



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

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15 **Abstract.** Stable nitrogen isotope composition ($\delta^{15}\text{N}$) offers new opportunities to address the long-standing and ongoing controversy regarding the origins of ambient ammonia (NH_3), a vital precursor of $\text{PM}_{2.5}$ inorganic components, in the urban atmosphere. In this study, the $\delta^{15}\text{N}$ 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
20 concentrations (ranging from 33 (vehicle) to over 6000 (human excreta) $\mu\text{g m}^{-3}$), different NH_3 sources have generally different $\delta^{15}\text{N}$ values (ranging from -52.0 to -9.6‰). Significantly high $\delta^{15}\text{N}$ values are seen as a characteristic feature of all vehicle-derived NH_3 samples ($-14.2\pm 2.8\text{‰}$), which can be distinguished from other sources emitted at environmental temperature (-29.1 ± 1.7 , -37.8 ± 3.6 , and $-50.0\pm 1.8\text{‰}$ for livestock, waste, and fertilizer, respectively).

25 The isotope $\delta^{15}\text{N}$ 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 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
30 fertilizer) during the three periods were 9.1 (15.1, 31.2, 23.7, and 30.0%), 7.3 (8.8, 24.9, 14.3, and



52.0%), and 12.7 (29.4, 23.6, 31.7, and 15.4%) $\mu\text{g m}^{-3}$, 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 58.7 (234.2), 0.9 (-5.0), 41.0 (120.8), and -87.6% (-70.5%) when compared with periods before (during) the summit, 35 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 40 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).

45 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 50 relatively high dry deposition velocity (Asman and van Jaarsveld, 1992), high rural NH_3 emissions do not generally influence extensive 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 55 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 agricultural processes (Kean et al., 2009). Based on a “bottom-up” methodology, a city-specific
60 non-agricultural NH₃ emission inventory for 113 Chinese cities was recently established (Chang, 2014),
in which traffic (32.2%) was identified as the largest NH₃ emission source. At the global scale,
non-agricultural NH₃ emissions are one or two orders of magnitude smaller than the gross flux of gaseous
NH₃ between the Earth’s surface and the atmosphere, which totals more than 50 Tg y⁻¹ (Schlesinger and
Hartley, 1992). Non-agricultural activities, however, are highly concentrated in urban areas and,
65 therefore, could be supposed to be significant sources of NH₃ in cities (Chang et al., 2012). Given the
important role of urban NH₃ emissions to form PM_{2.5}, NH₃ 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).

Although isotopic techniques have been extensively accepted as a useful tool for source apportionment
70 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 NH₃ in the
atmosphere (Felix et al., 2014; Liu et al., 2008). Greater scientific attention and regulatory efforts have
been giving to nitrogen oxides (NO_x=NO+NO₂) (Felix et al., 2012; Michalski et al., 2014; Walters and
75 Michalski, 2015; Walters et al., 2016; Walters et al., 2015) and sulfur dioxide (SO₂) (Barros et al., 2015;
Giesemann et al., 1994; Habicht and Canfield, 1997; Zhelezinskaia et al., 2014). Also, the conventional
method for analyzing δ¹⁵N, 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
considerable challenge for passive sampling devices (Skinner et al., 2006). To overcome this technical
80 restriction, a landmark paper was published by Felix et al. (2013), in which they tried to combine the
bromate (BrO⁻) oxidation of NH₄⁺ to NO₂⁻ with microbial denitrifier methods (bacteria converts NO₂⁻
to N₂O) to permit the N isotopic analysis of low concentration NH₄⁺ passive samples, featuring the high
throughput of sample mass and low toxicity of reagents. However, the microbial denitrifier they used
needs careful cultivation and maintenance, which is time-consuming and also may present a challenge
85 for many isotope laboratories. Recently, a novel and robust chemical method for δ¹⁵N-NH₄⁺ 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
90 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),
95 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
100 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.

105 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
110 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),
115 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 study, the three filters of one sampling event were combined for a single analysis. Hourly mass concentrations of gases (CO, SO₂, NO_x and O₃) 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/).

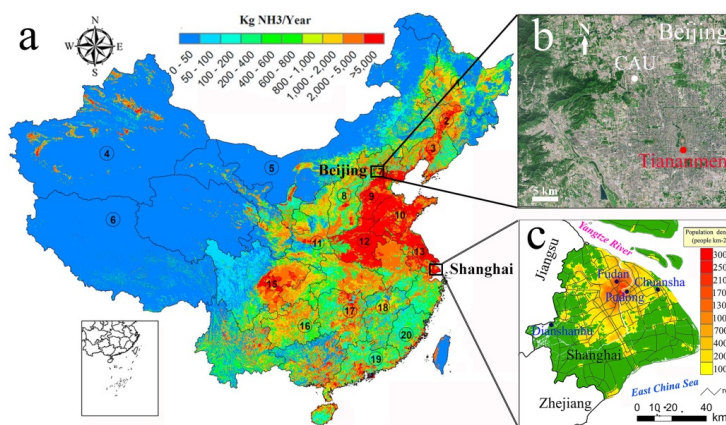


Figure 1. (a) 1 km×1 km gridded NH₃ emission inventory in China in 2006 (modified from Huang et al., (2012)). (b) Location of the sampling site (China Agricultural University or CAU) in this study and its spatial position relative to Tiananmen Square (Beijing urban center). (c) Atmospheric NH₃ monitoring network in Shanghai.

2.2 NH₃ Source Sampling

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 NH₃ 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, the Ogawa PSDs were used to collect NH₃ emitted from sources for isotopic analysis.



135 Six NH_3 emission sources were involved in this study, i.e., livestock (two pig sties), fertilizer
volatilization (laboratory simulation of NH_3 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). NH_3 emitted from fertilizer
140 volatilization was collected in the laboratory of Fudan University. To minimize the mixture of ambient
atmospheric $\text{NH}_3/\text{NH}_4^+$ (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.



