We thank the three referees for their useful comments and suggestions which have helped us to improve the manuscript. Our point-by-point responses are below, followed by the track-change manuscript. The referees' comments are in *Italic* and our responses are in normal font.

Referee 1:

The manuscript attempts to explain the observation of atmospheric ammonia in the urban atmosphere of Shanghai. The results are interesting and worthy of publication.

We thank the referee for his/her favorable comments.

This reviewer has a few minor comments for the authors considering. 1) P34728, line 5, 'the NH_3 concentrations varied between 0.03 and 39.2 μg m^{-3}'. This reviewer didn't believe that the detection limit of the MARGA can be as low as 0.03 μg m^{-3} because of highly non-linear response of NH_4^+ in the system.

Thanks for the comment. In our study, out of a total of 8447 hourly NH_3 data points, the ten lowest NH_3 values (μg m^{-3}) were 0.03, 0.06, 0.07, 0.08, 0.08, 0.09, 0.10, 0.11, 0.12, and 0.13 (all data are available as requested for reviewing purpose).

The performance of the MARGA has been systematically assessed by the US Environmental Protection Agency previously (Rumsey et al., 2014), and the detection limit for NH_3 at hourly resolution was identified as 0.05 μg m^{-3}. Strictly speaking, the values of higher than the twice of the detection limit are thought to be valid. Therefore, the lowest NH_3 concentration in the revised manuscript has been changed to 0.1 μg m^{-3}. The number of data points has also been corrected accordingly.

Reference:

Rumsey, I. C., Cowen, K. A., Walker, J. T. et al., An assessment of the performance of the Monitor for AeRosols and GAses in ambient air (MARGA): a semi-continuous method for soluble compounds, Atmos. Chem. Phys., 14, 5639-5658, doi:10.5194/acp-14-5639-2014, 2014.

2) P34728, lines 7-10, "This might be expected since Beijing and Xi'an are located in the North China Plain (NCP) and the Guanzhong Plain (GZP), respectively, two of the most intensive agricultural production regions in China." It is very difficult for this reviewer to understand that Beijing is one of the most intensive agricultural production regions in China.

We are sorry for making the reviewer confused and this sentence has been revised (page 34728, line 9). We would like to clarify that the North China Plain (NCP), instead of Beijing, is one of the most intensive agricultural production regions in China. The NCP (Figure 1), also known as ‘‘China’s granary’’, provides 40% and 25% of China’s wheat and corn production on 3.3% of the national area (Zhang et al., 2010). Application rates of mineral nitrogen fertilizers in the NCP are up to 600 kg N ha^{-1} yr^{-1} (Ju et al., 2009). Less than 30% efficiency in N application introduces about 40% N loss by various routes, including emissions of NH_3 (Ju et al., 2009). In addition, about 30% of national animal products are also from this area, which further increases the ammonia emission (Zhang et al., 2010). The NCP are recognized as a global hot spot for ammonia emissions (Clarisse et al., 2009). Beijing is situated at the northern tip of the NCP (Figure 1), and the southeasterly winds are prevailing in summer seasons (Sun et al., 2015). Therefore, Beijing is regarded as a receptor of agricultural NH_3 from the NCP (Ianniello et al., 2010).

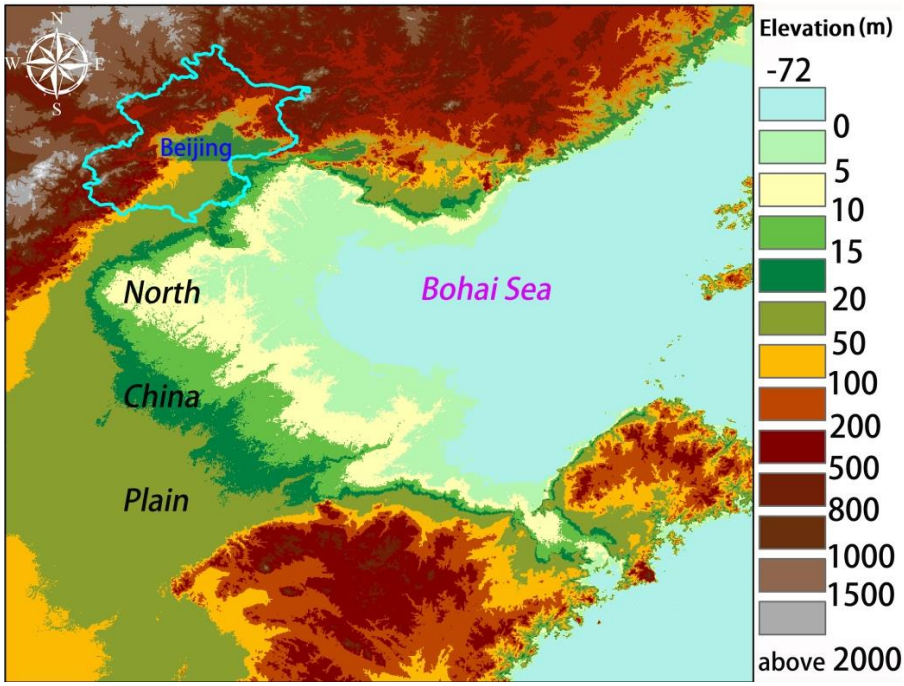


Figure 1. Topographic map of the North China Plain and its surrounding areas

Reference:

Clarisse, L., Clerbaux, C., Dentener, F., et al. Global ammonia distribution derived from infrared satellite observations. Nature Geosci., 2009, 2(7): 479-483.

Ju, X. T., Xing, G. X., Chen, X. P., et al. Reducing environmental risk by improving N management in intensive Chinese agricultural systems, PNAS, 2009, 106(9): 3041-3046.

Ianniello A, Spataro F, Esposito G, et al. Occurrence of gas phase ammonia in the area of Beijing (China), Atmos. Chem. Phys., 2010, 10(19): 9487-9503.

Sun, Y. L., Wang, Z. F., Du, W., et al. Long-term real-time measurements of aerosol particle composition in Beijing, China: seasonal variations, meteorological effects, and source analysis, Atmos. Chem. Phys., 2015, 15(10): 14549-14591.

Zhang, Y., Dore, A. J., Ma, L., et al. Agricultural ammonia emissions inventory and spatial distribution in the North China Plain, Environ. Pollut., 2010, 158(2): 490-501.

3) P34729, lines 11-12 "Smaller seasonal temperature differences and less agricultural activity in Shanghai could be the contributing factors." This could be reasons, but more direct evidences are needed.

We have to admit that it is very difficult to thoroughly isolate the effects of local emission, regional sources and changes in meteorology on measured ambient NH_3 concentrations. However, our conclusion lies on the well-established fact that almost no one questions the major contribution of agricultural activity to NH_3 emissions, and NH_3 volatilization from fertilizer and livestock waste is highly sensitive to the variations of meteorological parameters (particularly temperature).

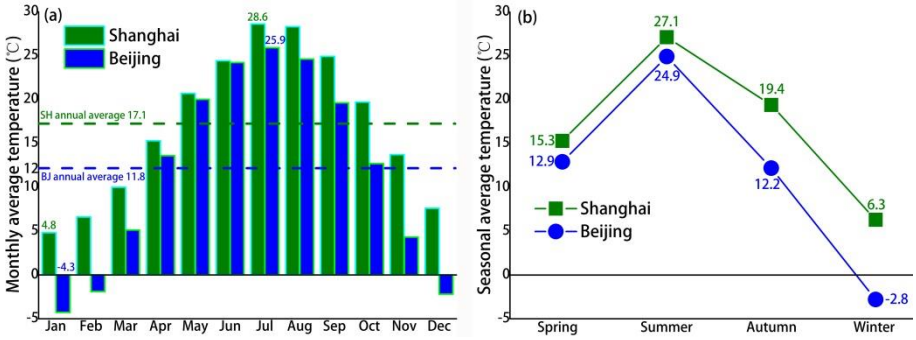


Figure 2. The variations of monthly (**a**) and seasonal (**b**) average temperature (normals 1971-2000) in Shanghai and Beijing.

Specifically, Figure 2 clearly shows that there is a smaller monthly and seasonal temperature difference in Shanghai compared to Beijing. Besides, according to Huang et al. (2012), the NH_3 emissions in Beijing were nearly twice than that of Shanghai in 2006. Moreover, as we mentioned above, Beijing is situated at the northern tip of the North China Plain, and the NCP is the most intensive agricultural production region in China. However, located in the mouth of the Yangtze River Delta in East China, Shanghai borders the regions of most developed city clusters in China, and is bounded to the east by the East China Sea.

Collectively, we think at the current stage, it is reasonable for us to conclude that "smaller seasonal temperature differences and less agricultural activities in Shanghai and its adjacent areas could be the contributing factors" to its smaller seasonal

ambient NH_3 concentration.

Reference:

Huang, X., Song, Y., Li, M., et al. A high-resolution ammonia emission inventory in China, Glob. Biogeochem. Cycl., 2012, 26(1), doi:10.1029/2011GB004161.

4) P34730, lines 3-8, "Although 19.6 mm of rainfall in the July period would be expected to lower NH_3 levels, the temperature on this high concentration date was much higher than on the low concentration March date. Over a longer time frame, even though rainfall in summer was around twice the amount of rainfall in other seasons, other factors such as greater NH_3 emissions at higher temperature outweigh the wet scavenging effects of rainfall yielding higher summertime NH_3 concentrations." The analysis needs to be revised. More and more on-line observations indicated that rainfall enhanced NH_3 emissions.

Taking advantage of fast (1 Hz) measurements of NH_3, we notice that Prof. Murphy's group found the significant increase in NH_3 concentrations followed by precipitation events (Ellis et al., 2011). There is substantial evidence that over certain land types both emission and deposition of NH_3 (known as bi-directional flux or exchange) can occur depending on the NH_3 compensation point (e.g. Farquhar et al., 1980; Sutton et al., 1993; Sutton et al., 1995; Asman et al., 1998; Nemitz et al., 2001). However, we would like to point out the underlying surface around PD supersite is dominated by buildings and roads (hard ground), which could hamper the production of biogenetic-related NH_3 emissions. Besides, given that NH_3 is readily water-soluble, the ambient NH_3 in the urban atmosphere of Shanghai can be expected to be scavenged after rainfall.

Reference:

Asman, W. A. H., Sutton, M. A., Schjørring, J. K., Ammonia: emission, atmospheric transport and deposition, New Phytol., 1998, 139(1): 27-48.

Ellis, R. A., Murphy, J. G., Markovic, M. Z., et al., The influence of gas-particle partitioning and surface-atmosphere exchange on ammonia during BAQS-Met, Atmos. Chem. Phys., 2011, 11(1): 133-145.

Farquhar, G. D., Firth, P. M., Wetselaar, R., et al. On the gaseous exchange of ammonia between leaves and the environment: determination of the ammonia compensation point, Plant Physiol., 1980, 66(4): 710-714.

Nemitz, E., Milford, C., Sutton, M. A., A two-layer canopy compensation point model for describing bi-directional biosphere-atmosphere exchange of ammonia, Q. J. Roy. Meteor. Soc., 2001, 127(573): 815-833.

Sutton, M. A., Schjorring, J. K., Wyers, G. P., et al., Plant-atmosphere exchange of ammonia, Philos. T. Roy. Soc., 1995, 351(1696): 261-278.

Sutton, M. A., Flower, D., Moncriefe, J. B., The exchange of atmospheric ammonia with vegetated surfaces. I: Unfertilized vegetation, Q. J. Roy. Meteor. Soc., 1993, 119(513): 1023-1045.

5) Section 3.2, to this reviewer, the correlation analysis was valid only if atmospheric NH_3 was derived from local sources. This has to be clarified.

Thanks for the comment. In this work, the potential source contribution function (PSCF) has been used to identify the possible geographic origins of NH_3 at different seasons. Figure 8c in our manuscript clearly illustrates that for all seasons, the source region of NH_3 in Shanghai is locally-dominated. In this regard, we think the correlation analysis should be still valid.

6) Section 3.3, in the morning, it has been well demonstrated that dew evaporation can also lead to the elevation of atmospheric NH_3. This should be added in the revision.

This is a very helpful comment and has been added in our revised manuscript. We also notice that pools of surface water (i.e. dew or fog), which form on nights that have a high RH, can act as NH_x reservoirs that release NH_3 upon evaporation in the mid-morning, particularly in spring seasons.

7) Section 3.4, Tunnel is an ideal place to study vehicle emission factors of NO_x, CO and BC, etc. This reviewer has concerns whether it is applicable to study the vehicle emission factor of NH_3. The potential biogenic emission of NH_3 in the ventilation system could be huge because of huge N sources for bacteria.

The ventilation system for the Handan tunnel was constructed by reinforced concrete. Based on our visual inspection (Figure 3), the ventilation orifice in Handan tunnel is not a good habitat for the growth and reproduction of bacteria. Besides, the NH_3 concentrations near the ventilation orifice (T_b and T_c) we measured did not support the assumption that “biogenic emission of NH_3 in the ventilation system could be huge”.

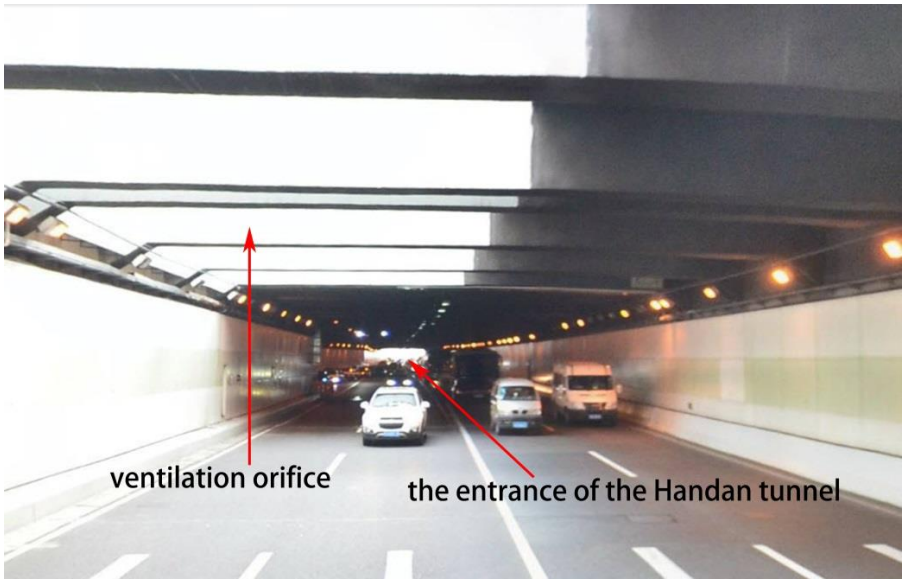


Figure 3. Photo shows the inner condition of Handan tunnel.

