Main revisions and response to reviewers' comments

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Title: Quantification and evaluation of atmospheric ammonia emissions with different methods: A case study for the Yangtze River Delta region, China

Authors: Yu Zhao, Mengchen Yuan, Xin Huang, Feng Chen, Jie Zhang

We thank very much for the valuable comments and suggestions from the two reviewers, which help us improve our manuscript significantly. The comments were carefully considered and revisions have been made in response to suggestions. Following is our point-by-point responses to the comments and corresponding revisions.

Reviewer #2

0. *This paper compares and contrasts two methodologies for estimating emissions of NH_3 in China, and illustrates the consequence through model simulations. The paper deals with an important subject, since the large uncertainties surrounding ammonia emissions need to be understood by modelers and policy experts. The paper is generally well written, and generally sound.*

Response and revisions:

We appreciate the reviewer's positive remarks on the importance of the work.

1. *I miss consideration of many of the factors omitted from the emission estimation procedure. This study basically used temperature, and agricultural statistics, to calculate emission factors (EFs). However, with respect to emissions from livestock/poultry, wind-speed is also a very important factor (e.g. Gyldenkaerne et al.,* *2005, Skjoeth et al., 2011, Flechard et al, 2013). Many other factors should also impact NH_3 emissions, such as radiation, rainfall (and other precipitation), leaf-wetness, atmospheric stability, large uncertainties in the so-called Gamma factors, or bi-directional exchange in general (Bash et al, 2013, Flechard et al., 2013, Massad et al, 2010, Wichink Kruit et al., 2012). Consideration of such factors might also help to explain some if the model discrepancies outlined in Section 3, and should at least be considered before trying to explain all such discrepancies in terms of temperature and a few selected variables only*

Response and revisions:

We thank and agree the reviewer's important comment. In this work, we mainly compared the magnitude and the spatial and temporal distribution of the YRD NH_3 emissions estimated with two different methodologies, and evaluated the two inventories through air quality modeling based on available satellite and ground observation within the region. Compared to E1, in particular, E2 included the impacts of the growing and farming cycles, soil properties (pH) and selected meteorological factor (temperature) on NH_3 emissions for fertilizer using sector, and those of manure management processes and ambient temperature for livestock/poultry breeding. Besides the parameters we are concerned with, however, some other factors and processes also play important roles on atmosphere-land exchange of NH_3, as pointed by the reviewer. Those factors/processes that were not considered in this work include given meteorological factors (e.g., wind speed, precipitation and leaf surface wetness), surface layer turbulence, air and surface heterogeneous-phase chemistry, and plant physiological conditions (Flechard et al, 2013). In general, those factors/processes could be integrated in the bi-directional surface–atmosphere exchange module coupled in the air quality modeling, and improved estimation of NH_3 flux (emissions and depositions) were expected. The modeling system with the bi-directional NH_3 exchange were reported to be able to reduce the biases and error in simulation of NHx (NH_3 +NH_4^+) wet deposition and ambient aerosol concentrations for both US and Europe (Bash et al, 2013; Wichink Kruit et al., 2012). Limited studies on the bi-directional NH_3 exchange were found for China (e.g., Fu et al., 2015). Out of the scope of current work, we did not focus on the bi-directional NH_3 exchange module and did not include the module for emission evaluation and comparison. We agree with the reviewer that the ignorance of given parameters/process in the estimation could potentially further explain the discrepancy between the simulation and observation. A more comprehensive evaluation and comparison in NH_3 emission inventories was thus suggested in the future, including the bi-directional NH_3 exchange and the top-down constraint with inversed modeling.

We have discussed this limitation and added relevant literatures **in lines 561-580, page 18 in the revised manuscript**.

2. *The authors use meteorology from ECMWF for their emissions, but why not the WRF model, since that is obviously available and is used for their CMAQ runs?*

Response and revisions:

We thank the reviewer's comment. We do not have very specific reason for using the ECMWF instead of WRF. When calculating the emissions, the underlying data open to the public were preferentially selected. ECMWF provided daily average data that satisfied our need of emission estimation and they were open to the public, thus we selected the dataset.

3. *The equations used are generally clearly written out, although it isn't always clear where they are coming from. For example, is it correct that equations 2 & 3 are a mixture of methods from Huang et al 2012 and EEA 2013? On the other hand, I read in various sections of EEA 2013 that temperature functions could not be provided (e.g. chap. 3.D crop production and agricultural soils) If from EEA, then it would also be good to cite the scientific papers underlying the EEA guidelines, and to be more specific as to which sections of EEA are being cited (it is a monster document).*

Response and revisions:

We appreciate the reviewer's comment. The specific EEA guidelines (EEA 2013a; 2013b; 2009) were provided in the revised manuscript. For Eq. 2 & 3, in particular, the linear relationships between NH_3 volatilization rate and temperature/soil pH were described in Chap. 4.D crop production and agricultural soils of EEA (2009)/Huang et al. (2012), and we specified them respectively **in lines 227-228, page 8 and lines 211-212, page 7 in the revised manuscript**.

4. *Some other points:*

P2. The abstract is rather long, and should be shortened for clarity.

Response and revisions:

We thank the reviewer's comment and the abstract was shortened.

P3, L67. NH_3 is said to react with NOx, but NOx usually means $NO+NO_2$. I think the authors mean HNO_3?

Response and revisions:

We thank the reviewer's reminder and it is corrected as nitric acid (HNO_3) in the revised manuscript.

P3, L78-81. The sentence is a little unclear. Clarify.

Response and revisions:

We thank the reviewer's comment. We mean that SO_2 and NO_X emissions have gradually decreased due to improved control, thus the NH_3 emissions was found to play a greater role on the secondary aerosol formation and nitrogen deposition, compared to previous years. The sentence is rewritten **in lines 72-76, page 3 in the**

revised manuscript:

Recently the SO_2 and NO_X emissions have gradually decreased due to implementation of various pollution control measures in China, thus NH_3 emissions were found to play a greater role on secondary aerosol formation and nitrogen deposition compared to previous years.

P4, L112. Methods of including meteorology in NH_3 emissions have been around for some time and should be mentioned, e.g. Gyldenkaerne et al., 2005, Skjoeth et al., 2011, Wichink Kruit et al., 2012, Bash et al., 2013.

Response and revisions:

We thank and agree the reviewer's comment. We have added the relevant papers and description **in lines 110-111, page 4 in the revised manuscript**.

P5, L148. Another source of human-related NH_3 emissions is pets. As shown in e.g. Sutton et al 1995, 2000, human pets can be as significant as human metabolism with regard to NH3 emissions.

Response and revisions:

We thank and agree the reviewer's comment. Due to lack of detailed statistic, we did not include pet emissions in current NH_3 inventories. Given the relatively small fraction in total emissions (e.g., less than 2% for United Kingdom by Sutton et al.), we believe that the uncertainty was limited. We have added the explanation **in lines 149-152, page 5 in the revised manuscript.**

P6, L168. Using should be used.

Response and revisions:

We thank the reviewer's reminder and it is corrected in the revised manuscript.

P7, L187. Give reference for radiometer

Response and revisions:

We thank the reviewer's reminder and the reference for radiometer is given in the revised manuscript (Davies et al., 2009).

P7, L202. The study of Huang et al 2012 uses a linear relationship between pH and EF. Why is the relation here said to be near-linear?

