Source apportionment of atmospheric ammonia before, during, and after the 2014 APEC summit in Beijing using stable nitrogen isotope signatures

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Abstract. Stable nitrogen isotope composition (δ^{15}N) offers new opportunities to address the long-standing and ongoing controversy regarding the origins of ambient ammonia (NH_3), a vital precursor of $PM_{2.5}$ inorganic components, in the urban atmosphere. In this study, the δ^{15}N values of NH_3 samples collected from various sources were constrained using a novel and robust chemical method coupled with standard elemental analysis procedures. Independent of the wide variation in mass concentrations (ranging from 33 (vehicle) to over 6000 (human excreta) µg m^{-3}), different NH_3 sources have generally different δ^{15}N values (ranging from -52.0 to -9.6‰). Significantly high δ^{15}N values are seen as a characteristic feature of all vehicle-derived NH_3 samples (-14.2±2.8‰), which can be distinguished from other sources emitted at environmental temperature (-29.1±1.7, -37.8±3.6, and -50.0±1.8‰ for livestock, waste, and fertilizer, respectively).

The isotope δ^{15}N signatures for a range of NH_3 emission sources were used to evaluate the contributions of the different sources within measured ambient NH_3 in Beijing, using an isotope mixing model (IsoSource). The method was used to quantify the sources of ambient NH_3 before, during and after the 2014 Asia-Pacific Economic Cooperation (APEC) summit, when a set of stringent air quality control measures were implemented. Results show that the average NH_3 concentrations (the overall contributions of traffic, waste, livestock, and fertilizer) during the three periods were 9.1 (20.3, 28.3,

23.6, and 27.7%), 7.3 (8.8, 24.9, 14.3, and 52.0%), and 12.7 (29.4, 23.6, 31.7, and 15.4%) μg m^{-3}, respectively, representing a 20.0% decrease first and then a 74.5% increase in overall NH$_3$ mass concentrations. During (after) the summit, the contributions of traffic, waste, livestock, and fertilizer decreased (increased) by 56.7 (234.2), 12.0 (-5.0), 39.4 (120.8), and -87.7% (-70.5%) when compared with periods before (during) the summit, respectively, signifying that future NH$_3$ control efforts in megacities like Beijing should prioritize traffic sector as well as livestock breeding. The results show that isotope ratio measurements of NH$_3$ to be a valuable tool to quantify the atmospheric sources of NH$_3$ in urban atmospheres.

1 Introduction

For more than a century, the Haber-Bosch process has been meeting the Earth's increasing demand for grain and protein through nitrogen fertilizer (Erisman et al., 2008; Sutton et al., 2011). But unintentionally, increasing the application of ammonia (NH$_3$) and its derivatives as fertilizer has altered the composition of the atmosphere (Fowler et al., 2009). Fertilizer application merged with livestock production is the largest contributor of NH$_3$ emissions (Aneja et al., 2008) which cause cascading effects on human health, ecosystems, and climate (Galloway et al., 2003).

Whilst the overwhelming contribution of agricultural activities to the global and regional NH$_3$ budgets is well accepted, a large number of observations show that the ambient levels of NH$_3$ concentration in cities are comparable with, or even higher than those in rural areas (e.g., Cao et al., 2009; Meng et al., 2011; Singh and Kulshrestha, 2014; Zbieranowski and Aherne, 2012). Given that the atmospheric behavior of NH$_3$ is characterized by a short lifetime (1-5 days or less) (Warneck, 1999), low transport height, and relatively high dry deposition velocity (Asman and van Jaarsveld, 1992), high rural NH$_3$ emissions do not generally influence urban areas strongly in the gaseous phase unless reacting with acidic gases locally to form particulate NH$_4^+$ (Flechard et al., 2013). Therefore, other non-agricultural sources must exist in urban areas (Chang, 2014; Sutton et al., 2000). Some authors argue that gasoline-powered vehicles equipped with three-way catalytic converters (TWCs) and diesel-powered vehicles fitted with the selective catalytic reduction system (SCRs) are a major contributor of non-agricultural NH$_3$ (Burgard et al., 2006; Liu et al., 2014c; Perrino et al., 2002). In the UK, for example, it is estimated that 15% of the national NH$_3$ emissions originate from non-agricultural activities (Sutton et al., 2000), and 5-6% of the

total NH_3 emissions in the U.S are derived from vehicles, with almost all the remaining NH_3 coming from

60 agricultural processes (Kean et al., 2009). Based on a "bottom-up" methodology, a city-specific

non-agricultural NH_3 emission inventory for 113 Chinese cities was recently established (Chang, 2014),

in which traffic (32.2%) was identified as the largest NH_3 emission source. At the global scale,

non-agricultural NH_3 emissions are one or two orders of magnitude smaller than the gross flux of gaseous

NH_3 between the Earth's surface and the atmosphere, which totals more than 50 Tg y^{-1} (Schlesinger and

65 Hartley, 1992). Non-agricultural activities, however, are highly concentrated in urban areas and,

therefore, could be supposed to be significant sources of NH_3 in cities (Chang et al., 2012). Given the

important role of urban NH_3 emissions to form $PM_{2.5}$, NH_3 emission reduction has been regarded as the

key to curb severe haze pollution in Chinese mega-cities (Ye et al., 2011; Wang et al., 2011; Wang et

al., 2013).