Referee 2:

General comment：

1. This paper deals with an important topic – the contribution of vehicle emitted NH_3 to the urban atmosphere. The study links a long term measurements with a short-term campaign performed in and out of a major freeway tunnel in Shanghai. Meteorological parameters from the WRF model and the Hysplit model simulations were used to support the analysis of measured NH_3 concentrations. The authors show some interesting results, however some explanations and analysis are not always clear.

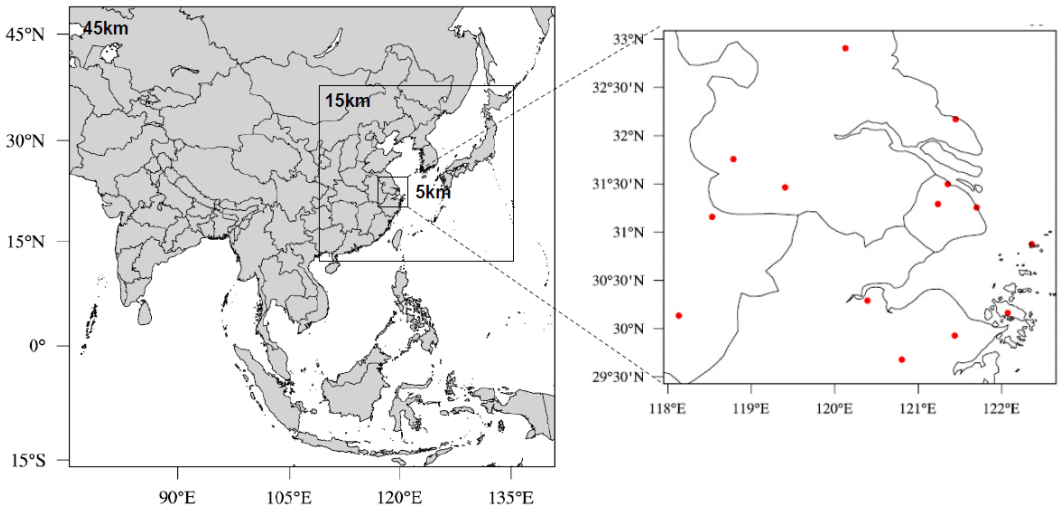
We thank the referee for the critical comments. One thing we would like to emphasize is that meteorological parameters such as RH, temperature and rainfall we used in this study were from observations except for PBLH which was derived from the WRF modeling results. Based on the specific comments as below, we have responded to all the comments point-by-point and made corresponding changes in the manuscript.

2. My main comments are: 1. P34730, chapter 3.2. The authors use the boundary layer height (PBLH) from the WRF model simulations and try to interpret the relations between PBLH for different seasons. There is no information on the WRF model domains, spatial resolution, simulation period. Did you verified the WRF modelled PBLH against observations or are there any other studies on this for this region. So, in this context the statement that the boundary layer is similar for four seasons and is not relevant for NH_3 concentrations has to be reconsidered.

Thanks for the comments. In the revised manuscript, we now added more details about the WRF configuration (page 34724, line 8).

The Weather Research and Forecasting (WRF) model v3.5.1 (Skamarock et al., 2008) is used for simulating the height of planetary boundary layer. The WRF simulation was performed from a mother domain with a 45 × 45 km horizontal resolution over Asia, and nested down to a second domain of 15 × 15 km covering Eastern China, Korea and Japan, and further nested down to a third domain of 5 × 5 km covering the Yangtze Delta River region. Lambert conformal conic projection was used with true latitude limits of 4° and 44° and standing longitude of 115°. The coverage of three domains is shown in Supplement Fig. S4. We chose the RRTM longwave radiation scheme and the Dudhia shortwave radiation scheme. The Yonsei University scheme was used for the planetary boundary layer option. The WRF model configurations can be found elsewhere (Huang et al., 2013a).The National Centers for Environmental Prediction (NCEP) Final (FNL) Operational Global Analysis dataset (http://rda.ucar.edu/datasets/ds083.2/) with a horizontal resolution of a resolution of 1.0 × 1.0° are incorporated as initial and boundary conditions for the model. An one-way nested approach with four-dimensional data assimilation (FDDA) in WRF is

applied. We have performed model evaluations of major meteorological parameters against the NCDC surface meteorological network (National Climate Data Center, http://www7.ncdc.noaa.gov/CDO/cdo) within the YRD region (red dots marked in Supplement Fig. S4). A Meteorology/Chemistry Interface Processor (MCIP) (Otte and Pleim, 2010) v4.1 is used to post-process the WRF results by outputting the atmospheric height of the planetary boundary layer field, one of the standard MCIP outputs. The simulation period is consistent with the observation, i.e. from April, 2014 to April, 2015. In this study, PBLH derived from the third domain is used.



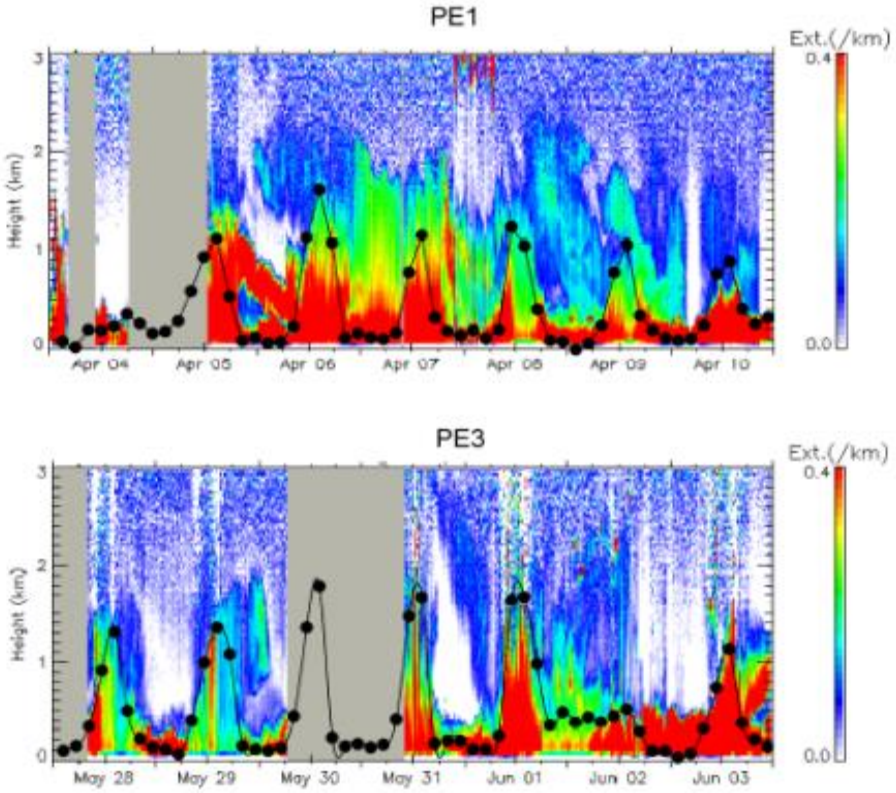
We have performed model evaluations of major meteorological parameters against the NCDC network (National Climate Data Center, http://www7.ncdc.noaa.gov/CDO/cdo), which is limited to the surface observation. The available NCDC sites within the YRD region are marked in the right figure. The evaluation results of wind speed, temperature, and humidity are show in the table below. It could be seen that these meteorological parameters are within the benchmarks (First column in the table) during most of the months, suggesting our WRF modeling results are reliable.

		JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Wind Speed (m/s)	Mean Obs	2.56	2.87	2.98	3.18	3.65	3.22	3.86	3.37	3.34	2.81	2.51	2.43
Benchmark	Mean Sim	3.08	3.38	2.88	3.23	3.92	2.94	3.5	3.45	3.38	2.94	2.84	2.62
$\leq \pm 0.5$	Mean Bias	0.52	0.51	-0.1	0.05	0.27	-0.28	-0.36	0.08	0.04	0.13	0.33	0.19
≤ 2	Gross Error	1.3	1.29	1.19	1.36	1.53	1.16	1.22	1.21	1.14	1.11	1.33	1.22
	RMSE	1.72	1.72	1.65	1.79	1.94	1.51	1.59	1.54	1.44	1.4	1.74	1.6
≥ 0.6	IOA	0.77	0.77	0.81	0.78	0.66	0.73	0.74	0.72	0.79	0.74	0.79	0.78
Temperature (K)	Mean Obs	272.95	278.54	281.18	287.25	293.62	298.5	301.93	302.64	296.17	294.34	281.42	274.53
Benchmark	Mean Sim	273.63	278.3	281.16	287.09	293.8	298.84	301.89	302.27	296.57	294.68	282.45	275.72
$\leq \pm 0.5$	Mean Bias	0.68	-0.24	-0.02	-0.16	0.18	0.34	-0.04	-0.37	0.4	0.34	1.03	1.19
≤ 2	Gross Error	1.29	1.32	1.41	1.47	1.68	1.71	1.39	1.26	1.28	1.23	1.51	1.69
	RMSE	1.61	1.75	1.83	1.89	2.09	2.19	1.8	1.61	1.59	1.57	1.86	2.06
≥ 0.8	IOA	0.98	0.97	0.96	0.94	0.86	0.87	0.85	0.9	0.89	0.91	0.98	0.97
Humidity (g/kg)	Mean Obs	3.61	4.15	4.84	6.93	11.18	16.35	20.4	19.98	13.97	12.22	5.72	3.72
Benchmark	Mean Sim	4.26	3.67	4.9	7.36	10.2	14.92	19.28	19.21	13.24	11.36	6.68	4.36
$\leq \pm 1$	Mean Bias	0.65	-0.48	0.06	0.43	-0.98	-1.43	-1.12	-0.77	-0.73	-0.86	0.96	0.64
≤ 2	Gross Error	0.51	0.92	0.92	1.45	1.54	1.7	1.06	1.02	0.98	1.34	1.15	0.72
	RMSE	0.63	1.13	1.13	1.76	1.93	2.41	1.56	2.14	1.43	1.7	1.38	0.87
≥ 0.6	IOA	0.86	0.78	0.78	0.73	0.59	0.6	0.71	0.72	0.69	0.58	0.87	0.87

$$\text{Mean Bias} = \frac{1}{N}\sum_{i=1}^{N} C_m - C_o \text{ , GE} = \frac{1}{N}\sum_{i=1}^{N} |C_m - C_o| \text{ , RMSE} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(C_m - C_o)^2} \text{ , IOA} = 1 - \frac{\sum_{i=1}^{N}(C_m - C_o)^2}{\sum_{i=1}^{N}(|C_m - \overline{C_o}| + |C_o - \overline{C_o}|)^2}$$

There are very rare observations of PBLH in Shanghai as it may require setup of instruments such as Lidar or Ceilometer. In our previous work (Huang et al., 2012), we compared the vertical profile of aerosol extinction measured by a Lidar to the 3-hour resolution PBLH extracted from the NCEP reanalysis data (http://www.atmos-chem-phys-discuss.net/11/C10382/2011/acpd-11-C10382-2011-supplement.pdf). As shown in the figure below, the temporal variations of NCEP PBLH (black dotted lines) are relatively consistent with the PBLH as visualized from the Lidar measured aerosol extinction at most times during two periods. As the NCEP reanalysis data is used for the inputs for the WRF model, we think the WRF simulated PBLH is capable of reasonably simulating the PBLH.

However, as we didn't have Lidar observations in this study (April 2014-April 2015), we couldn't verify the model simulated PBLH at this moment. We hope the reviewer could understand our difficulty that no observations of PBLH are available.



Reference:

Huang, K., Zhuang, G., Fu, J. S., et al., Typical types and formation mechanisms of haze in an Eastern Asia megacity, Shanghai, Atmos. Chem. Phys., 2012, 12, 105-124.

Huang, K., Fu, J. S., Hsu, N. C., Gao, Y., Dong, X., Tsay, S. C. and Lam, Y. F.: Impact assessment of biomass burning on air quality in Southeast and East Asia during BASE-ASIA, Atmos. Environ., 78, 291-302, doi: 10.1016/j.atmosenv.2012.03.048, 2013a.

Otte, T. L., and Pleim, J. E.: The Meteorology-Chemistry Interface Processor (MCIP) for the CMAQ modeling system: updates through MCIPv3.4.1, Geosci. Model Dev., 3(1), 243-256, doi:10.5194/gmd-3-243-2010, 2010.

3. *P34728, line 22: "The variations of NH_3 in spring and summer were generally consistent with fluctuations of temperature (Fig. 2a)." The variation of ammonia is also consistent with fluctuations of temperature in winter and autumn. This issue needs to be reconsidered*.

Thanks for the comment. In winter, temperature and NH_3 concentration did co-varied but the correlation was much lower than spring (Figure 5). However, in autumn, there was a sustained drop in temperature while the NH_3 concentrations remained quite flat

during autumn days (Figure 4).

In the revised manuscript, this sentence has been revised as "The variations of NH_3 in spring and summer were generally consistent with fluctuations of temperature (Fig. 2a). In winter, their correlations turned to be much weaker (Fig. 5). While in autumn, no significant correlation between temperature and NH_3 was observed (Fig. 5)."

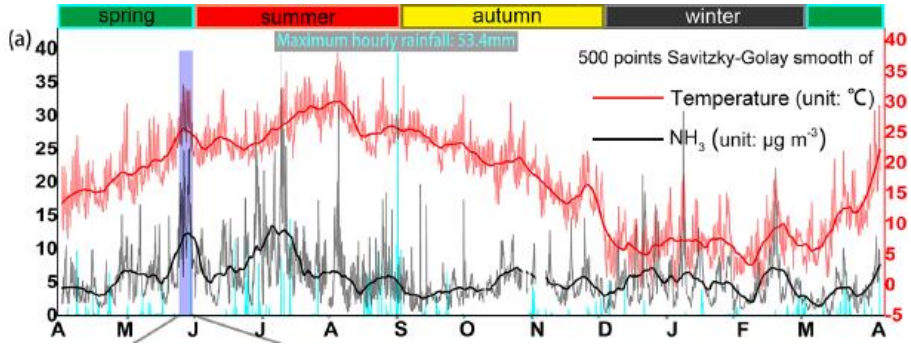


Figure 4. Temporal variations of hourly NH_3 concentrations (gray) and temperature (red), along with 500-point Savitzky-Golay smoothed records in Shanghai from 3 April 2014 to 2 April 2015.