Response and revisions:

We thank the reviewer's reminder and it is corrected as linear in the revised manuscript.

P7. What is the time-resolution of the EF calculations?

Response and revisions:

The time-resolution of EF calculation is monthly. In the method, the fertilization method (top or basal dressing) was month-dependent, and monthly average temperature was applied for the EF calculation. We have added the information **in lines 212-213, page 7 and line 220, page 8 in the revised manuscript.**

P8, L232. Surely fertilizer application at 15-20cm affects the pH of the soil; doesn't this affect the assumptions made when using global pH data from IIASA?

Response and revisions:

We thank and agree the reviewer's comment. Previous domestic experimental studies in China (e.g, Zhong et al., 2006) indicated that the fertilizer application would increase the soil pH, particularly for the acidic soils. Bias thus existed in soil pH from the global database, without considering the detailed schedule and method of fertilizer application. As the quantitative relation between the fertilizer application and soil pH was still lacking at the regional scale in China, we ignored the interaction between the fertilizer application and soil pH in Eqs.(2). We acknowledged the limitation and added the explanation **in lines 243-248, page 8 in the revised manuscript.**

P9. The basic references of the CMAQ model should be given, not just a web-address.

Response and revisions:

We thank the reviewer's reminder and the basic operational guidance of CMAQ by University of North Carolina was provided in the revised manuscript (UNC, 2010).

P10. Which version of MEGAN was used? Did you use data provided by Sindelarova, or did you use the MEGAN model itself? If the latter, a Guenther et al ref would seem more

Response and revisions:

We thank the reviewer's comment. We used the MEGAN 2.1. The literature (Guenther et al., 2012) has been added in the revised manuscript.

P10. Again, give reference to the model developers - this time for WRF.

Response and revisions:

We thank the reviewer's reminder and the reference of WRF is provided in the revised manuscript (Skamarock et al., 2008).

P11. The Lanciki 2018 reference for MARGA is missing.

Response and revisions:

We thank the reviewer's reminder and the information of Lanciki (2018) is provided in the revised manuscript.

P15. The citation of Wei et al (2015) is in Chinese, and thus not helpful for most authors. This instrument has been around for many years, and the artifacts documented elsewhere. Please find some citations in English for the problems mentioned.

Response and revisions:

We thank the reviewer's comment and provided English papers for the problem **in lines 484-485, page 16 in the revised manuscript.** (Chen et al., 2017; Schaap et al., 2011; Stieger et al., 2018).

P28, Use molecule not "mole.", to avoid confusion with the mole unit.

Response and revisions:

We thank the reviewer's reminder and molecule is used in the revised manuscript.

P31. Table 3. Correlation coefficients should be added, and the time-resolution of the statistics mentioned.

Response and revisions:

We thank the reviewer's comment. The correlation coefficients between the observation and simulation were added in the revised Table 3, and the time-resolution of the statics was hourly, as mentioned in the revised caption of the table.

P31 cont. for all Tables make it clear if statistics are calculated from hourly, daily or monthly values.

Response and revisions:

We thank the reviewer's reminder. The statistics in Tables 3 and 6 were calculated based on the hourly values, and those in Tables 4 and 5 were from the daily values (the value of one hour (9:30am for satellite observation and the average of 9:00am-10:00am for simulation) per day). The information has been added **in the revised captions of Tables 3-6**.

There are small English misses throughout, for example with regard to singular or plural, or omission of the definite article (the).

Response and revisions:

We thank the reviewer's comment and the grammar errors are corrected in the revised manuscript.

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Reviewer #3

0. *The manuscript develops and presents two gridded NH3 emission inventories, one based on emission factors from the literature and a second with more process information. The two are compared against one other, as well as to two ground sites. CMAQ output was also be compared against satellite columns. This is a good exploration of what is known about NH3 emission patterns in the heavily populated Yangtze River Delta region. That said, without well understanding the methods E1 and E2, it was difficult to fully review manuscript.*

Response and revisions:

We appreciate the reviewer's positive remarks on the importance of the work.

1. *Emission inventories with general emission factors or more detailed process have always been used, so at first read I am not sure why this is considered as case study of the methodology versus something like "Quantification and evaluation of atmospheric ammonia emissions for the Yangtze River Delta region, China". The exact methods used for E1 and E2 are fairly confusing. The "constant emission factors" method that is referenced throughout are actually based on annual emission factors, with a monthly and spatial allocation schemes given on L179-L188. This needs to be clearer early on in the manuscript. Also, to confirm, neither allocation affects the total yearly emission? Are the activity factors different in E1 than what are used in E2?*

Response and revisions:

We appreciate the reviewer's important comment and acknowledged that some descriptions on the principles of the two methods were unclear in the original manuscript. The reviewer was correct for E1. It was developed based on the constant annual emission factors at the prefectural city level (as most of the activity data could be obtained at the prefectural city level). Spatial and monthly allocations of emissions were then conducted, without changes in total yearly emissions. Following the reviewer's suggestion, we mentioned this at the beginning of Section 2.1 (**lines 143-145, page 5 in the revised manuscript**). It is a relatively quick and simple method, based on the previous understanding of NH_3 emissions at regional scale (both the emission factor and temporal distribution). The effects of actual environmental conditions and agricultural activities on emission rate were not considered at a high temporal and spatial resolution.

In E2, the method for fertilizer application and livestock/poultry breeding (the main source categories of NH_3) was improved. In particular, the emission factors were developed at the monthly resolution, integrating the effects of soil, meteorology and agricultural processes. Therefore the method did not only change the temporal pattern of emissions but also the magnitude of the annual emissions, as the emission factors developed in this method varied from the ones applied in E1, which were directly taken from previous studies.

It should also be noted that the annual activity data were the same for the two inventories at the prefectural city level, although the monthly distributions were different. We have clearly stated the relation between the activity data in the two inventories **in lines 196-197, page 7 in the revised manuscript.** Please also see our response to Question 2 of the reviewer.

2. *Sect 2.2.1 about E2: please check each use of 'corrected' to make sure it is clear what/how/why something is being corrected. Specifically, L198 why does the fertilizer use need to be corrected? Where do the relationships in Table S2 come from?*

Response and revisions:

We appreciate the reviewer's comment and acknowledged some "corrected" were confusing. In E2, the emissions from fertilizer use and livestock/poultry breeding were recalculated with a different method from E1. In general, it is not a correction of E1. Therefore we deleted unnecessary "corrected" in the methodology section of E2

(Section 2.2). Regarding the word "corrected" fertilizer as pointed by the reviewer, in particular, we actually means that the monthly fertilizer used was estimated in E2 combining the information of investigated farming cycles. The annual total fertilizer was the same as E1. We also added an example of early-season rice for better understanding the method. The relevant texts have been revised **in lines 199-209, page 7 in the revised manuscript**.

Regarding Table S2, we clearly stated that the annual total amount of fertilizer used were the same by prefecture city and type in the two inventories **in lines 196-197, page 7 in the revised manuscript.** The method of estimating the annual amount of fertilizer by prefecture city and type in Table S2 was described in lines **in lines 165-171, page 6 in the revised manuscript.**

3. *Specific technical/style: L206 EFbase -> EFbasal and Tbase -> Tbasal*

Response and revisions:

We thank the reviewer's reminder and terms are corrected in the revised manuscript.

