Revisiting the concentration observations and source apportionment of atmospheric ammonia

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While China's Air Pollution Prevention and Control Action Plan on particulate matter since 2013 has reduced sulfate significantly, aerosol ammonium nitrate remains high in east China. As the high nitrate abundances are strongly linked with ammonia, reducing ammonia emissions is becoming increasingly important to improve the air quality of China. Although satellite data provides evidence of substantial increases in atmospheric ammonia concentrations over major agricultural regions, long-term surface observation of ammonia concentrations are sparse. In addition, there is still no consensus on whether agricultural or non-agricultural emissions dominate the urban ammonia budget. Identifying the ammonia source by nitrogen isotope helps in designing a mitigation strategy for policy makers, but existing methods have not been well validated. Revisiting the concentration measurement and identifying source apportionment of atmospheric ammonia is thus an essential step towards reducing ammonia emissions.

1. The need for ammonia monitoring in the atmosphere

Ammonia (NH_3) is the most abundant alkaline gas in the atmosphere. While NH_3 has a beneficial role in buffering acid rain (Wang et al. 2012), after deposition it can detrimentally affect Earth's ecosystems through soil acidification, water eutrophication, and biodiversity loss (Liu et al. 2019). The overabundance of NH_3 in the lower atmosphere is suggested to promote the formation of secondary ammoniated aerosol particles (Wang et al. 2016), with significant impacts on visibility deterioration and human health (An et al. 2019). Recently, NH_3 and ammonium nitrate particles were also found in the upper troposphere during the Asian monsoon and play a hitherto neglected role in ice cloud formation and aerosol indirect radiative forcing (Höpfner et al. 2019). However, the severe lack of NH_3 measurements with sufficient spatial and temporal coverage is currently a barrier to understanding the vital role of NH_3 in air pollution, ecosystem protection, and climate change. It has

resulted in unclear regulatory guidelines for mitigating these effects (Pan et al. 2020b).

2. Current status of ammonia observations and limitations

Anthropogenic emissions of NH_3 in China are more significant than the total emissions of the U.S. and the European Union (Liu et al. 2019). To date, there is still no national NH_3 concentration monitoring network operated by the Chinese government. Following the guidelines of the National Atmospheric Deposition Program in the U.S., the Institute of Atmospheric Physics, Chinese Academy of Sciences established a Regional Atmospheric Deposition Observation Network in the North China Plain (READ-NCP). The READ-NCP, included 10 sites covering different land-use types started monitoring NH_3 concentrations in 2007, and has also obtained significant results of atmospheric deposition on the nitrogen, carbon, sulfate, and metals. Based on the observations at the READ-NCP from 2008 to 2010, NH_3 was found to be a significant contributor to nitrogen deposition in this region (Pan et al. 2012). Thus, clarification of NH_3 levels in China can aid policy-makers in the protection of ecosystems from excess nitrogen deposition. Due to the lack of data, however, the whole picture of NH_3 distribution in China was poorly understood. In 2015, the READ-NCP was extended to a spatially dense and cost-efficient network focusing on NH_3 observations in China (AMoN-China) (Pan et al. 2018). The system currently consists of approximately 100 sites, which is similar to that of the U.S. AMoN (Figure 1). While the NH_3 concentration was relatively low in the U.S., there is an increasing importance of deposition of reduced nitrogen due to the significant reduction in oxidized nitrogen (Li et al. 2016).

Besides AMoN in China (Pan et al. 2018) and the U.S. (http://nadp.slh.wisc.edu/AMoN), the monitoring of surface NH_3 is also conducted at other networks (Figure 1), e.g., EANET (The Acid Deposition Monitoring Network in East Asia, https://www.eanet.asia), EMEP (the Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants,