70 Although isotopic techniques have been extensively accepted as a useful tool for source apportionment

of gases and PM (e.g., Cao et al., 2011; Felix et al., 2012; Liu et al., 2014b; Rudolph et al., 1997; Wang

et al., 2016; Xiao et al., 2012; Xiao et al., 2015; Xiao and Liu, 2002), there have been few studies to

date in terms of directly observing or quantifying the contribution of non-agricultural NH_3 in the

atmosphere (Felix et al., 2014; Liu et al., 2008). Greater scientific attention and regulatory efforts have

75 been giving to nitrogen oxides ($NO_x=NO+NO_2$) (Felix et al., 2012; Michalski et al., 2014; Walters and

Michalski, 2015; Walters et al., 2016; Walters et al., 2015) and sulfur dioxide (SO_2) (Barros et al., 2015;

Giesemann et al., 1994; Habicht and Canfield, 1997; Zhelezinskaia et al., 2014). Also, the conventional

method for analyzing $\delta^{15}N$, using elemental analyzer (EA) combustion with isotope-ratio mass

spectrometry (IRMS), normally requires more than 20 μg N for a single solid sample, which poses a

80 considerable challenge for passive sampling devices (Skinner et al., 2006). To overcome this technical

restriction, a landmark paper was published by Felix et al. (2013), in which they tried to combine the

bromate (BrO^-) oxidation of NH_4^+ to NO_2^- with microbial denitrifier methods (bacteria converts NO_2^- to

N_2O) to permit the N isotopic analysis of low concentration NH_4^+ passive samples, featuring the high

throughput of sample mass and low toxicity of reagents. However, the microbial denitrifier they used

85 needs careful cultivation and maintenance, which is time-consuming and also may present a challenge

for many isotope laboratories. Recently, a novel and robust chemical method for $\delta^{15}N$-NH_4^+ at natural

abundance has been developed (Liu et al., 2014a), which has major advantages over previous

approaches: (i) substantially simplified preparation procedures and reduced preparation time particularly compared to the methods in which diffusion or distillation is involved since all reactions occur in the same vial and separation of NH_4^+ from solution is not required; and (ii) greater suitability for low volume samples including those with low N concentration, having a blank size of 0.6 to 2 nmol.

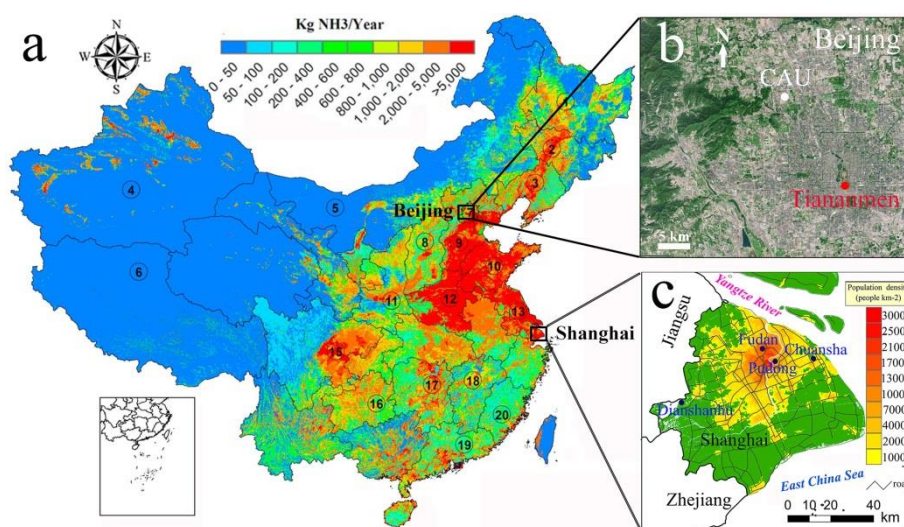
The 2014 Asia-Pacific Economic Cooperation (APEC) summit, another major international event after the 2008 Olympic Games, was hosted in Beijing on 3-12, November. To ensure good air quality and traffic flow during the APEC Summit, a set of stringent measures to control atmospheric pollutants, including regulating vehicle travel (restricting traffic based on the odd and even number plate rule), delaying winter heating (for a week), suspending coal-based industries and closing construction sites, were implemented in Beijing and its neighboring provinces over a month before and during the APEC summit (Chen et al., 2015; Li et al., 2015a; Tang et al., 2015; Xu et al., 2015b). This provided a unique city-wide experiment to isotopically examine the response of various NH_3 sources to such comprehensive and intensive mitigation efforts. In the present study, the isotopic signatures of various NH_3 sources in China were determined for the first time. Moreover, the ambient NH_3 concentrations and their isotopic compositions were investigated before, during and after the APEC control period in Beijing. Based on the isotopic signatures of major sources we developed, a stable isotope mixing model was used to quantify the contributions of each NH_3 source so as to examine the effect of the control measures.

2 Methodology

2.1 Ambient NH_3 Monitoring

The Adapted Low-Cost Passive High Absorption (ALPHA) samplers (Centre for Ecology and Hydrology, Edinburgh, UK), one of the most widely recognized passive sampling devices (PSDs) (Puchalski et al., 2011; Tang et al., 2001; Xu et al., 2015a), were used to collect ambient NH_3 in this study. The ALPHA sampler is a circular polyethylene vial (26 mm height, 27 mm diameter) with one open end. The vial contains a position for a 25 mm phosphorous acid-impregnated filter and a PTFE membrane for gaseous NH_3 diffusion. In the current study, triplicate ALPHA filters were used to collect NH_3 for IRMS at weekends (from Saturday to Monday) or weekdays (from Monday to Saturday) on the roof of a 4-floor building (12 m a.g.l) in the campus of the China Agricultural University (CAU),

Beijing (116.289 °E, 40.032 °N) before (18th-20th-25th-27th October-1st-3rd November), during (3rd-8th-10th-15th November), and after (15th-17th-22nd-24th-29th November) the APEC summit (normally at 8:00 local time). The site of the CAU campus represents a general urban background with relatively low-rise buildings in the surrounding area, ca. 16.3 km Northwest of Tiananmen Square (Fig. 1). In this

120   study, the three filters of one sampling event were combined for a single analysis. Hourly mass concentrations of gases (CO, SO_2, NO_x and O_3) and $PM_{2.5}$ in Beijing are averaged from the data obtained from the 14 state-controlled environmental monitoring stations across the city (http://datacenter.mep.gov.cn/).