L206-207 Are Tbasal and T0 in different units? Otherwise, 273.15 wouldn't be needed

Response and revisions:

We thank the reviewer's reminder and 273.15 was deleted in the revised manuscript.

L213 'method' -> 'application method'? (if I'm guessing correctly). What are the possible methods?

Response and revisions:

We thank the reviewer's reminder and it is revised as application method (basal dressing).

L347-L349 where is this shown about the EFs being from hot seasons?

Response and revisions:

We appreciate the reviewer's comment. Most of the measurements on emission factor of ammonia from fertilizer application were conducted in summer or late spring (Cai et al., 2002; Huo et al., 2015; Su et al., 2006), especially those using micrometeorological method. It is expectable since that the basal dressing of single-season rice and maize as well as top dressing of wheat are usually conducted in late spring or summer. However, the crop rotation varies a lot in China, and part of the nitrogen-containing fertilizer actually is not applied in hot seasons. Emission estimation based on those emission factors may thus overestimate the emission intensity of ammonia (Huo et al., 2015; Wang et al., 2011; Zhang et al., 2010). We have provided relevant literatures and added the above discussion **in lines 361-369, page 12 in the revised manuscript.**

L518-L519 Please reword. IASI is an instrument, so it cannot 'provide' an averaging kernel.

Response and revisions:

We thank the reviewer's reminder and the sentence is rewritten **in lines 537-538, page 17 in the revised manuscript:**

As the ESPRI product of NH_3 VCDs we applied in the study does not provide the averaging kernel…

Figure 1 caption: "Studying area and research domain" -> aren't study area and research domain the same?

Response and revisions:

We thank the reviewer's reminder, and they are the same. We delete the "Studying area" in the figure caption.

Figure 3 and Figure 6: ‘Januray” -> “January”

Response and revisions:

We thank the reviewer’s reminder and the errors are corrected.

Figure 4: emissions misspelled in the y-axis label Figure 4: Suggest giving fertilizer and livestock consistent colors, then keeping E1 as solid fill but E2 as hatched for easier reading

Response and revisions:

We thank the reviewer’s reminder and the figure is improved as required.

Figure 6: colorscales could have greater consistency

Response and revisions:

We thank the reviewer’s reminder and the figure is improved as required.

Figure 9: the subplots should have a consistent axis font size

Response and revisions:

We thank the reviewer’s reminder and the same font size is applied in all the subplots.

Figure 10; from caption, shouldn’t axis limits be same as Figure 9? Also, helpful to add the border lines like in Figure 9 so one is orientated where they are looking

Response and revisions:

We thank the reviewer’s reminder and revised the axis limits. The border lines have also been added in the revised Figure 10.

Figure S4: there is one main cluster of data along the black line, but why is there seem to also be a second one? Also, what is the significance of the red dots, which do not fit well especially for the ABC panel?

Response and revisions:

The black line is obtained through linear regression based on all the blue dots (including the "second cluster" mentioned by the reviewer).

Different from blue dots that are calculated for all the grids within the research domain of this study, the red dots are taken from available field measurement studies, as we mentioned in the figure caption. The gap between them, in particular at lower soil pH, explained the possible uncertainty in current method, i.e., the current linear assumption between the soil pH and NH_3 volatilization rate might not be appropriate for soil with low pH values for eastern China. We discuss it **in lines 553-560, page 18 in the revised manuscript.**

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Quantification and evaluation of atmospheric ammonia emissions with different methods: A case study for the Yangtze River Delta region, China

Yu Zhao[1,2*], Mengchen Yuan[1], Xin Huang[3], Feng Chen[4], Jie Zhang[4]

1. State Key Laboratory of Pollution Control & Resource Reuse and School of the Environment, Nanjing University, 163 Xianlin Ave., Nanjing, Jiangsu 210023, China

2. Jiangsu Collaborative Innovation Center of Atmospheric Environment and Equipment Technology (CICAEET), Nanjing University of Information Science & Technology, Jiangsu 210044, China

3. School of Atmospheric Science, Nanjing University, 163 Xianlin Ave., Nanjing, Jiangsu 210023, China

4. Jiangsu Provincial Academy of Environmental Science, 176 North Jiangdong Rd., Nanjing, Jiangsu 210036, China

*Corresponding author: Yu Zhao

Phone: 86-25-89680650; email: yuzhao@nju.edu.cn

Abstract

To explore the effects of data and method on emission estimation, two inventories of NH_3 emissions of the Yangtze River Delta (YRD) region in eastern China were developed for 2014 based on the constant emission factors (E1) and those characterizing the agricultural processes (E2), respectively. The latter derived the monthly emission factors and activity data integrating the local information of soil, meteorology and agricultural processes. The total emissions were calculated at 1765 and 1067 Gg, respectively, and clear differences existed in seasonal and spatial distributions. Elevated emissions were found in March and September in E2, attributed largely to the increased top dressing fertilization and to the enhanced NH_3 volatilization under high temperature, respectively. Relatively large discrepancy between the inventories existed in northern YRD with abundant croplands. With the estimated emissions 38% smaller in E2, the average of simulated NH_3 concentrations with an air quality model using E2 were 27% smaller than those using E1 at two ground sites in YRD. At the suburban SHPD site, the simulated NH_3 concentrations with E1 were generally larger than observations, and the modeling performance was improved indicated by the smaller NMEs when E2 was applied. In contrast, very limited improvement was found at the urban site JSPAES, as E2 failed to improve the emission estimation of transportation and residential activities. Compared to NH_3, the modeling performance for inorganic aerosols was better for most cases, and the differences between the simulated concentrations with E1 and E2 were clearly smaller, at 7%, 3% and 12% (relative to E1) for NH_4^+, SO_4^{2-}, and NO_3^-, respectively. Compared to the satellite-derived NH_3 column, application of E2 significantly corrected the overestimation in vertical column density for January and October with E1, but did not improve the model performance for July. The NH_3 emissions might be underestimated with the assumption of linear correlation between NH_3 volatilization and soil pH for acidic soil, particularly in warm seasons. Three additional cases, i.e., 40% abatement of SO_2, 40% abatement of NO_X, and 40% abatement of both species were applied to test the sensitivity of NH_3 and inorganic aerosol concentrations to precursor emissions. Under an NH_3-rich condition, estimation of SO_2 emissions was detected to be more effective on simulation of secondary inorganic aerosols compared to NH_3. Reduced SO_2 would restrain the formation of $(NH_4)_2SO_4$, and thereby enhance the NH_3 concentrations. To improve the air quality more effectively and

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efficiently, NH_3 emissions should be substantially controlled along with SO_2 and NO_X in the future.