http://ebas.nilu.no/Default.aspx) and the IDAF (IGAC-DEBITS-AFRICA) program for African ecosystems (Adon et al. 2010). Most of these networks employed a cost-effective approach by using passive samplers, including ALPHA, Analyst, Radiello, and Ogawa, which have advantages in characterizing the spatial distribution and long-term trends of NH_3. However, the accuracy of these passive NH_3 sampling techniques is not well validated in the field, which represents one of the biggest challenges in NH_3 monitoring (Martin et al. 2019). For example, it is reported that the NH_3 concentration collected by Radiello passive samplers were approximately 40% lower than the denuder-based reference method (Puchalski et al. 2011). The low NH_3 concentration bias in the passive collection samplers was suggested to be the result of inaccurate effective sampling rates due to incorrect mass transfer correction factors for the environmental conditions (Pan et al. 2020a). Thus, questions remain as to whether the NH_3 concentrations from different networks can be directly compared if they employed different passive samplers. Concurrent measurements of the passive samplers used in various networks are thus further needed, with a collocated reference method, e.g., annular denuders and continuous real-time instruments employing wet chemistry technique (Martin et al. 2019; Pan et al. 2020a; von Bobrutzki et al. 2010).

3. Source debate on ammonia in urban atmosphere

The need for source apportionment has increased in recent years as atmospheric NH_3 concentrations, and deposition fluxes showed little change or even increased following more stringent air pollutant controls (Liu et al. 2018). Long-term satellite observation from the Atmospheric Infrared Sounder (AIRS) aboard NASA's Aqua satellite also implied that NH_3 levels over agricultural regions had experienced significant increasing trends between 2002 and 2013, with an annual increase rate of 2.6%, 1.8% and 2.3% in the U.S., the European Union, and China, respectively (Warner et al. 2017). The increment of atmospheric NH_3 concentrations tends to continue between 2013 and 2017, as observed from space with the Cross-track Infrared Sounder (CrIS) (Shephard et al. 2020). While agricultural activities

(fertilization and livestock volatilization) are known to dominate the emissions of NH_3, accounting for over 60 and 80% of the global and Asian inventory (Bouwman et al. 1997; Huang et al. 2012), non-agricultural sources have been suggested as a major NH_3 source at the urban scale (Chang et al. 2019; Felix et al. 2014; Pan et al. 2016; Sun et al. 2017; Walters et al. 2020a).

Ammonia emissions in developing cities are especially important because of their high emissions ratios to CO_2 and rapidly expanding vehicle fllets (Sun et al. 2017). For example, vehicular emissions were found to be a critical NH_3 source in urban Beijing (Ianniello et al. 2010; Meng et al. 2011). Industrial NH_3 emissions, rather than those from vehicles, were also identified in the megacity of Shanghai (Wang et al. 2015). However, in contrast to previous results, Teng et al. (2017) suggested that urban green spaces and evaporation of deposited NH_x (NH_3+NH_4^+) on wet surfaces, rather than traffic and agricultural emissions, were the primary source for NH_3 in an urban environment during winter in NCP. Thus, there is still no consensus on whether these emissions are among the major sources of urban atmospheric NH_3. Currently, the rapid development of isotope techniques is promising (Liu et al. 2014) and may provide scientists and policymakers with a more robust methodology and reliable evidence to track atmospheric NH_3 sources (Chang et al. 2019; Felix et al. 2014; Pan et al. 2016; Walters et al. 2020a).

4. Constraining ammonia sources utilizing nitrogen isotopes

The use of nitrogen isotopic composition of NH_3 (δ^{15}N-NH_3) as a fingerprint identification of NH_3 emissions sources requires distinguishable isotopic signatures (Felix et al. 2013). While this technique has been widely used in Chinese cities, e.g., Beijing (Pan et al. 2016; Zhang et al. 2020) and Shanghai (Chang et al. 2019), considerable uncertainties remain in characterizing the endmembers. In particular, current collection methods were almost exclusively based on passive samplers, which have not been verified for their suitability to characterize δ^{15}N-NH_3 accurately. Recently, Walters and Hastings (2018) validated an active sampling collection

technique using an acid-coated honeycomb denuder to characterize $\delta^{15}N\text{-}NH_3$ under a variety of laboratory-controlled conditions and also under field conditions. As a reference to this new verified method, Walters et al. (2020a) also found a substantial low bias of 15‰ in the ALPHA passive sampler in characterizing $\delta^{15}N\text{-}NH_3$ from traffic plumes. Such a low bias of passive samplers in characterizing $\delta^{15}N\text{-}NH_3$ was also confirmed in field observations in urban Beijing by Pan et al. (2020a). Thus, previous source apportionment needs to be reevaluated if using an inventory of $\delta^{15}N\text{-}NH_3$ based on passive samplers, especially the ALPHA sampler.

