We thank two referees for their careful considerations of the manuscript and their well thought-out comments. These certainly helped to significantly improve the paper. We've addressed all comments and questions below in the form of point-by-point responses. The referees' comments are in *Italic* and our responses are in normal font. Text changes in the revised manuscript are highlighted in color (including a mistake we mentioned in our short comments).

Referee 1:

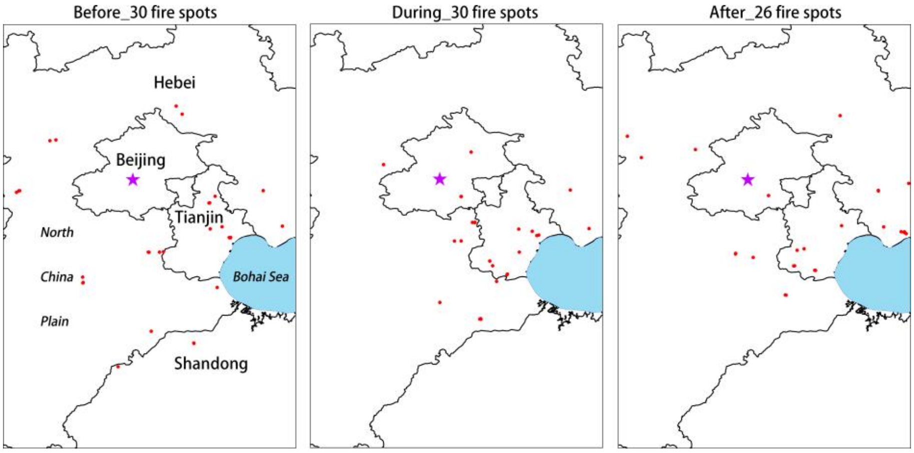
The manuscript by Chang et al. studied the sources of atmospheric ammonia before, during, and after the 2014 APEC summit in Beijing using stable nitrogen isotope signatures coupled with an isotope mixing model. The source contributions of traffic, waste, livestock, and fertilizer were quantified and compared. The results showed a substantial decrease (58.7%) of traffic emission during the APEC period with strict emission controls. The results also showed that non-agricultural sources (traffic and waste) of NH_3 *play an important role in particle pollution in the megacity of Beijing, which has important implications for future air pollution mitigating strategies. This is a pioneer study by applying isotopic measurements into source apportionment of* NH_3*. Such an approach could be very powerful in future source apportionment studies particularly if combining with more collocated measurements. I recommend it for publication after addressing the following two comments.*

Thanks for the encouraging comments, and also useful suggestions, which will certainly be taken into account in our field measurements in the future.

One of the assumptions of this study is that the contribution of biomass burning is considered minimal. The authors need to address the uncertainties of this assumption because Xu et al. (2015) showed that biomass burning contributed 12-19% to total organic aerosols before and during APEC in Beijing.

Firstly, biomass burning is well-known as a major source of ambient organic aerosols (OA). The factors/sources of OA in non-refractory submicron aerosols identified by aerosol mass spectrometer typically (including Xu *et al.* (2015)) include HOA, COA, biomass-burning (BBOA), coal combustion (CCOA), semi-volatile OOA (SV-OOA), and low volatility OOA (LV-OOA). Although biomass burning (e.g., crop residues, wild fires) also contribute to NH_3 emissions, their emission factors are much less than that of OA and its large group of precursors (Akagi *et al.*, 2011; Stockwell *et al.*, 2014).

Secondly, we illustrated the locations (red dots) and number of fire spots (https://firms.modaps.eosdis.nasa.gov/) in Beijing and its neighboring region from 18th October to 29th November 2014. The figure below clearly showed that fire spots in each period were sparse, indicating the magnitude of open burning activities was very limited. Such a result can be expected because all crops grown in open-field (e.g. maize and cotton) in Northern China had been harvested before the APEC summit.



Before_30 fire spots During_30 fire spots After_26 fire spots

Thirdly, there is a considerable amounts of wood burning for heating in EU and US (Clark *et al*., 2013; Saffari*et al*., 2013). While this is not the case in Northern China where coal-based heating is overwhelmingly popular (Chen *et al*., 2013). Besides, wood burning for cooking only exists in some rural areas of China that are far away from our sampling site in Beijing. Moreover, regions having wood burning for cooking also having intensive agricultural activities (e.g., livestock production), which makes NH_3 emissions from wood burning relatively insignificant. In addition, 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).