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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 NH_3 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).

150 The ambient average NH_3 concentration was less than $6 \mu\text{g m}^{-3}$ (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
 HNO_3 by DELTA active samplers causing the instrument now to be coated with NaCl to avoid this
155 interference with HNO_3 measurements. The Ogawa filters used for trapping NH_3 were impregnated
with citric acid. Using a Discrete Auto Analyzer (Smartchem 200, AMS, Italy; the detection limit for
 $\text{NO}_2^- \text{-N}$ 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 ~~don't~~^{don'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 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 ($2809^{+5803}_{-2661} \mu\text{g m}^{-3}$) 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 $\delta^{15}\text{N-NH}_3$ values of daily samples varied widely (± 10 per mil), suggesting that the isotope fractionation may occur during the process of 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 $\delta^{15}\text{N-NH}_3$ values of weekly (-11.9‰; -11.2‰), semimonthly (-11.7‰; -12.5‰) and monthly samples ($-12.0 \pm 1.8\%$; $n=4$) in the exit of Handan tunnel were almost identical, suggesting that passive NH_3 collection is an effective approach for isotopic analysis procedures.

2.3 Stable Isotope Analysis

175 A newly developed chemical method for $\delta^{15}\text{N-NH}_4^+$ 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 $\text{M}\Omega\cdot\text{cm}$). 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 (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)

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(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 N₂ as follows:

$$\delta^{15}\text{N}(\text{‰}) = \frac{\left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{sample}} - \left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{N}_2}}{\left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{N}_2}} \times 1000 \quad (1)$$

190 Three international NH₄⁺ standards (IAEA N1, USGS 25, and USGS26 with δ¹⁵N 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 N₂O. The standard deviation of δ¹⁵N measurements is less than 0.3‰. Moreover, to enhance our confidence in the results determined by the PT-IRMS method, the δ¹⁵N values of fertilizer-, vehicle-, human excreta-, and solid waste-derived NH₃ were also examined by the
195 EA-IRMS method at the *Shanghai Institutes of Life Sciences, Chinese Academy of Sciences* (SI Text S1).

2.4 Isotope Mixing Model

A ~~stable~~ isotope mixing models offer a statistical framework to estimate the relative contributions of multiple sources to a mixture, such as food-web structure, plant water use, air pollution, and many
200 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 well tested in numerous studies (e.g., Cole et al., 2011; Dai et al., 2015; Jautzy et al., 2015; Wang et al.,
205 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 predicted values are then examined to determine which ones fall within some tolerance range (typically
210 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 (prior information) to constrain the emission sources in the mixing model analysis: (1) there was no
215 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 be neglected; and (3) previous work indicated that miscellaneous NH_3 sources like pets and household
220 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 emissions. The $\delta^{15}\text{N}$ average values for these four NH_3 emission sources will be built and served as the
225 baseline input to the IsoSource. For the traffic source, given that the relatively larger difference in terms of their $\delta^{15}\text{N}$ values in different seasons (see Table 1), the wintertime average value of $\delta^{15}\text{N}$ 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 -50.0‰, respectively (Table 1 and SI Table S1). The source increment and mass balance tolerance
230 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

3.1 Isotopic Signatures of NH_3 Emission Sources

235 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 44 NH_3 source samples in this study, $\delta^{15}\text{N}$ values and NH_3 concentrations of these samples ranged from -52.0 to -9.6‰, and 33 to 6211 $\mu\text{g m}^{-3}$, respectively (all data are presented in SI Table S1). These NH_3 sources can be
240 classified into four categories, i.e., fertilizer, livestock, traffic, and waste. For most sources, there was



no significant difference in terms of their $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N-NH}_3$ values (-56.1 to -2.2‰) from major NH_3 emission sources (including livestock, marine, vehicle, and fertilizer sources) as those presented here. These two independent studies determining the $\delta^{15}\text{N}$ values of major NH_3 sources arrive at the same conclusion: NH_3 emitted from volatilized sources has relatively low $\delta^{15}\text{N}$ values, allowing them to be distinctly differentiated from NH_3 emitted from traffic sources that are characterized by relatively high $\delta^{15}\text{N}$ values.

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

Category	Sub-category	Location	Season	NH_3 conc. ($\mu\text{g m}^{-3}$)	$\delta^{15}\text{N-NH}_3$ (‰)	N
Livestock	pig	Shanghai pig farm	summer	1329.6 \pm 175.8	-30.3 \pm 1.3	3
			winter	586.6 \pm 113.2	-28.2 \pm 1.5	4
Traffic	on-road vehicle	Handan Tunnel	summer	85.2 \pm 6.2	-12.0 \pm 1.8	4
			winter	46.7 \pm 14.3	-16.5 \pm 1.1	4
Waste	solid waste	municipal waste transfer stations	summer	443.4 \pm 92.6	-31.1 \pm 1.0	4
			winter	315.0 \pm 48.5	-36.6 \pm 0.9	4
	wastewater	wastewater treatment plant	summer	246.3 \pm 9.3	-41.3 \pm 0.7	4
			winter	143.8 \pm 12.3	-40.7 \pm 1.1	4
human excreta	septic tanks	summer	4578.4 \pm 1400.3	-38.4 \pm 0.9	4	
		winter	4440.1 \pm 1288.6	-38.6 \pm 1.0	4	
Fertilizer	urea	Fudan lab	/	396.3 \pm 199.9	-50.0 \pm 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 $\delta^{15}\text{N-NH}_3$ values collected from a heavily used tunnel like the Handan tunnel (around 120000 vehicles passing per day; an average of 65.9 $\mu\text{g m}^{-3}$ 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 $\delta^{15}\text{N-NH}_3$ values of vehicle exhausts that we collected from the Handan tunnel (-17.8 to -9.6‰; n=8)



are lower than the $\delta^{15}\text{N-NH}_3$ 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.