To evaluate the potential influences of the low bias of $\delta^{15}N\text{-}NH_3$ by passive samplers, we revisited the sources of atmospheric NH_3 in urban Beijing using a Bayesian isotope mixing model (SIAR, Stable Isotope Analysis in R) (Kendall et al. 2008). Two scenarios were performed based on an isotopic inventory with and without correction for the passive collection $\delta^{15}N\text{-}NH_3$ bias (Figure 2). Accordingly, the model was run with $\delta^{15}N\text{-}NH_3$ values of −18.2‰ (corrected) and −33.2‰ (original uncorrected) as input for ambient samples. The latter value represented an annual mean $\delta^{15}N\text{-}NH_3$ value in urban Beijing based on a year-round and weekly collection by the passive ALPHA sampler (Zhang et al. 2020).

Figure 3a demonstrates that non-agricultural sources contributed only 57% of NH_3 using the inventory without correction (Figure 2), which is lower than the original estimation of ~72% by Zhang et al. (2020). This difference implied the impacts of different selection of source signatures in these two studies. Also, we have apportioned the source of NH_3 with corrected $\delta^{15}N\text{-}NH_3$ values of both inventories and samples by adding 15‰ to the corresponding passive sampler measurement data. The results showed that 66% of NH_3 was from non-agricultural emissions (Figure 3b). This attribution may be more reliable due to the updated inventory. The different contributions between Figures 3a and 3b for each source, in particular for fertilizers, industry, and vehicles, indicated the uncertainty introduced by the low $\delta^{15}N\text{-}NH_3$ bias of passive samplers.

5. Outlook

It is important to note that tropospheric NH_3 concentrations can be reduced through tight control measures; else they will continue to increase. Constraining NH_3 sources utilizing stable nitrogen isotopes can aid policy-makers to draft a mitigation strategy for NH_3 emissions. But this method depends on an accurate characterization of $\delta^{15}N\text{-}NH_3$ from both source and receptor sites. While the isotopic inventory has significant impacts on the source apportionment, a verified collection technique is warranted to improve the source inventory of $\delta^{15}N\text{-}NH_3$. Due to the different lifetime of NH_3 and NH_4^+ in the atmosphere, the sources of NH_3 and NH_4^+ at a given site may also be different. Thus, a better knowledge of nitrogen fractionation via atmospheric processes, e.g., gas-to-particle conversion, also helps in source apportionment of atmospheric NH_3 and NH_4^+. To address this concern, the concurrent determination of different chemical speciation (i.e., $\delta^{15}N\text{-}NH_3$ and $\delta^{15}N\text{-}NH_4^+$) is highly needed.