In conclusion, we are confident that the contribution of biomass burning to ambient NH_3 concentrations was minimal during our sampling period in Beijing.

Reference:

Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J. D., and Wennberg, P. O.: Emission factors for open and domestic biomass burning for use in atmospheric models, Atmos. Chem. Phys., 11, 4039-4072, doi:10.5194/acp-11-4039-2011, 2011.

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.

Chen, Y., Ebenstein, A., Greenstone, M., and Li, H.: Evidence on the impact of sustained exposure to air pollution on life expectancy from China's Huai River policy, Proc. Natl. Acad. Sci., 6, 110, 12936-12941, doi: 10.1073/pnas.1300018110, 2013.

Clark, M. L., Peel, J. L, Balakrishnan K, Breysse, P. N., Chillrud, S. N., Naeher, L. P., Rodes, C. E., Vette, A. F., and Balbus, J. M.: Health and household air pollution from solid fuel use: the need for improved exposure assessment, Environ. Health Perspect., 121, 1120-1128, doi: org/10.1289/ehp.1206429, 2013.

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.

Saffari, A, Daher, N, Samara, C, et al.: Increased biomass burning due to the economic crisis in Greece and its adverse impact on wintertime air quality in Thessaloniki, Environ. Sci. Technol., 47, 13313-13320, doi: 10.1021/es403847h, 2013.

Stockwell, C. E., Yokelson, R. J., Kreidenweis, S. M., Robinson, A. L., DeMott, P. J., Sullivan, R. C., Reardon, J., Ryan, K. C., Griffith, D. W. T., and Stevens, L.: Trace gas emissions from combustion of peat, crop residue, domestic biofuels, grasses, and other fuels: configuration and Fourier transform infrared (FTIR) component of the fourth Fire Lab at Missoula Experiment (FLAME-4), Atmos. Chem. Phys., 14, 9727-9754, doi:10.5194/acp-14-9727-2014, 2014.

Warneck, P.: Chemistry of the Natural Atmosphere, pp. 426-441, Academic Press, San Diego, Calif., 1999.

Xu, W. Q., Sun, Y. L., Chen, C., Du, W., Han, T. T., Wang, Q. Q., Fu, P. Q., Wang, Z. F., Zhao, X. J., Zhou, L. B., Ji, D. S., Wang, P. C., and Worsnop, D. R.: 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, 2015.

Coal combustion is the dominant source of aerosol particles during the heating season in Beijing. Unfortunately, such a source is missed in this study, which will affect the source apportionment results.

We appreciate the constructive criticism. We fully agree with the reviewer that coal combustion is the dominant source of aerosol particles during heating season in Beijing. However, we also think coal combustion-derived NH_3 emissions could be largely neglected **in this study**.

First of all, the emission control measures taken by the Chinese government were really comprehensive and aggressive. For example, Beijing took half of the cars off local roads, closed more than 1000 heavy industrial plants within a 120-mile radius of the city. More importantly, although the convention was held during a heating period, coal-fired power plants operation and urban coal-based heating services in Beijing and Tianjin were suspended until the summit was closed (Zhang, 2014).

Besides, coal combustion is not necessary an important source of gaseous NH_3. In fact, we have collected NH_3 emissions from coal combustion in a combustion chamber by a glass-fritted bubbler system, and the initial results do not support the view that coal combustion is an important source of NH_3 emissions (unpublished). Li *et al.* (2016) recently provided more robust evidence, suggesting that the average NH_3 emission factors for burning 13 kinds of coal in a traditional heating stove was 1.01 mg g^{-1}, and the advanced heating stove with a highly modified combustion efficiency had a much lower average NH_3 EF of 0.13 mg g^{-1}. Supposing an amount of 19 Mt coal consumption in 2014, the annual NH_3 emissions from coal combustion in Beijing was only 247-1919 t, which cannot be comparable with any other major NH_3 sources (e.g., N fertilizer and animal manure/urine emissions).

Lastly, some may argue that coal-fired power plant (CFPP) NH_3 slip is a major NH_3 source in Beijing. But we do not think this can be true. In September 2013, a five-year plan was introduced in Beijing to slash coal consumption, and there were only four CFPPs operating near the city's urban areas during wintertime (China Daily, 2015). In 2016, all CFPP in Beijing will be shut down and replaced with gas-fired power plants to cut pollution. The replacement by the four gas-fired power plants will help cut emissions by 10000 t of sulfur dioxide and 19000 t of nitric oxide annually (China Daily, 2015). Although NH_3 slip is a common issue with SCR (Selective Catalytic Reduction) technology used in CFPP for removal of nitric oxide, the mass concentration of ammonia (typically 3-5 mg NH_3 m^{-3}) in flue gases is two or three orders of magnitude smaller than that of NO_x (MOE of China, 2014). Moreover, although there are many CFPPs surrounded Beijing in the North China Plain, most of which are co-located with intensive agricultural production areas.