1. Introduction

As the most important alkaline composition in the atmosphere, ammonia (NH_3) exerts crucial influences on atmospheric chemistry and nitrogen cycle. NH_3 participates in chemical reactions with sulphuric acid (H_2SO_4) and nitric acid (HNO_3), and contributes to formation of secondary inorganic aerosols (SIA) including sulfate (SO_4^{2-}), nitrate (NO_3^-), and ammonium (NH_4^+) and to thereby the elevated concentrations of fine particulate matters (PM). In the developed regions in eastern China, for example, SIA was observed to account for over 50% of $PM_{2.5}$ mass concentrations (Yang et al., 2011; Zhang et al., 2012; Huang et al., 2014), and NH_3 emissions were estimated to contribute 8-11% of $PM_{2.5}$ (Wang et al., 2011). Recent studies reported that existence of NH_3 could accelerate the heterogeneous oxidation of SO_2 and thereby sulfate formation by neutralizing aerosol acidity (Wang et al., 2016; Cheng et al., 2016; Paulot et al., 2017). Deposition of gaseous NH_3 and NH_4^+ aerosols results in soil acidification and water eutrophication. Reduced nitrogen (NH_3+NH_4^+) was monitored to contribute over 70% of total nitrogen deposition in China, revealing the importance of NH_3 on ecosystem (Pan et al., 2012). Recently the SO_2 and NOx emissions have gradually decreased due to implementation of air pollution control measures in China, thus NH_3 emissions were found to play a greater role on secondary aerosol formation and nitrogen deposition compared to previous years (Liu et al., 2013; Fu et al., 2017; Pan et al., 2018).

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Quantification of NH_3 sources helps better understanding its atmospheric and ecosystem effects. In contrast to SO_2 and NO_X that are largely from industrial plants, NH_3 comes mainly from agricultural activities that are more difficult to track, including livestock farming and fertilizer use, and relatively large uncertainty in NH_3 emission inventories existed. Given the intensive agriculture across the country, various methods were developed to estimate China's NH_3 emissions at the national level for last twenty years, but clear discrepancies existed between studies, as summarized by Zhang et al. (2018). With meteorology, soil property, the method of fertilizer application and different processes of manure management considered in emission factor (emissions per unit level of activity) determination, in particular, the national NH_3 emissions estimated by Peking University group (Huang et al., 2012; Kang et al., 2016) was 39-46% smaller than those by Tsinghua University group (Dong et al., 2010; Zhao et al., 2013). Emissions of certain sectors differed significantly between various methods. For example, Zhao et al. (2013) and Kurokawa et al. (2013) calculated China's NH_3 emissions from fertilizer use at 9.5-9.8 Tg, over three times of the estimation by Kang et al. (2016). With a fertilizer modeling system that couples an air quality model and an agro-ecosystem model, Fu et al. (2015) made an estimate at 3.0 Tg, similar with Kang et al. (2016). Besides the annual emission level, discrepancies existed as well in the inter-annual trend of emissions. Kang et al. (2016) estimated that the national NH_3 emissions reached the peak in 1996 and declined thereafter, while Zhang et al. (2017) and Kurokawa et al. (2013) expected a continuous growth till 2008 and 2015, respectively. The growth in NH_3 emissions got supported by satellite observation. Based on the measurement of Atmospheric Infrared Sounder (AIRS), for example, Warner et al. (2017) suggested an annual increasing rate of NH_3 concentrations at 2.3% from 2002 to 2016 in China, and it was partly attributed to the elevated emissions from fertilizer use.

Although varied methods and data resulted in discrepancies between inventories and big uncertainty in NH_3 emission estimation, very little attention has been paid to those discrepancies and the underlying reasons. At the regional scale, in particular, inclusion of high-resolution information on meteorology and land use would potentially improve the spatial and seasonal distribution of agricultural NH_3 emissions in the inventory. Previous studies have demonstrated that including meteorology field could improve NH_3 emission estimation for both Europe and North America compared to simple static methodology (Bash et al., 2013; Gyldenkaerne et al., 2005; Skjoeth et al., 2011; Wichink Kruit et al., 2012), while the inter-comparison studies have not sufficiently been conducted for China. Moreover, few studies were conducted to evaluate NH_3 emission inventories incorporating air quality model and available ground and satellite observations. One possible reason is the lack of sufficient ground observation data on NH_3 and NH_4^+ aerosols open to public, as they are currently not regulated air pollutants in China and thus not regularly monitored by the government. In addition, uncertainty also existed in satellite observation on NH_3 columns and the retrieved data needs further validation (van Damme et al., 2015). Without comparison of different inventories in details and appropriate assessment based on model performance, the limitations of current emission estimates and the

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future steps for inventory improvement remained unclear.

In this study, therefore, we chose the Yangtze River Delta (YRD) region to develop and evaluate the emission inventories of NH_3 with different methods and data sources. Located in eastern China, the YRD region contains the city of Shanghai and the provinces of Jiangsu, Zhejiang and Anhui (see Figure 1 for its location and prefectural cities), and is one of China's most developed and heavy-polluted regions (Xiao et al., 2011; Cheng et al., 2013; Guo et al., 2017). It is an important area of agriculture production, and was identified as a "NH_3-rich" region regarding the SIA formation (Wang et al., 2011). We developed two NH_3 emission inventories for 2014 based on the constant emission factors (E1) and those characterizing the agricultural processes (E2), respectively. The two inventories were compared against each other to reveal the differences in spatial and seasonal patterns of NH_3 emissions and their origins. Evaluation of the two inventories was further conducted using a Models-3 Community Multi-scale Air Quality (CMAQ) system and available observations from ground station and satellite. Environmental parameters that might influence NH_3 simulation were identified through the model performance. Finally, the effects of SO_2 and NOx emission estimates on NH_3 and NH_4^+ aerosol simulation were evaluated through sensitivity analysis, and the policy implication of air quality improvement were accordingly suggested.

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2. Data and methods

2.1 Emission inventory based on the constant emission factors (E1)

The annual NH_3 emissions of the YRD region for 2014 were estimated with a bottom-up method based on the constant emission factors, and then allocated to the monthly level based on the previously investigated temporal profile of emissions. The inventory contained eight source categories, i.e., fertilizer application, livestock/poultry breeding, fuel combustion, biomass burning, transportation, sewage/waste treatment, industrial process, and human metabolization (see Table 1 for the details). Note that the emissions from pets were not included in the current work, due to lack of detailed information. Given their relative small fraction in total emissions, e.g., less than 2% in United Kingdom (Sutton et al., 1999; 2000), we believed that the uncertainty was limited. The annual emissions were calculated by prefectural city with the Eq. 1:

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$$E_i = \sum_j \left(AL_{i,j} \times EF_j \times 10^{-3}\right) \qquad (1)$$

where E is the emissions, metric ton (t); i and j indicate the prefectural city and source type, respectively; AL is the activity level, which indicated the amount of livestock, the amount of used fertilizer, the fuel burned or the industrial production, depending on the source type; and EF is the annual emission factor, kg-NH_3/unit AL.

The activity data were mainly taken or estimated from official statistics at the prefectural city (if available) or provincial level. For livestock/poultry breeding, the year-end stock and slaughtered numbers were used respectively for animals with the breeding cycle more and less than one year. If the city-level stock was unavailable, the output of livestock products by prefectural city was applied as the scaling factor to calculate the number from the provincial data. Table S1 in the supplement summarizes the annual numbers of livestock and poultry by prefectural city in YRD. The amount of fertilizer used by prefectural city and type was calculated as the product of sown area of cropland and fertilizer rate per unit area of cropland. The sown area by crop type was taken from city-level statistics, and the application rate by fertilizer type was obtained at provincial level from a national investigation by NDRC (2015). The detailed results of fertilizer activity data are summarized in Table S2 in the supplement. As can be seen as well in the table, the aggregated amount of fertilizer used by province was close to the provincial-level statistics, and the deviation relevant to the official statistics was 2.3% for the whole YRD. The methods and data sources for activity levels of other source categories were provided in our previous studies (Zhou et al., 2017; Zhao et al., 2017; Yang and Zhao, 2019).