125   **Figure 1**. (**a**) 1 km×1 km gridded NH_3 emission inventory in China in 2006 (modified from Huang et al., (2012). (**b**) Location of the sampling site (China Agricultural University or CAU) in this study and its spatial position relative to Tiananmen Square (Beijing urban center). (**c**) Atmospheric NH_3 monitoring network in Shanghai.

2.2 NH_3 Source Sampling

130   The Ogawa passive sampling device (Ogawa & Co., FL, USA) is another popular PSD that has been successfully applied in the U.S. (Butler et al., 2015; Puchalski et al., 2011) and China (Chang et al., 2015; Meng et al., 2011) to determine the time-integrated NH_3 concentrations. The Ogawa PSD is a double-sided passive diffusion sampler equipped with a diffusive end cap, followed by a stainless-steel screen, and a 14mm quartz filter impregnated with phosphoric acid by the manufacturer. In this study,

135   the Ogawa PSDs were used to collect NH_3 emitted from sources for isotopic analysis.

Six NH₃ emission sources were involved in this study, i.e., livestock (two pig sties), fertilizer volatilization (laboratory simulation of NH₃ volatilization from urea-fertilized soil), human excreta (septic tanks of a residential building and a teaching building), waste water (sewage water treatment plant), solid waste (municipal waste transfer stations in a residential community and an educational area), and vehicle (a heavily used urban tunnel) (Table 1 and SI Table S1). NH₃ emitted from fertilizer volatilization was collected in the laboratory of Fudan University. To minimize the mixture of ambient atmospheric NH_3/NH_4^+ (see Fig. 2 and SI Fig. S1 for two examples) and to examine the potential influence of the macro environment, non-laboratory samples were collected within a confined space in short periods (e.g., several hours) during both the warm (summer) and cold seasons (winter) between June 2014 and January 2015. Descriptions of the sampling processes are detailed in SI Table S1.

Figure 2. Field photos of a solid waste container in the solid waste transfer station we used for source sampling at Fudan University. Before sampling, an Ogawa passive sampler for NH₃ is attached on a plastic strip (1.5 m in length). The sampler is fitted into the container through the holes (shown on the right panel).

The ambient average NH₃ concentration was less than 6 μg m⁻³ (Chang et al., 2016), which was between 1 and 3 orders of magnitude smaller than all emission sources we investigated (Table 1). Therefore, the interference of ambient air to all source samples is not a major concern in our study. HONO has been measured in significant concentrations in the UK and interfered with measurements of HNO₃ by DELTA active samplers causing the instrument now to be coated with NaCl to avoid this interference with HNO₃ measurements. The Ogawa filters used for trapping NH₃ were impregnated with citric acid. Using a Discrete Auto Analyzer (Smartchem 200, AMS, Italy; the detection limit for NO_2^--N is 0.002 mg L⁻¹), we recently analyzed nearly 100 passive filter samples collected from our passive ammonia network in Shanghai (Fig. 1). No detectable nitrite was found for almost all these

160   samples (including samples collected from a busy road tunnel (Chang et al., 2016), which provides compelling evidence that passive collection of ammonia doesn't introduce interference of nitrite in this study.

In our pilot study, the sampling period of each source was optimized to avoid insufficiency of NH_3 absorption, but more importantly, to minimize potential effects of N isotope fractionation. Taking the

165   source of human excreta for example, the concentrations of NH_3 in the exhausts of 15 ceiling ducts from collecting septic tanks in 13 buildings with 6 functions (2809^{+5803}_{-2661} μg m^{-3}) were higher than those in ambient air by 3 orders of magnitude (Chang et al., 2015). Therefore, the insufficiency of NH_3 absorption is of no significant concern. However, the δ^{15}N-NH_3 values of daily samples varied widely (±10 per mil), suggesting that the isotope fractionation may occur during the process of

170   sampling/storage. After many tests by trial and error, we found that a sampling period of 2 hours could provide sufficient N-NH_3 as well as avoid potential fractionation. Another example is the on-road traffic source. The δ^{15}N-NH_3 values of weekly (-11.9‰; -11.2‰), semimonthly (-11.7‰; -12.5‰) and monthly samples (-12.0±1.8‰; n=4) in the exit of Handan tunnel were almost identical, suggesting that passive NH_3 collection is an effective approach for isotopic analysis procedures.

175   **2.3 Stable Isotope Analysis**

A newly developed chemical method for δ^{15}N-NH_4^+ of low NH_4^+ samples was used in the current study. The detailed analytical procedures are given elsewhere (Liu et al., 2014a). Briefly, this method is based on the isotopic analysis of N_2O, which is much less abundant in the atmosphere than N_2 and thus causes minimal atmospheric contamination. Filter samples were firstly soaked with ultra-pure water (18.2

180   MΩ.cm). Concentrations of NH_4^+ were then analyzed using an ion chromatographic system (883 Basic IC plus, Metrohm Co., Switzerland) equipped with a Metrosept C4/4.0 cation column. The eluent was 1.0 mM HNO_3 + 0.5 mM PDA. The detection limit for NH_4^+ was 0.0028 mg L^{-1}. After the measurement of the NH_4^+ concentration, NH_4^+ in every sample was initially oxidized to NO_2^- by hypobromite (BrO^-) in a vial. NO_2^- was then quantitatively converted into N_2O by hydroxylamine

185   (NH_2OH) under strongly acid conditions. The produced N_2O was analyzed by a purge and cryogenic trap system (Gilson GX-271, IsoPrime Ltd., Cheadle Hulme, UK) coupled to an IRMS (PT-IRMS)

(IsoPrime 100, IsoPrime Ltd., Cheadle Hulme, UK) at the *Stable Isotope Ecology Laboratory of Institute of Applied Ecology, Chinese Academy of Sciences*.