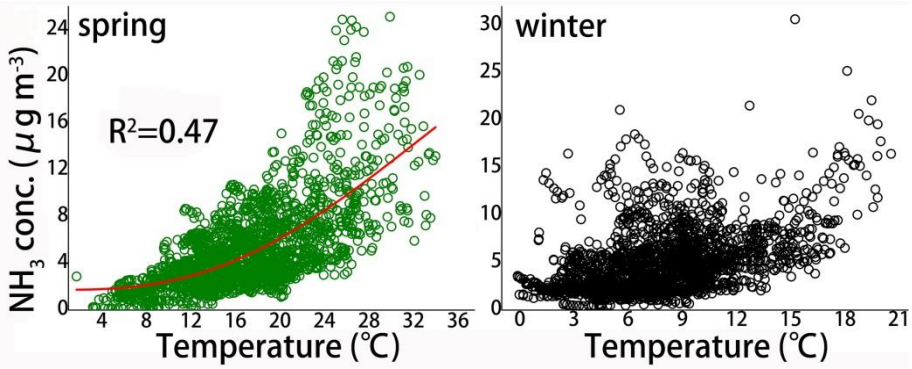


Figure 5. The relationship between hourly NH_3 concentration and hourly temperature in spring (left) and winter during our study period.

4. *P34730-31 You have not clarified what is the source of the meteorological data you used, like e.g. temperature, relative humidity, rainfall. Only PBLH data were described in the Methods section. It has to be clarified.*

Sorry for our negligence. We have clarified in the revised manuscript (page 34724, line 8) that meteorological parameters including temperature, relative humidity, and rainfall were monitored by an automatic meteorological station (Met One Instruments, US), which was co-located at the rooftop of the Pudong supersite.

5. *P34732 "However, it is unexpected that in Shanghai, almost all high NH_3 concentration values in summer are concentrated in the direction of South-Southwest-West (Supplement Fig. S3b), which strongly indicates that the urban area is one of the most important NH_3 emission regions in Shanghai." This is not clear – from the map 1 it is clear that there are rice fields in the south and west from the city. What is the wind direction frequency for this season – it could also influence the results*.

We think this question has been well discussed in our manuscript. In terms of emission inventory, the NH_3 emissions in the region of Shanghai (including rural and urban areas) were dominated by agricultural activity and, we agree with the reviewer that there are rice fields in the south and west from the city. However, our PSCF analysis indicated that independent of investigated season, the NH_3 sources in Shanghai were locally dominated during our study period (Figure 6c). This is particularly true in summer: both CO and NH_3 were sourced near the city and therefore yield the highest correlation coefficient (Figure 6b). Moreover, although a much higher temperature in summer tends to enhance the contribution of agricultural NH_3 emissions, almost all high NH_3 concentration values in summer were occurred within the city (indicated by rather low wind speed (lower than 1 m s^{-1}) in Supplement Fig. S3b). This suggests that even in hot summer, there was a strong contribution of NH_3 emissions within the city (e.g., on-road traffic).

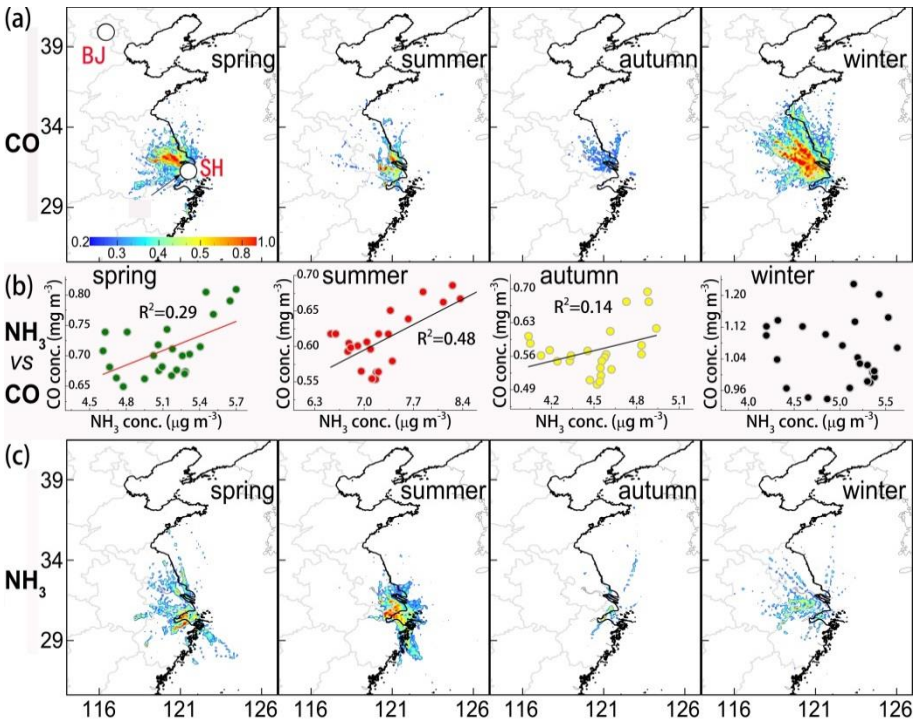


Figure 6. PSCF of CO (**a**) and NH_3 (**c**) during four seasons. The cities marked in each panel are Beijing (BJ) and Shanghai (SH). The color scales indicate the values of PSCF. (**b**) Relationship between hourly NH_3 and CO during four seasons.

The wind rose (wind speed/wind direction) in different season during our study period

is shown in Figure 7. It is clear that the winds in summer mainly came from the directions of North and Northwest instead of South-Southwest- West.

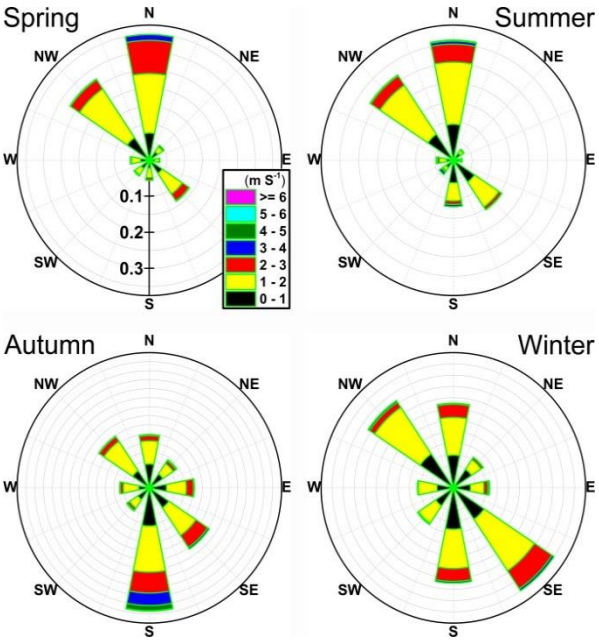


Figure 7. Wind rose plots, color coded by wind speed for each season during our study period. The frequencies are set to the same scales for all seasons.

6. *P34733 "NH_3 also displays a clear bimodal profile during all four seasons, similar to the CO diurnal profile, suggesting a significant influence of on-road traffic (with daily commuting) on ambient NH_3 concentrations in the urban environment of Shanghai." – concerns fig.7 Similar profiles were previously observed for agricultural stations (e.g. in (Aas et al., 2012) or (Schaap et al., 2011)). Please compare the profiles you got to other studies. Aas, W., Tsyro, S., Bieber, E., Bergström, R., Ceburnis, D., Ellermann, T., Fagerli, H., Fröhlich, M., Gehrig, R., Makkonen, U., Nemitz, E., Otjes, R., Perez, N., Perrino, C., Prévôt, A. S. H., Putaud, J.-P., Simpson, D., Spindler, G., Vana, M. and Yttri, K. E.: Lessons learnt from the first EMEP intensive measurement periods, Atmos. Chem. Phys., 12(17), 8073–8094, doi:10.5194/acp-12-8073-2012, 2012. Schaap, M., Otjes, R. P. and Weijers, E. P.: Illustrating the benefit of using hourly monitoring data on secondary inorganic aerosol and its precursors for model evaluation, Atmos. Chem. Phys., 11(21), 11041–11053, doi:10.5194/acp-11-11041-2011, 2011.*

Thanks for the comment. As suggested, we bring out the observed and modeled NH_3 diurnal profiles from agricultural stations in Aas et al. (2012) and Schaap et al. (2011) that are shown in Figure 8 and Figure 9, respectively. It is very clear to tell the difference between the urban station (Shanghai Pudong supersite; Figure 10) and the agricultural stations in terms of their diurnal variation pattern of NH_3. In Shanghai

urban areas (Figure 10), "NH_3 displays a clear bimodal profile during all four seasons". In Schaap et al. (2011), the variation of NH_3 at Cabauw was clearly characterized of a single modal profile and didn't show any peaks during the evening rush hours (Figure 9). As similar as in Aas et al. (2012), generally there were no high peaks during the rush hours in different seasons (Figure 8). Specifically, at the Ispra site, high values of NH_3 occurred during the daytime which was clearly related to the agricultural activities.

Overall, we found out significant differences of the NH_3 diurnal profiles between our urban site and the agricultural sites. We thank the reviewer for providing these references.

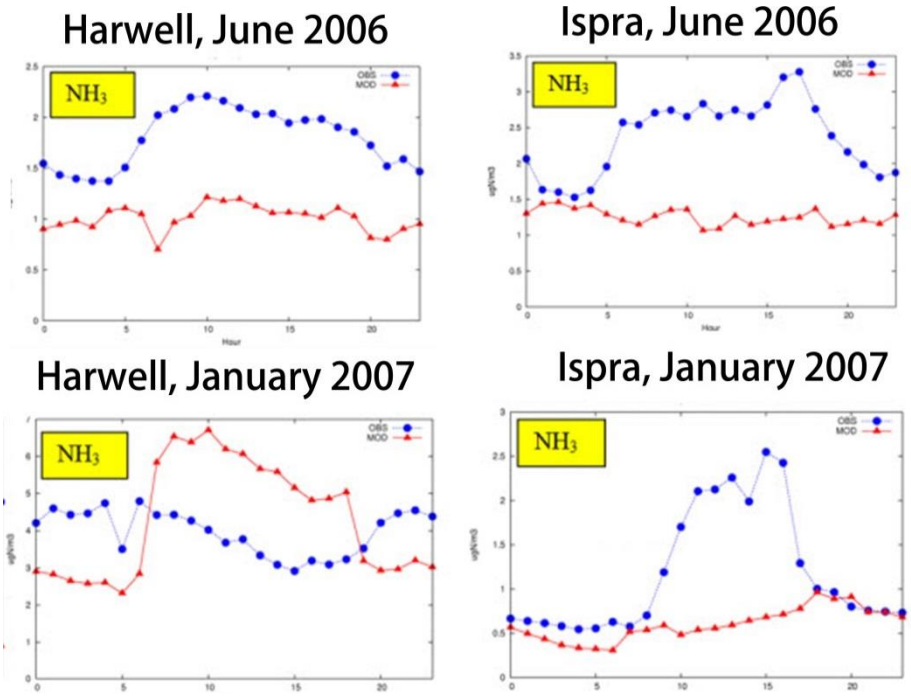


Figure 8. Diurnal variations of ambient NH_3 from some of the intensive measurements compared with the EMEP model. This figure was modified from Figure 8 in Aas et al. (2012).

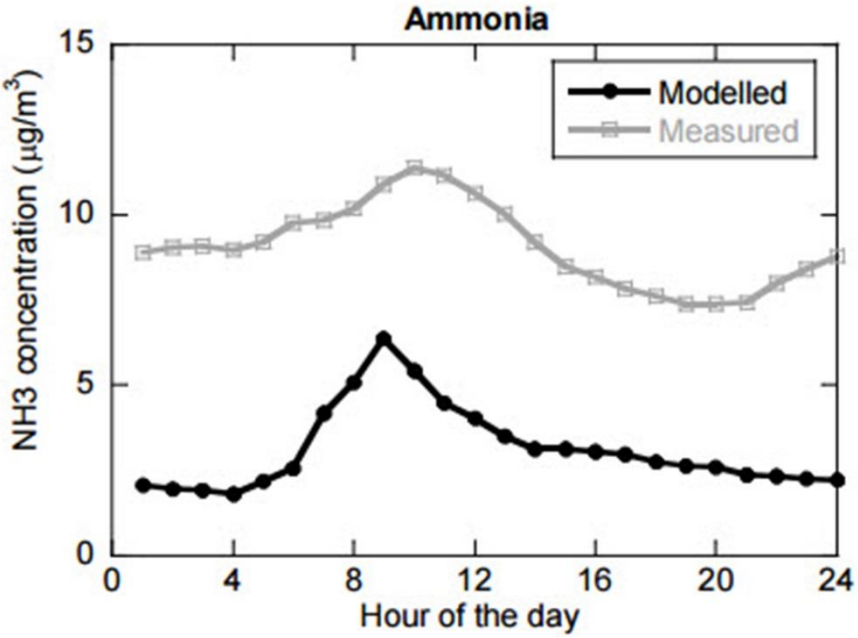


Figure 9. Comparison of the measured (grey) diurnal cycle for NH_3 at Cabauw with 7 km grid resolution estimates (black) of the LOTOS-EUROS model. This figure was modified from Figure 6 in Schaap et al. (2011).