The annual NH_3 emission factors were obtained based on a thorough literature review and summarized by source category in Table S3 in the supplement. The results from domestic field measurements were preferentially selected. For sources without suitable domestic measurements, the emission factors were also obtained from previous inventories that shared similar studying period with this work. The values from US and Europe, e.g., AP-42 database (USEPA, 2002) and the EMEP/EEA guidebook (EEA, 2013a; b), were adopted when above information was lacking.

The monthly distribution of emissions by source was taken from domestic investigations in YRD (Li, 2012; Zhao et al., 2015; Zhou et al., 2017). For the purpose of air quality modeling, the emissions by sector were allocated into a grid system with a horizontal resolution at 9×9 km based on selected proxies. Those proxies included

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the distribution of land use (for fertilization), density of total population (for human metabolization and sewage/waste treatment) and rural population (for livestock/poultry breeding and residential solid fuel burning), gross domestic product (for industrial fuel combustion and processes), road net (for transportation), and the satellite-derived fire points from Moderate Resolution Imaging Spectroradiometer (for open biomass burning, Davies et al., 2009).

2.2 The method characterizing the agricultural processes (E2)

The emissions from fertilizer use and livestock/poultry breeding were recalculated integrating the detailed regional information of soil, meteorology and agricultural processes. The same annual activity data as E1 (e.g., livestock/poultry numbers in Table S1 and fertilizer used in Table S2) were applied.

2.2.1 Fertilizer use

The growing seasons of crops affects the temporal distribution of fertilizer use and thereby that of NH_3 emissions. We investigated the growing and farming cycles by crop type in YRD from the regional farming database by the Ministry of Agriculture (MOA, http://202.127.42.157/moazzys/nongshi.aspx) and other publication (Zhang et al., 2009). Taking the early-season rice as an example, the basal dressing was usually conducted in mid-April, with all the complex-fertilizer and half of the other nitrogen fertilizer used. The top dressing was conducted three times, i.e., 10% and 10% of nitrogen fertilizer used 7 days and 14 days after transplanting, and the left 30% used for sprouting, respectively. With that information incorporated, we estimated the monthly amount of fertilizer usage by prefectural city and fertilizer type based on the annual amount in Table S2.

Emission factors of fertilization were expected to be influenced by soil acidity, temperature, and the fertilization rate. We assumed a linear correlation between the soil pH and NH_3 volatilization rate (Huang et al., 2012), and calculated the monthly emission factors of two fertilization types (basal dressing and top dressing) with Eq. 2 and 3, respectively:

$$EF_{basal} = [(a_{pH} \times pH + b_{pH}) + (T_{basal} - T_0) \times k_T] \times CF_{rate} \times CF_{method} \quad (2)$$

$$EF_{top} = [(a_{pH} \times pH + b_{pH}) + (T_{top} - T_0) \times k_T] \times CF_{rate} \quad (3)$$

where EF_{basal} and EF_{top} are the emission factors for basal dressing and top dressing, respectively; a_{pH} and b_{pH} are the slope and intercept depending on soil pH; T_0 and k_T

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are the reference temperature and the slope depending on temperature, respectively; T_{basal} and T_{top} are the monthly average temperature of basal dressing and top dressing, respectively; and CF_{rate} and CF_{method} are the correction factors for fertilization rate and application method (basal dressing), respectively.

The spatial distribution of soil pH at a horizontal resolution of 1×1km was obtained from a world soil database by International Institute for Applied Systems and Analysis (IIASA, http://webarchive.iiasa.ac.at/Research/LUC/External-World-soil-database/HTML/). The correlation data between temperature and NH_3 volatilization rate were obtained from EEA (2009). T_{basal} and T_{top} were determined combining the information of farming season by MOA and the daily temperature data from European Centre for Medium-Range Weather Forecasts (ECMWF, http://apps.ecmwf.int/datasets/data/interim-full-daily/levtype=sfc/#userconsent#). All the relevant data for emission factor correction were summarized in Table S4 in the supplement. The monthly NH_3 volatilization rates of urea and ammonium bicarbonate (ABC), the mostly applied two types of fertilizer over the YRD region, were illustrated by season in Figure S1 in the supplement. Larger volatilization rates were found in northern YRD for both fertilizer types, consistent with the distribution of soil pH across the region. Taking urea as an example, the volatilization rates in April and October were commonly smaller than the uniform value applied in E1 at 17.4%, while those in July were larger. This discrepancy came partly from the consideration of fertilization types in E2. In April and October, basal dressing fertilization was commonly applied at the soil depth of 15-20 centimeters, restraining the NH_3 volatilization. In contrast, the relatively high temperature and top dressing fertilization conducted in July elevated the NH_3 volatilization. It should be noted that the local fertilizer application introduced some bias to the soil pH from the global database by IIASA. Basal dressing would increase the soil pH (particularly for the acidic soils) as indicated in previous domestic study (Zhong et al., 2006). Due to lack of the quantitative relation between the fertilizer application and soil pH at the regional scale in China, we ignored the interaction between the them in Eqs.(2).

Through the methodology mentioned above, the gridded emission factors and monthly activity levels were obtained to improve the spatial and temporal distributions of NH_3 emissions from fertilization. Figure 2 compares the spatial

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distribution of the monthly fertilizer usage between E1 and E2, indicated by the relative deviation (*RD*):

$$RD = (E_1 - E_2)/(E_1 + E_2)/2 \quad (4)$$

In January and July, top dressing fertilization was conducted with limited crop types like rape, corn and paddy rice, while considerable basal dressing fertilization was investigated in April and October. Inclusion of those details in E2 resulted in smaller estimates of fertilizer use in winter and summer but larger in spring and autumn compared to E1.

2.2.2 Livestock/poultry breeding

In contrast to E1 that calculated the NH_3 emissions based on livestock numbers and annual EFs, a mass-flow approach was applied in E2 considering the nitrogen transformation at different stages of manure management (Beusen et al., 2008; EEA, 2013a; Huang et al., 2012). Commonly applied at the global or national scale, the approach calculated NH_3 emissions of manure management processes from a pool of total ammoniacal nitrogen (TAN) for three main raising systems, as shown in Figure S2 in the supplement. In the YRD region, only intensive and free-range systems were considered, and the TAN was calculated by livestock/poultry type based on the breeding duration, the amount and nitrogen contents of urine/feces, and the mass fraction of TAN. The parameters were taken from Yang (2008) and Huang et al (2012), as summarized in Table S5 in the supplement. According to the nitrogen flow and phase of manure management, the activity levels were then classified into seven categories, including outdoor, housing (solid), housing (liquid), storage (solid), storage (liquid), spreading (solid) and spreading (liquid). NH_3 emissions from livestock are calculated as the product of TAN of each category and corresponding emission factors. As provided in Table S6 in the supplement, the temperature-dependant emission factors by stage/phase were taken from Huang et al. (2012), and the gridded emission factors can then be derived over the YRD region combining the meteorology data from ECMWF.

