Assessing Contributions of Agricultural and Nonagricultural Emissions to Atmospheric Ammonia in a Chinese Megacity

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ABSTRACT: Ammonia (NH₃) is the predominant alkaline gas in the atmosphere contributing to formation of fine particles—a leading environmental cause of increased morbidity and mortality worldwide. Prior findings suggest that NH₃ in the urban atmosphere derives from a complex mixture of agricultural (mainly livestock production and fertilizer application) and nonagricultural (e.g., urban waste, fossil fuel-related emissions) sources; however, a citywide holistic assessment is hitherto lacking. Here we show that NH₃ from nonagricultural sources rivals agricultural NH₃ source contributions in the Shanghai urban atmosphere. We base our conclusion on four independent approaches: (i) a full-year operation of a passive NH₃ monitoring network at 14 locations covering urban, suburban, and rural landscapes; (ii) model-measurement comparison of hourly NH₃ concentrations at a pair of urban and rural supersites; (iii) source-specific NH₃ measurements from emission sources; and (iv) localized isotopic signatures of NH₃ sources integrated in a Bayesian isotope mixing model to make isotope-based source apportionment estimates of ambient NH₃. Results indicate that nonagricultural sources and agricultural sources are both important contributors to NH₃ in the urban atmosphere. These findings highlight opportunities to limit NH₃ emissions from nonagricultural sources to help curb PM₂.₅ pollution in urban China.

1. INTRODUCTION

Atmospheric ammonia (NH₃) is the predominant alkaline gas in the atmosphere and actively involved in atmospheric chemistry. In reactions with sulfuric acid and nitric acid, formed via the oxidation of SO₂ and NOₓ, respectively, NH₃ contributes to the formation of NH₄⁺ salts, which typically make up from 20% to 80% of atmospheric particulate matter with an aerodynamic diameter less than 2.5 μm (PM₂.₅).¹⁻⁵ This fine particle formation has led to huge health and economic costs.⁶⁻¹⁰

There is an increasing importance of NH₃ emissions relative to SO₂ and NOₓ worldwide due to relatively slow reduction of NH₃ emissions.¹¹⁻¹⁵ Over 90% of NH₃ emissions in China, the United States, and many European countries result from agriculture, mainly including livestock production and NH₃-based fertilizer application;⁶⁻¹⁵,¹⁸⁻²² thus, agricultural NH₃ emissions are often blamed for high levels of ammonium-containing PM₂.₅.¹⁻⁶,⁷,¹²,²³,²⁴ However, in urban areas where agricultural activities are mostly absent, a growing body of evidence suggests that nonagricultural activities like wastewater treatment,¹³⁻¹⁷ coal combustion,¹⁶⁻¹⁷ solid garbage,¹⁸⁻¹⁹ vehicular exhaust,¹⁶⁻¹⁷ and urban green space¹⁶⁻¹⁷ also contribute to NH₃ emissions.¹⁶⁻¹⁷ For example, large vehicular NH₃ emissions from noble metal-based three-way catalysts (TWCs) have been detected in chassis dynamometer vehicle experiments, road tunnel tests, and ambient air measurements dating back to the 1980s.¹⁶⁻¹⁷ Nevertheless, Yao et al.⁴³ and Teng et al.²⁹ suggest that vehicular NH₃ emissions can be neglected and proposed urban green spaces as the dominant contributor to urban...
In China, while there have been no long-term and nationwide NH₃ monitoring studies like the U.S. passive Ammonia Monitoring Network (AMoN, http://nadp.sws.uiuc.edu/amon) affiliated with the National Atmospheric Deposition Program (NADP), 47—49 numerous researchers have measured NH₄⁺ concentrations in wet deposition (i.e., precipitation) for more than 30 years. 50,51 The data show that the annual flux of NH₄⁺ in wet deposition in China has increased in conjunction with the growth in animal production and fertilizer application. 17,50,52,53 Further, China’s recent economic boom has been coupled with accelerated urbanization. 54,55 In 1978 less than 20% of Chinese residents lived in cities. The population of its cities has quintupled over the past 40 years, reaching 813 million or nearly 60% of the total population. 56 At present, there are three super-regions or city clusters in China: the Pearl River Delta (PRD), next to Hong Kong; the Yangtze River Delta (YRD), which surrounds Shanghai; and Jing-jin-ji (J3), centered on Beijing. 57 In particular, the YRD region is arguably the most concentrated set of adjacent urban conurbations in the world. 58 Huge cities place huge demands on resource consumption and associated nonagricultural NH₃ emissions. 44 For example, the region has released high-resolution (100 x 100 m² per pixel) population map of China in 2010 (worldpop.org.uk).