Isotope ratio values are reported in parts per thousand relative to atmospheric N_2 as follows:

190
$$\delta^{15}N\left(‰\right)=\frac{\left(^{15}N/^{14}N\right)_{sample} - (^{15}N/^{14}N)_{N_2}}{\left(^{15}N/^{14}N\right)_{N_2}}\times1000 \quad (1)$$

Three international NH_4^+ standards (IAEA N1, USGS 25, and USGS26 with $\delta^{15}N$ values of +0.4‰, -30.4‰ and +53.7‰, respectively) were used to correct for the reagent blank and drift during isotope analysis of the produced N_2O. The standard deviation of $\delta^{15}N$ measurements is less than 0.3‰. Moreover, to enhance our confidence in the results determined by the PT-IRMS method, the $\delta^{15}N$
195 values of fertilizer-, vehicle-, human excreta-, and solid waste-derived NH_3 were also examined by the EA-IRMS method at the *Shanghai Institutes of Life Sciences*, *Chinese Academy of Sciences* (SI Text S1).

2.4 Isotope Mixing Model

Stable isotope mixing models offer a statistical framework to estimate the relative contributions of
200 multiple sources to a mixture, such as food-web structure, plant water use, air pollution, and many other environments (Cole et al., 2011; Dai et al., 2015; Jautzy et al., 2015; Wang et al., 2016). A common problem, however, is having too many possible sources relative to isotopes to allow unique linear mixing solutions based on mass balance equations. To this end, Phillips and Gregg (2003) developed the model IsoSource, which solves iteratively for feasible mixing solutions, and has been
205 well tested in numerous studies (e.g., Cole et al., 2011; Dai et al., 2015; Jautzy et al., 2015; Wang et al., 2016). The model does not generate exact values for proportional contributions of each source, but instead provides a range of possible contributions or feasible solutions. The IsoSource addresses every possible combination of source proportions (summing to 100%) incrementally (e.g., 1%), then calculates the predicted isotope value for each combination using linear mass-balance equations. These
210 predicted values are then examined to determine which ones fall within some tolerance range (typically 0.1‰) of the observed consumer isotope value, and all of these feasible solutions are recorded. The IsoSource model is available at https://www.epa.gov/eco-research/stable-isotope-mixing-models-estimating-source-proportions.

Considering the large number of possible sources for ambient NH_3, we use multiple lines of evidence

215 (prior information) to constrain the emission sources in the mixing model analysis: (1) there was no crop harvest activity in the North China Plain (NCP) during the APEC summit in Beijing. Besides, harvesting forests for fuelwood and timber has nearly disappeared in Beijing. Therefore, the contribution of biomass burning is considered minimal; (2) Beijing is 150 km inland from the Bohai Sea (the nearest sea) via Tianjin Municipality in the southeast. Therefore, marine source in Beijing can

220 be neglected; and (3) previous work indicated that miscellaneous NH_3 sources like pets and household products are minor NH_3 emissions in Beijing urban areas (Chang, 2014), which thus can be largely neglected.

In conclusion, ambient NH_3 in Beijing during our study period has been shown to be due to four main sources: livestock production, N-fertilizer application, on-road traffic emissions, and waste-derived

225 emissions. The $\delta^{15}N$ average values for these four NH_3 emission sources will be built and served as the baseline input to the IsoSource. For the traffic source, given that the relatively larger difference in terms of their $\delta^{15}N$ values in different seasons (see Table 1), the wintertime average value of $\delta^{15}N$ was used in this study because the APEC summit was held during winter. In brief, the N isotopic signatures for the sources of waste, livestock, traffic, and fertilizer are set as -37.8‰, -29.1‰, -16.5‰, and

230 -50.0‰, respectively (Table 1 and SI Table S1). The source increment and mass balance tolerance parameter values of 1% and 0.1‰, respectively, were applied. Model output files include all the feasible source combinations, with histograms and descriptive statistics on the distributions for each source. Results are expressed as box-and-whisker plots for these distributions.

3. Results and Discussion

235 **3.1 Isotopic Signatures of NH_3 Emission Sources**

Using N isotope as a tool to discriminate the contribution of various sources to ambient NH_3 concentration requires (i) well-established N isotopic compositions of NH_3 emission sources and (ii) well-constrained N isotope fractionation to allow separating different sources. In total of 44 NH_3 source samples in this study, $\delta^{15}N$ values and NH_3 concentrations of these samples ranged from -52.0 to -9.6‰,

240 and 33 to 6211 $\mu g\ m^{-3}$, respectively (all data are presented in SI Table S1). These NH_3 sources can be classified into four categories, i.e., fertilizer, livestock, traffic, and waste. For most sources, there was

no significant difference in terms of their δ^{15}N values in different seasons (Table 1), indicating the effectiveness of our sampling strategy. The work of Felix et al. (2013) addressed some of the same issues and we found and reported similar results for the range of δ^{15}N-NH$_3$ values (-56.1 to -2.2‰)

245 from major NH$_3$ emission sources (including livestock, marine, vehicle, and fertilizer sources) as those presented here. These two independent studies determining the δ^{15}N values of major NH$_3$ sources arrive at the same conclusion: NH$_3$ emitted from volatilized sources has relatively low δ^{15}N values, allowing them to be distinctly differentiated from NH$_3$ emitted from traffic sources that are characterized by relatively high δ^{15}N values.