Reference:

China Daily: Beijing closes coal power plant to cut pollution, http://www.chinadaily.com.cn/china/2015-03/20/content_19869722.htm. (accessible August 13, 2016)

Li, Q., Jiang, J., Cai, S., Zhou, W., Wang, S., Duan, L., and Hao, J.: Gaseous ammonia emissions from coal and biomass combustion in household stoves with different combustion efficiencies, Environ. Sci. Technol. Lett., 3, 98-103, doi: 10.1021/acs.estlett.6b00013, 2016.

MOE of China, Emission standard of air pollutants for thermal power plants (GB13223-2003), 2014.

Zhang, S. R.: Beijing smog: The day after 'APEC Blue', 2014, http://thediplomat.com/2014/11/beijing-smog-the-day-after-apec-blue/. (accessible August 13, 2016)

Referee 2:

The authors have presented data which increases the inventory of isotopic signatures of ammonia emission sources, an area lacking in data. The authors have characterized isotopic signatures of NH_3 emissions sources in China, a region of the world where this has not been done, and the data agrees closely with data obtained in other areas of the world. This data can be employed by researchers to quantify NH_3 emissions contributing to ambient atmosphere. This is valuable as many NH_3 emission sources are nonpoint sources making them difficult to quantify. Using the nitrogen isotope signatures the authors have estimated urban source contribution before and after a major event in Beijing in which air quality measures were employed during the event. The authors provide isotopic evidence that vehicles are a major contributor to urban

NH_3 concentrations and the isotopic signature in the city changed to reflect the reduction in vehicle emissions resulting from air quality measures. The estimation of other source contributions is likely confounded by potentially overlapping source signatures and this should be more adequately addressed by the authors. This a novel approach to assessing NH_3 source contributions in an urban setting and the authors have presented the data in a clear and concise manner. If the major and minor issues below are addressed, I believe the manuscript could be accepted to ACP.

Thanks for the recognition of our contribution. Please check our point-by-point responses to the major and minor issues raised.

The authors use an isotope mixing model to predict NH_3 source apportionment. The endmember signatures used in the model are vehicles, fertilizer, livestock waste, and human waste. The authors provide evidence that the vehicle endmember signature is significantly different from the other three endmembers but the other endmembers signatures are similar and with more sampling it is likely that these signatures will overlap. This is because the three sources are essentially the same "volatilized NH_3" source and if the literature data is taken into consideration, these sources' signatures are observed to overlap. I don't think the authors have a viable case for assigning the source signatures they present to each source. I do however believe they could combine the "volatilized NH_3" sources as one endmember and vehicles as another endmember. While this would only provide insight to vehicle source apportionment, I think it is a more realistic approach. If the authors keep the mixing model as is, they need to explain the caveats associated with the estimates of the "volatilized NH_3" sources and include error analysis. Rather than reporting specific values a range should be reported that represents the deviation and error involved in the calculations.

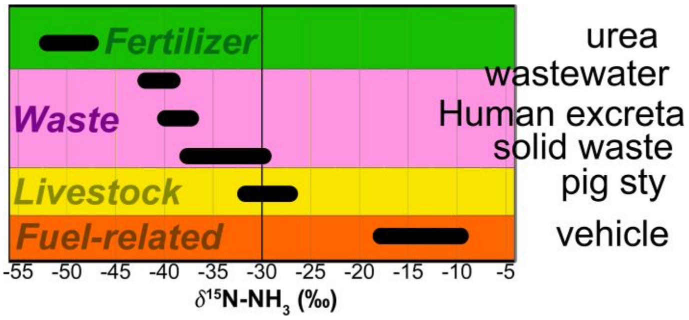
(1) We agree with the reviewer's comments that some of the isotopic signatures of volatilized sources could overlap and this problem should be addressed properly.

We think the source classification in our study is reasonable.