2.3 Configuration of air quality modeling

The Models-3 Community Multi-scale Air Quality (CMAQ) version 4.7.1 was applied to evaluate the NH_3 emission inventories for YRD. CMAQ is a three-dimensional Eulerian model designed for understanding the complex

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interactions of atmospheric chemistry and physics (UNC, 2010). The model has been widely applied and tested in China (Qin et al., 2015; Zhou et al., 2017; Zheng et al., 2019). As shown in Figure 1, two nested domains were applied with the spatial resolutions of 27 and 9 km respectively, on a Lambert Conformal Conic projection centered at (110°E, 34°N). The mother domain (D1, 177×127 cells) covered most parts of China, and the second domain (D2, 118×121 cells) covered the whole YRD region. The two inventories of YRD NH_3 emissions developed in this work were applied in D2. Emissions from other pollutants of anthropogenic origin in D1 and D2 outside Jiangsu were obtained from the Multi resolution Emission Inventory for China (MEIC, http://www.meicmodel.org/) with an original spatial resolution of 0.25°×0.25°. Population density was applied to relocate MEIC to each modeling domain. A high-resolution inventory that incorporates more information of local emission sources was applied for Jiangsu (JS, Zhou et al., 2017). Both MEIC and JS inventories are for 2012. The emissions for 2014 were obtained using a simple scaling method based mainly on changes in activity levels (e.g., energy consumption and industrial production) between the three years. Biogenic emission inventory was from the Model Emissions of Gases and Aerosols from Nature 2.1 (MEGAN2.1, Guenther et al., 2012; Sindelarova et al., 2014), and the emission inventories of Cl, HCl and lightning NO_X were from the Global Emissions Initiative (GEIA, Price et al., 1997). Meteorological fields were provided by the Weather Research and Forecasting Model (WRF) version 3.4, a state-of-the-art atmospheric modeling system designed for both meteorological research and numerical weather prediction (Skamarock et al., 2008), and the carbon bond gas-phase mechanism (CB05) and AERO5 aerosol module were adopted. Other details on model configuration and parameters were given in Zhou et al. (2017). The simulations were conducted for January, April, July and October to represent the four typical seasons in 2014. A 5-day spin-up period of each month was used to minimize the influences of initial conditions in the simulations.

Using the observation data of US National Climate Data Center (NCDC) at 43 stations in YRD (see Figure 1 for the locations of the stations), the WRF modeling performance was evaluated with statistical indicators including averages of simulations and observations, bias, normalized mean bias (NMB), normalized mean error (NME), root mean squared error (RMSE) and index of agreement (IOA). As can be found in Table S7 in the Supplement, discrepancies between simulation and

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observation met the criteria by Emery et al. (2001) for most cases, implying the reliability of meteorological simulation. However, bigger errors were found for the simulation of wind direction.

2.4 Ground-based and satellite observations

There were very limited continuous ground measurement data available for ambient NH_3 and NH_4^+ aerosol in the YRD region 2014, particularly at rural/remote sites that are more representative for the regional atmospheric environment. We conducted on-line hourly measurements using the MARGA (Monitor for AeRosols and Gases in ambient Air, ADI2080) at an urban site in the western downtown of Nanjing (32.03°N, 118.44°E) from August 2014. The MARGA is a state-of-art instrument which monitors near real-time water-soluble ions in aerosols and their gaseous precursors (Lanciki, 2018), and it was able to capture rapid compositional changes in $PM_{2.5}$ (Chen et al., 2017). The site was on the roof of the building of Jiangsu Provincial Academy of Environmental Science (30 m above the ground) surrounded by residential and commercial buildings and heavy traffic (JSPAES: Li et al., 2015; Chen et al., 2019). The data of October 2014 were applied in this work to evaluate the NH_3 inventories through air quality simulation. Besides, the hourly data of online measurement with MARGA were available at a suburban site in Pudong, Shanghai (SHPD) for April, July and October 2014 (unpublished data from Shanghai Environmental Monitoring Center).

Regarding satellite observation, the daily NH_3 vertical column densities (VCDs) measured through Infrared Atmospheric Sounding Interferometer (IASI) were downloaded from ESPRI data center (http://cds-espri.ipsl.upmc.fr/etherTypo/index.php?id=1700&L=1). We used the data in the domain (114.2°E-124.1°E, 26.1°N-35.4°N) with a 9:30am equator local crossing time to evaluate the NH_3 emissions. Only pixels with radiative cloud fraction<25%, relative error <100% and absolute error<5×10^{15} molec/cm^2 were used following the criteria of previous studies (van Damme et al., 2014; 2015). The monthly average VCDs for January, April, July and October 2014 were calculated and allocated into a grid system of 0.5° (longitude)×0.25° (latitude) using the Kriging interpolation method, as shown in Figure 3.

3. Results and discussions

3.1 Comparison between the two inventories

Table 2 summarizes the NH_3 emissions estimated with E1 and E2 by source category and province for the YRD region in 2014. Agricultural activities (livestock farming and fertilizer) were identified as the most important sources of NH_3, with the fraction to total emissions ranged 74-84% in the two methods. Applying the constant emission factors, E1 derived a total NH_3 emission estimate 60% larger than that by E2 that characterized the agricultural processes. In particular, emissions from agricultural activities in E1 were calculated as twice of those in E2. At the national scale, similarly, Dong et al. (2016) applied the constant emission factors and estimated the total NH_3 emissions at 16.1 Tg for China, 64% larger than 9.8 Tg by Huang et al. (2012) with the agricultural processes characterized. The clearly larger estimation by constant emission factors was due partly to the fact that most domestic measurements on the emission factors of NH_3 from fertilizer application were conducted in hot seasons (late spring and summer), when the basal dressing of single-season rice and maize and top dressing of wheat were usually conducted (Cai et al., 2002; Huo et al., 2015; Su et al., 2006). However, the crop rotation varied a lot in China, and part of the nitrogen fertilizer was actually not applied in hot seasons. Emission estimation based on those emission factors may thus overestimate the NH_3 emission intensity (Huo et al., 2015; Wang et al., 2011; Zhang et al., 2010). Among the provinces, the fraction of Jiangsu to YRD emissions was ranged 45-47% in the two methods, followed by Anhui around 37%. Agricultural activities were relatively intensive in the two provinces: Jiangsu and Anhui contributed 46% and 33% of the economic output of agriculture and livestock/poultry farming in YRD, and the collective fraction of fertilizer use by the two provinces reached 84%. In contrast, agricultural activities were limited in Shanghai and Zhejiang, with smaller emissions estimated in both inventories.

The monthly distribution of NH_3 emissions in the two inventories were illustrated in Figure 4. Both inventories indicated the relatively large emissions in summer (from June to August), and the elevated emissions were also found in March and September in E2, The difference comes mainly from the effect of farming season on fertilization process. For example, the top dressing fertilization for winter wheat was conducted mostly during the seedling establishment and elongation stage in the following spring, resulting in enhanced use of nitrogen fertilizer in March. Moreover,

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September was the month with the highest temperature following summer in YRD 2014, and the elevated NH_3 volatilization led to large emissions in E2. Compared to the fertilizer use, less variation of monthly emissions were found for livestock/poultry breeding, as very limited change in livestock amount was detected in both inventories.

Illustrated in Figure 5 are the spatial distributions of emissions from fertilizer use, livestock/poultry breeding and all categories in the two inventories. Both inventories indicated the large emission intensities in northern Jiangsu (Xuzhou and Yancheng) and northern Anhui (Fuyang, Bozhou and Suzhou) with abundant agricultural production. Xuzhou and Yancheng collectively contributed 36%, 31% and 41% of the provincial fertilizer use, agricultural economic product, and livestock/poultry farming product in Jiangsu, respectively. Similarly, Fuyang, Bozhou and Suzhou collectively contributed 36%, 36% and 35% of the provincial sown area, agricultural economic product, and livestock/poultry farming product in Anhui, respectively.