The population density in Shanghai, which was retrieved from a newly released high-resolution (100 x 100 m² per pixel) population map of China in 2010 (worldpop.org.uk).

Figure 1. Shanghai passive ammonia monitoring network. The natural-color satellite image in the left panel shows the urban area of Shanghai in 2016, along with its major island Chongming. The right panel presents the population density in Shanghai, which was retrieved from a newly released high-resolution (100 x 100 m² per pixel) population map of China in 2010 (worldpop.org.uk).

2. MATERIALS AND METHODS

2.1. Site Description. The Yangtze River Delta or YRD region encompasses the nation’s largest population center, Shanghai, and major agricultural fields in eastern China. In order to obtain information regarding the spatial and temporal variability of NH₃ concentrations in Shanghai, we established a regional monitoring network of 14 sites covering urban (FD, HK, YP, HP, PT, JA, LW, XH, and PD), suburban (ZJ and CJ), and rural (DH, SY, and CM) landscapes (Figure 1). Of particular importance are PD and DH, which also serve as supersites intended to represent urban and rural settings, respectively. In Shanghai, all ten state-control stations (SCS) of China’s Ministry of Environmental Protection were utilized. The advantages of selecting these SCS sites include (i) their deliberate locations away from point and local sources of pollution, such as transportation corridors, agricultural fields, livestock operations, and industrial emissions; (ii) they have well-trained staff with long-term employment to sustain continuous measurements; and (iii) they are equipped with refrigerators so that the collected samples can be quickly stored to prevent potential contamination or sample degradation. More detailed site descriptions can be found elsewhere. 36,61 The meteorology in Shanghai is typical of a subtropical monsoon system with four distinct seasons. A summary of the average meteorological conditions can be found in Supporting Information, SI, Figure S1.

2.2. Field Sampling. In order to obtain the spatial distributions of NH₃ concentrations over the Shanghai region, from May 2014 to June 2015, weekly Ogawa PSDs (passive sampling devices, Ogawa, FL, U.S.A.) were deployed at each site (from March 2017 to March 2018 for CM and SY sites) under the protection of an opaque shelter for collecting ambient NH₃. Between June and August of 2014, two Ogawa PSDs were deployed for monthly collection at the urban PD site and the rural DH site for N isotopic analysis of NH₃. The Ogawa PSD consists of a solid cylindrical polymeric body (2 cm diameter, 3 cm long) housing a citric acid-coated glass fiber disk at each end as a duplicate to trap NH₃. 48 All PSD components (including filters) were purchased from Ogawa U.S.A., and sampling procedures provided by the manufacturer (http://www.ogawausa.com) were strictly followed through-

NH₃ concentrations between field measurements and chemical transport model simulations, and (3) using stable isotopes as a tool to quantify source category contributions to ambient NH₃ concentrations in the rural and urban atmospheres.
out the campaign. After exposure, the filters were transferred with tweezers into plastic vials (15 mL) and stored at −18 °C immediately. The samples were delivered to the analytical laboratory monthly. The average relative percent difference between duplicate Ogawa PSD samples was 5.5%.

In order to relate temporal variations of NH3 concentrations to potential NH3 sources, the PD (urban), and DH (rural) sites were equipped with a Monitor for AeRosols and Gases (MARGA, Applikon B.V., NL), allowing continuous characterization of the inorganic components of PM2.5 (NH4+, N O3−, SO2−4, Cl−, Na+, K+, Ca2+, Mg2+) and water-soluble gases (NH3, SO2, HCl, HONO, and HNO3) at hourly resolution. This effort builds upon our earlier effort36 to look at the influence of on-road traffic on ambient NH3 variability with different meteorology at the PD site. Details of the MARGA instrument and its performance can be found elsewhere.61 To complement the information obtained from the MARGA monitoring campaign, additional measurements of tailpipe-emitted NH3 from 19 different vehicles equipped with three-way catalytic converters were carried out in Nanjing, a megacity in the western Yangtze River Delta region, during April 2016, following a method described elsewhere63 and briefly summarized in SI Text S1.