Our NH_3 source classification (Figure below) is based on:

a. The difference of isotopic signatures.
In our MS we concluded that "NH_3 emitted from volatilized sources has relatively low $\delta^{15}N$ values, allowing them to be distinctly differentiated from NH_3 emitted from traffic sources that are characterized by relatively high $\delta^{15}N$ value". Obviously, traffic-derived and fertilizer-volatized NH_3 has the highest and the lowest $\delta^{15}N$ values, respectively. However, "three sources are essentially the same volatilized NH_3" does not necessarily signify that all volatilized NH_3 has a similar variation range of $\delta^{15}N$-NH_3 values (data overlap), nor does it mean that these volatilized NH_3 sources should be classified as a single source category. Temperature is an important parameter, but not the only parameter in determining the differences of $\delta^{15}N$-NH_3 values among different NH_3

sources. In other words, even if data overlap may occur within volatilized sources, they can still be further classified as several sub-categories because of their fundamentally different emission mechanisms (e.g., organic N *vs*. inorganic N; see discussion later);



Variation range of isotopic signatures for different NH_3 sources in our study.

b. The results of emission inventories or the practical emission situation of our targeted study area.
If our sampling site is located in rural areas, then we agree with the reviewer that all volatilized sources can be combined as a single source because NH_3 source contributions in rural areas are much simpler: agricultural volatilized sources predominate the NH_3 emission budget. However, in urban areas, except for on-road traffic, there are many other important non-agricultural NH_3 sources (also volatized sources). Urban wastewater treatment plants and solid waste are arguably two of the most important NH_3 sources in urban China. As a case study, we've identified that human excreta stored in septic tanks in Shanghai is a stable and important source of atmospheric NH_3, contributing to over 11% of the total NH_3 emissions in the Shanghai urban areas. Therefore, it is of critical importance to incorporate the isotopic signatures of waste-related NH_3 sources into the isotope mixing model.

More importantly, even in natural/rural areas, we still need to take account of emission inventory information. If we combined all volatilized sources as a single source, the underlying logic is that every volatilized source contributes equally to ambient NH_3 concentrations. However, wastewater and solid waste, generally, have an insignificant contribution to the rural NH_3 budget. Besides, **if we simply separate all NH_3 sources into two categories (volatilized source and combustion source) without the consideration of the emission inventory, then we are highly likely to get into a trouble: some δ^{15}N values of ambient NH_3 samples may be beyond the endmember, or the isotopic signatures of NH_3 sources.**

To facilitate our explanation, we would like to give a counterexample. In a recent paper entitled "Fossil fuel combustion-related emissions dominate atmospheric ammonia sources during severe haze episodes: Evidence from ^{15}N-stable isotope in size-resolved aerosol ammonium", Pan *et al.* (2016) presented the isotopic measurements of size-resolved aerosols in Beijing, summarizing that fossil fuel-related ammonia emissions (including traffic, coal combustion and power plants NH_3 slip) have overtaken agricultural activities as the dominant source of atmospheric NH_3 during the hazy days of 2013.

There are three NH_3 sources, i.e., agricultural NH_3 volatilization, fossil fuel combustion, and power plant NH_3 slip, considered in Pan *et al.* (2016), and the average $\delta^{15}N$ values (specific values) of these sources were used as isotope signatures ($\delta^{15}N$-NH_3) to estimate their relative contributions to the ambient NH_3 in Beijing. We fully understand the author's consideration in terms of the classification of NH_3 sources: agricultural ammonia is emitted at environmental temperature, the process of fossil fuel combustion can directly emit ammonia at high temperature, and ammonia slipped from power plant is the residue of gaseous reductants (typically anhydrous ammonia, aqueous ammonia or urea) that are subjected to medium temperature, and the isotopic signatures of these sources can be separated based on various temperatures.

However, we have to point out that temperature-only-based NH_3 source classification has a few severe problems, which may lead to wrong conclusions and therefore could potentially mislead China's policy on future NH_3 emissions reduction.

It is well accepted that agricultural activities-fertilizer application merged with livestock production-are the largest contributors of NH_3 emissions at a regional or global scale. However, recent works reveal that NH_3 volatilized from fertilizer application and livestock waste have distinct $\delta^{15}N$ values, which can also be reflected by the large variation range of $\delta^{15}N$ values for agricultural source in Pan *et al.* (2016) (see Figure 3). This is because fertilizer application and livestock waste generally represent two totally different nitrogen forms, i.e., inorganic and organic nitrogen, respectively. Situated on the northern edge of the North China Plain, one of the most intensive agricultural regions in China, Beijing is regarded as a receptor of agricultural ammonia from rural areas. In Pan *et al.* (2016), fertilizer application and livestock waste were combined as a single source (volatilized source), which could inevitably underestimate the contribution of agricultural activities to the ambient NH_3 in Beijing.