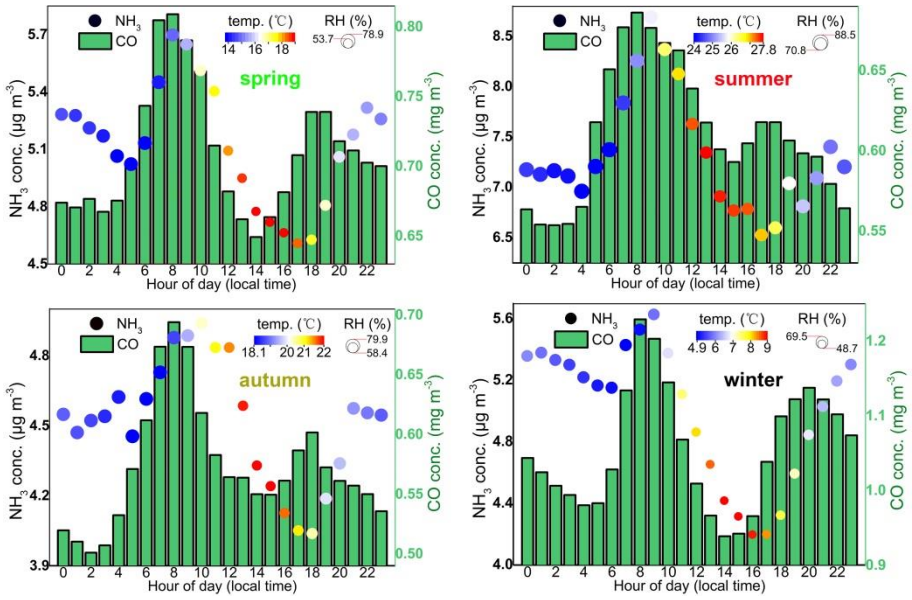


Figure 10. Seasonal diurnal profiles of NH_3 and CO concentrations determined at the Pudong supersite in our study. Color coded by hourly temperature and circle radius coded by hourly relative humidity.

Reference:

Aas, W., Tsyro, S., Bieber, E., et al., Lessons learnt from the first EMEP intensive

measurement periods, Atmos. Chem. Phys., 2012, 12(17): 8073-8094.

Schaap, M., Otjes, R. P., Weijers, E. P., Illustrating the benefit of using hourly monitoring data on secondary inorganic aerosol and its precursors for model evaluation, Atmos. Chem. Phys., 2011, 11(21): 11041-11053.

7. *P34736 "During spring, ambient NH_3 concentrations appeared to be influenced to some extent by temperature-dependent emissions, likely from agricultural activities including crop fertilization. No such relationship was apparent during other seasons" This is not true. NH_3 concentrations seem to be dependent on temperature also for other seasons. It is visible in fig. 2. Please clarify*.

Please refer to our response to *comment 2*.

8. *P34736 While mixing height of planetary boundary layer and relative humidity were not the main factors influencing seasonal NH_3 concentrations. The PBL issue has to be reconsidered after the explanation of the PBLH data quality used in this study (please see also comment 1). Compare your results on PBLH with other studies*.

Please refer to our response to *comment 3*.

9. *The diurnal profile of NH_3 concentrations showed a typical bimodal cycle during four seasons, with maxima in the morning and the evening rush hours, suggesting a persistent influence of on-road traffic (with daily commuting) on ambient NH_3 levels in Shanghai. It has to be reconsidered (please see comment 5).*

Please refer to our response to *comment 5*.

Referee 3:

General comments

Ammonia is regarded mainly as emissions from agricultural sources (e.g. ammonium-based N fertilizers and animal husbandry). However, ammonia emissions from non-agricultural or urban sources have been paid much less attention currently. This manuscript provides strong evidence that traffic vehicles are significant urban ammonia sources which contribute to ground level NH_3 in megacity of Shanghai. The authors use a one-year continuous monitoring data from a super cite in Pudong (east of Shanghai) and monitoring results from an urban tunnel (west of Shanghai) to support their conclusions. In addition, using bottom-up approach, they have estimated overall annual vehicle emissions of ammonia in the megacity of Shanghai (1300 t yr^{-1}) for the first time, in spite of some uncertainties. Although non-agricultural source NH_3 emission is not new topic, the manuscript systematically proves the non-negligible contribution of traffic vehicles, as an important non-agricultural source, to urban ammonia pollution. The related results may provide implications for haze or $PM_{2.5}$ pollution in megacities worldwide. I strongly support the publication of the manuscript after minor revisions as suggested in the specific comments.

We are grateful to Prof. Liu for his strong support and highly praised to our work.

Specific comments

1. *The title of the paper could be slightly modified as "Non-negligible contribution of vehicle emissions to atmospheric ammonia in the megacity of Shanghai".*

We think the word “non-negligible” has some sort of ambiguity. After personal communication with Prof. Liu, we would like to keep our original title.

2. *In the section of Results and Discussion, I suggest the authors provide a combined analysis of ammonia and ammonium (ion) dynamics in $PM_{2.5}$ at the PD super site.*

The analysis of water-soluble traces gases and ions data in $PM_{2.5}$ concentrations by MARGA is not presented in the present manuscript, although models applied to the MARGA database is usefull to investigate the contribution and processess of NH_3 to secondary inorganic aerosol formation. Such work will be addreessed in details, with further tests in the near future.

3. *Legend (of land use) in Figure 1: using "upland cropland" instead of "drought land".*

Revised accordingly.

4. *Lines 7-8 in Page 38422: "Despite the focus on ammonia sources mainly from agricultural and rural environments,...".*

In the revised manuscript, we've corrected our statement as suggested by the referee.

5. *Mileage emission factor for NH_3 in this study is quite different from other reports and it can be discussed for details in the revision*.

Both performed in two of China's megacities (Shanghai and Guangzhou), the emission factor (EF) for vehicle-emitted NH_3 in our study is much lower than that work of Liu et al. (2014). In fact, the EF we derived is very similar to that observed for the Gurbrist tunnel in Switzerland (31 ± 4 mg km^{-1}) (Emmenegger et al., 2004) and the Caldecott tunnel in California (49 ± 3 mg km^{-1}) (Kean et al., 2000). Yunhua Chang (the first author of the manuscript) had tried to discuss this with one of the co-authors of Liu et al., (2014) via email, but unfortunately, no feedback has yet been received.

In collaboration with Yunting Fang, Professor of the Institute of Applied Ecology, Chinese Academy of Sciences, we recently measured the vehicle-emitted NH_3 directly from vehicular tailpipes. We found that varying at different stages, the NH_3 concentrations ranged from 300 ppb to 500 ppb (unpublished data). We have no intention to judge any work related to the EF of vehicle-emitted NH_3, however, we still think the NH_3 concentrations measured at the exit of the Zhujiang tunnel in Guangzhou by Liu et al. (2014) were unexpectedly high (729 ± 497 ppb). Here we call for more research to be undertaken to pinpoint this parameter in order to accurately quantify the level of NH_3 emitted from vehicles.

Reference:

Emmenegger, L., Mohn, J., Sigrist, M., Marinov, D., Steinemann, U., Zumsteg, F., and Meier, M., Measurement of ammonia emissions using various techniques in a comparative tunnel study, Int. J. Environ. Pollut., 2004, 22, 326–341, doi:10.1504/IJEP.2004.005547.

Kean, A. J., Harley, R. A., Littlejohn, D., and Kendall, G. R., On-road measurement of ammonia and other motor vehicle exhaust emissions, Environ. Sci. Technol., 2000, 34, 3535–3539, doi:10.1021/es991451q.

Liu T, Wang X, Wang B, et al., Emission factor of ammonia (NH_3) from on-road vehicles in China: tunnel tests in urban Guangzhou, Environ. Res. Lett., 2014, 9(6), doi:10.1088/1748-9326/9/6/064027.

The importance of vehicle emissions as a source of atmospheric ammonia in the megacity of Shanghai

Y. H. Chang[1, 2], Z. Zou[23], C. R. Deng[1,32], K. Huang[1, 2, 5], J. L. Collett Jr.[4], J. Lin[1], and G. S. Zhuang[1, 2]

[1]Center for Atmospheric Chemistry Study, Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, China

[2]Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP[3]), Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, China

[32]Pudong New Area Environmental Monitoring Station, Shanghai 200135, China

~~[3]Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP[3]), Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, China~~

[4]Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80523, USA

[5]Department of Civil and Environmental Engineering, The University of Tennessee, Knoxville, TN 37996, USA

Correspondence to: C. R. Deng (congruideng@fudan.edu.cn) and G. ~~S.~~ Zhuang (gzhuang@fudan.edu.cn)

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Abstract

Agricultural activities are a major source contributing to NH_3 concentrations in Shanghai and most other regions of China; however, there is a long-standing and ongoing controversy regarding the contributions of vehicle-emitted NH_3 to the urban atmosphere. From April 2014 to April 2015, we conducted measurements of a wide range of gases (including NH_3) and the chemical properties of $PM_{2.5}$ at hourly resolution at a Shanghai urban supersite. This large dataset shows NH_3 pollution events, lasting several hours with concentrations four times the annual average of 5.3 μg m^{-3}, caused by the burning of crop residues in spring. There are also generally higher NH_3 concentrations (mean ±1σ) in summer (7.3 ±4.9 μg m^{-3}; n=2181) because of intensive emissions from temperature-dependent agricultural sources. However, the NH_3 concentration in summer was only an average of 2.4 μg m^{-3} or 41% higher than the average NH_3 concentration of other seasons. Furthermore, the NH_3 concentration in winter (5.0 ±3.7 μg m^{-3}; n=2113) was similar to that in spring (5.1 ±3.8 μg m^{-3}; n=~~2204~~2198) but slightly higher, on average, than that in autumn (4.5 ±2.3 μg m^{-3}; n=1949). Moreover, other meteorological parameters like planetary boundary layer height and relative humidity were not major factors affecting seasonal NH_3 concentrations. These findings suggest that there may be some climate-independent NH_3 sources present in the Shanghai urban area. Independent of season, the concentrations of both NH_3 and CO present a marked bimodal diurnal profile, with maxima in the morning and the evening. A spatial analysis suggests that elevated concentrations of NH_3 are often associated with transport from regions west-northwest and east-southeast of the city, areas with dense road systems. The spatial origin of NH_3 and the diurnal concentration profile together suggest the importance of vehicle-derived NH_3 associated with daily commuting in the urban environment. To further examine vehicular NH_3 emissions and transport, sampling of the NH_3 concentration was performed in (from the entrance to the exit of the tunnel) and out (along a roadside transect spanning 310 m perpendicular to the tunnel) of a heavily trafficked urban tunnel during the spring 2014. NH_3 concentrations in the tunnel exit were over 5 and 11 times higher than those in the tunnel entrance and in the ambient air, respectively. Based on the derived mileage-based NH_3 emission factor of 28 mg km^{-1}, a population of 3.04 million vehicles in Shanghai produced around 1300 t NH_3 in 2014, which accounts for 12% of total NH_3 emissions in the urban area. Collectively, our results clearly show that vehicle emissions associated with combustion are an important NH_3 source in Shanghai urban areas and may have potential implications for $PM_{2.5}$ pollution in the urban atmosphere.

1 Introduction

Ammonia (NH_3) is one of the most abundant nitrogen-containing substances and the principal reduced nitrogen component in the atmosphere. It plays a strong role in local and regional scale tropospheric chemistry and air quality by serving as a precursor to particulate ammonium (pNH_4^+) (Seinfeld and Pandis, 2012). Although major efforts have been made towards regulating NO_x and SO_2 emissions to improve air quality in China (Wang et al., 2014; Zhao et al., 2013), a major portion of the nation's population presently lives in environments of non-compliance with national standards for fine particulate matter ($PM_{2.5}$, representing particles with aerodynamic diameters smaller than 2.5 microns) (Huang et al., 2014; Lin et al., 2010; Ma et al., 2014; Ma et al., 2015). NH_3 emission reduction has been proposed as a cost-effective strategy to lower ambient $PM_{2.5}$ levels (Heald et al., 2012; Pinder et al., 2007; Wang et al., 2011; Wang et al., 2013; Ye et al., 2011). However, the emission sources of NH_3 and their relative contributions to ambient concentrations, especially in urban atmospheres, remain uncertain (Chang, 2014; Felix et al., 2014; Yao et al., 2013).

Emission sources of NH_3 have been previously reviewed (e.g., Asman et al., 1998; Reis et al., 2009; Sutton et al., 2008). Major sources include volatilization of N-containing fertilizers and excreta from animal husbandry, which together contribute over 80% of total global NH_3 emissions (Bouwman et al., 1997; Clarisse et al., 2009; Olivier et al., 1998; Schlesinger and Hartley, 1992). Thus it is not surprising that previous investigations of NH_3 emissions were mainly performed adjacent to dairy operations (Mount et al., 2002), animal housing (Gay et al., 2003), livestock facilities (Kawashima and Yonemura, 2001), slurry lagoons (Aneja et al., 2000), pit latrines (Rodhe et al., 2004), and croplands (Yan et al., 2003), where elevated levels of NH_3 are often observed. Varying significantly in time and space, biomass burning (including agricultural waste, savanna and forest fires) may contribute up to 12% of the global NH_3 emissions flux (Behera et al., 2013; Lamarque et al., 2010). Despite the focus on ammonia sources mainly from ~~is typical of~~ agricultural and rural environments, a number of studies reveal that ambient NH_3 concentrations in urban areas can be comparable to (Cao et al., 2009; Stanier et al., 2012) or even higher than (Bettez et al., 2013; Meng et al., 2011; Singh and Kulshrestha, 2014) those in rural areas. These observations strongly suggest that there must be other non-agricultural NH_3 sources present in urban areas.

Starting in the 1980s, the introduction of three-way catalytic converters (TWCs) on automobiles dramatically mitigated pollutant emissions from vehicle tailpipes (Shelef and

McCabe, 2000). An unwanted side effect of the use of TWCs for gasoline powered vehicles and selective catalytic reduction (SCR) for control of nitrogen oxides emissions from diesel powered vehicles, has been an increase in NH_3 emissions from motor vehicles, a significant source of non-agricultural NH_3 that has been documented directly through laboratory dynamometer studies (Durbin et al., 2002; Heeb et al., 2008; Heeb et al., 2006; Huai et al., 2005; Livingston et al., 2009; Suarez-Bertoa et al., 2014; Suarez-Bertoa et al., 2015) and on-road measurements (including mobile chase systems and tunnel tests) (Brito et al., 2013; Fraser and Cass, 1998; Kean et al., 2009; Liu et al., 2014; Moeckli et al., 1996; Pierson and Brachaczek, 1983; Pierson et al., 1996; Sun et al., 2014), or indirectly through correlation analysis between ambient NH_3 concentrations and other recognized traffic tracers (e.g., CO, NO_x) (Bishop and Stedman, 2015; Gong et al., 2011; Gong et al., 2013; Ianniello et al., 2010; Nowak et al., 2010; Pandolfi et al., 2012; Phan et al., 2013; Reche et al., 2012). In the U.S., it is estimated that 5% of the national NH_3 emissions are due to motor vehicles (Kean et al., 2009), while this figure is estimated at 12% for the UK (Sutton et al., 2000), with almost all the remaining NH_3 coming from agricultural processes. At a regional level, motor vehicle emissions make a small contribution to the total. Nevertheless, they are locally concentrated in urban areas where agricultural sources of NH_3 are mostly absent. Therefore, a disproportionately greater impact of motor vehicles on the urban NH_3 budget and subsequent secondary $PM_{2.5}$ formation can be expected (Chang, 2014). On the other hand, we notice that several important studies did not detect evidence of an influence of on-road traffic on ambient NH_3 concentrations (Pryor et al., 2004; Saylor et al., 2010; Yao et al., 2013). Therefore, more efforts needed to be made to elucidate the contribution of vehicle-emitted NH_3 to the urban atmosphere.