### 2.3. Laboratory Analysis.

NH4+ concentrations in the H2SO4 absorbing solutions were measured using a Dionex ICS-5000+ system (Thermo Fisher Scientific, Sunnyvale, U.S.A.) at the clean laboratory (class 1000) of Nanjing University of Information Science and Technology (NUIST) Center on Atmospheric Environment. The IC system was equipped with an automated sampler (AS-DV). NH4+ in solutions was measured using an IonPac CG12A guard column and CS12A separation column with an aqueous methanesulfonic acid (MSA, 30 mM L−1) eluent at a flow rate of 1 mL min−1. For the Ogawa passive samples, each filter pad was soaked in 8 mL deionized water (18 MΩ·cm) in a 15 mL vial for 30 min with occasional shaking. Concentrations of NH4+ in extracts were analyzed using an ion chromatography system (883 Basic IC plus, Metrohm Co., Switzerland) equipped with a Metrosep C4/4.0 cation column. The eluent was 1.0 mmol L−1 HNO3 + 1.0 mmol L−1 2,6-pyridine dicarboxylic acid. The detection limit for NH4+ was 2.8 μg L−1, corresponding to an ambient NH3 concentration of 0.1 ppb for a seven-day sample.

For isotopic analysis, a robust and quantitative chemical method was used to determine δ15N-NH3 based on the isotopic analysis of nitrous oxide (N2O),64 as detailed and successfully applied in our previous studies.61,65 One of the advantages of this method is that it is more suitable for low volume samples including those with low nitrogen concentration. The standard deviation of δ15N measurements determined from the replicates is less than 0.3‰.

### 2.4. Ammonia Modeling.

The Community Multiscale Air Quality (CMAQ, v5.0.1) chemical transport model was used to simulate hourly NH3 and NH4+ concentrations in Shanghai with a 12 × 12 km2 grid resolution.66 Meteorological inputs were generated with the Weather Research and Forecasting (WRF v3.6.1) model and the National Centers for Environmental Prediction FNL Operational Model Global Tropospheric Analyses. The tropospheric analyses data set was used to provide initial and boundary conditions. A multisolution emission inventory for China developed by Tsinghua University (http://www.meicmodel.org) was used to define monthly anthropogenic emissions from China. Anthropogenic emissions in 2012 including NH3, SO2, NOx volatile organic compounds, and PM were regridded to the model grids. Open biomass burning emissions were generated from the Fire Inventory from NCAR, which is based on satellite observations.66 Dust and sea salt emissions were generated online during the CMAQ simulations. Biogenic emissions were generated using the Model for Emissions of Gases and Aerosols from Nature (v2.1).66 The model configurations of CMAQ and WRF are similar to those utilized in a previous nationwide study.66

#### 2.5. Bayesian Mixing Model.

Isotopic mixing models allow us to estimate the proportional contributions of multiple sources (emission sources of NH3 in this study) within a mixture (the ambient NH3 in this study).67 By explicitly reflecting the uncertainties associated with multiple sources, isotope fractionation, and isotopic signatures, the application of Bayesian methods to stable isotope mixing models is able to generate robust probability estimates of source proportions, being more appropriate in natural systems than simple linear mixing models.68,69 Here a novel Bayesian methodology for analyzing mixing models implemented in the software package SIAR (Stable Isotope Analysis in R)70 was used to resolve multiple NH3 source categories by generating potential solutions of source apportionment as true probability distributions. The generation of such source contribution probability distributions is helpful in estimating likely ranges of source contributions when the system solution is under-constrained (i.e., the number of sources exceeds the number of different isotope system tracers +1). The SIAR package is available to download from the packages section of the Comprehensive R Archive Network site (CRAN)–http://cran.r-project.org/, and has been widely applied in a number of fields.71–75 Model frame and computing methods are detailed in SI Text S2.

A comprehensive pool of isotopic source signatures of NH3 (IS_NH3) has been established in our previous work with the exception of “NH3 slip from coal-fired power plant”.65 These IS_NH3 are typically found to lie between −50‰ and −10‰, with occasional overlap between signatures from different source types.67,76 The NH3 emissions were defined by four distinct source categories (Table 1): livestock breeding (−29.1 ± 1.7‰), N-fertilizer application (−50.0 ± 1.8‰; urea application), combustion-related sources (−14.0 ± 2.7‰; urban waste, solid waste, wastewater, human excreta, vehicle (road tunnel), power plant (NH3 slip))