260 The $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N-NH}_3$ 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 $\delta^{15}\text{N}$ values are a function of the initial $\delta^{15}\text{N}$ values of animal waste and fertilizer and variations in the bacteria populations, as well as other factors (temperature, wind, pH
265 etc.) that influence kinetic fractionation rates associated with NH_3 volatilization. Long-term (30 days) monitoring of $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ values of livestock- and fertilizer-derived NH_3 .

270 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
275 present study, the concentrations of NH_3 in the ceiling ducts ($4509.3 \pm 1248.0 \mu\text{g m}^{-3}$; n=8) outweigh those in the open air by 3 orders of magnitude, and the $\delta^{15}\text{N-NH}_3$ values are seasonally consistent ($-38.4 \pm 0.9\text{‰}$ in summer and $-38.6 \pm 1.0\text{‰}$ 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
280 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 $\delta^{15}\text{N}$ values of wastewater-originated NH_3 ($-41.0 \pm 0.9\text{‰}$; 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 $\delta^{15}\text{N}$ values of municipal solid



285 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 NH₃ in Beijing

Hourly observations of major air pollutants (including PM_{2.5}, NO_x, CO, SO₂ and O₃) in Beijing are show in SI Fig. S2. The meteorological differences (e.g., temperature and wind speed) for the three
290 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. Therefore, the before-during comparison of some pollutants like SO₂ are not in stark contrast in terms
295 of their mass concentration (SI Fig. S2). The evolution of ambient NH₃ 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), NH₃ 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 NH₃ 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 NH₃ 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).

On the basis of the δ¹⁵N values of NH₃ emission sources and ambient δ¹⁵N-NH₃ samples (Table 2), the
305 ranges (within 5 and 95 percentiles) of relative contribution fractions of each NH₃ 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 δ¹⁵N-NH₃ values of the ambient atmosphere are closer to the latter two. For example, after the APEC summit in our study period, the δ¹⁵N-NH₃ values of the ambient atmosphere averaged -30.7‰, which is very close
310 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).

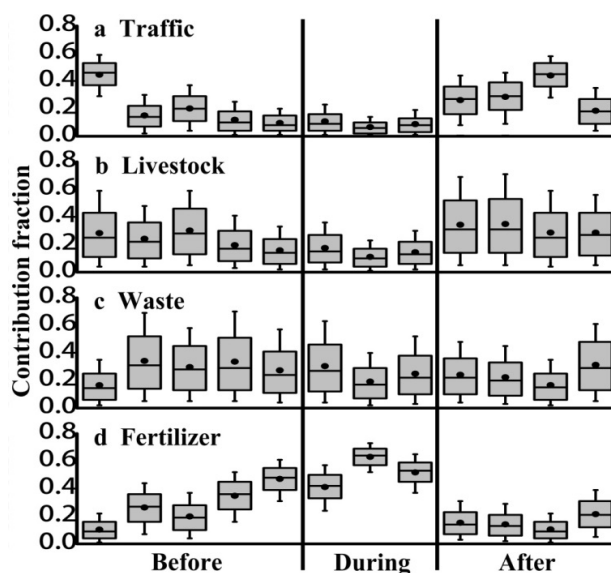


Figure 3. Time series of the box-whisker plots of the contribution fraction of ambient NH_3 from different sources estimated from the IsoSource model. The box boundaries represent the 25th and 75th percentile; the horizontal line is the median, and the whiskers mark the 10th and 90th percentile. The dots denote the mean values of the distribution.

For each sample, information regarding the $\delta^{15}\text{N}$ value, the NH_3 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 18.3, 27.1, 24.0, and 30.6% of the whole period (Table 2), respectively. Specifically, the contribution of traffic initially decreased by 58.7% and then doubled, and this represents the largest change among the four sources (Table 2). Considering the absolute contributions of different sources to ambient NH_3 , 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 NH_3 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 NH_3 emissions in the Pearl River Delta region and Shanghai urban areas, respectively. With a total of 5.5 million vehicles in 2014, the traffic fleet in Beijing was far ahead of other cities. Thus vehicle sources might contribute more than 20% of the total NH_3 to the air within Beijing.



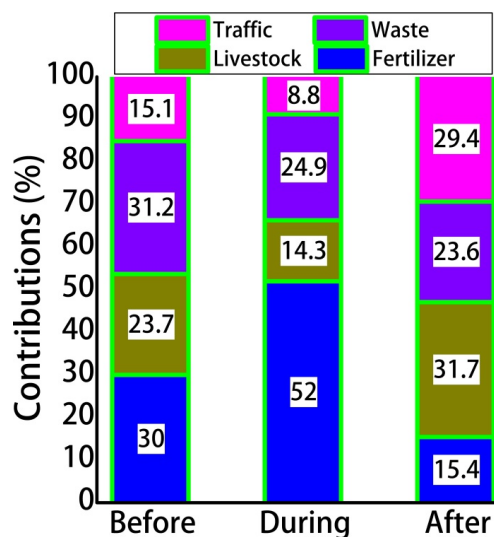
Table 2. $\delta^{15}\text{N}$ values, NH_3 concentrations and source contributions for all samples collected before, during, and after the APEC summit in Beijing.