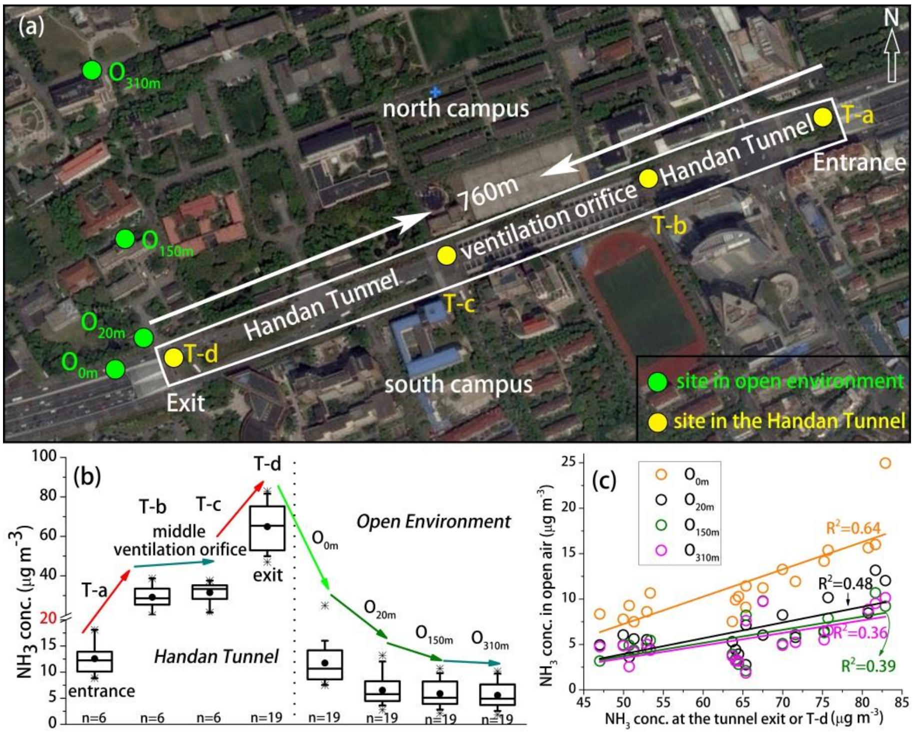
If temperature is a decisive factor, then power plant NH_3 slip considered as a major NH_3 source in Pan *et al.* (2016) should be reasonable. However, Pan *et al.* (2016) claimed that during haze periods, **49%** of NH_3 in the ambient atmosphere of Beijing was derived from power plant NH_3 slip, which can hardly be true. In September 2013, a five-year plan was introduced in Beijing to slash coal consumption, and there were only four coal-fired power plants (CFPP) operating near the city's urban areas during wintertime. In 2016, all CFPP in Beijing will be shuttled and replaced with gas-fired power plants to cut pollution. The replacement by the four gas-fired power plants will help cut emissions by 10000 t of sulfur dioxide and 19000 t of nitric oxide annually. Although ammonia slip is a common issue with SCR (Selective Catalytic Reduction) technology used in CFPP for removal of nitric oxide, the mass concentration of ammonia (typically 3-5 mg NH_3 m^{-3}) in flue gases is two or three orders of magnitude smaller than that of NO_x. Moreover, it is necessary to consider that although there are many CFPPs surrounding Beijing in the North China Plain, most of these are co-located with intensive agricultural production areas.

(2) We also fully agree with the reviewer that the range of isotopic values, instead of a specific value of a given NH_3 source should be served as input into isotopic mixing model. Unfortunately, the isotopic mixing model-IsoSource-used in the current study only allows a fixed isotopic value input for each NH_3 source. The good news is that the isotopic signatures of each source in our study have very narrow variation range, and there is only a few data overlap between the source signatures of waste and livestock (see figure above). These could significantly reduce the uncertainty of source apportionment by IsoSource. Besides, the uncertainty of model simulation also reported in Figure 3 in the MS. Nevertheless, we think future studies should include the adoption of more sophisticated Bayesian mixing models.