Shanghai, like many other cities in eastern China, is suffering severe air pollution problems, such as high $PM_{2.5}$ concentrations and resulting poor visibility (Huang et al., 2013b; Huang et al., 2012). Although there are many studies aimed at understanding PM pollution, little is known about the characteristics of NH_3 in the largest city of China. In an effort to curb its severe air pollution, China recently launched an air pollution monitoring research program (known as the supersite program) in several major cities. In 2014, a new in situ atmospheric station equipped with state-of-the-art instruments was installed in the Shanghai region, allowing comprehensive characterization of $PM_{2.5}$ and associated precursor gases. Here seasonal trends, diurnal variations and pollution episodes retrieved from one year of real-time

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measurement of NH_3 are presented and interpreted in order to explore the sources and parameters controlling the NH_3 concentrations across Shanghai. Meanwhile, an additional source-specific campaign was performed to examine the emission and transport of vehicle-emitted NH_3 from an urban heavily trafficked tunnel in Shanghai.

2 Methods

2.1 Long-term monitoring at Pudong supersite

In situ continuous observations of the chemical and optical properties of atmospheric aerosols and associated precursor gases were made on the rooftop (18 m above ground level) of the Pudong Environmental Monitoring Center (PEMC; 121.5446 °E, 31.2331 °N), 5 km east of the Shanghai urban center (the People's Square) (Figure 1). The site is located in a mixed-use urban area (office, commercial, residential and traffic) east of downtown Shanghai, with no obvious NH_3 point source within 5 km (Zou et al., 2015). As one of the state-controlled sites, Pudong (PD) supersite was designed by the Ministry of Environemtal Protection of China and operated by the Shanghai Environmental Monitoring Center, being responsible for the release of hourly air quality data for PM_{10}, $PM_{2.5}$, and other criteria pollutants (CO, SO_2, NO_x and O_3).

From 3 April 2014 to 2 April 2015, using a MARGA instrument (Measurement of Aerosols and Reactive Gases Analyzer, Metrohm Applikon B.V., NL), water-soluble gases (NH_3, HNO_3, HONO, HCl and SO_2) and $PM_{2.5}$ components (NO_3^-, Cl^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) were measured with hourly temporal resolution. The MARGA removes soluble gases in a rotating, wet-walled denuder, while a steam-jet aerosol collector is used for fine particle collection. Meanwhile, aerosol light absorption coefficients (b_{abs}) were retrieved every 5 min from an AE31 Aethalometer using seven wavelengths (370, 470, 520, 590, 660, 880 and 950 nm) with a $PM_{2.5}$ cut-off inlet. Black carbon (BC) concentrations for the whole data set were calculated from the absorption coefficient at 880 nm. The measurement process was subjected to rigorous quality assurance and quality control procedures according to the Technical Guideline of Automatic Stations of Ambient Air Quality in Shanghai based on the national specification HJ/T193-2005. Meteorological parameters including temperature, relative humidity, and rainfall were monitored by an automatic meteorological station (Met One Instruments, US), which was co-located at the rooftop of the PD supersite.

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To explore the comparability between on-line and off-line methods for NH_3 measurement, an Ogawa **p**assive **s**ampling **d**evice (PSD) was co-located with MARGA at PD to passively measure weekly ambient NH_3 concentration from May 2014 to June 2015. The Ogawa PSD is a double-sided passive sampler equipped with two 14 mm quartz filters (serving as duplicates) impregnated with phosphoric acid provided by the manufacturer. Following the manufacturer's protocols (http://www.ogawausa.com), exposed filter samples were soaked with 8 ml ultra-pure water (18.2 MΩ.cm) and analyzed by an ion chromatography system (883 Basic IC plus, Metrohm Co., Switzerland). The detection limit for NH_4^+ in the passive sampler extracts was 2.8 μg L^{-1}; this corresponds to an ambient NH_3 concentration detection limit of approximately 0.1 ppb for a 7-day sample. The NH_3 concentrations measured by the MARGA (ppb) were averaged over the same time period as the Ogawa PSDs (ppb). SI Figure S1 shows a good correlation (y=0.82x+0.56, n=53, R^2=0.84, p<0.001) between the two NH_3 measurement methods, validating the reliability of NH_3 data from the MARGA platform.

2.2 On-road measurement of NH_3 concentration in and out of a tunnel

To complement the information obtained from the main monitoring campaign described above, additional measurements of NH_3 concentration were performed at eight sites in and out the Handan tunnel from April 9 to May 21, 2014. The Handan tunnel is a 720 m long urban freeway in the northeast of Shanghai, separating the campus of Fudan University into two parts (Figure 9a). It contains an array of ventilation orifices in the middle section of the tunnel, 200 m in total. The tunnel has two traffic bores; each bore has a cross section of 70 m^2 and four lanes with typically 120000 vehicles (of which 85% of are light-duty vehicles) passing per day (Li, 2007). Driven by a group of high power fans, the average wind speed measured at the exit of the tunnel was approximately 5±1 m s^{-1}. The maximum vehicle speed limit in the tunnel is 80 km h^{-1}, with typical driving speeds of 50-60 km h^{-1}. Inside the northern bore of the tunnel, four sampling points were located at both ends of the tunnel (10 m from the exit and entrance of the tunnel, or T-d and T-a, for short) and the two ends of an array of ventilation orifices located in the middle section of the tunnel (Figure 9a; the site near the entrance and the exit named as T-b, and T-c for short, respectively). Outside the tunnel, a roadside transect involving four sites perpendicular to the tunnel was established, spanning the distance from 0 m (O_{0m}, for short), 20 m (O_{20m}), 150 m (O_{150m}), to 310 m (O_{310m}). Figure 9a shows the layout of the tunnel and the sampling points.

Using US EPA Method 207.1 (Determination of Ammonia Emissions from Stationary Sources), the NH_3 concentration at each site was measured. Briefly, for each sample, ambient air was pumped through two fritted glass bubblers (containing 10 ml 0.005 mol L^{-1} H_2SO_4 absorbing solution in each bubbler) for two hours at a flow rate of 1 L min^{-1}. These two bubblers were connected in series, and the NH_3 collection efficiency of the sampling trains was 95% or better (checked by using four bubblers in series in our pilot study, the collection efficiency=100*(the sum of the values of the first two bubblers)/the sum of the values of the four bubblers). Measurements were made during the morning (between 08:00 and 11:00 local time) and afternoon (between 14:00 and 19:00). Due to the proximity of the monitoring sites to the laboratory, all samples could be collected and analyzed by IC swiftly to avoid potential contamination, and field blanks were below the detection limit. Due to the dangers to personnel of sampling at the T-a, T-b and T-c sites, six samples were collected synchronously at these three sites. 19 paired samples were successfully collected and determined at the site of T-d, O_{0m}, O_{20m}, O_{150m} and O_{310m}.

2.3 Planetary boundary layer height simulation

The Weather Research and Forecasting (WRF) model v3.5.1 (Skamarock et al., 2008) is used for simulating the height of planetary boundary layer. The WRF simulation was performed from a mother domain with a 45 × 45 km horizontal resolution over Asia, and nested down to a second domain of 15 × 15 km covering Eastern China, Korea and Japan, and further nested down to a third domain of 5 × 5 km covering the Yangtze Delta River region. Lambert conformal conic projection was used with true latitude limits of 4° and 44° and standing longitude of 115°. The coverage of three domains is shown in Supplement Fig. S4. We chose the RRTM longwave radiation scheme and the Dudhia shortwave radiation scheme. The Yonsei University scheme was used for the planetary boundary layer option. The WRF model configurations can be found elsewhere (Huang et al., 2013a).The National Centers for Environmental Prediction (NCEP) Final (FNL) Operational Global Analysis dataset (http://rda.ucar.edu/datasets/ds083.2/) with a horizontal resolution of a resolution of 1.0 × 1.0° are incorporated as initial and boundary conditions for the model. An one-way nested approach with four-dimensional data assimilation (FDDA) in WRF is applied. We have performed model evaluations of major meteorological parameters against the NCDC surface meteorological network (National Climate Data Center, http://www7.ncdc.noaa.gov/CDO/cdo) within the YRD region (red dots marked in Supplement Fig. S4). The evaluation results of

surface wind speed, temperature, and humidity are show in Supplement Table S2. It could be seen that these meteorological parameters are within the benchmarks during most of the months, suggesting our WRF modeling results are reliable. A Meteorology/Chemistry Interface Processor (MCIP) (Otte and Pleim, 2010) v4.1 is used to post-process the WRF results by outputting the atmospheric height of the planetary boundary layer field, one of the standard MCIP outputs. The simulation period is consistent with the observation, i.e. from April, 2014 to April, 2015. In this study, PBLH derived from the third domain is used.~~The National Centers for Environmental Prediction (NCEP) Final (FNL) Operational Global Analysis dataset (http://dss.ucar.edu/datasets/ds083.2) with a horizontal resolution of a resolution of 1.0 °×1.0 ° are incorporated as initial and boundary conditions for the model. An one-way nested approach with four-dimensional data assimilation (FDDA) in WRF is applied. The WRF model configurations can be found elsewhere (Huang et al., 2013a). A Meteorology/Chemistry Interface Processor (MCIP) (Otte and Pleim, 2010) v4.1 is used to postprocess the WRF output. The atmospheric height of the planetary boundary layer field, one of the standard MCIP outputs, is used in this study.~~ Additionally, the planetary boundary layer depths at 3-hour resolution were obtained from the US National Oceanic and Atmospheric Administration (NOAA) READY archived Global Data Assimilation System (GDAS) meteorological data (1 ° × 1 °) based on Coordinated Universal Time (UTC). All UTC values are converted to local time (UTC + 8).

2.4 Potential source contribution analysis

24 h back trajectories arriving at the PD supersite at a height of 500 m were calculated at 1 h time intervals for each of the four seasons using NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model with GDAS one degree archive meteorological data (Draxler and Rolph, 2015). An in-depth back trajectory analysis, the potential source contribution function (PSCF), is useful for identifying the possible geographic origin of emission sources; this method calculates the ratio of the number of points with concentration higher than a threshold value (m_{ij}) to the total number of points (n_{ij}) in the ijth grid cell. Higher PSCF values indicate higher potential source contributions to the receptor site. In this study, the domain for the PSCF was set within the range of (26-42 °N, 112.5-125.5 °E) in 0.1 °×0.1 ° grid cells. The 75th percentile for CO and NH_3 during the four seasons was used as the threshold value m_{ij}. To reduce the uncertainties of m_{ij}/n_{ij} for those grid cells with a limited

number of points, a weighting function recommended by (Polissar et al., 2001) was applied to the PSCF in each season. Visualizations of the PSCF were mapped using ArcMap 10.2.

3 Results and discussion

3.1 Temporal evolution of NH_3 concentrations

The temporal patterns of hourly gaseous NH_3 concentrations determined by the MARGA at the Pudong supersite are reported in Figure 2. Summary statistics for NH_3 concentrations (μg m^{-3}) during April 3, 2014-April 2, 2015 are shown in Table 1. Using a variety of chemical, physical and optical techniques, numerous studies have examined ambient NH_3 concentrations over the last three decades; however, few of them were conducted in urban areas. As a comparison, we compiled previous work related to the measurement of urban NH_3 concentrations in Table 2.

The one year dataset (n=~~8447~~8441; data availability 96.4%) in the current study represents one of the longest on-line continuous measurement series of atmospheric NH_3 in China. During the study period, the NH_3 concentrations varied between 0.1~~0.03~~ and 39.2 μg m^{-3}, with an average (±1σ) of 5.5±3.9 μg m^{-3}. Domestically, the annual average NH_3 concentrations in Beijing and Xi'an were much higher than in Shanghai (see Table 2). This might be expected since Beijing and Xi'an are located in the North China Plain (NCP) and the Guanzhong Plain (GZP), respectively~~,~~. The NCP and GZP are two of the most intensive agricultural production regions in China. Moreover, the NH_3 loss from soil increases with an increase in soil pH value (Ju et al., 2009). Shanghai and its surrounding regions are dominated by the acid soils of paddy fields (Figure 1) (Zhao et al., 2009), while Beijing and Xi'an are dominated by the alkaline soils of dry land (Wei et al., 2013). Internationally, the NH_3 concencentration level in Shanghai was similar to observations from cities in developed and middle-income countries, but much lower than those cities in emerging countries. This is particularly true when comparing with cities in South Asia (e.g., Delhi in India and Lahore in Pakistan), where there is a lack of basic sanitation facilities (e.g., public flush toilets) and significant animal populations (such as cow) coexist with people in urban areas. The higher NH_3 concentrations measured at surface sites in South Asia are consistent with spatial patterns from recent satellite remote sensing observations (Clarisse et al., 2009; Van Damme et al., 2014).

277 The variations of NH_3 in spring and summer were generally consistent with fluctuations of
278 temperature (Figure 2a). In winter, their correlations turned to be much weaker (Fig. 4a).
279 While in autumn, no significant correlation between temperature and NH_3 was observed (Fig.
280 4a). Monthly, from March to September, the NH_3 concentration first increased steadily, with
281 the highest value in July, then decreased gradually, along with falling temperature (Figure 2c).
282 In summer (June to August), high temperatures favor NH_3 volatilization from urea and other
283 N fertilizers applied to croplands (Fu et al., 2013; Huang et al., 2011; Ianniello et al., 2010;
284 Meng et al., 2011). High temperatures in summer also favor NH_3 emission from other sources,
285 such as animal housing, landfills, laystalls and pit latrines, animal manure, natural and
286 fertilized soils, vegetation, and municipal solid waste (Fu et al., 2013; Huang et al., 2011).
287 Moreover, given that the equilibrium between ammonium nitrate particles and gaseous
288 ammonia and nitric acid favors the gas phase compounds at higher temperature, warmer
289 summer conditions promote dissociation of ammonium nitrate particles, shifting the
290 ammonium/ammonia partitioning toward the gas phase (Behera et al., 2013). In this study, the
291 average NH_3 concentration in summer (7.3 ± 4.9 μg m^{-3}; n=2181) was 2.4 μg m^{-3} or 41%
292 higher than the average of other seasons. The gap between summer and winter in Shanghai
293 was similar to New York, but generally much lower than many other cities. Taking Beijing
294 for example, according to Ianniello et al. (2010), the NH_3 concentration in summer was 460%
295 higher than in winter; this figure was 320% in Xi'an between 2006 and 2007 (Cao et al.,
296 2009). Smaller seasonal temperature differences and less agricultural activity in Shanghai
297 could be the contributing factors.