The differences in spatial pattern between the two inventories were further investigated for total and fertilizer use emissions by month, through the indicator *RD* calculated with Eq. (4). As shown in Figure 6, larger *RD* was found in northern Jiangsu, northern Anhui, and eastern Zhejiang, while smaller in western Zhejiang. The emissions in E1 were commonly larger than that in E2 across the YRD region for January and April. In contrast, larger emissions in E2 were found in northern Jiangsu (e.g., Xuzhou and Yancheng) and northern Anhui for July and October. The discrepancy resulted from the combined effect of varied activity data and emission factors as described in Section 2.2: top dressing fertilization and high temperature led to enhanced volatilization rate and thereby emissions of NH_3 in E2, and the abundant fertilizer use in the broad cropland in northern YRD was the main reason for the high emissions in October.

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Figure 7 compares the NH_3 emissions by province and source category in this work and other available downscaled national (MEIC) or provincial inventories in the YRD region. Results from other studies were commonly ranged between E1 and E2 for agriculture, the most important NH_3 source. With the constant emission factors applied, the MEIC estimates were similar to those in E1. Most current provincial inventories made some corrections for emissions from fertilizer use or livestock/poultry breeding, but the local geographical and meteorological information was seldom applied in the emission estimation. For example, Liu and Yao (2016) calculated the emissions from livestock/poultry breeding for Jiangsu based on TAN,

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but did not consider the impacts of varied monthly temperatures on the emissions. Zheng et al. (2016) calculated the agricultural NH_3 emissions for Anhui based on a national guideline of NH_3 emission inventory development (MEP, 2014), and ignored the impact of soil condition (e.g., pH) on NH_3 volatilization from fertilizer use.

3.2 Evaluation of the inventories with transport modeling and ground observation

Figures 8 illustrates the observed and simulated hourly concentrations for gaseous NH_3 and inorganic aerosol species (NH_4^+, SO_4^{2-} and NO_3^-) in $PM_{2.5}$ for April, July and October at SHPD and October at JSPAES. The normalized mean biases (NMB) and normalized mean errors (NME) between observed and simulated concentrations, and the monthly average concentrations from observation and simulation are summarized in Table 3. The simulated monthly average concentrations were close to the observed ones at both sites. The biggest discrepancy was found at SHPD for April, where the monthly average NH_3 was simulated 56% larger than observation with E1, and the smallest at JSPAES for October, where the simulated was 1.7% smaller than observation with E1. The simulated temporal variation, however, was much larger than the observation, leading to relatively large NME, particularly at SHPD for April. Clear difference was found for the simulation under two NH_3 inventories. In general, the average of simulated NH_3 concentrations at the two sites for available months was 27% smaller in E2 than that in E1 (note the total NH_3 emissions in E2 was 38% smaller than that in E1 for the whole YRD region). At SHPD site, application of E1 in CMAQ overestimated the NH_3 concentration, indicated by the positive NMB values and the larger simulated concentrations than observation. Such overestimation was corrected when E2 was applied, and the NMEs with E2 were substantially reduced as well, as shown in Table 3. The better modeling performance implies the improved estimation and spatiotemporal distribution of emissions. At JSPAES, the air quality modeling with both inventories underestimated the NH_3 concentrations, and the simulated monthly average concentration with E1 was much closer to observation than that with E2. The close NMEs between the two inventories indicated very limited improvement at the site, in contrast to SHPD. Located in urban area, JSPAES might be largely affected by the local sources like transportation and residential activities. NH_3 emissions of such source categories, however, were not improved in E2.

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To reduce the impact of the highly uncertain hourly meteorology simulation and emission data on air quality modeling, the daily NH_3 concentrations derived from simulation and observation were further compared for October at JSPAES. As illustrated in Figure S3 in the supplement, better agreement between observation and simulation was achieved for the daily concentrations than the hourly, and the NMEs for E1 and E2 were reduced respectively from 56.9% and 53.7% to 37.0% and 32.5%, respectively. Besides the emission data, uncertainty in meteorology simulation also contributed to the discrepancy between simulation and observation. For example, both inventories overestimated the concentration on 7th October but underestimated that on 21st-22nd. In contrast to the southeasterly wind observed at ground meteorology station in Nanjing, the simulated wind direction on 7th was from north, enhancing the NH_3 transport from Yancheng and Xuzhou in northern Jiangsu with intensive agricultural activities. On 21st-22nd, the underestimation NH_3 concentration resulted largely from the overestimation in wind speed by WRF.

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Compared to NH_3, the modeling performance for inorganic aerosols (NH_4^+, SO_4^{2-}, and NO_3^-) is better for most cases, indicated by the smaller NMEs and larger correlation coefficients (r) in Table 3. Some exceptions exist at SHPD for NH_4^+ and SO_4^2 in October and NO_3^- in January. Application of E2 reduced the NMEs and improved the simulation of NH_4^+ and SO_4^2 moderately, but there were no significant changes between the modeling results with E1 and E2. The averages of simulated concentrations at the two sites for available months was 7%, 3% and 12% smaller in E2 than those in E1 for NH_4^+, SO_4^{2-}, and NO_3^-, respectively, and the differences were clearly smaller than that for NH_3 at 27%. As large fraction of inorganic aerosols comes from secondary chemistry reaction, they are more representative for the regional atmosphere condition other than the local environment around the measurement site. Therefore, the air quality modeling at a horizontal resolution at 9×9 km is expected to be able to better simulate the concentrations for SIA than the primary gaseous pollutants, particularly when emissions from some local sources are not sufficiently quantified. The simulated concentrations were commonly larger than observation for NH_4^+ and SO_4^{2-}, particularly at SHPD in July and October. The uncertainty of model could be an importance source of the discrepancy, as the recent reported mechanisms of gas to particle conversion were not sufficiently applied in the CMAQ we used (Wang et al., 2016; Cheng et al., 2016). In addition, positive or negative artifacts also existed in ground observation with MARGA, resulting from the

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unexpected reaction between acid gaseous pollutants and nitrate aerosol (Chen et al., 2017; Schaap et al., 2011; Stieger et al., 2018; Wei et al., 2015). From an emission perspective, the overestimation was partly corrected when smaller NH_3 emissions in E2 were applied instead of E1 in the model. Due to missing information on individual industrial plants, moreover, the inventory we used in CMAQ failed to fully capture the progress of emission control in the YRD region and probably overestimated the SO_2 emissions (Zhang et al., 2019). The formation of sulfate ammonium aerosols could then be enhanced through the irreversible reaction between SO_2 and NH_3. The process simultaneously reduced the amount of NH_3 reacted with HNO_3, leading further to the underestimation of nitrate aerosols. As shown in Table 3, application of E2 with less NH_3 emissions than E1 could not improve the modeling performance of nitrate aerosols. The impact of SO_2 and NO_X emission on SIA modeling will be further discussed in Section 3.4.