Vehicle sampling Unlike the US, a major urban NH_3 *source in China is human waste which has been found to have a* $\delta^{15}N$-NH_3 *value of ~ -41 to -30 per mil in this study. The vehicle exhaust in this study was sampled in a tunnel not directly from tailpipe. Most highly trafficked tunnels have ventilation systems that flush the tunnel with ambient air constantly. If the urban ambient air* NH_3 *is mainly from waste and the tunnels are flushed with ambient air, this mixing would lower the* $\delta^{15}N$ *value of the* NH_3 *sampled at the tunnel. Do these tunnels have ventilation systems? Could mixing with ambient air confound the* $\delta^{15}N$ *vehicle signal?*

The tunnel we chose does have ventilation system and the air in the tunnel is absolutely the mixture of vehicle exhaust and ambient air (even without the ventilation system). We think the mixing with ambient air (including NH_3 emissions from human excreta) in the tunnel is not an important problem. Two reasons are as follows:

(1) The NH_3 conc. in the Tunnel (T-d in figure below; samples for isotopic analysis were also collected at) is nearly **11** times than that in ambient air (O_{310m} and O_{150m} in figure below) (Chang *et al.*, 2016). Therefore, it is safe to conclude that the NH_3 emissions in the Tunnel are dominated by vehicles instead of ambient air.



(**a**) Location of the eight sampling points in (labeled in yellow; inside the tunnel from the entrance to the exit) and out (labeled in green; varying in distance from the tunnel) of the Handan tunnel. The campus of Fudan University was separated into north and south parts by the tunnel. (**b**) Box-whisker plots of the NH_3 concentration sampled at each site, setting 20 as the breaking point of y axis. The box boundaries represent the 25th and 75th percentile, the horizontal line is the median, and the whiskers mark the 10th and 90th percentiles. (**c**) Relationship between the NH_3concentration at T-d (the exit of the Handan tunnel) and the other four sites varying in distance from the Handan road in the open environment.

(2) For NH_3 emission from human excreta, we recently quantified that that the population of ~21 million people living in the urban areas of Shanghai annually emitted approximately 1386 t NH_3, which corresponds to over 11.4% of the total NH_3 emissions in the Shanghai urban areas (Chang *et al*., 2015). Therefore, we don't think human excreta is a major (but still important) urban NH_3 source in Chinese megacities like Beijing.

Line 119: All three filters from a sampling event were combined for single analysis. Why? Was there not enough N for analysis? This doesn't allow for reporting of the deviation, if any among samplers. Did the authors evaluate deviation among samplers? If so this should be included.

Yes, ensuring enough N for isotopic analysis was our top priority. Efficient NH_3 PSD for short-term sampling and for N isotope analysis is still missing. In our previous work, two Ogawa filter samples collected monthly in Shanghai often cannot absorb enough

NH_3-N for isotopic analysis. Although the ALPHA PSDs used in Beijing had larger filters to absorb more NH_3, the sampling time in our study was shortened. Therefore, we combined three ALPHA filters for a single analysis. Although we didn't have isotopic deviation among samplers, we had noticed the potential deviation of NH_3 concentrations among different filters. We had two co-located ALPHA PSDs simultaneously operating at our sampling site as part of our monitoring campaign. We didn't find any significant difference between the combined samples (for isotopic analysis) and these single filter samples.

Line 166: When sampling exhaust from septic tanks the authors state "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 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" It seems the daily samples would be more representative of the source and the fractionation that is occurring is representative of the source. The magnitude of fractionation is going to change under varying environmental conditions but this is a symptom of the source type and should be evaluated as the range in source signature.*

Compared with previous work, we have every confidence that we had optimized our sampling to provide sufficient N-NH_3 and avoid potential fractionation. As to the sampling period we chosen, please note that the NH_3 conc. in the ceiling ducts were very high. A whole day sampling was unpractical because the sampling filters could be overloaded. Besides, NH_3 conc. in the ceiling ducts only came from septic tanks without the interference of ambient air.

We cannot agree more that "the magnitude of fractionation is going to change under varying environmental conditions". If the fluctuation of daily environmental conditions could alter the δ^{15}N-NH_3 values, then we can expect a much larger difference between different seasons. However, our results show that even sampling in different seasons, the δ^{15}N-NH_3 values of the samples collected from septic tanks didn't show significant difference.

Line 400: The authors state "However, as a direct product of NO reduction on the catalyst surface of TWCs ($2NO+5H_2 \rightarrow 2NH_3+2H_2O$ *and/or* $2NO+2CO+3H_2 \rightarrow 2NH_3+2CO_2$*),* NH_3 *emitted from light-duty vehicle exhausts can be expected to have similar* δ^{15}*N-values to vehicle-emitted* NO_x*." This reasoning is not sound. NO produced may have a different original* δ^{15}*N value then the* NH_3 *being used in the TWC and the fractionation factor of the two different compounds caused by the TWC process could be very different. There is not valid evidence to state that the* δ^{15}*N of vehicle* NO_x *and* NH_3 *would be the same.*

To avoid misunderstanding, we decided to delete this sentence in our revised MS (line 390-405).