298 Based on the "bottom-up" methodologies, previous emission inventories indicate that
299 livestock feeding and N-fertilizer application contribute around 50% (48%-54.9%) and 35%
300 (33.4%-40%) of the total NH_3 emissions in the Yangtze River delta region (YRD for short,
301 including Shanghai as well as 24 cities in the provinces of Jiangsu and Zhejiang), respectively
302 (Fu et al., 2013; Huang et al., 2011; Huang et al., 2012). Agricultural production is also the
303 dominant source of NH_3 emissions in most other regions worldwide (Bouwman et al., 1997;
304 Olivier et al., 1998; Reis et al., 2009). However, performed at an urban level, many studies in
305 Table 2 concluded that the concentrations and evolution of ambient NH_3 in urban areas were
306 influenced by traffic emissions. As one of the world's largest megacities, Shanghai might
307 expect contributions of vehicle-emitted NH_3 as well. NH_3 concentrations in the atmosphere,
308 however, are also sensitive to other important factors such as changes in temperature, wind

speed or direction, and boundary layer depth; other influential factors might include local or regional NH_3 emissions, dry and wet deposition, and gas-to-particle partitioning. The relative importance of such factors in controlling ambient NH_3 concentration may vary seasonally. For example, the highest and lowest daily NH_3 concentrations in Shanghai were observed on 10-11 July 2014 (23.4 ± 6.7 μg m^{-3}) and 10-11 March 2015 (0.5 ± 0.4 μg m^{-3}), respectively. For the two periods, there was no significant difference between them in terms of wind speed and planetary boundary layer height (the relative humidity data in March period was missed). Although 19.6 mm of rainfall in the July period would be expected to lower NH_3 levels, the temperature on this high concentration date (28.4 ℃) was much higher than on the low concentration March date (4.7 ℃). Over a longer time frame, even though rainfall in summer was around twice the amount of rainfall in other seasons, other factors such as greater NH_3 emissions at higher temperature outweigh the wet scavenging effects of rainfall yielding higher summertime NH_3 concentrations. High NH_3 concentration episodes during burning of agricultural wheat residues, indicated by a strong and synchronous rise of trace aerosols from biomass burning (e.g., K^+ and BC), were also evident in late spring (Figure 2b). The evolution of this pollution episode induced by biomass burning and its influence of on the air quality of Shanghai has been examined in our recent paper (Zou et al., 2015).

3.2 Effects of meteorological parameters

In the following, we will examine the (synergistic) effects of various meteorological parameters on measured NH_3 concentrations in Shanghai, because these factors may mask the effect of vehicular emissions on the measured NH_3 concentrations. Summary statistics for meteorological parameters during April 3, 2014-April 2, 2015 are shown in Table 3.

Planetary boundary layer (PBL) height plays a vital role in determining the vertical dispersion of air pollutants that are emitted from the Earth surface. Decreasing height of PBL can normally hold the pollutants within the shallow surface layer so as to suppress the vertical atmospheric dilution. In many previous studies, as described above, the NH_3 concentrations in winter were much lower than those in summer. However, the NH_3 concentrations observed here in Shanghai during winter are relatively high. One may argue that weaker vertical mixing and shallow PBL layers in winter could trap NH_3 and contribute to elevated concentrations. In Figure 3a, although the simulated average PBL height in winter is the lowest during our study period, there is no significant difference among different seasons. In Figure 3b, the average

PBL height in winter is even higher than that in spring and summer. Therefore, a relatively high NH_3 concentration in winter at PD cannot be fully explained by the strength of vertical mixing or PBL height in this study.

Figure 4a suggests that temperature (*T*) is an important driver of the increase of NH_3 concentration in spring. No clear relationship is seen for other seasons. As the transitional period between winter and summer, springtime in Shanghai has the highest standard deviation of temperature during our study period (Table 3). Additionally, spring is known as the sowing season in South China, with the greatest application of N-containing fertilizers (mainly in the form of urea) of the year. Warming temperature tends to increase the rate of urea hydrolysis and ammonium conversion to NH_3, and therefore volatilization. For example, an increase in temperature from 7.2 ℃ to 15.6 ℃ can double volatilization loss when moisture content is kept the same (Ernst and Massey, 1960). For relative humidity (RH), there is no clear evidence to suggest RH as an important factor controlling the dynamics of NH_3 concentrations in any of the seasons (Figure 4b). Figure S2 shows the RH and *T* dependent distributions of NH_3 concentration for each season. Given the generally poor relationship between the NH_3 concentration and *T* and RH as discussed above, NH_3 concentrations have no clear dependence on *T* and RH seasonally.

In Figures 5a and b the distribution of hourly average wind speeds was calculated for values between 0 m s^{-1} and 4.0 m s^{-1} (99.5% of occurrence). Figure 5a shows that there is a highly significant relationship between WS and NH_3 concentration (R^2=0.91, p<0.001). The highest average NH_3 concentrations were measured under the lowest wind speeds and the lowest concentrations were measured at the highest wind speeds. There is no clear relationship between wind frequency (the number of wind occurrence) and average NH_3 concentration or WS during the study period (Figure 5c). Figure S3 shows WS/WD dependence of NH_3 concentrations in different seasons. The distribution of NH_3 concentration showed an obvious concentration gradient as a function of WS. Seasonally, there are different preferential wind directions for the highest NH_3 concentration values. Generally, an overwhelming higher *T* in summer tends to greatly enhance the contribution of temperature-dependent emissions to the urban NH_3 budget from agricultural areas. And the nearby rural areas around Pudong supersite are in the direction of Southeast (Nanhui) and Northeast (Chongming) (Figure 6d). However, it is unexpected that in Shanghai, almost all high NH_3 concentration values in summer are concentrated in the direction of South-Southwest-West (SI Figure S3b), which

strongly indicates that the urban area is one of the most important NH_3 emission regions in Shanghai.

Figures 6a and 6b show the RH and *T* dependent distributions of NH_3 and WS for the entire study period, respectively. Although the distribution of higher NH_3 favors the condition of high *T* (>25 ℃), low RH (<60%) and low WS (<1.2 m s^{-1}), Figure 6a shows that there is no obvious concentration gradient as a function of RH and *T* (Note that in SI Figure S2d, higher NH_3 concentrations in winter tend to occur at higher *T* for a given RH range of 60% to 80%). This can be explained by the dominance of low WS (often lower than 1.2 m s^{-1}) during east-southeast and west-northwest wind directions associated with intense local sources for NH_3 within the city (Figure 6c). In brief, our results suggest that there are some temperature-independent and important NH_3 sources in the urban area of Shanghai.

3.3 NH_3 diurnal profiles and insight into sources

Hourly observations over long-term periods offer a unique opportunity to provide robust diurnal profiles for each season. Figure 7 shows the average diurnal profiles of NH_3 and CO concentrations across seasons. Historically, CO emissions in Shanghai and its surrounding YRD region mainly came from iron and steel manufacturing and on-road vehicles, which contributed 34% and 30% of the total, respectively in 2007 (Huang et al., 2011). Due to changing economic activity, emission sources of air pollutants in China are changing rapidly. For example, over the past several years, China has implemented a portfolio of plans to phase out its old-fashioned and small steel mills, and raise standards for industrial pollutant emissions (Chang et al., 2012). In contrast, China continuously experienced double digit growth in terms of auto sales during the same period, and became the world's largest automobile market since 2009 (Chang, 2014). Consequently, on-road traffic has overtaken industrial sources as the dominant source of CO emissions in Eastern China (Zhao et al., 2012). In Figure 7, CO shows a well-marked bimodal diurnal profile, with maxima in the morning (starting at 05:00 local time) and the evening (starting at 16:00), consistent with the variation of traffic flow in Shanghai (Liu et al., 2012). Therefore, CO variation can be utilized as a robust indicator of vehicle emissions. NH_3 also displays a clear bimodal profile during all four seasons, similar to the CO diurnal profile, suggesting a significant influence of on-road traffic (with daily commuting) on ambient NH_3 concentrations in the urban environment of Shanghai. We also notice that pools of surface water (i.e. dew or fog), which form on nights

that have a high RH, can act as NH_x reservoirs that release NH_3 upon evaporation in the mid-morning, particularly in spring seasons.

Interestingly however, NH_3 shows different degrees of positive relationship with CO as a function of season (Figure 8b). Specifically, during summertime, NH_3 displays a significant relationship with CO (R^2=0.48, p<0.001), while this positive relationship is not observed during the winter season, when heavy traffic volume also occurs. As discussed above, the seasonal variation of NH_3 concentration in Shanghai during our study period was quite flat. The seasonal average CO concentrations at PD were 0.71, 0.61, 0.58, and 1.1 ppmv in spring, summer, autumn, and winter, respectively. And the CO level in wintertime was higher than other seasons. Moreover, Figure 8c suggests that for all seasons, the source region of NH_3 in Shanghai is local-dominated. However, the atmospheric lifetime of CO is much longer than that of NH_3 (typically several hours depending on meteorology) (Asman et al., 1998). PSCF analysis for CO in winter suggests important contributions from north of Shanghai (Figure 8a), a region that does not appear as important as a NH_3 source (Figure 8c). Consequently, elevated regional background levels of CO from long-range transport appear to yield a poorer relationship between NH_3 and CO in wintertime (Figure 8b).

3.4 The emission and transport of vehicle-sourced NH_3

SI Table S1 summarizes statistics of the NH_3 concentrations (μg m^{-3}) measured at each sampling point in and out of the Handan tunnel, which have been also been visualized in Figure 9b. As expected, the highest average NH_3 concentration occurred at the exit of the tunnel (T-d). Although NH_3 concentration varied temporally, throughout the two months of observations, a large spatial gradient in NH_3 concentration at near-road sites was present in every sampling event, suggesting that an intensive NH_3 source from on-road traffic (not meteorological parameters) is the leading factor in governing the variation of ambient NH_3 concentration in a road-side environment. The NH_3 concentrations in the tunnel were increased with distance from the entrance of the tunnel (T-a). The NH_3 concentration at T-d (64.9±11.5 μg m^{-3}) was over 5 times that at T-a (12.6±3.3 μg m^{-3}). Moreover, the lowest NH_3 concentration value obtained at T-d (47.0 μg m^{-3}) was still nearly 10 μg m^{-3} or 20% higher than the highest value of other sites (SI Table S1). These observations provide compelling evidence that on-road traffic is an important emission source of NH_3 in the urban atmosphere. Given that there is a significant loss of vehicle exhaust from the tunnel through an array of

ventilation orifices in the middle section of the tunnel, the NH_3 concentration at T-b (29.2±6.6 μg m^{-3}) was close to that at T-c (31.5±5.9 μg m^{-3}). If we taking into account of the **P**hysical **D**istance (PD; 300 m) and the NH_3 **C**oncentration **G**ap (**CG**; 33.4±11.5 μg m^{-3}) between T-c and T-d, the **C**ross **S**ection of tunnel bore (CS; 70 m^3), the average **W**ind **S**peed (WS; 5 m s^{-1}) and **T**raffic **F**low (TF; 120000 vehicles day^{-1}), we can obtain an approximate mileage-based NH_3 **E**mission **F**actor (EF) of 28±5 mg km^{-1} for a single vehicle using the following equation:

$$EF = \frac{CG \times CS \times WS \times 86400}{TF \times PD} \quad (1)$$

where 86400 is the number of seconds in a day. This NH_3 emission factor was similar to that observed for the Gurbrist tunnel in Switzerland (31±4 mg km^{-1}) (Emmenegger et al., 2004) and the Caldecott tunnel in California (49±3 mg km^{-1}) (Kean et al., 2000), while much lower than that recently measured in Guangzhou, China (230±14 mg km^{-1}) (Liu et al., 2014). Based on the emission factor we developed, a population of 3.04 million vehicles (average mileage of 15000 km yr^{-1}) in Shanghai would produce around 1300 t NH_3 in 2014. This is very close to the "bottom-up" emission inventory in Shanghai for 2010 (1581.1 t) (Chang, 2014). Previous emission inventories in Shanghai (e.g., Huang et al. (2011) and Fu et al. (2012)) made a significant underestimation of the NH_3 emissions from city areas. When compared with the NH_3 emissions from city area, the contribution of on-road traffic can reach 12% of the total NH_3 emissions in Shanghai city areas (10742 t) (Chang, 2014). Moreover, model results have shown that over half of agricultural NH_3 emissions would be deposited downwind of its source within 10 km depending on local meteorological conditions (Asman et al., 1998). Therefore, the relative contribution of NH_3 emissions from on-road traffic to urban PM pollution could be higher than the share of its mass contribution. Given that precisely estimating the EF of NH_3 from on-road traffic is beyond the scope of this paper, more research is needed to pinpoint this parameter in order to accurately quantify the amount of NH_3 emissions from vehicles.

From the tunnel exit to the open environment, the average NH_3 concentration at T-d (64.9±11.5 μg m^{-3}) was 11 times more than that at O_{310m} (5.6±2.5 μg m^{-3}), and a general negative relationship was found between distance and ambient NH_3 concentration. Over the total measured distance, the maximum percent decrease was observed between the sites of T-d and O_{0m} (50 m apart), indicating a rapid dispersion of vehicle-emitted NH_3 from the road

tunnel. Still, Figure 9c clearly shows that 64% (48%) of the NH_3 concentration we observed at the site of O_{0m} (O_{20m}) can be explained by the simultaneous measurements of NH_3 concentration at T-d. No significant decrease in the gradients of NH_3 concentration was observed between the sites of O_{150m} (5.9±2.5 μg m^{-3}; n=6) and O_{310m} (5.6±2.5 μg m^{-3}; n=6), suggesting that the strongest impact of NH_3 emission and transport from local traffic flow on ambient NH_3 concentrations in the Shanghai urban area lies within 150 m distance.