Sample ID	$\delta^{15}\text{N}$ (‰)	NH_3 conc. ($\mu\text{g m}^{-3}$)	Absolute contribution of NH_3 conc. ($\mu\text{g m}^{-3}$)				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	18.5	31.3	28.6	21.6	
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	18.3±10.6	27.1±5.7	24.0±8.1	30.6±16.8	
Before	-34.8	9.1	1.4	2.9	2.2	2.6	15.1	31.2	23.7	30.0	
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↑	58.7↓	0.9↓	41.0↓	87.6↑
	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, 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* septic 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). 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 at a regional scale. However, the results show that within urban areas, non-agricultural sources are very



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

350 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
limited. However, our results show that fertilizer is the largest contributor, accounting for 30.6%
355 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 km^2 in 1956 to 16808 km^2 in 1958 led to the increased adoption of peri-urban
agriculture. Such “suburban agriculture” contributed ~70% of non-staple food in Beijing, mainly
consisting of vegetables and milk, to be produced by the city itself in the 1960s and 1970s (Cai, 2003).
360 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
365 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
370 considered as an overlooked NH₃ 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 NH₃ sources. Considering the current nascent stage of partitioning NH₃ sources
using stable isotope approach, there are several unsolved problems that could potentially undermine the
375 above-mentioned results. One of our fundamental assumptions in this study is that the measured NH₃
was directly from NH₃ emission sources. In other words, we treated the measured NH₃ as the mixture
of primary NH₃ sources without “gas-aerosol conversion” fractionation. But in fact, NH₃↔NH₄⁺
equilibrium will cause ¹⁴N to be preferentially associated with NH₃ and ¹⁵N to be enriched in NH₄⁺ of
PM due to the stronger associative strength of ¹⁵N than ¹⁴N in NH₄⁺ (Kawashima and Kurahashi, 2011;
380 Yeatman et al., 2001). In Beijing, earlier studies confirmed that the atmosphere in Beijing was
NH₃-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 NH₃ to exert substantial isotopic effect through NH₃↔NH₄⁺ equilibrium. Still, it is critical
to develop a controlled laboratory system to fundamentally understand the characteristics and
385 mechanisms of N isotope fractionations during the process of NH₃ transformation (Li et al., 2012).

Several additional factors could introduce uncertainty in the solutions of isotope mixing model. Given
the complexity of urban NH₃ sources, no definitive solution exists in a linear mixing model with one
isotope system tracer ($\delta^{15}\text{N}$) in the current study. Recommended future studies should include the
combinations of different types of isotope ratio measurements and the adoption of more sophisticated
390 Bayesian mixing models. ~~The isotopic signature of sources like on road traffic still remains uncertain.~~
~~Some may argue that since NH₃ (also NO_x) is known to be a component of vehicle emitted exhaust,~~



~~why not collect vehicle-emitted NH₃ directly from the tailpipes. To our knowledge the $\delta^{15}\text{N}$ of vehicle-emitted NH₃ has not previously been assessed. However, a recent research paper from Walters et al. (2015) addressing the $\delta^{15}\text{N}$ of vehicle-emitted NO_x may shed some light on this issue. In that paper, the $\delta^{15}\text{N}$ -values of NO_x emitted from 26 different vehicles ranged from -19.1‰ to +9.8‰, much higher than the variation of $\delta^{15}\text{N}$ -NH₃ collected from the Handan tunnel in our research. In road diesel Selective Catalytic Reduction (SCR) applications, a urea in water solution is used as the reduction agent. Urea is injected in the exhaust line and is decomposed over a catalyst to NH₃. In this case, the $\delta^{15}\text{N}$ values of vehicle-emitted NO_x and NH₃ can hardly be the same. However, as a direct product of NO reduction on the catalyst surface of TWCs ($2\text{NO} + 5\text{H}_2 \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O}$ and/or $2\text{NO} + 2\text{CO} + 3\text{H}_2 \rightarrow 2\text{NH}_3 + 2\text{CO}_2$), NH₃ emitted from light duty vehicle exhausts can be expected to have similar $\delta^{15}\text{N}$ -values to vehicle-emitted NO_x. In this regard, the tunnel test has a unique advantage in measuring the overall isotopic signatures of vehicle-emitted pollutants. Therefore, we believe that the $\delta^{15}\text{N}$ -NH₃ 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 NH₃ 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 NH₃ sources in urban atmosphere where policy efforts relating to emissions abatement can be directed to deliver the largest impact.

410 4. Conclusions

Firstly, we establish a pool of isotopic signatures ($\delta^{15}\text{N}$ -NH₃) for the major NH₃ emission sources in China. The $\delta^{15}\text{N}$ -NH₃ source inventory confirms that NH₃ emitted from on-road traffic has much higher $\delta^{15}\text{N}$ 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‰).

415 Secondly, we demonstrated that the isotopic source signatures of NH₃ represent an emerging tool for partitioning NH₃ 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 NH₃ mass concentrations is 18.3%,



420 27.1%, 24.0%, and 30.6%, 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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Reference

- 435 Aneja, V. P., Schlesinger, W. H., and Erisman, J. W.: Farming pollution, *Nat. Geosci.*, 1, 409-411, doi: 10.1038/ngeo236, 2008.
- Asman, W. A., and van Jaarsveld, H. A.: A variable-resolution transport model applied for NH_x in Europe, *Atmos. Environ.*, 26, 445-464, doi: 10.1016/0960-1686(92)90329-J, 1992.
- Barros, C., Pinho, P., Durão, R., Augusto, S., Máguas, C., Pereira, M. J., and Branquinho, C.:
440 Disentangling natural and anthropogenic sources of atmospheric sulfur in an industrial region using biomonitors. *Environ. Sci. Technol.*, 49, 2222-2229, doi: 10.1021/es505292t, 2015.
- Burgard, D. A., Bishop, G. A., and Stedman, D. H.: Remote sensing of ammonia and sulfur dioxide from on-road light duty vehicles, *Environ. Sci. Technol.*, 40, 7018-7022, doi: 10.1021/es061161r, 2006.
- Butler, T., Marino, R., Schwede, D., Howarth, R., Sparks, J., and Sparks, K.: Atmospheric ammonia
445 measurements at low concentration sites in the northeastern USA: Implications for total nitrogen