Minor comments

Line 28: APEC should not be abbreviated Line 51: delete "extensive" Line 160: "don't" should be replaced with "doesn't" Line 198: "A" should be deleted Lin329: The wording "far ahead" is not the appropriate descriptor here and should be changed.

Revised accordingly. "far ahead" has been replaced by "much more than" in the revised MS.

Figure 3: The x-axis labeling isn't sufficient. Are the boxes in order of sampling period? If so, provide the timeframe on the axis.

Timeframe has been added on the axis.

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Atmospheric Chemistry and Physics
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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 ($\delta^{15}N$) 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 $\delta^{15}N$ 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 $\delta^{15}N$ values (ranging from -52.0 to -9.6‰). Significantly high $\delta^{15}N$ 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 $\delta^{15}N$ 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 ~~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 (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%) 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 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, 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 ~~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 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

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from 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 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).

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 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 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 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 $\delta^{15}N\text{-}NH_4^+$ 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

(3^{rd}-8^{th}-10^{th}-15^{th} November), and after (15^{th}-17^{th}-22^{nd}-24^{th}-29^{th} 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, 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/).

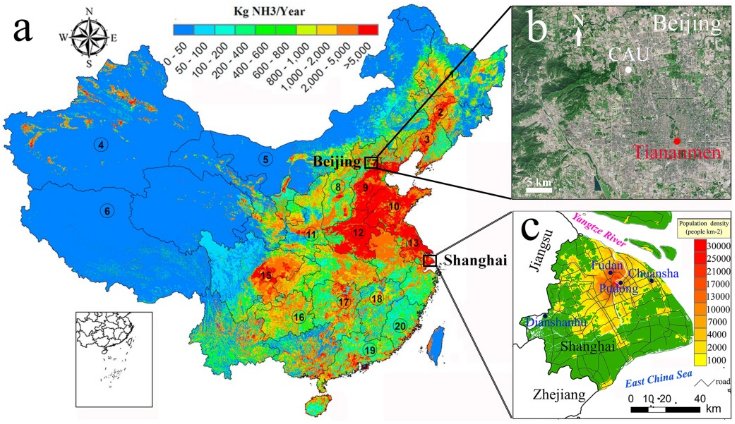

Figure 1. (**a**) 1 km×1 km gridded NH_3 emission inventory in China in 2006 (modified from Huang et al., (2012). (**b**) Location of the sampling site (China Agricultural University or CAU) in this study and its spatial position relative to Tiananmen Square (Beijing urban center). (**c**) Atmospheric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

2.2 NH_3 Source Sampling

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

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 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.

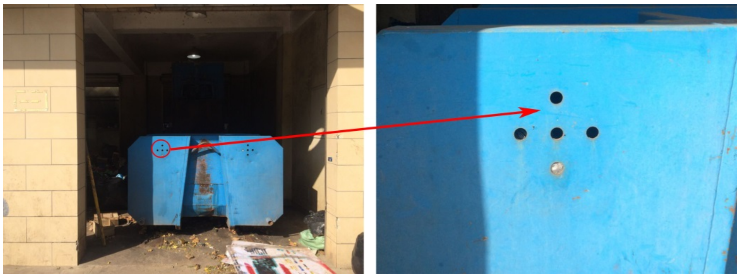

Figure 2. Field photos of a solid waste container in the solid waste transfer station we used for source sampling at Fudan University. Before sampling, an Ogawa passive sampler for NH_3 is attached on a plastic strip (1.5 m in length). The sampler is fitted into the container through the holes (shown on the right panel).

The ambient average NH_3 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 HNO_3 by DELTA active samplers causing the instrument now to be coated with NaCl to avoid this 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 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 samples (including samples collected from a busy road tunnel (Chang et al., 2016), which provides compelling evidence that passive collection of ammonia ~~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} 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 $\delta^{15}N$-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 $\delta^{15}N$-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.