4 Conclusions and outlook

This study linked a long-term and near real-time measurement of NH_3 at one of China's flagship supersites with a vehicle source-specific campaign performed in and out of a major freeway tunnel in Shanghai. The conclusions are shown as below:

- The average NH_3 concentration (mean±1σ) between April, 2014 and April, 2015 was 5.5±3.9 μg m^{-3}. Seasonal NH_3 concentration levels varied in the following sequence: summer (7.3±4.9 μg m^{-3}) > spring (5.1±3.8 μg m^{-3}) ≈ winter (5.0±3.4 μg m^{-3}) > fall (4.5±2.3 μg m^{-3}).

- During spring, ambient NH_3 concentrations appeared to be influenced to some extent by temperature-dependent emissions, likely from agricultural activities including crop fertilization. No such relationship was apparent during other seasons. Measured NH_3 concentrations were highly dependent on wind speed, while mixing height of planetary boundary layer and relative humidity were not the main factors influencing seasonal NH_3 concentrations.

- The diurnal profile of NH_3 concentrations showed a typical bimodal cycle during four seasons, with maxima in the morning and the evening rush hours, suggesting a persistent influence of on-road traffic (with daily commuting) on ambient NH_3 levels in Shanghai.

- The NH_3 concentration in the exit of the Handan tunnel (64.9±11.5 μg m^{-3}) was over 5 and 11 times higher than that in the tunnel entrance (12.6±3.3 μg m^{-3}) and the ambient air (5.6±2.5 μg m^{-3}), respectively, providing further compelling evidence that on-road traffic is an important NH_3 source. 1300 t vehicle-emitted NH_3 in 2014 was calculated based on a mileage-based NH_3 emission factor of 28±5 mg km^{-1} we developed.

- A negative relationship was found between the distance and ambient NH_3 concentration in

our near-road gradient experiment. Up to 64% of ambient NH_3 concentration out of the tunnel can be explained by the vehicle-emitted NH_3 from the tunnel.

Unlike NH_3 emissions in agricultural areas, the NH_3 emissions in urban areas originate from a variety of stationary sources (industrial coal/oil/gas combustion, wastewater, landfill, compost and incineration), mobile sources and area sources (e.g., humans, green land, domestic fuel combustion). As a start, our study is far from fully elucidating the complex origins of urban NH_3 in Shanghai. Vehicle-emitted NH_3, while important, is likely not the only major source of NH_3. Additional useful investigative steps could include:

- Using isotopes as a source apportionment tool. Isotopic techniques have been proven to be useful tools for sources apportionment of gases and PM. Although the $\delta^{15}N$ values of NH_4^+ in rainwater and aerosols have been examined (Xiao et al., 2015; Xiao and Liu, 2002; Xiao et al., 2012), atmospheric NH_3 has received much less attention. According to Felix et al., (2013), NH_3 emitted from volatilized sources has relatively low $\delta^{15}N$ values, allowing them to be distinctly differentiated from NH_3 emitted from fuel-related sources (e.g., on-road traffic) that are characterized by relatively high $\delta^{15}N$ values.

- Using chemical transport modeling (CTM) as a cost-effective analysis tool. CTM has the potential to capture the complex atmospheric behavior of NH_3. Moreover, NH_3 emission reduction targets are represented as constraints in the optimization problem, and have a major influence on overall costs of a cost-effective solution and their distribution across different sources and economic sectors. Through sensitivity analyses of specific emission source or assuming possible emission control scenarios, CTM can contribute to the setting of effective emission reduction strategies to achieve cost-effective improvements in air quality.

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Table 1. Summary statistics of the NH_3 concentrations (μg m^{-3}) measured in Shanghai during April 3, 2014-April 2, 2015. P10 and P90 represent the 10th and 90th concentration percentile, respectively.

	N	Mean	SD	Minimum	P10	Medium	P90	Maximum
All	~~8447~~8441	5.5	3.9	~~0.03~~0.10	2.0	4.6	10.2	39.2
Spring	~~2204~~ 2198	5.1	3.8	~~0.03~~0.10	1.7	4.1	9.6	25.1
Summer	2181	7.3	4.9	0.65	2.6	6.3	12.7	39.2
Autumn	1949	4.5	2.3	0.57	2.3	3.9	7.2	19.7
Winter	2113	5.0	3.4	0.43	1.8	4.3	9.3	30.7

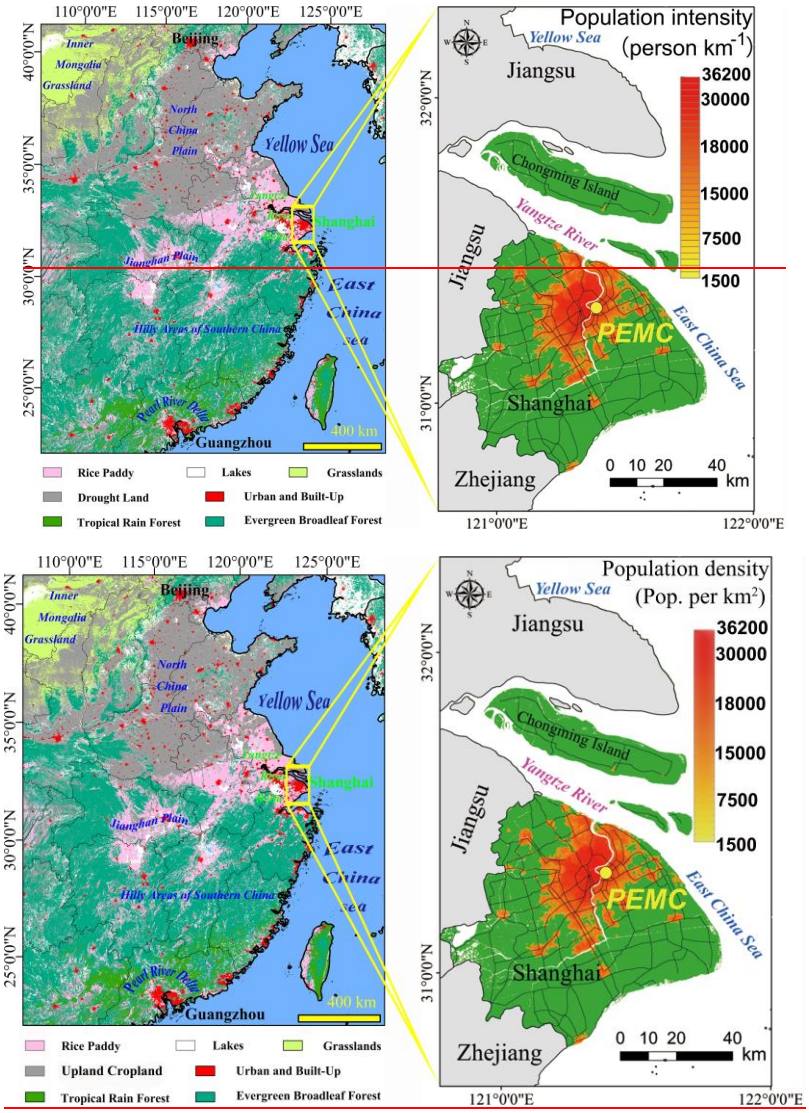
Table 2. Ambient NH_3 concentration measurements in the urban atmosphere of China and other countries/regions.

Location	Period	Methodology	Time resolution	Concentration (μg m^{-3})	Reference
East Asia					
Shanghai, CN	2014.4-2015.4	MARGA online monitor	hourly	5.5±3.9	This study
Beijing, CN	2008.2-2010.7	Ogawa passive sampler	weekly	14.2±10.6 (2008), 18.1±13.8 (2009)	Meng et al., 2011
Beijing, CN	2007.1-2, 8	Annular diffusion denuder	daily	5.5±3.8 (winter), 25.4±6.9 (summer)	Ianniello et al., 2010
Xi'an, CN	2006.4-2007.4	Ogawa passive sampler	weekly	12.9/6.4/20.3 (annual/winter/summer)	Cao et al., 2009
Nanjing, CN	2012.8-9	HRToF-CIMS (a)	1 Hz	1.3±1.8 (industrial area)	Zheng et al., 2015
Nanjing, CN	2013.7-8	Portable NH_3 online detector	hourly	6.7 (near road)	Wang et al., 2015
Guangzhou, CN	2010.11	OP-DOAS (b)	2.5 min	1.6	Wang et al., 2012
Urumqi, CN	2009.9-2010.8	Radiello passive sampler	biweekly	6.5	Li et al., 2013
Hong ~~kong~~Kong, CN	2003.10-2006.5	Ogawa passive sampler	weekly	0.7 (rooftop) -7.1 (near road)	Tanner, 2009
Taichung, TW	2002.1-12	Annular diffusion denuder	12 h	8.5±3.0	Lin et al., 2006
~~Yokohama~~Yokohama, JP	1987.1-1991.12	Glass flask sampling	3 h	2.5±1.4 (winter), 8.7±3.1 (summer)	Yamamoto et al., 1995
Nara, JP	1994.6-1995.5	Annular diffusion denuder	12 h	1.7 (winter), 1.6 (summer)	Matsumoto and Okita, 1998
Seoul, KP	1996.10-1997.9	Annular diffusion denuder	daily;	4.3/0.7/38.6 (annual/winter/summer)	Lee et al., 1999
Seoul, KP	2010.1-12	MARGA online monitor	hourly	6.8±3.3 (spring), 11.2±3.9 (summer)	Shon et al., 2013
Seoul, KP	2010.9-2011.8	MARGA online monitor	hourly	8.4±3.3	Phan et al., 2013
North America					
New York, US	1999.1-2000.6	Annular diffusion denuder	daily	5.0/4.1/6.1 (annual/winter/summer)	Bari et al., 2003
New York, US	2004.1-2	TDLAS (c)	<1 min	0.6 (winter)	Li et al., 2006
Chicago, US	1990.4-1991.3	Annular diffusion denuder	12 h	1.6±1.7	Lee et al., 1993
Pittsburgh, US	1993.7-9	Annular diffusion denuder	daily	3.9±4.4 (summer)	McCurdy et al., 1999
Los Angeles, US	1988.5-1994.9	Annular diffusion denuder	12 h	8.3	Blanchard et al., 2000
Sacramento, US	1988.10-1994.9	Annular diffusion denuder	12 h	9.5	Blanchard et al., 2000
Santa Barbara, US	1988.5-1994.9	Annular diffusion denuder	12 h	2.7	Blanchard et al., 2000
Farmington, US	2006.12-2007.12	Ogawa passive sampler	3 week	1.2±0.4	Sather et al., 2008
Clinton, US	2000.1-12	Annular diffusion denuder	12 h	2.6 (winter), 6.2 (summer)	Walker et al., 2004
Kinston, US	2000.1-12	Annular diffusion denuder	12 h	0.5 (winter), 2.7 (summer)	Walker et al., 2004
Morehead, US	2000.1-12	Annular diffusion denuder	12 h	0.3 (winter), 0.7 (summer)	Walker et al., 2004
Houston, US	2010.8	Quantum laser spectrometer	10 min	2.3±1.9 (summer)	Gong et al., 2011
Commerce, US	1978.11-12	~~Customed~~ Custumed passive sampler	two days	2.6 (winter)	Cadle et al., 1982
Vinton, US	1995.5-9	Ogawa passive sampler	biweekly	1.3±0.4 (summer)	Leaderer et al., 1999
Mexico city, MX	2006.3	Quantum laser spectrometer	6 min	17.7±11.0 (spring)	Fountoukis et al., 2009
Hamilton,CA	1992-1994	Annular diffusion denuder	daily	4.3	Brook et al., 1997
Europe					
Edinburgh, UK	2002.4-5	ALPHA passive sampler	bimonthly	4.8 (spring)	Cape et al., 2004
Münster, DE	2004.3-7	AMANDA (d)	10 min	3.9 (spring-summer)	Vogt et al., 2005
Toulouse, FR	1985.3-1986, 3	Nylon filter pack method	daily	3.8 (near road) – 19.8 (residential)	Giroux et al., 1997
Rome, IT	2001.5-2002.3	Annular diffusion denuder	30 min	17.2±2.7 (near road)	Perrino et al., 2002
Al-Ain, AE	2005.4-2006.4	Ogawa passive sampler	biweekly	9.7±4.8	Salem et al., 2009
Barcelona, ES	2011.5-9	AiRRmonia online analyzer	1 min	2.2±1.0 (near road), 5.6±2.1 (mixed)	Pandolfi et al., 2012
Barcelona, ES	2010.7, 2011.1	ALPHA passive sampler	biweekly	4.4 (winter), 9.5 (summer)	Reche et al., 2012
Barcelona, ES	2010.7, 2011.1	ALPHA passive sampler	biweekly	4.5±2.1 (winter), 9.2±6.6 (winter)	Reche et al., 2015
Madrid, ES	2011.3, 2011.7	ALPHA passive sampler	biweekly	2.3±1.3 (winter), 2.6±1.8 (summer)	Reche et al., 2015
Valencia, ES	2010.6, 2011.2-3	ALPHA passive sampler	biweekly	1.5±0.9 (winter), 0.5±0.4 (summer)	Reche et al., 2015
Huelva, ES	2010.11, 2011.5-6	ALPHA passive sampler	biweekly	2.8±3.8 (winter), 1.2±0.9 (summer)	Reche et al., 2015
Aveiro, PT	1988.8-1989.5	Nylon filter pack method	daily	3.5±1.9	Pio et al., 1991
South America					
Santiago, CL	2008.4-6	Ogawa passive sampler	monthly	15.0±3.8 (spring)	Toro et al., 2014
Sou~~r~~th Asia					
Lahore, PK	2005.12-2006.2	Annular diffusion denuder	12 h	50.1±16.9	Biswas et al., 2008
Dayalbagh, IN	1997.7, 1998.2	Annular diffusion denuder	3 h	12.5±2.2	Parmar et al., 2001
Delhi, IN	2008.9-10, 2009.9-10	Chemiluminescence analyzer	1 h	13.5±2.5 (2008), 14.4±3.7 (2009)	Sharma et al., 2011
Delhi, IN	2010.4-2011.11	Glass flask sampling	5 h	35.0±16.8	Singh and Kulshrestha, 2012
Delhi, IN	2012.10-2013.9	Glass flask sampling	8 h	40.7±16.8	Singh and Kulshrestha, 2014

Note: (a): High resolution time-of-flight chemical ionization mass spectrometry. (b): Open-path differential optical absorption spectroscopy. (c): Tunable diode laser absorption spectrometer. (d): Horizontal continuous-flow wet denuder.