250 **Table 1.** δ^{15}N-NH$_3$ values of ammonia sources, source location, and summer-winter comparison (mean $\pm$ SD).

Category	Sub-category	Location	Season	NH$_3$ conc.(μg m^{-3})	δ^{15}N-NH$_3$ (‰)	N
Livestock	pig	Shanghai pig farm	summer	1329.6±175.8	-30.3±1.3	3
			winter	586.6±113.2	-28.2±1.5	4
Traffic	on-road vehicle	Handan Tunnel	summer	85.2±6.2	-12.0±1.8	4
			winter	46.7±14.3	-16.5±1.1	4
Waste	solid waste	municipal waste transfer stations	summer	443.4±92.6	-31.1±1.0	4
			winter	315.0±48.5	-36.6±0.9	4
	wastewater	wastewater treatment plant	summer	246.3±9.3	-41.3±0.7	4
			winter	143.8±12.3	-40.7±1.1	4
	human excreta	septic tanks	summer	4578.4±1400.3	-38.4±0.9	4
			winter	4440.1±1288.6	-38.6±1.0	4
Fertilizer	urea	Fudan lab	/	396.3±199.9	-50.0±1.8	5

Road tunnels are excellent locations to provide emissions from a large number of vehicles mixed with SCRs and TWCs under 'real world conditions' (Liu et al., 2014c). Here we assume that the δ^{15}N-NH$_3$ values collected from a heavily used tunnel like the Handan tunnel (around 120000 vehicles passing per day; an average of 65.9 μg m^{-3} NH$_3$ or 12.4 times the levels of open environment (Chang et al., 2016) can be accepted as the isotopic signatures of vehicles in China. Nevertheless, we note the δ^{15}N-NH$_3$ values of vehicle exhausts that we collected from the Handan tunnel (-17.8 to -9.6‰; n=8)

are lower than the δ^{15}N-NH$_3$ values determined by Felix et al. (2013) in the Squirrel Hill Tunnel, Pittsburgh (-4.6‰ and -2.2‰; n=2). This Sino-US difference may be partially attributed to a higher usage of TWCs in the traffic in the US.

The δ^{15}N values of NH$_3$ from livestock (-31.7 to -27.1‰) and fertilizer (-52.0 to -47.6‰) that we measured are slightly lower than the range of δ^{15}N-NH$_3$ values collected monthly from two dairy barns (-28.5 to -22.8‰) and a cornfield treated with urea-ammonia-nitrate fertilizer (-48.0 to -36.3‰) by Felix et al. (2013). These ranges of δ^{15}N values are a function of the initial δ^{15}N values of animal waste and fertilizer and variations in the bacteria populations, as well as other factors (temperature, wind, pH etc.) that influence kinetic fractionation rates associated with NH$_3$ volatilization. Long-term (30 days) monitoring of δ^{15}N and NH$_3$ emissions of manure measured by Lee et al. (2011) indicated that the dynamics of N isotope fractionation may be complicating the usefulness of the isotope approach as a tool for estimating NH$_3$ emissions in field conditions. In this sense, the shorter sampling period in our work should reflect the essence of δ^{15}N values of livestock- and fertilizer-derived NH$_3$.

As a normal metabolic process, the release of NH$_3$ from human excreta has been well documented. However, most emission inventories involving human excreta have focused on pit latrines in rural areas of developing and middle income countries. In urban China, human excreta are typically stored in a three-grille septic tank under the building before disposal. After a series of anaerobic decomposition processes, a substantial amount of NH$_3$ will be generated and emitted through a ceiling duct. In the present study, the concentrations of NH$_3$ in the ceiling ducts (4509.3±1248.0 μg m^{-3}; n=8) outweigh those in the open air by 3 orders of magnitude, and the δ^{15}N-NH$_3$ values are seasonally consistent (-38.4±0.9‰ in summer and -38.6±1.0‰ in winter; Table 1), suggesting that human excreta may be an important and consistent source of NH$_3$ in urban areas. These data suggest that emissions of NH$_3$ from human excreta for an urban population of ~21 million people in Shanghai contribute 1386 Mg NH$_3$ annually to the atmosphere within the city, which corresponds to 11.4% of the total NH$_3$ emissions in the Shanghai urban areas (Chang et al., 2015). The δ^{15}N values of wastewater-originated NH$_3$ (-41.0±0.9‰; n=8) are close to that of human excreta and also show no seasonal variation. Sampling in a stable and closed physical environment may be responsible for such a small range of isotopic variation. However, although also sampled in a closed environment, the δ^{15}N values of municipal solid

waste demonstrate a much greater variation (-37.6 to -29.9‰), which may be due to the variable composition of solid waste.