<table>
<thead>
<tr>
<th>category</th>
<th>subcategory</th>
<th>NH3 (μg m−3)</th>
<th>δ15N-NH3 (%)</th>
<th>N</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>livestock breeding (LB)</td>
<td>pig breeding</td>
<td>462.2 to 1502.8</td>
<td>−31.7 to −27.1</td>
<td>7</td>
<td>65</td>
</tr>
<tr>
<td>N-fertilizer application (FA)</td>
<td>urea</td>
<td>165.6 to 623.7</td>
<td>−52.0 to −47.6</td>
<td>5</td>
<td>65</td>
</tr>
<tr>
<td>urban waste (UW)</td>
<td>solid waste</td>
<td>271.2 to 542.4</td>
<td>−37.6 to −29.9</td>
<td>8</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>wastewater</td>
<td>127.2 to 258.5</td>
<td>−41.9 to −39.2</td>
<td>8</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>human excreta</td>
<td>3238.0 to 6211.0</td>
<td>−39.6 to −37.3</td>
<td>8</td>
<td>61</td>
</tr>
<tr>
<td>fossil fuel-related (FF)</td>
<td>vehicle (road tunnel)</td>
<td>33.2 to 87.4</td>
<td>−17.8 to −9.6</td>
<td>8</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>power plant (NH3 slip)</td>
<td>not available</td>
<td>−14.6, −11.3</td>
<td>2</td>
<td>76</td>
</tr>
</tbody>
</table>

Table 1. Mass Concentrations and Isotopic Signatures (δ15N) of Major NH3 Sources
on-road traffic, NH$_3$ slip from coal-fired power plants), and urban waste volatilized sources (−37.8 ± 3.6‰; wastewater treatment, municipal solid waste, and human excreta).

2.6. Ancillary Information. Hourly meteorological parameters (MSO Weather Sensor, MetOne Instruments, U.S.A.; including wind direction, wind speed, relative humidity or RH, and temperature or $T$) in Shanghai were provided by the Shanghai Meteorological Bureau. Bivariate polar plots (BPP) were used to demonstrate how NH$_3$ concentrations vary with wind direction and wind speed in polar coordinates, an effective diagnostic technique for discriminating different source regions. BPPs were used to illustrate spatial distributions rather than temporal variations of NH$_3$ due to their relatively coarse time resolution.

Taking the results of all weekly samples as a whole, atmospheric NH$_3$ concentrations in Shanghai range from 1.2 to 23.1 ppb, with a mean (±σ) and median value of 7.3 (±3.1) and 6.8 ppb, respectively. Domestically, the annual average NH$_3$ concentrations in northern China (e.g., Beijing (23.5 ± 18.0 ppb) and Xi’an (18.6 ppb on average)) are much higher than our observations in Shanghai (Table 2). This can be partly explained by a higher soil pH in the North China Plain and the Guanzhong Plain where Beijing and Xi’an are located, respectively, which promotes loss of NH$_3$. Instead, the Yangtze River Delta region (including Shanghai) is dominated by acid soils of paddy fields. Internationally, the average NH$_3$ level we measured in Shanghai is generally similar to observations in developed cities like Seoul in S. Korea and Houston in the U.S.A., but much lower than in some cities in developing countries. This is particularly true when comparing

Figure 2. Sample-specific and group-averaged mixing ratios of ambient NH$_3$ measured with Ogawa passive samplers at 14 surface locations in Shanghai. Excepting the green color in the map (indicating rural areas), the color scheme is population density with the scale the same as that in Figure 1 (retrieved from worldpop.org.uk).
with cities in South Asia (e.g., Delhi in India; Table 2), where there is a lack of basic sanitation facilities (e.g., public flush toilets), and significant animal populations (such as cows) coexist with people in urban areas. The high NH$_3$ concentrations measured at surface sites in South Asia are consistent with the spatial patterns determined from recent satellite remote sensing observations. It is worth noting that from measurements in the Shanghai Jinshan chemical industry park (Figure 2), Wang et al. showed a much higher NH$_3$ concentration (17.6 ± 9.5 ppb) with abrupt concentration changes on an hourly basis, a result of the strong influence of variable industrial emissions in the vicinity. NH$_3$ levels were found to exhibit modest gradients across the study region, with mean NH$_3$ concentrations ranging from 4.8 (CM rural site) to 9.7 ppb (HP urban site) (Figures 2 and 3c). As discussed above, on a regional scale, NH$_3$ is mainly emitted from animal housing, manure storage, and land-spread manure, and to a smaller extent from mineral fertilizer application. The emission strengths of these sources are primarily determined by the activity of microbes, which is highly dependent on temperature. Hence, rural areas with strong agricultural sources, are expected to experience increased emissions in summertime. Indeed, in our study, the average NH$_3$ concentrations in summer are higher than in other seasons for each land use category (Figure 3b) and site (Figure 3d), signifying the importance of volatilized NH$_3$ sources in the region (see discussion later). Somewhat surprisingly, however, the lowest average ambient NH$_3$ concentrations are found at rural sites such as CM (4.8 ± 2.6 ppb) and SY (6.3 ± 4.1 ppb), which are in active agricultural areas (Figure 3c). Although the average NH$_3$ concentration at the rural DH site (7.4 ± 4.1 ppb) is higher than the rural DH site (7.4 ± 4.1 ppb) of the other 13 sites (Figure 3c), the overall average NH$_3$ concentration observed at urban sites (7.8 ± 2.9 ppb) is significantly higher than at suburban (6.8 ± 3.1 ppb, p < 0.01) and rural (6.2 ± 3.8 ppb, p < 0.01) sites (Figure 3d). In fact, urban enrichment of NH$_3$ in Shanghai is not unique. In Table 2 we compile previous studies in which urban NH$_3$ concentrations are comparable with or higher than suburban and rural NH$_3$ concentrations. In brief, our results demonstrate that urban areas, without agricultural activities, can also be an important source of NH$_3$ emissions.