Table 3. The average of temperature (^{o}C), relative humidity (%), accumulated rainfall (mm) and simulated planetary boundary layer (PBL) height (m) in Shanghai (mean ±1σ) during April 3, 2014-April 2, 2015.

	Temperature	Relative humidity	Accumulated rainfall	Simulated PBL height
All	17.1 ±8.2	72.4 ±16.1	1271.5	454.0 ±309.2
Spring	16.1 ±6.1	63.7 ±19.5	298.3	448.8 ±311.9
Summer	25.7 ±3.4	78.4 ±12.5	550.7	460.6 ±293.2
Autumn	19.8 ±4.4	76.5 ±13.0	221.4	482.6 ±321.6
Winter	6.7 ±3.3	67.0 ±15.6	192.1	428.0 ±307.4



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978 **Figure 1**. Location of the Pudong Environmental Monitoring Center (PEMC) supersite in
979 Shanghai. The left panel shows various types of land use in eastern and southern China
980 (adopted from (Broxton et al., 2014)). The red areas and black lines in the right panel
981 represent the urban areas and main roads in Shanghai, respectively.

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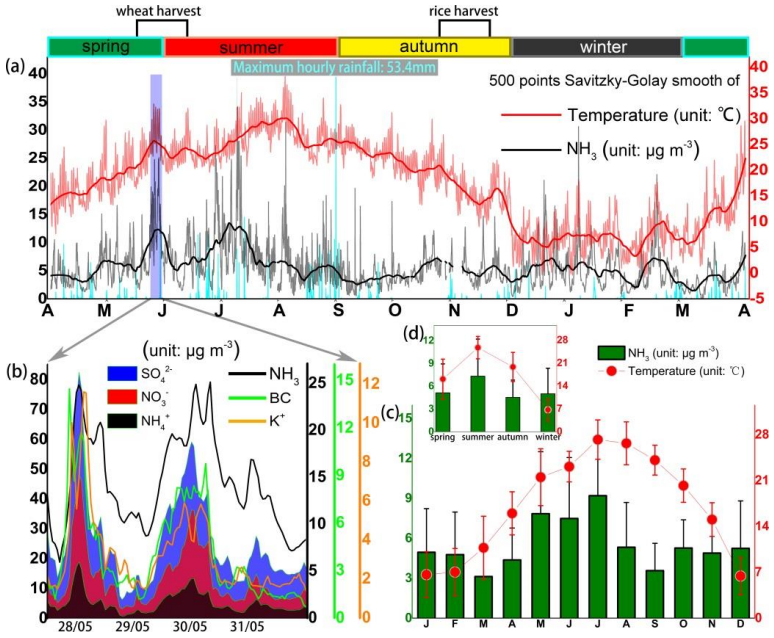

Figure 2. (**a**) Temporal variations of hourly NH_3 concentrations (gray) and temperature (red), along with 500-point Savitzky-Golay smoothed records in Shanghai from 3 April, 2014 to 2 April, 2015. Rainfall is shown in cyan. The vertical blue rectangle highlights NH_3 pollution episodes that occurred during the wheat harvest season. (**b**) Time series of NH_3, BC, SO_4^{2-}, NO_3^-, NH_4^+, and K^+ concentrations during periods of pollution associated with biomass burning. Monthly (**c**) and seasonal (**d**) variations of NH_3 average concentrations and temperature.

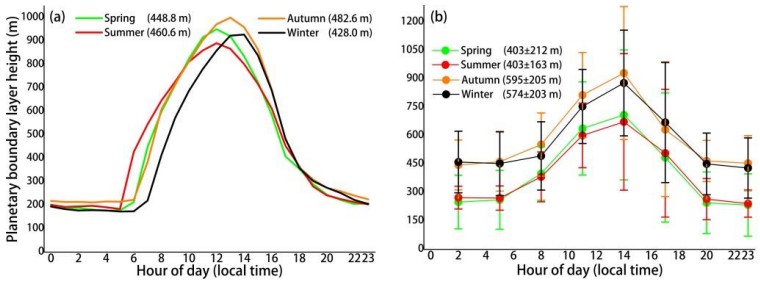

Figure 3. (**a**) Simulated diurnal profiles of the planetary boundary layer height in Shanghai during April 3, 2014-April 2, 2015. (**b**) Daily evolution of the planetary boundary layer height (NOAA READY achieved GDAS data) in Shanghai from 12 April, 2014 to 11 April, 2015. The number in the legend represents the average planetary boundary layer height, by time of day, in different seasons.

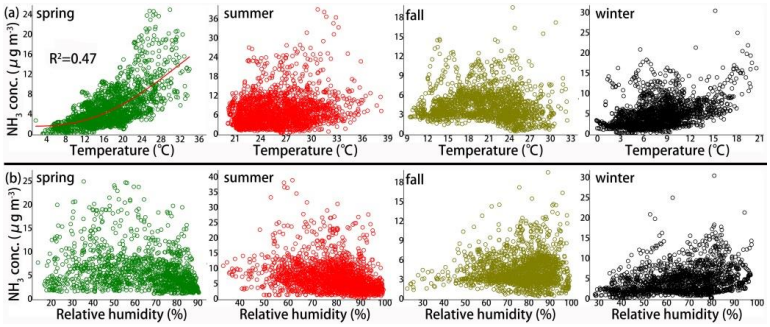

Figure 4. The relationship between hourly NH_3 concentration and hourly temperature (**a**) and hourly relative humidity (**b**) in four seasons at Pudong supersite between during April 3, 2014-April 2, 2015.

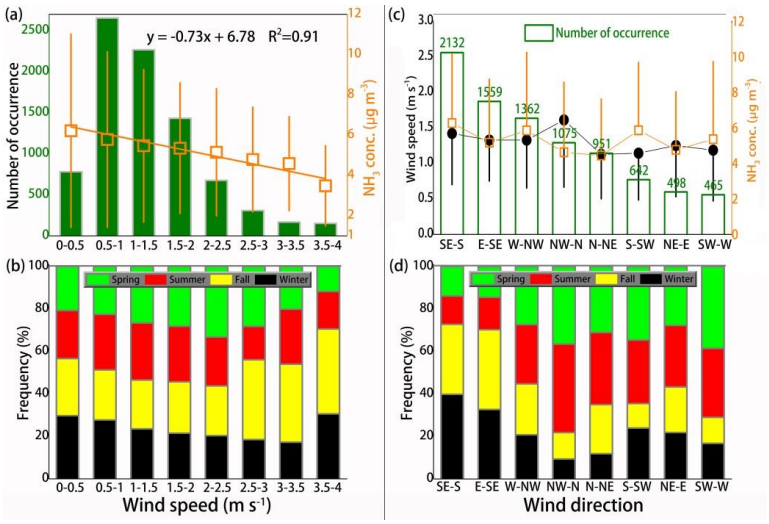

Figure 5. (**a**) Linear fitting of average NH_3 concentrations at different ranges of wind speed. The number of occurrences of wind (NOW) within each specific range of wind speed is shown as green columns. (**b**) Seasonal frequency distribution (%) of NOW at each specific range of wind speed. (**c**) The green boxes showing a descending order of the number of occurrences of wind at different wind directions. The points in black and the squares in orange represent the average wind speed and NH_3 concentration for each specific wind direction, respectively. (**d**) Seasonal frequency distribution (%) of NOW at each specific wind direction.

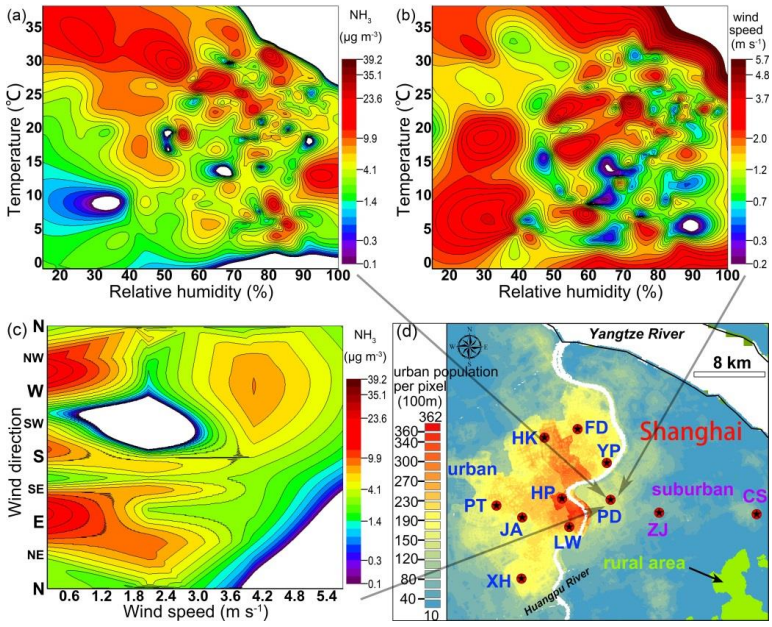

Figure 6. RH/*T* dependence of (**a**) NH_3 mass concentration and (**b**) WS, and (**c**) WS/WD dependence of NH_3 mass concentration at Pudong (PD) supersite for the year sampled. (**d**) The spatial distribution of ~~environemtal~~ environmental monitoring network in Shanghai. FD represents Fudan university. The base map is the 2010 urban population density, derived from a newly released high-resolution (100 m×100 m per pixel) population map of China (http://www.worldpop.org.uk/).

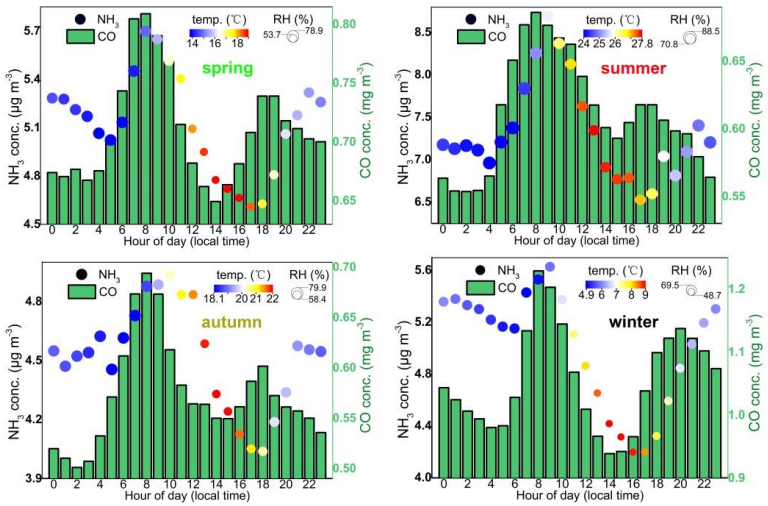

Figure 7. Seasonal diurnal profiles of NH_3 and CO concentrations in Shanghai. Color coded by hourly temperature and circle radius coded by hourly relative humidity.

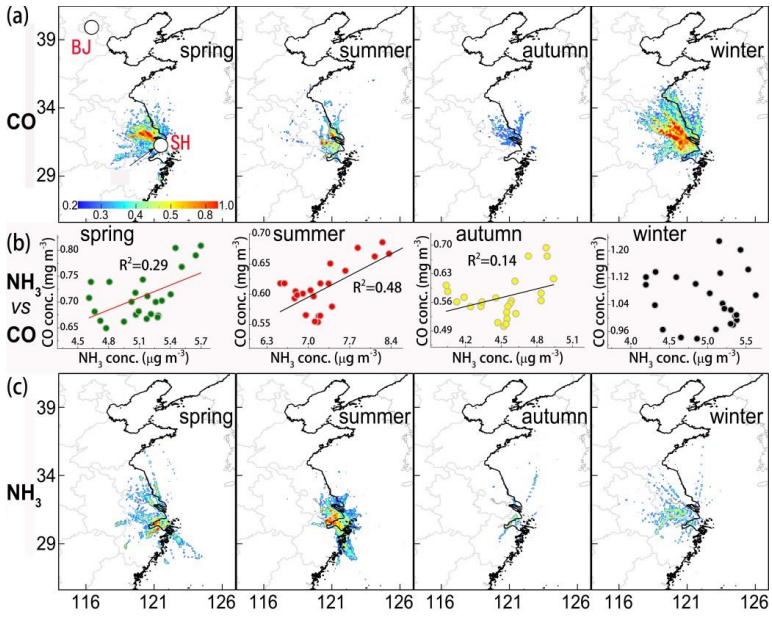

Figure 8. PSCF of CO (**a**) and NH_3 (**c**) during four seasons. The cities marked in each panel are Beijing (BJ) and Shanghai (SH). The color scales indicate the values of PSCF. (**b**) Relationship between hourly NH_3 and CO during four seasons.

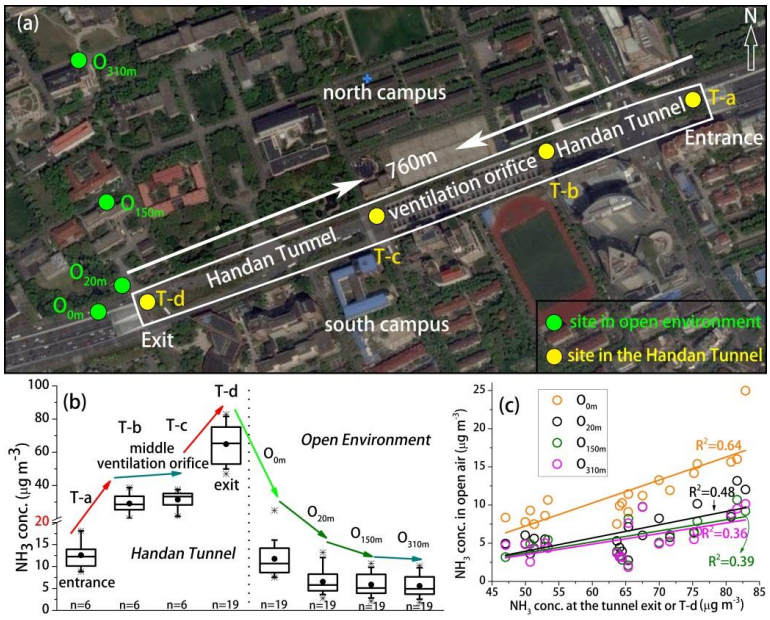

Figure 9. (**a**) Location of the eight sampling points in (labeled in yellow; inside the tunnel from the entrance to the exit) and out (labeled in green; varying in distance from the tunnel) of the Handan tunnel where atmospheric concentrations of NH_3 were measured using fritted glass bubblers. The 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_3 concentration 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.