3.2 Source Apportionment of Ambient NH$_3$ in Beijing

Hourly observations of major air pollutants (including PM$_{2.5}$, NO$_x$, CO, SO$_2$ and O$_3$) in Beijing are
290   show in SI Fig. S2. The meteorological differences (e.g., temperature and wind speed) for the three periods pre, during and post APEC are not significant, suggesting that emission reduction strategies implemented during the APEC summit were successful (SI Fig. S2). It should be noted that several control measures, i.e., closing factories within 200 km of the city center and stopping the entrance of out-of-city vehicles, had been undertaken in Beijing and its neighboring regions before the summit.
295   Therefore, the before-during comparison of some pollutants like SO$_2$ are not in stark contrast in terms of their mass concentration (SI Fig. S2). The evolution of ambient NH$_3$ mass concentrations measured at CAU shows a similar pattern with CO and NO$_x$ (SI Fig. S3). Before the opening of the summit (from 18th October to 3rd November), NH$_3$ concentrations averaged 9.9 μg m^{-3} and ranged from 6.9 to 11.0 μg m^{-3}. During the summit session (from 3rd to 15th November, the ending date of the summit is 13th November), this was reduced to 7.3 μg m^{-3} with a range of 5.8 to 8.6 μg m^{-3}. After the APEC summit
300   (from 15th to 29th November), the NH$_3$ concentration levels rebounded to an average of 12.7 μg m^{-3} (ranging from 10.7 to 17.7 μg m^{-3}). In other words, the NH$_3$ concentrations were reduced by 20.0% during the APEC summit compared with the period before it. Compared with the period after control, the concentrations were 74.5% lower than that during the summit (Table 2).

305   On the basis of the δ^{15}N values of NH$_3$ emission sources and ambient δ^{15}N-NH$_3$ samples (Table 2), the ranges (within 5 and 95 percentiles) of relative contribution fractions of each NH$_3$ source to the ambient atmosphere were modeled by the IsoSource and depicted in Fig. 3a-d. Of these, sources of traffic and fertilizer are better constrained than livestock and waste. This is because the δ^{15}N-NH$_3$ values of the ambient atmosphere are closer to the latter two. For example, after the APEC summit in
310   our study period, the δ^{15}N-NH$_3$ values of the ambient atmosphere averaged -30.7‰, which is very close to the isotopic signature of livestock (-29.1‰), thus leading to weaker constraint with 5 and 95 percentiles ranges from near 0 to 0.7 (Fig. 3).

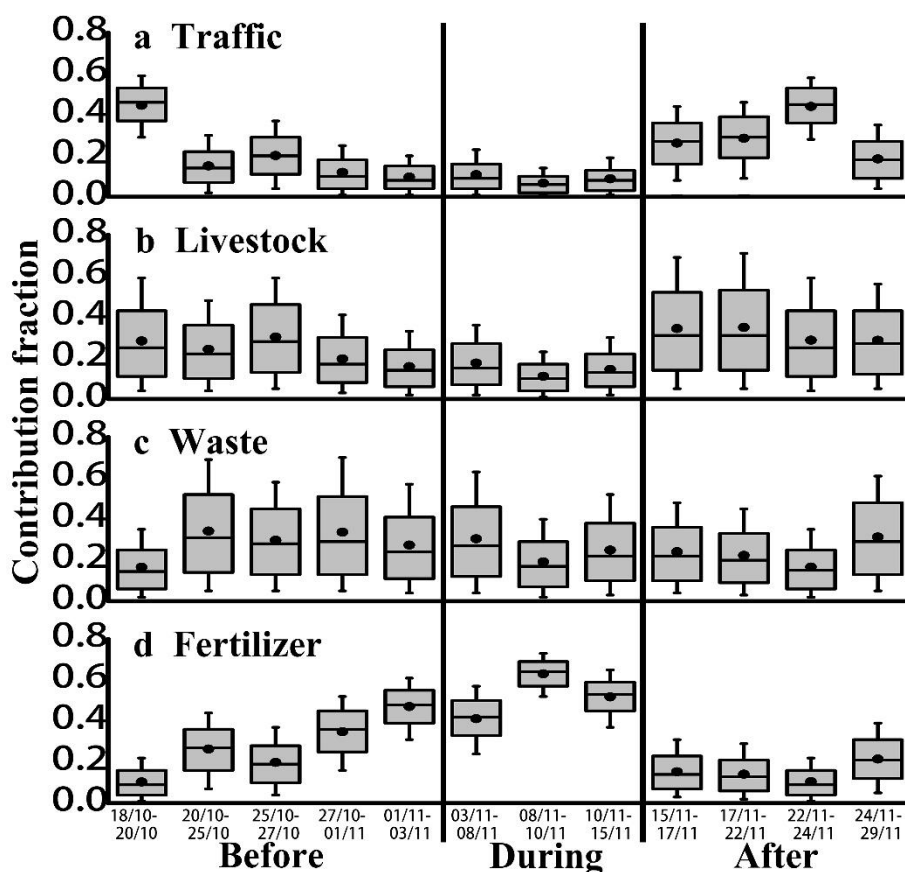



Figure 3. Time series of the box-whisker plots of the contribution fraction of ambient NH₃ from different sources estimated from the IsoSource model. The box boundaries represent the 25th and 75th percentile; the horizontal line is the median, and the whiskers mark the 10th and 90th percentiles. The dots denote the mean values of the distribution.

For each sample, information regarding the δ^{15}N value, the NH₃ concentration and its source contributions is listed in Table 2. Fig. 4 illustrates the overall source contribution proportions before, during and after the summit, in which traffic, waste, livestock, and fertilizer comprised 20.4, 25.9, 24.0, and 29.7% of the whole period (Table 2), respectively. Specifically, the contribution of traffic initially decreased by 56.7% and then doubled, and this represents the largest change among the four sources (Table 2). Considering the absolute contributions of different sources to ambient NH₃, these results show that traffic is the most sensitive source to the emission control measures. This result was expected since over half the vehicles in Beijing were banned from entering the city during the APEC summit (Note that before the summit, out-of-city vehicles had already been banned from entering Beijing). Based on the vehicle NH₃ emission factor obtained from real-world tunnel tests, Liu et al. (2014c) and Chang et al. (2016) recently reported that vehicles contribute 8.1% and 12.0% to total NH₃ emissions in

the Pearl River Delta region and Shanghai urban areas, respectively. With a total of 5.5 million vehicles
330 in 2014, the traffic fleet in Beijing was much more than other cities. Thus vehicle sources might contribute more than 20% of the total NH_3 to the air within Beijing.