![Figure 3. Comparison of the ambient NH$_3$ concentrations (mean ±1σ) among (a) different site types (urban/suburban/rural), (b) different seasons (spring/summer/fall/winter) within a specific site type, (c) different individual sites, and (d) different seasons (spring/summer/fall/winter) within a specific site.](image)

**Table 2. Comparison of Atmospheric NH$_3$ Concentrations (in ppb) between Urban and Suburban/Rural Areas in Different Regions**

<table>
<thead>
<tr>
<th>location</th>
<th>period</th>
<th>average NH$_3$ concentration</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shanghai, CN</td>
<td>2014.5−2015.6</td>
<td>7.8</td>
<td>urban: 6.8/6.2, this study</td>
</tr>
<tr>
<td>Xi’an, CN</td>
<td>2006.4−2007.4</td>
<td>18.6</td>
<td>suburban/rural: 20.3, 83</td>
</tr>
<tr>
<td>Beijing, CN</td>
<td>2007.1−2010.7</td>
<td>22.8</td>
<td>urban: 10.2, 82</td>
</tr>
<tr>
<td>Hong Kong, CN</td>
<td>2003.10−2006.5</td>
<td>10.2</td>
<td>suburban/rural: 0.2, 95</td>
</tr>
<tr>
<td>Delhi, IN</td>
<td>2012.10−2013.9</td>
<td>52.8</td>
<td>urban: 65.6, 90</td>
</tr>
<tr>
<td>Rome, IT</td>
<td>2001.5−2002.3</td>
<td>5.3</td>
<td>suburban/rural: 3.5, 96</td>
</tr>
<tr>
<td>Toronto, CA</td>
<td>2003−2011.9</td>
<td>2.3−3.0</td>
<td>urban: 0.1−4, 97</td>
</tr>
</tbody>
</table>

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Temperature is the key driver of NH$_3$ emissions from volatility-driven sources; observations of NH$_3$ volatilization by Sommer et al. found that NH$_3$ emissions after 6 h of surface applied cattle slurry were exponentially related to temperature ($r^2 > 0.80$). As shown in Figures 2 and 3d, the average NH$_3$ concentrations are higher in summer and lower in winter. This is particularly true at rural sites, consistent with dominant, temperature-sensitive emission of NH$_3$ from agricultural sources like livestock waste and fertilizer application. There are also other temperature-sensitive sources in urban areas like wastewater, household garbage, golf turf, and human excreta; the latter two are often overlooked but important NH$_3$ sources in urban China. Although still recognized as a luxury sport by most Chinese people, golf is increasingly popular. In contrast to Western industrialized countries, human excreta in urban China is typically first stored in a three-grille septic tank beneath the building. After a series of anaerobic decomposition processes, a substantial amount of odors (including NH$_3$) will be generated and emitted through a ceiling duct.

From a climate perspective, differences in temperature and other meteorological parameters (e.g., precipitation, wind speed, planetary boundary layer) over the Shanghai region are minor. Interestingly, the lowest NH$_3$ concentrations at urban Shanghai sites were not observed in the winter, while the NH$_3$ difference between summer and winter is much lower at urban sites than at rural sites in our data set (Figure 3). These observations suggest that there may be some other temperature-independent NH$_3$ sources present in urban areas.

3.2. Significant Influences of Nonagricultural NH$_3$ Emissions in the Urban Atmosphere. The analysis of weekly NH$_3$ samples collected from our network of sites spanning various land use categories indicates that the enhancement of atmospheric NH$_3$ at urban sites reflects a mix of agricultural and nonagricultural NH$_3$ emissions. To further explore and compare the influences of various NH$_3$ sources on ambient NH$_3$ in urban and rural atmospheres, we can examine the year-round, hourly observations of NH$_3$ at the urban PD and rural DH sites (Figure 1). By combining hourly concentration, wind speed, and wind direction measurements, bivariate polar plots (BPP) can be constructed to identify source regions of near-ground pollutants like NH$_3$, an approach that has proven to be a more suitable tool than back trajectory-based methods.