- deposition and comparison with CMAQ estimates, *Biogeochem.*, 122, 191-210, doi: 10.1007/s10533-014-0036-5, 2015.
- Cai, J.: Periurban agriculture development in China: a new approach in Xiaotangshan, Beijing, *Urban Agri. Mag.*, 9, 40-42, 2003.
- 450 Cao, J. J., Chow, J. C., Tao, J., Lee, S. C., Watson, J. G., Ho, K. F., Wang, G. H., Zhu, C. S., and Han, Y. M.: Stable carbon isotopes in aerosols from Chinese cities: Influence of fossil fuels, *Atmos. Environ.*, 45, 1359-1363, doi: 10.1016/j.atmosenv.2010.10.056, 2011.
- Cao, J. J., Zhang, T., Chow, J. C., Watson, J. G., Wu, F., and Li, H.: Characterization of atmospheric ammonia over Xi'an, China, *Aerosol Air Qual. Res.*, 9, 277-289, doi: 10.4209/aaqr.2008.10.0043, 455 2009.
- Chang, Y. H., Liu, X. J., Dore, A. J., and Li, K. H.: Stemming PM_{2.5} pollution in China: Re-evaluating the role of ammonia, aviation and non-exhaust road traffic emissions, *Environ. Sci. Technol.*, 46, 13035-13036, doi: 10.1021/es304806k, 2012.
- Chang, Y. H.: Non-agricultural ammonia emissions in urban China, *Atmos. Chem. Phys. Discuss.*, 14, 460 8495-8531, doi: 10.5194/acpd-14-8495-2014, 2014.
- Chang, Y. H., Deng, C. R., Dore, A. J., and Zhuang, G. S.: Human Excreta as a Stable and Important Source of Atmospheric Ammonia in the Megacity of Shanghai, *Plos One*, 10, e0144661, doi: 10.1371/journal.pone.0144661, 2015.
- Chang, Y. H., Zou, Z., Deng, C. R., Huang, K., Collett, J. L., Lin, J., and Zhuang, G. S.: The importance 465 of vehicle emissions as a source of atmospheric ammonia in the megacity of Shanghai, *Atmos. Chem. Phys.*, 16, 3577-3594, doi: 10.5194/acp-16-3577-2016, 2016.
- Chen, C., Sun, Y. L., Xu, W. Q., Du, W., Zhou, L. B., Han, T. T., Wang, Q. Q., Fu, P. Q., Wang, Z. F., Gao, Z. Z., Zhang, Q., and Worsnop, D. R.: Characteristics and sources of submicron aerosols above the urban canopy (260 m) in Beijing, China, during the 2014 APEC summit, *Atmos. Chem. Phys.*, 15, 470 12879-12895, doi: 10.5194/acp-15-12879-2015, 2015.
- Cole, J. J., Carpenter, S. R., Kitchell, J., Pace, M. L., Solomon, C. T., and Weidel, B.: Strong evidence for terrestrial support of zooplankton in small lakes based on stable isotopes of carbon, nitrogen, and hydrogen, *Proc. Natl. Acad. Sci.*, 108, 1975-1980, doi: 10.1073/pnas.1012807108, 2011.



- 475 Dai, Y., Zheng, X. J., Tang, L. S., and Li, Y.: Stable oxygen isotopes reveal distinct water use patterns of
two Haloxylon species in the Gurbantonggut Desert, *Plant Soil*, 389, 73-87, doi:
10.1007/s11104-014-2342-z, 2015.
- Erisman, J. W., Sutton, M. A., Galloway, J., Klimont, Z., and Winiwarer, W.: How a century of
ammonia synthesis changed the world, *Nat. Geosci.*, 1, 636-639, doi: 10.1038/ngeo325, 2008.
- 480 Felix, J. D., Elliott, E. M., Gish, T. J., Maghirang, R., Cambal, L., and Clougherty, J.: Examining the
transport of ammonia emissions across landscapes using nitrogen isotope ratios, *Atmos. Environ.*, 95,
563-570, doi: 10.1016/j.atmosenv.2014.06.061, 2014.
- Felix, J. D., Elliott, E. M., Gish, T. J., McConnell, L. L., and Shaw, S. L.: Characterizing the isotopic
composition of atmospheric ammonia emission sources using passive samplers and a combined
oxidation-bacterial denitrifier approach, *Rapid Commun. Mass Sp.*, 27, 2239-2246, doi:
485 10.1002/rcm.6679, 2013.
- Felix, J. D., Elliott, E. M., and Shaw, S. L.: Nitrogen isotopic composition of coal-fired power plant NO_x :
influence of emission controls and implications for global emission inventories, *Environ. Sci.
Technol.*, 46, 3528-3535, doi: 10.1021/es203355v, 2012.
- 490 Flechard, C., Massad, R. S., Loubet, B., Personne, E., Simpson, D., Bash, J., Cooter, E., Nemitz, E., and
Sutton, M. A.: Advances in understanding, models and parameterizations of biosphere-atmosphere
ammonia exchange, *Biogeosci.*, 10, 5183-5225, doi: 10.5194/bg-10-5183-2013, 2013.
- Fowler, D., Pilegaard, K., Sutton, M. A., Ambus, P., Raivonen, M., Duyzer, J., Simpson, D., Fagerli, H.,
Fuzzi, S., and Schjørring, J. K.: Atmospheric composition change: Ecosystems-atmosphere
interactions, *Atmos. Environ.*, 43, 5193-5267, doi: 10.1016/j.atmosenv.2009.07.068, 2009.
- 495 Fu, X., Wang, S., Zhao, B., Xing, J., Cheng, Z., Liu, H., and Hao, J.: Emission inventory of primary
pollutants and chemical speciation in 2010 for the Yangtze River Delta region, China, *Atmos.
Environ.*, 70, 39-50, doi: 10.1016/j.atmosenv.2012.12.034, 2013.
- Galloway, J. N., Aber, J. D., Erisman, J. W., Seitzinger, S. P., Howarth, R. W., Cowling, E. B., and
Cosby, B. J.: The nitrogen cascade, *Biosci.*, 53, 341-356, doi:
500 10.1641/0006-3568(2003)053[0341:TNC]2.0.CO;2, 2003.
- Giesemann, A., Jäger, H. J., Norman, A., Krouse, H., and Brand, W.: Online sulfur-isotope
determination using an elemental analyzer coupled to a mass spectrometer, *Anal. Chem.*, 66,
2816-2819, doi: 10.1021/ac00090a005, 1994.