Table 2. $\delta^{15}N$ values, NH_3 concentrations and source contributions for all samples collected before, during, and after the APEC summit in Beijing.

Sample ID	$\delta^{15}N$ (‰)	NH_3 conc. (μg m^{-3})	Absolute contribution of NH_3 conc. (μg m^{-3})				Relative contribution of NH_3 conc. (%)			
			Traffic	Waste	Livestock	Fertilizer	Traffic	Waste	Livestock	Fertilizer
Before-1	-27.1	11.0	2.0	3.4	3.1	2.4	44.6	16.6	28.3	10.4
Before-2	-35.7	8.9	1.3	3.1	2.2	2.4	15.1	34.2	24.3	26.4
Before-3	-33.3	10.2	2.1	3.0	3.1	2.0	20.2	29.7	30.2	19.9
Before-4	-37.8	8.6	1.0	2.9	1.7	3.0	12.0	33.6	19.6	34.8
Before-5	-40.1	6.9	0.7	1.9	1.1	3.3	9.7	27.4	15.8	47.1
During-1	-39.0	8.6	0.9	2.6	1.5	3.5	10.8	30.4	17.5	41.2
During-2	-43.1	5.8	0.4	1.1	0.6	3.7	6.7	19.2	11.1	63.1
During-3	-41.0	7.5	0.7	1.9	1.1	3.9	8.8	25.0	14.4	51.8
After-1	-31.1	11.6	3.0	2.8	4.0	1.8	26.2	24.1	34.4	15.3
After-2	-30.4	17.7	5.1	4.0	6.2	2.5	28.6	22.4	34.9	14.1
After-3	-27.2	10.7	4.7	1.8	3.1	1.1	44.1	16.7	28.7	10.5
After-4	-34.0	11.0	2.0	3.4	3.2	2.4	18.5	31.3	28.6	21.6
Overall	-35.0±5.4	9.9±3.1	2.0±1.6	2.7±0.8	2.6±1.6	2.7±0.8	20.4±13.1	25.9±6.2	24.0±8.1	29.7±17.7
Before	-34.8	9.1	1.4	2.9	2.2	2.6	20.3	28.3	23.6	27.7
During	-41.1	7.3	0.7	1.9	1.1	3.7	8.8	24.9	14.3	52.0
After	-30.7	12.7	3.7	3.0	4.1	1.9	29.4	23.6	31.7	15.4
Change (%) During *VS.* Before	17.9↓	20.0↓	53.8↓	34.7↓	51.8↓	42.2↑	56.7↓	12.0↓	39.4↓	87.7↑
Change (%) After *VS.* During	25.3↑	74.5↑	462.7↑	60.5↑	280.6↑	47.5↓	234.2↑	5.0↓	120.8↑	70.5↓

The waste-originated percentages in Fig. 3 and 4 remain fairly constant over the sampling period,
335 appearing to be a stable and important NH_3 contributor in Beijing. Compared with wastewater and solid water, NH_3 emissions from human excreta through *in situ* sceptic tank system are far from quantified. Based on an extensive measurement campaign, we estimated that the population of ~21 million people living in the urban areas of Shanghai annually emitted approximately 1386 Mg NH_3, which corresponds to over 11.4% of the total NH_3 emissions in the urban areas (Chang et al., 2015).
340 Non-agricultural sources-merged with waste and traffic NH_3 emissions-collectively account for nearly 50% of ambient NH_3 before and after the APEC summit, which cannot be explained by previous work

of emission inventories (e.g., Fu et al., 2013; Huang et al., 2011; Huang et al., 2012; Kang et al., 2016; Li et al., 2015b; Zhang et al., 2009; Zhang et al., 2010). Our results do not contradict a commonly held belief that agriculture is responsible for the vast majority (normally >90%) of total ammonia emissions

345   at a regional scale. However, the results show that within urban areas, non-agricultural sources are very important. A consequence of the new results is that measures to improve air quality in urban areas of China need to include measures to reduce both agricultural and non-agricultural sources of NH_3.

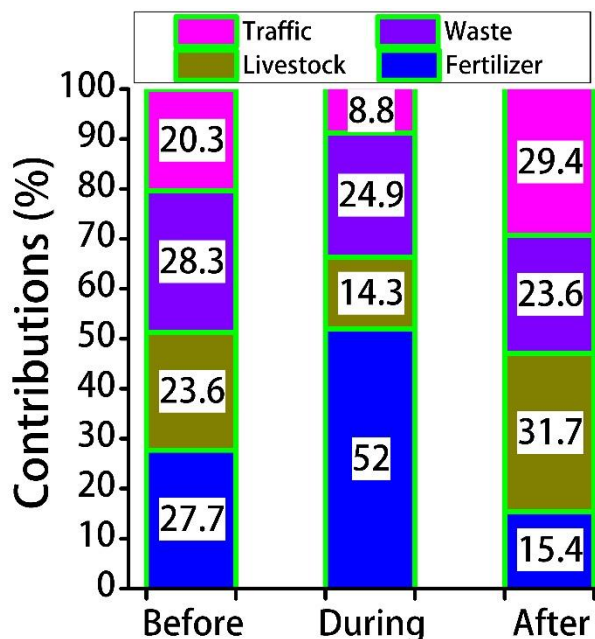



Figure 4. The overall contribution proportion (%) of the four sources to ambient NH_3 identified by the