As illustrated in Figure 4a, there are large temporal variations in NH$_3$ concentrations at the urban PD and rural DH site, with their hourly NH$_3$ concentrations ranging from 0.1 to 36.4 μg m$^{-3}$ (mean ± 1σ = 5.9 ± 4.5 μg m$^{-3}$; median = 4.8 μg m$^{-3}$; $n$ = 7897; 90.1% data availability) and 0.1 to 33.0 μg m$^{-3}$ (mean ± 1σ = 6.6 ± 4.1 μg m$^{-3}$; median = 5.9 μg m$^{-3}$; $n$ = 8204; 93.7% data availability), respectively. The NH$_3$ concentration spikes at both sites are concentrated in summer (June, July, and August), and their smoothed trends are generally consistent with the variation of temperature. These findings suggest that volatilized NH$_3$ emissions are a regionally important NH$_3$ source in Shanghai. Also included in Figure 4 are, to help further identify specific sources, the diurnal profiles of NH$_3$ and temperature at DH and PD. At the rural DH site, diurnal variations of NH$_3$ concentrations are highly correlated with temperature ($r^2 = 0.98$, $p < 0.01$; Figure 4b), indicating the predominant role of volatilization-related NH$_3$ sources in rural areas. In eastern China (including Shanghai), agricultural sources (livestock feeding and N-fertilizer application) make up nearly 90% of the total NH$_3$ emissions. Indeed, in Figure 5a, the BPP analysis shows that high NH$_3$ concentrations at DH are associated with...
NH₃ and carbon monoxide (CO) in the Shanghai urban observations have also shown coincident enhancements of NH₃ concentration and temperature on a diurnal basis (Figure 4c and d), suggesting a complex mix of NH₃ source contributions. Specificaly, there is no correlation between NH₃ concentration and temperature on a diurnal basis (Figure 4d). The average concentrations of NH₃ show a well-marked bimodal pattern, which is generally similar to the diurnal evolution of urban traffic flow in Shanghai. Previous observations have also shown coincident enhancements of NH₃ and carbon monoxide (CO) in the Shanghai urban atmosphere. Following a stable period of NH₃ concentrations between 22:00 and 5:00 (5.7 ± 0.1 μg m⁻³), the maximum NH₃ concentration occurs in the morning rush hour (7.0 μg m⁻³, 10:00), 22% higher than the overnight level. In Figure 5b, the Shanghai metropolitan area to the southwest is covered by intensive cultivation areas, with modern agriculture facilities. The areas to the southeast of the sampling site have been described as the “backyard garden” of Shanghai, renowned for its idyllic scene, and are a regional hot spot of agricultural NH₃ emissions.

At the urban PD site, however, distinctly different pictures of the diurnal profiles of NH₃ and temperature are observed (see Figure 4c and d), suggesting a complex mix of NH₃ source contributions. Specifically, there is no correlation between NH₃ concentration and temperature on a diurnal basis (Figure 4d). The average concentrations of NH₃ show a well-marked bimodal pattern, which is generally similar to the diurnal evolution of urban traffic flow in Shanghai. Previous observations have also shown coincident enhancements of NH₃ and carbon monoxide (CO) in the Shanghai urban atmosphere. Following a stable period of NH₃ concentrations between 22:00 and 5:00 (5.7 ± 0.1 μg m⁻³), the maximum NH₃ concentration occurs in the morning rush hour (7.0 μg m⁻³, 10:00), 22% higher than the overnight level. In Figure 5b, the Shanghai metropolitan area to the southwest is covered by intensive cultivation areas, with modern agriculture facilities. The areas to the southeast of the sampling site have been described as the “backyard garden” of Shanghai, renowned for its idyllic scene, and are a regional hot spot of agricultural NH₃ emissions.

To further examine the NH₃ emission potential from vehicles, we measured NH₃ concentrations emitted from tailpipe exhaust of 19 different vehicles equipped with TWCs. The average NH₃ concentration of the total 57 samples (10.2 ppm) is 4 orders of magnitude higher than the ambient NH₃ concentrations. Considering the huge automobile inventory in Shanghai (nearly 3.3 million in 2015), our study strongly suggests that on-road traffic is an important NH₃ source in the urban atmosphere.