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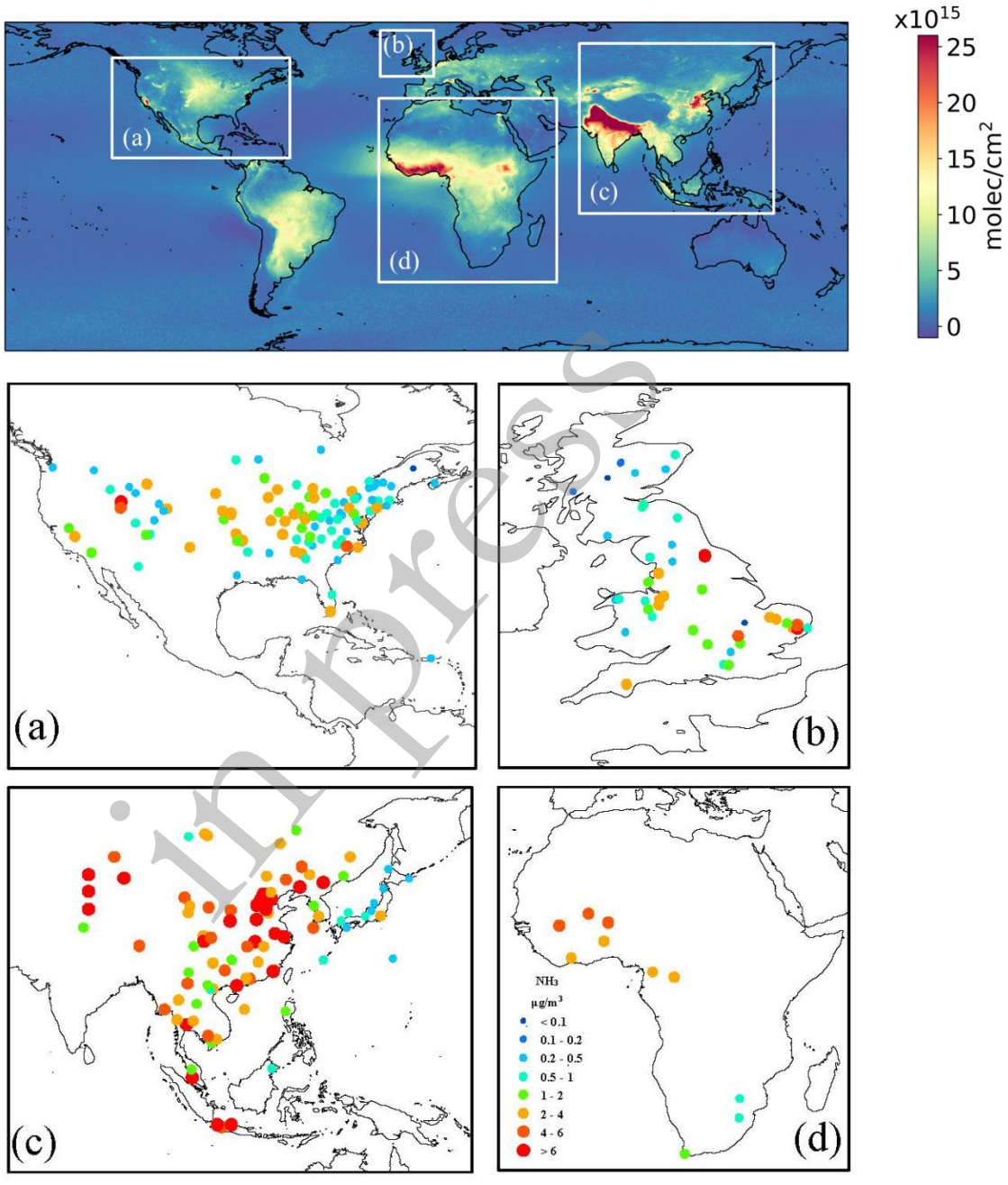


Figure 1. Surface ammonia concentrations during 2015-2016 observed by AMoN in the U.S. (a) (http://nadp.slh.wisc.edu/AMoN/), U.K. (b) (https://uk-air.defra.gov.uk/), and East Asia (https://www.eanet.asia) including China (c) (Pan et al. 2018). Long-term surface

measurements of ammonia in Africa within the framework of the IDAF (IGAC-DEBITS-AFRICA) program were mean values from 1998 to 2007 (d) (Adon et al. 2010). Global ammonia morning column measurements (2008-2016) observed from space by IASI were also shown (https://doi.pangaea.de/10.1594/PANGAEA.894736).

