁵N standard deviation of less than 0.3‰ and often less than 0.1‰ based on replicates (n = 3–5).

2.2. Prediction of δ¹⁵N-NH₃ gas from aerosol δ¹⁵N-NH₄⁺

During the campaign, NH₄⁺ was predominantly present in the fine fraction for all the samples, constituting 89% of the total NH₄⁺. We calculated the acid status of the fine aerosols using the equivalent ratio of NH₄⁺ to the sum of SO₄²⁻ and NO₃⁻ 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 NH₃. Nitrogen fractionation may occur under these conditions, with excess NH₃ remaining in the atmosphere. To circumvent this problem, the δ¹⁵N values of the initial NH₃ were calculated using an isotopic mass-balance model in a well-mixed closed system, as follows:

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

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