3.3. NH₃ from Nonagricultural Rival Agricultural Emissions in the Urban Atmosphere. Figure 6 compares model simulations and measurements of hourly NH₃ concentration at the rural DH and urban PD sites. The average measured and predicted NH₃ concentrations at DH are similar, although the variability in the model predictions is much larger than the observations, perhaps reflecting the coarse time resolution of the emission inventory used. It is noteworthy that the average NH₃ concentration at the rural DH site is accurate without any nonagricultural NH₃ emissions being included in the model, consistent with our conclusion above that agricultural activities are the predominant NH₃ source in rural areas. At the urban PD site, the simulation with only agricultural NH₃ emissions yields an average predicted NH₃ concentration (3.6 μg m⁻³) that is 47% lower than the average measured concentration (6.7 μg m⁻³), suggesting that (nonsimulated) emissions from nonagricultural activities are important contributors to urban NH₃. Although other factors could contribute to under-prediction of urban NH₃ (e.g., incorrectly modeled transport from rural agricultural sources or overestimation of the rate of dry deposition of NH₃ emitted by agricultural sources), past studies suggest that ambient NH₃ concentrations most strongly depend on NH₃ emissions rather than atmospheric processes. Suggesting that ignoring nonagricultural NH₃ emissions is likely one of the most important reasons for the low concentration model bias at PD.

A quantitative and accurate assessment of NH₃ sources in the urban atmosphere is difficult to obtain solely using the approach described above. Below we demonstrate the complementary use of N isotopes to better constrain NH₃ source contributions at the PD site. Although there is generally not a compelling need to differentiate agricultural vs nonagricultural emissions contributions in rural areas, the relative contributions of N-fertilizer application and livestock feeding are certainly of interest and isotopic signatures are also used to constrain these source contributions at the rural DH site.

Isotope-based source apportionment of atmospheric NH₃ requires a well-established pool of NH₃ isotopic source signatures (δ¹⁵N-NH₃) to allow a separation of different sources. From a total of 44 NH₃ source samples in our previous study, we have established a pool of isotopic signatures for the major NH₃ emission sources in Eastern China (Table 1). The NH₃ concentrations and δ¹⁵N values of these samples ranged from 33 to 6211 μg m⁻³ and −52.0 to −9.6‰, respectively. Recently, NH₃ slip from coal-fired power plants equipped with selective catalytic reduction (SCR) technology was reported as an important source of NH₃; thus,
its isotopic signature, as reported by Felix et al.\textsuperscript{76} is also considered in this study. Table 1 shows that these NH$_3$ sources can be clearly classified into four categories by specific isotope signatures: NH$_3$ emitted from combustion-related sources has relatively high $\delta^{15}$N values, allowing them to be distinguished from NH$_3$ emitted from volatilization processes. The $\delta^{15}$N values (mean $\pm 1\sigma$) of the Shanghai urban PD site environmental samples collected in July and August of 2015 were $-31.72 \pm 3.36\%$ (ranging from $-36.01\%$ to $-25.40\%$, $n = 10$), close to the $\delta^{15}$N-NH$_3$ values observed in Beijing ($-34.0\%$ to $-27.2\%$, $n = 4$; a period without strict air quality control measures)\textsuperscript{68} and higher than at the rural DH site ($-41.03\%$, $-36.53\%$), suggesting a stronger influence of combustion-related sources in the urban atmosphere.  

At the rural DH site, our earlier analysis demonstrated that rural NH$_3$ concentrations can be solely attributed to agricultural NH$_3$ emissions, i.e., livestock breeding (LB) and fertilizer application (FA). Therefore, the isotopic signatures of two sources, i.e., LB and FA, are used as input into the SIAR Bayesian mixing model. The results suggest that on average, LB and FA contribute 51.9% and 48.1% to the measured NH$_3$ concentrations, respectively (not shown). From the perspective of the emissions inventory, the NH$_3$ emissions from LB and FA contribute 48% and 40% to the total in Eastern China, respectively,\textsuperscript{7} in general agreement with our results.  

At the PD urban site with its more complex NH$_3$ sources, normal distributions and variation ranges (within 5 and 95 percentiles) of the relative contribution fractions of each source to the ambient NH$_3$ concentrations were estimated and are depicted in Figure 7. As a reminder, the availability of only a single isotopic tracer vs four hypothesized source types, means that there is no unique solution for the system;\textsuperscript{102,103} however, we can identify all possible sets of source contributions that reproduce the observed isotopic signature. The utility of this analysis will depend, to a large extent, on how narrow the source contribution ranges are for each source. In our analysis, fossil fuel-related sources (FF) and fertilizer application (FA) have relatively low variation ranges (Figure 7), indicating that they are better constrained than livestock breeding (LB; $-31.7\%$ to $-27.1\%$) and urban waste volatilized (UW; $-41.9\%$ to $-29.9\%$) sources. This is because the isotopic signatures of LB and UW are distributed in the middle of the source pool, where their contributions to the $\delta^{15}$N values of the ambient NH$_3$ ($-36.01\%$ to $-25.40\%$) are less well constrained. The pie chart in Figure 7 illustrates the overall mean contribution proportions. While estimates of the mean values are inherently uncertain,\textsuperscript{104} the four source contribution distribution estimates strongly suggest that all four source types make substantial contributions to the NH$_3$ concentrations measured at the urban PD site. Further, this isotopic analysis lends further confidence to our earlier conclusion from the WRF-CMAQ model vs observations comparison that nonagricultural sources rival agricultural sources in terms of contributing to ambient NH$_3$ in the urban atmosphere.  