350   IsoSource before, during, and after the APEC summit in Beijing.

The North China Plain (NCP) is one of the most intensive agricultural regions in China, enjoying a good reputation of "China's granary" (Ju et al., 2009). Situated on the northern edge of the NCP with mountains to the North and West, Beijing is a receptor of agricultural NH_3 from rural areas. During our study period, crops in the NCP had been harvested and thus fertilizer application would have been very

355   limited. However, our results show that fertilizer is the largest contributor, accounting for 29.7% throughout the sampling periods (Table 2). One explanation might be the prevalence of intensive urban agricultural production with high nitrogen fertilizer input in the suburban areas. Beijing's increase in land area from 4822 km² in 1956 to 16808 km² in 1958 led to the increased adoption of peri-urban agriculture. Such "suburban agriculture" contributed ~70% of non-staple food in Beijing, mainly

360   consisting of vegetables and milk, to be produced by the city itself in the 1960s and 1970s (Cai, 2003).

In the late 1990s, recognizing the importance of urban agriculture to sustainable urban development, Beijing's municipal government launched an official program encouraging multi-function urban agriculture in peri-urban areas by supporting the development of "agro-parks", which not only produce food but also attract tourism and are used as educational tools (Cai, 2003). One of the recent experiments in urban agriculture is the Modern Agricultural Science Demonstration Park in Xiaotangshan Town, Changping District (Cai, 2003). Today, Beijing is leading the way in using smart-city technologies to make urban farming more sustainable. In addition to suburban agriculture, there are 17 golf courses with 2280 ha. greens in Beijing; some of them are located at the urban areas (Chang, 2014). The turf grass of golf course typically needs 200-400 kg N ha^{-1} yr^{-1} as N fertilizer to achieve high performance (Wong et al., 1998; Wong et al., 2002; Zhang, 2002), which should be considered as an overlooked NH$_3$ contributor in Beijing.

3.3 Limitations and Outlook

The dataset reported in this study represents, to the best of our knowledge, the first attempt to partition urban atmospheric NH$_3$ sources. Considering the current nascent stage of partitioning NH$_3$ sources using stable isotope approach, there are several unsolved problems that could potentially undermine the above-mentioned results. One of our fundamental assumptions in this study is that the measured NH$_3$ was directly from NH$_3$ emission sources. In other words, we treated the measured NH$_3$ as the mixture of primary NH$_3$ sources without "gas-aerosol conversion" fractionation. But in fact, NH$_3$↔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$_4^+$ (Kawashima and Kurahashi, 2011; Yeatman et al., 2001). In Beijing, earlier studies confirmed that the atmosphere in Beijing was NH$_3$-limited, suggesting that acidic gases could not be fully neutralized to form ammonium salts (Ianniello et al., 2010; Wang et al., 2016). Therefore, ammonium salts had much less opportunity to volatilize to NH$_3$ to exert substantial isotopic effect through NH$_3$↔NH$_4^+$ equilibrium. Still, it is critical to develop a controlled laboratory system to fundamentally understand the characteristics and mechanisms of N isotope fractionations during the process of NH$_3$ transformation (Li et al., 2012).

Several additional factors could introduce uncertainty in the solutions of isotope mixing model. Given the complexity of urban NH$_3$ sources, no definitive solution exists in a linear mixing model with one

isotope system tracer ($\delta^{15}N$) in the current study. Recommended future studies should include the
combinations of different types of isotope ratio measurements and the adoption of more sophisticated
Bayesian mixing models. The isotopic signature of sources like on-road traffic still remains uncertain.
Some may argue that since NH_3 (also NO_x) is known to be a component of vehicle-emitted exhaust,
why not collect vehicle-emitted NH_3 directly from the tailpipes. To our knowledge the $\delta^{15}N$ of
vehicle-emitted NH_3 has not previously been assessed. The tunnel test has a unique advantage in
measuring the overall isotopic signatures of vehicle-emitted pollutants. We believe that the $\delta^{15}N$-NH_3
values of the samples collected from Handan tunnel in this study are representative as the isotopic
signatures of vehicles in China.

Despite the potential limitations in this study, given the importance of NH_3 to $PM_{2.5}$ formation, this
work can be expected to enrich the discussion on the methodologies (including stable isotope analysis)
in terms of identifying the largest NH_3 sources in urban atmosphere where policy efforts relating to
emissions abatement can be directed to deliver the largest impact.

4. Conclusions

Firstly, we establish a pool of isotopic signatures ($\delta^{15}N$-NH_3) for the major NH_3 emission sources in
China. The $\delta^{15}N$-NH_3 source inventory confirms that NH_3 emitted from on-road traffic has much higher
$\delta^{15}N$ values (-14.2±2.8‰), allowing them to be differentiated from other sources, such as livestock
(-29.1±1.7‰), waste (-37.8±3.6‰), and fertilizer (-50.0±1.8‰).

Secondly, we demonstrated that the isotopic source signatures of NH_3 represent an emerging tool for
partitioning NH_3 sources. Taking advantage of the implementation of stringent air quality control
measures during the APEC summit in Beijing, the IsoSource modeling results indicate that the overall
contribution of traffic, waste, livestock, and fertilizer to ambient NH_3 mass concentrations is 20.4%,
25.9%, 24.0%, and 29.7%, respectively, in which traffic is the most sensitive to control measures. Our
results clearly show that non-agricultural sources (traffic and waste) of NH_3 are of critical importance
in megacities like Beijing. Therefore, in addition to current SO_2 and NO_x controls, China also needs to
allocate more scientific, technical, and legal resources on controlling non-agricultural NH_3 emissions in
the future.

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