- Habicht, K. S., and Canfield, D. E.: Sulfur isotope fractionation during bacterial sulfate reduction in
505 organic-rich sediments, *Geochim. Cosmochim. Ac.*, 61, 5351-5361, doi:
10.1016/S0016-7037(97)00311-6, 1997.
- Huang, C., Chen, C. H., Li, L., Cheng, Z., Wang, H. L., Huang, H. Y., Streets, D., Wang, Y., Zhang, G.,
and Chen, Y. R.: Emission inventory of anthropogenic air pollutants and VOC species in the Yangtze
River Delta region, China, *Atmos. Chem. Phys.*, 11, 4105-4120, doi: 10.5194/acp-11-4105-2011,
510 2011.
- Huang, X., Song, Y., Li, M., Li, J., Huo, Q., Cai, X., Zhu, T., Hu, M., and Zhang, H.: A high-resolution
ammonia emission inventory in China, *Global Biogeochem. Cy.*, 26, doi: 10.1029/2011GB004161,
2012.
- Ianniello, A., Spataro, F., Esposito, G., Allegrini, I., Rantica, E., Ancora, M. P., Hu, M., and Zhu, T.:
515 Occurrence of gas phase ammonia in the area of Beijing (China), *Atmos. Chem. Phys.*, 10, 9487-9503,
doi: 10.5194/acp-10-9487-2010, 2010.
- Jautzy, J. J., Ahad, J. M., Gobeil, C., Smirnov, A., Barst, B. D., and Savard, M.M.: Isotopic evidence for
oil sands petroleum coke in the Peace-Athabasca Delta, *Environ. Sci. Technol.*, 49, 12062-12070, doi:
10.1021/acs.est.5b03232, 2015.
- 520 Ju, X. T., Xing, G. X., Chen, X. P., Zhang, S. L., Zhang, L. J., Liu, X. J., Cui, Z. L., Yin, B., Christie,
P., Zhu, Z. L., and Zhang, F. S.: Reducing environmental risk by improving N management in
intensive Chinese agricultural systems, *Proc. Natl. Acad. Sci.*, 106, 3041-3046, doi:
10.1073/pnas.0813417106, 2009.
- Kang, Y., Liu, M., Song, Y., Huang, X., Yao, H., Cai, X., Zhang, H., Kang, L., Liu, X., and Yan, X.:
525 High-resolution ammonia emissions inventories in China from 1980 to 2012, *Atmos. Chem. Phys.*, 16,
2043-2058, doi: 10.5194/acp-16-2043-2016, 2016.
- Kawashima, H., and Kurahashi, T.: Inorganic ion and nitrogen isotopic compositions of atmospheric
aerosols at Yurihonjo, Japan: Implications for nitrogen sources, *Atmos. Environ.*, 45, 6309-6316, doi:
10.1016/j.atmosenv.2011.08.057, 2011.
- 530 Kean, A. J., Littlejohn, D., Ban-Weiss, G. A., Harley, R. A., Kirchstetter, T. W., and Lunden, M. M.:
Trends in on-road vehicle emissions of ammonia, *Atmos. Environ.*, 43, 1565-1570, doi:
10.1016/j.atmosenv.2008.09.085, 2009.



- Lee, C., Hristov, A. N., Cassidy, T., and Heyler, K.: Nitrogen isotope fractionation and origin of ammonia nitrogen volatilized from cattle manure in simulated storage, *Atmos.*, 2, 256-270, doi: 10.3390/atmos2030256, 2011.
- 535
- Li, J., Xie, S. D., Zeng, L. M., Li, Y., Li, Y. Q., and Wu, R. R.: Characterization of ambient volatile organic compounds and their sources in Beijing, before, during, and after Asia-Pacific Economic Cooperation China 2014, *Atmos. Chem. Phys.*, 15, 7945-7959, doi: 10.5194/acp-15-7945-2015, 2015.
- Li, L., Lollar, B. S., Li, H., Wortmann, U. G., and Lacrampe-Couloume, G.: Ammonium stability and nitrogen isotope fractionations for $\text{NH}_4^+ - \text{NH}_3(\text{aq}) - \text{NH}_3(\text{gas})$ systems at 20-70 °C and pH of 2-13: Applications to habitability and nitrogen cycling in low-temperature hydrothermal systems, *Geochim. Cosmochim. Ac.*, 84, 280-296, doi: 10.1016/j.gca.2012.01.040, 2012.
- 540
- Li, M., Zhang, Q., Kurokawa, J., Woo, J. H., He, K. B., Lu, Z., Ohara, T., Song, Y., Streets, D. G., Carmichael, G. R., Cheng, Y. F., Hong, C. P., Huo, H., Jiang, X. J., Kang, S. C., Liu, F., Su, H., and Zheng, B.: MIX: a mosaic Asian anthropogenic emission inventory for the MICS-Asia and the HTAP projects, *Atmos. Chem. Phys. Discuss.*, 15, 34813-34869, doi: 10.5194/acpd-15-34813-2015, 2015b.
- 545
- Liu, D., Fang, Y., Tu, Y., and Pan, Y.: Chemical method for nitrogen isotopic analysis of ammonium at natural abundance, *Anal. Chem.*, 86, 3787-3792, doi: 10.1021/ac403756u, 2014.
- Liu, J., Li, J., Zhang, Y., Liu, D., Ding, P., Shen, C., Shen, K., He, Q., Ding, X., Wang, X., Chen, D., Szidat, S., and Zhang, G.: Source apportionment using radiocarbon and organic tracers for $\text{PM}_{2.5}$ carbonaceous aerosols in Guangzhou, South China: Contrasting local- and regional-scale haze events, *Environ. Sci. Technol.*, 48, 12002-12011, doi: 10.1021/es503102w, 2014b.
- 550
- Liu, T., Wang, X., Wang, B., Ding, X., Deng, W., Lü, S., and Zhang, Y.: Emission factor of ammonia (NH_3) from on-road vehicles in China: Tunnel tests in urban Guangzhou, *Environ. Res. Lett.*, 9, 064027, doi: 10.1088/1748-9326/9/6/064027, 2014.
- 555
- Liu, X. Y., Xiao, H. Y., Liu, C. Q., Li, Y. Y., and Xiao, H. W.: Atmospheric transport of urban-derived NH_x : Evidence from nitrogen concentration and $\delta^{15}\text{N}$ in epilithic mosses at Guiyang, SW China, *Environ. Pollut.*, 156, 715-722, doi: 10.1016/j.envpol.2008.06.011, 2008.
- Meng, Z. Y., Lin, W. L., Jiang, X. M., Yan, P., Wang, Y., Zhang, Y. M., Jia, X., and Yu, X. L.: Characteristics of atmospheric ammonia over Beijing, China, *Atmos. Chem. Phys.*, 11, 6139-6151, doi: 10.5194/acp-11-6139-2011, 2011.
- 560