Fossil fuel-related sources are identified as an important contributor to ambient NH$_3$ concentrations at PD. Although NH$_3$ emissions from coal and biomass burning are observed,\textsuperscript{26,30} they are not comparable with the magnitude of vehicular NH$_3$ emissions and NH$_3$ slip from SCR-equipped coal-fired power plant (CFPP).\textsuperscript{30,59} Recently, a five-year plan was introduced in China to slash coal consumption from CFPP and household sectors.\textsuperscript{77} For example, in 2016, all CFPPs in Beijing were replaced with gas-fired power plants to cut pollution.\textsuperscript{77} The replacement by the four gas-fired power plants will help cut emissions by 10 000 tons of SO$_2$ and 19 000 tons of NO annually.\textsuperscript{7} Although NH$_3$ slip is a common issue with SCR technology used in CFPP for the removal of NO, the mass concentration of NH$_3$ (typically 3–5 mg NH$_3$ m$^{-3}$) in flue gases is two or 3 orders of magnitude smaller than that of NO.\textsuperscript{77} Therefore, we suspect that the share of NH$_3$ emissions from SCR-equipped CFPP in urban areas is relatively small and will decrease continuously in China. In the U.S.A., it is estimated that 5% of the national NH$_3$ emissions are derived from motor vehicles, while this figure is estimated at 12% for the U.K., with almost all the remaining NH$_3$ coming from agricultural processes.\textsuperscript{44} In China, all new light-duty vehicles were required to install TWC since 2009.\textsuperscript{44} In Table S1, we have provided direct evidence that TWC-equipped vehicles are an important urban source of NH$_3$. Thus, expanding vehicular NH$_3$ emissions in urban China can be expected. Indeed, the average contribution of fossil fuel-related sources derived from the Bayesian isotopic mixing model (28.6%) is close to the share of on-road traffic (22.3%), we estimated the above based on NH$_3$ concentration analysis at PD. This suggests that fossil fuel-derived NH$_3$ concentrations in urban Shanghai are primarily emitted from on-road traffic.  

4. IMPLICATIONS AND OUTLOOK  

The present study outlines a framework to integrate NH$_3$ concentration measurements, atmospheric transport modeling, and isotope-based source apportionment to address a longstanding and ongoing controversy regarding sources of NH$_3$ in the urban atmosphere. We validate the feasibility of this approach by application to the Yangtze River Delta region, with a focus on the megacity of Shanghai. Results from a Shanghai passive NH$_3$ monitoring network (14 locations) reveal a broadly homogeneous distribution of NH$_3$ concentrations throughout the region and pinpoint urban areas as a hot spot of NH$_3$. The acquired data also provide a baseline toward tracking future NH$_3$ emissions changes. The year-round online measurements of NH$_3$ at an urban and rural site, and a comparison against concentrations simulated by the WRF-CMAQ chemical transport model, demonstrate that NH$_3$ in the rural atmosphere can be attributed to emissions from agricultural sources, while there is a significant contribution from nonagricultural NH$_3$ emissions, particularly vehicular NH$_3$ emissions, in the urban atmosphere. Isotope-
based source apportionment of NH₃ in the urban atmosphere further indicates that nonagricultural NH₃ emissions, missing from the current emission inventory, could well rival agricultural NH₃ emissions in terms of contributing to ambient NH₃.

Given the central role of NH₃ in the formation of secondary inorganic aerosols and resulting haze, our results are of critical importance for China as it seeks to curb its severe PM₂.₅ pollution. Additional useful investigative steps could include: (1) sensitivity analyses with the WRF-CMAQ model to further diagnose the importance of nonagricultural NH₃ emissions through developing a gridded nonagricultural NH₃ emissions inventory with high time resolution; (2) collecting NH₃ and aerosol NH₄⁺ for simultaneously determining the mass concentrations and isotopic compositions at high time resolution; and (3) improving the pool of isotopic source signatures of NH₃ from fuel-related sources.

**REFERENCES**


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