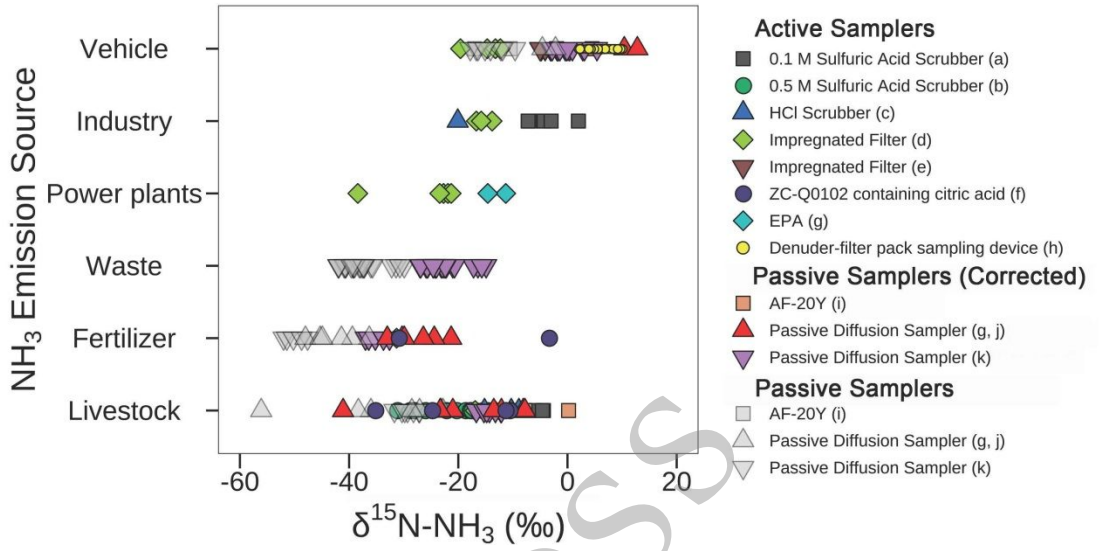
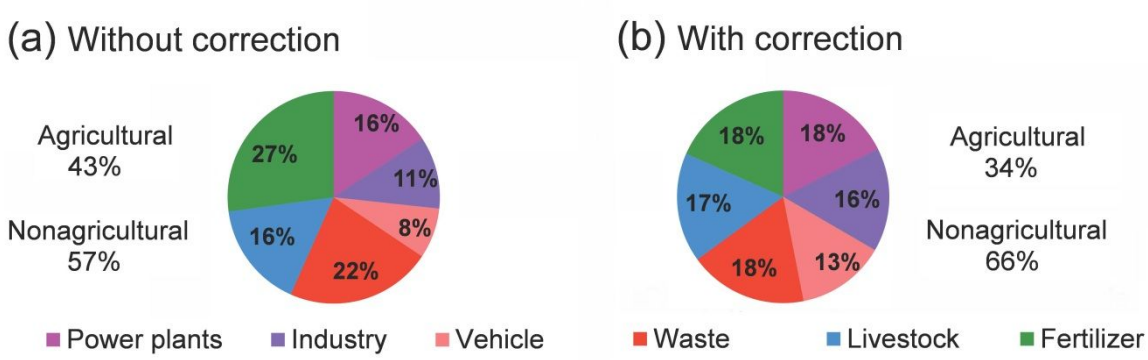


Figure 2. The nitrogen isotopic composition of ammonia characterized at various endmembers. Recent reported isotopic signatures from traffic plumes, fertilizer. and livestock (Kawashima 2019; Ti et al. 2018; Walters et al. 2020a) were updated based on the previous summary by Walters and Hastings (2018). Note that the field sampling was employed by different collection method (legend) and grouped by passive against active samplers (symbols with colors). To correct the low bias of passive data (grey symbols), 15‰ was added to the original values and is shown as corrected (symbols with colors) accordingly. Symbols with the same color and shape represent a series of observations during the same campaign. Data source, a: (Freyer 2016); b: (Hristov et al. 2009); c: (Heaton 1987); d: (Savard et al. 2017); e: (Smirnoff et al. 2012); f: (Ti et al. 2018); g: (Felix et al. 2013); h: (Walters et al. 2020b); i: (Kawashima 2019); j: (Felix et al. 2014); (k): (Chang et al. 2016).



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411 **Figure 3.** Source apportionment of atmospheric ammonia in urban Beijing based on isotopic
412 inventory without (a) and with correction (b) for the passive collection bias in characterizing
413 nitrogen isotopic composition of ammonia, as shown in Figure 2. The nitrogen isotopic values
414 of −18.2‰ (corrected) and −33.2‰ (original) were selected as input for ambient ammonia
415 samples. The original isotope data of −33.2‰ was the annual mean values observed between
416 March 2016 and March 2017 by Zhang et al. (2020).

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