- Michalski, G., Bhattacharya, S. K., and Girsch, G.: NO_x cycle and the tropospheric ozone isotope anomaly: an experimental investigation, *Atmos. Chem. Phys.*, 14, 4935-4953, doi: 10.5194/acp-14-4935-2014, 2014.
- 565 Perrino, C., Catrambone, M., Di Bucchianico, A. D. M., and Allegrini, I.: Gaseous ammonia in the urban area of Rome, Italy and its relationship with traffic emissions, *Atmos. Environ.*, 36, 5385-5394, doi: 10.1016/S1352-2310(02)00469-7, 2002.
- Phillips, D. L., and Gregg, J. W.: Source partitioning using stable isotopes: Coping with too many sources, *Oecologia*, 136, 261-269, doi: 10.1007/s00442-003-1218-3, 2003.
- 570 Puchalski, M. A., Sather, M. E., Walker, J. T., Lehmann, C. M., Gay, D. A., Mathew, J., and Robarge, W. P.: Passive ammonia monitoring in the United States: Comparing three different sampling devices, *J. Environ. Monit.*, 13, 3156-3167, doi: 10.1039/C1EM10553A, 2011.
- Rudolph, J., Lowe, D. C., Martin, R., and Clarkson, T.: A novel method for compound specific determination of $\delta^{13}\text{C}$ in volatile organic compounds at ppt levels in ambient air, *Geophys. Res. Lett.*, 575 24, 659-662, doi: 10.1029/97GL00537, 1997.
- Schlesinger, W. H., and Hartley, A. E.: A global budget for atmospheric NH₃, *Biogeochem.*, 15, 191-211, doi: 10.1007/BF00002936, 1992.
- Singh, S., and Kulshrestha, U. C.: Rural versus urban gaseous inorganic reactive nitrogen in the Indo-Gangetic plains (IGP) of India, *Environ. Res. Lett.*, 9, 125004, doi: 580 10.1088/1748-9326/9/12/125004, 2014.
- Skinner, R., Ineson, P., Jones, H., Sleep, D., and Theobald, M.: Sampling systems for isotope-ratio mass spectrometry of atmospheric ammonia, *Rapid Commun. Mass Sp.*, 20, 81-88, doi: 10.1002/rcm.2279, 2006.
- Sutton, M. A., Dragosits, U., Y. Tang, and Fowler, D.: Ammonia emissions from non-agricultural 585 sources in the UK, *Atmos. Environ.*, 34, 855-869, doi: 10.1016/S1352-2310(99)00362-3, 2000.
- Sutton, M. A., Oenema, O., Erisman, J. W., Leip, A., van Grinsven, H., and Winiwarter, W.: Too much of a good thing, *Nature*, 472, 159-161, doi: 10.1038/472159a, 2011.
- Tang, G., Zhu, X., Hu, B., Xin, J., Wang, L., Munkel, C., Mao, G., and Wang, Y.: Impact of emission controls on air quality in Beijing during APEC 2014: Lidar ceilometer observations, *Atmos. Chem. Phys.*, 590 15, 12667-12680, doi: 10.5194/acp-15-12667-2015, 2015