2.3 Stable Isotope Analysis

A newly developed chemical method for $\delta^{15}N$-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 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 (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:

$$\delta^{15}N\left(‰\right)=\frac{\left({}^{15}\mathrm{N}/{}^{14}\mathrm{N}\right)_{\mathrm{sample}}-\left({}^{15}\mathrm{N}/{}^{14}\mathrm{N}\right)_{\mathrm{N_2}}}{\left({}^{15}\mathrm{N}/{}^{14}\mathrm{N}\right)_{\mathrm{N_2}}}\times 1000 \qquad (1)$$

Three international NH_4^+ standards (IAEA N1, USGS 25, and USGS26 with δ^{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 δ^{15}N measurements is less than 0.3‰. Moreover, to enhance our confidence in the results determined by the PT-IRMS method, the δ^{15}N 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

~~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 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., 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 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 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 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 $\delta^{15}N$ 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 -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

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 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‰, and 33 to 6211 μg 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‰) 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.

Table 1. δ^{15}N-NH_3 values of ammonia sources, source location, and summer-winter comparison (mean ± 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 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. 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 (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).

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 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).

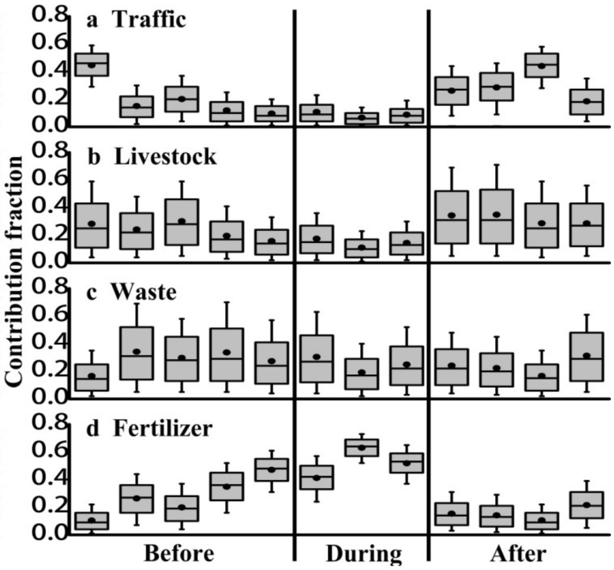

Figure 3. Time series of the box-whisker plots of the contribution fraction of ambient NH_3 from different sources estimated from the IsoSource model. The box boundaries represent the 25th and 75th percentile; the horizontal line is the median, and the whiskers mark the 10th and 90th percentiles. The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

For each sample, information regarding the $\delta^{15}N$ 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. $\delta^{15}N$ 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. ($\mu g\ m^{-3}$)	Absolute contribution of NH_3 conc. ($\mu g\ m^{-3}$)				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* 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). 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 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.

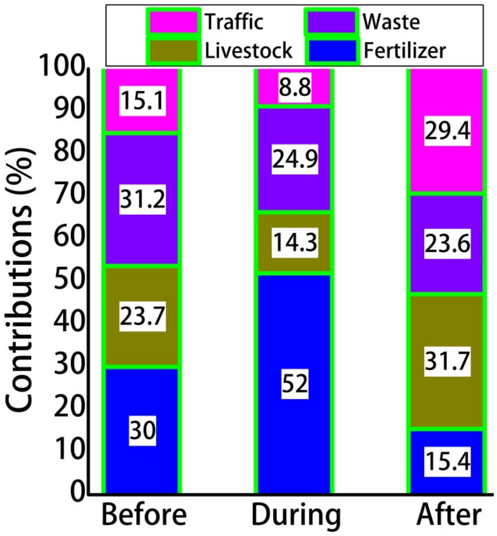

Figure 4. The overall contribution proportion (%) of the four sources to ambient NH_3 identified by the IsoSource before, during, and after the APEC summit in Beijing.

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% 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 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, $NH_3 \leftrightarrow NH_4^+$ 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 $NH_3 \leftrightarrow NH_4^+$ 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. However, a recent research paper from Walters et al. (2015) addressing the $\delta^{15}N$ of vehicle-emitted NO_x may shed some light on this issue. In that paper, the $\delta^{15}N$-values of NO_x emitted from 26 different vehicles ranged from -19.1‰ to +9.8‰, much higher than the variation of $\delta^{15}N$-NH_3 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 NH_3. In this case, the $\delta^{15}N$ values of vehicle-emitted NO_x and NH_3 can hardly be the same. However, as a direct product of NO reduction on the catalyst surface of TWCs ($2NO+5H_2 \rightarrow 2NH_3+2H_2O$ and/or $2NO+2CO+3H_2 \rightarrow 2NH_3+2CO_2$), NH_3 emitted from light-duty vehicle exhausts can be expected to have similar $\delta^{15}N$-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 $\delta^{15}N$-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 18.3%, 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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