- Tang, Y., Cape, J., and Sutton, M. A.: Development and types of passive samplers for monitoring atmospheric NO₂ and NH₃ concentrations, *Sci. World J.*, 1, 513-529, doi: 10.1100/tsw.2001.82, 2001.
- Walters, W. W., and Michalski, G.: Theoretical calculation of nitrogen isotope equilibrium exchange fractionation factors for various NO_y molecules, *Geochim. Cosmochim. Ac.*, 164, 284-297, doi: 595 10.1016/j.gca.2015.05.029, 2015.
- Walters, W. W., Simonini, D. S., and Michalski, G.: Nitrogen isotope exchange between NO and NO₂ and its implications for δ¹⁵N variations in tropospheric NO_x and atmospheric nitrate, *Geophys. Res. Lett.*, 43, 440-448, doi: 10.1002/2015GL066438, 2016.
- Walters, W. W., Tharp, B. D., Fang, H., Kozak, B. J., and Michalski, G.: Nitrogen isotope composition of 600 thermally produced NO_x from various fossil-fuel combustion sources, *Environ. Sci. Technol.*, 49, 11363-11371, doi: 10.1021/acs.est.5b02769, 2015.
- Wang, S. X., Xing, J., Jang, C. R., Zhu, Y., Fu, J. S., and Hao, J. M.: Impact assessment of ammonia emissions on inorganic aerosols in East China using response surface modeling technique, *Environ. Sci. Technol.*, 45, 9293-9300, doi: 10.1021/es2022347, 2011.
- 605 Wang, Y., Zhang, Q. Q., He, K., Zhang, Q., and Chai, L.: Sulfate-nitrate-ammonium aerosols over China: response to 2000-2015 emission changes of sulfur dioxide, nitrogen oxides, and ammonia, *Atmos. Chem. Phys.*, 13, 2635-2652, doi: 10.5194/acp-13-2635-2013, 2013.
- Wang, Y. L., Liu, X. Y., Song, W., Yang, W., Han, B., Dou, X. Y., Zhao, X. D., Song, Z. L., Liu, C. Q., and Bai, Z. P.: Isotopic partitioning of nitrogen in PM_{2.5} at Beijing and a background site of China, 610 *Atmos. Chem. Phys. Discuss.*, 1-33, doi: 10.5194/acp-2016-187, 2016.
- Warneck, P.: *Chemistry of the Natural Atmosphere*, pp. 426-441, Academic Press, San Diego, Calif., 1999.
- Wong, J., Chan, C., and Cheung, K.: Nitrogen and phosphorus leaching from fertilizer applied on golf course: Lysimeter study, *Water Air Soil Pollut.*, 107, 335-345, doi: 10.1023/A:1005096122921, 1998.
- 615 Wong, J. W. C., Chan, C. W. Y., and Cheung, K. C.: Research progress about the impact of fertilizer and pesticide on the environment of golf course, *Grassland and Turf*, 4, 6-10, 2002. (In Chinese with English abstract)
- Xiao, H. W., Xiao, H. Y., Long, A. M., and Wang, Y. L.: Who controls the monthly variations of NH₄⁺ nitrogen isotope composition in precipitation? *Atmos. Environ.*, 54, 201-206, doi: 620 10.1016/j.atmosenv.2012.02.035, 2012.



- Xiao, H. W., Xie, L. H., Long, A. M., Ye, F., Pan, Y. P., Li, D. N., Long, Z. H., Chen, L., Xiao, H. Y., and Liu, C. Q.: Use of isotopic compositions of nitrate in TSP to identify sources and chemistry in South China Sea, *Atmos. Environ.*, 109, 70-78, doi: 10.1016/j.atmosenv.2015.03.006, 2015.
- Xiao, H. Y., and Liu, C. Q.: Sources of nitrogen and sulfur in wet deposition at Guiyang, southwest China, *Atmos. Environ.*, 36, 5121-5130, doi: 10.1016/S1352-2310(02)00649-0, 2002.
- 625 Xu, W., Luo, X., Pan, Y., Zhang, L., Tang, A., Shen, J., Zhang, Y., Li, K., Wu, Q., and Yang, D.: Quantifying atmospheric nitrogen deposition through a nationwide monitoring network across China, *Atmos. Chem. Phys.*, 15, 12345-12360, doi: 10.5194/acp-15-12345-2015, 2015a.
- Xu, W., Sun, Y. L., Chen, C., Du, W., Han, T., Wang, Q., Fu, P., Wang, Z., Zhao, X., and Zhou, L.: Aerosol composition, oxidation properties, and sources in Beijing: results from the 2014 Asia-Pacific Economic Cooperation summit study, *Atmos. Chem. Phys.*, 15, 13681-13698, doi: 10.5194/acp-15-13681-2015, 2015b.
- 630 Ye, X. N., Ma, Z., Zhang, J., Du, H., Chen, J., Chen, H., Chen, H., Yang, X., Gao, W., and Geng, F.: Important role of ammonia on haze formation in Shanghai, *Environ. Res. Lett.*, 6, 024019, doi: 10.1088/1748-9326/6/2/024019, 2011.
- Yeatman, S., Spokes, L., Dennis, P., and Jickells, T.: Comparisons of aerosol nitrogen isotopic composition at two polluted coastal sites, *Atmos. Environ.*, 35, 1307-1320, doi: 10.1016/S1352-2310(00)00408-8, 2001.
- Zbieranowski, A. L., and Aherne, J.: Ambient concentrations of atmospheric ammonia, nitrogen dioxide and nitric acid across a rural-urban-agricultural transect in southern Ontario, Canada, *Atmos. Environ.*, 62, 481-491, doi: 10.1016/j.atmosenv.2012.08.040, 2012.
- 640 Zhang, Q., Streets, D. G., Carmichael, G. R., He, K. B., Huo, H., Kannari, A., Klimont, Z., Park, I., Reddy, S., and Fu, J.: Asian emissions in 2006 for the NASA INTEX-B mission, *Atmos. Chem. Phys.*, 9, 5131-5153, doi: 10.5194/acp-9-5131-2009, 2009.
- 645 Zhang, R. L., Research advances on fertilizers application to lawn, *Trop. Agric. Sci.*, 22, 77-81, 2002. (In Chinese with English abstract)
- Zhang, Y., Dore, A. J., Ma, L., Liu, X. J., Ma, W. Q., Cape, J. N., and Zhang, F. S.: Agricultural ammonia emissions inventory and spatial distribution in the North China Plain, *Environ. Pollut.*, 158, 490-501, doi: 10.1016/j.envpol.2009.08.033, 2010.



650 Zhelezinskaia, I., Kaufman, A. J., Farquhar, J., and Cliff, J.: Large sulfur isotope fractionations associated with Neoproterozoic microbial sulfate reduction, *Science*, 346, 742-744, doi: 10.1126/science.1256211, 2014.