3.3 Evaluation of the inventories with transport modeling and satellite observation

To be consistent with the local crossing time of IASI at 9:30am, the average of simulated hourly NH_3 concentrations at 9:00 am and 10:00 am were applied to calculate the NH_3 VCDs, using the following equations:

$$n_{NH3} = \sum_{k=1}^{23} m_k \times \Delta H_k \times 100 \qquad (5)$$

$$\Delta H_k = H \times \ln\left(\frac{p_k}{p_{k+1}}\right) \qquad (6)$$

where n_{NH3} is the NH_3 VCDs from CMAQ model (molec./cm^2); m_k is the simulated NH_3 concentrations at vertical layer k in the CMAQ (molec./cm^3); $\triangle H$ is the height of layer k (m); H represents the height when the pressure of atmosphere declines to 1/e of the original value; and p is the air pressure. Figure 9 illustrates the simulated NH_3 VCDs with E1 and E2 for January, April, July, and October. Similar spatial patterns are found with the two inventories, i.e., relatively large NH_3 VCDs were simulated mostly in northern Jiangsu and northern Anhui province, consistent with the hotspot of NH_3 emissions. The simulated NH_3 VCDs with E1 were 53% larger than those with E2 across the whole YRD region, with the maximum and minimum monthly difference calculated at 73% and 31% for April and October, respectively. The NMB, NME, and correlation coefficient (r) between the observed and simulated VCDs, and the monthly average VCDs from observation and simulation are summarized in Table

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4. Application of both inventories resulted in larger NH_3 VCDs than those from satellite observation for January and October, while the simulated VCDs for April and July were smaller. Besides the uncertainty from monthly distribution of NH_3 emissions, the bias from WRF modeling on temperature might also contribute to the discrepancy between simulated and observed VCDs. As shown in Table S7 in the supplement, WRF overestimated the monthly temperature in January and October with the NMBs calculated at 26.6% and 0.34%, and underestimated it in April and July with the NMBs calculated at-1.62% and -2.51%, respectively. Compared to E1, application of E2 significantly reduced the NMEs from 83.8% to 37.5% for January and largely corrected the overestimation in VCD simulation for January and October. The simulated VCDs were 4.3% larger and 1.4% smaller than observation for the two months, respectively. The results implied satisfying agreement between the simulated and observed VCDs over the YRD region. Improvement in NH_3 VCD simulation was also found for April when E2 instead of E1 was applied in the air quality modeling, with the NME reduced from 65.8% to 60.7%. For July, however, application of E2 did not improve the model performance, implying that current method in E2 could possibly underestimate the NH_3 volatilization when the actual ambient temperature was high. Besides the emissions, the discrepancy could result from various factors including the uncertainty in chemical mechanisms in CMAQ and environmental condition. Errors from satellite retrieval could also contribute to the inconsistence between simulation and observation. van Damme et al. (2014), for example, estimated an error of 19% for the total NH_3 columns in Asia. As the ESPRI product of NH_3 VCDs we applied in the study does not provide the averaging kernel, moreover, uncertainty in NH_3 column retrieval could result from the reduced sensitivity of satellite measurement towards the surface.

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To further investigate the impact of soil pH on the emissions and thereby the modeling performance on NH_3 VCDs, the soil in the YRD region was classified to three types, acidic soil (pH≤6.5), neutral soil (6.5<pH≤7.5), and alkali soil (pH>7.5), and the NMBs and NMEs between the simulated and observed NH_3 VCDs were calculated by soil type and month, as summarized in Table 5. For neutral and acidic soil, application of E2 that considers the effect of farming season, geophysical condition and manure management on NH_3 emission rates resulted in clearly smaller NMEs than E1, implying the improvement in emission estimation. For acidic soil, however, the NMBs were negative for all the months when E2 was applied, and the

NMEs were elevated compared to E1 except for January. Moreover, application of E2 resulted in negative NMBs for neutral and alkali soil in April and July as well. Those results implied that E2 possibly underestimated the NH_3 emissions for acidic soil particularly for warm seasons. With the correction of pH and temperature, the NH_3 volatilization rate from basal dressing fertilization was relatively low, indicating that the current linear assumption between the soil pH and NH_3 volatilization rate might not be appropriate for soil with low pH values for eastern China. As shown in Figure S4 in the supplement, the measured NH_3 volatilization rates from urea and ABC fertilizer use under relatively high soil pH (Zhang et al., 2002; Zhong et al., 2006) were close to the estimated values in E2, but the measured results for acidic soil were clearly larger than those in E2.

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Limitation should be acknowledged in the emission comparison and evaluation. Besides those we paid extra attention to in E2 (e.g., temperature, soil property, fertilizer application method and manure management process), other factors could also be influential on air-surface exchange of NH_3 and thereby NH_3 emissions, including meteorology parameters (wind speed, precipitation, and leaf surface wetness), surface layer turbulence, air and surface heterogeneous-phase chemistry, and plant physiological conditions (Flechard et al, 2013; Gyldenkaerne et al., 2005, Skjoeth et al., 2011). With those factors integrated in a bi-directional surface–atmosphere exchange module in air quality modeling, the NH_3 emission inventories were improved and the biases in simulation of NH_3 and NH_4^+ aerosol concentrations were reduced for both US and Europe (Bash et al, 2013; Wichink Kruit et al., 2012). The ignorance of given parameters/process in current work could thus partly explain the discrepancy between the simulation and observation. Applying the bi-directional NH_3 exchange module, for example, Wichink Kruit et al. (2012) found increased NH_3 concentrations for agricultural source areas due to the elevated life time and transport distance of NH_3 in the model. The result implied a possible correction on the underestimation in NH_3 concentrations, as shown in Tables 3 and 4. Therefore, a more comprehensive evaluation and comparison in NH_3 emissions was thus suggested in the future, including the bi-directional NH_3 exchange and the top-down constraint with inversed modeling.

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3.4 Impacts of SO_2 and NOx emission estimates on simulated NH_3 and aerosols

Besides the meteorology condition, NH_3 emissions, and soil pH, the estimates of SO_2 and NO_X emissions could influence the NH_3 and SIA simulation as well. SO_2 can be transformed to S (IV) through liquid phase reaction and then be oxidized to S (VI) by O_3, or can be directly oxidized to H_2SO_4 by H_2O_2 or hydroxyl radical (•OH). HNO_3 can be formed through NO_2 oxidation by •OH at daytime, or through hydrolysis of N_2O_5 at aerosol surface at night. Normally NH_3 preferentially reacts with H_2SO_4 and relatively stable $(NH_4)_2SO_4$ is produced, while NH_4NO_3 could easily be decomposed under high temperature or low humidity condition. Therefore, the ambient NH_3 concentrations and formation of NH_4^+ aerosols are influenced by the balance between acidic (SO_2 and NO_X) and alkaline component (NH_3) emissions.

As described in Section 2.3, the SO_2 and NO_X emissions for 2014 used in this work were scaled from those for 2014 based on the changes in activity data. Ignorance of emission control progress during 2012-2014 would probably result in overestimation in emissions. The bias was evaluated through satellite observation. The daily planetary boundary layer (PBL) SO_2 and tropospheric NO_2 VCDs were obtained from the OMSO2 Level-3 product (http://disc.sci.gsfc.nasa.gov/Aura/data-holdings/OMI/omso2e_v003.shtml) and the POMINO Level-3 product from Ozone Monitoring Instrument (OMI), respectively. As shown in Table S8 in the supplement, all the provinces in YRD had their SO_2 and NO_2 VCDs substantially reduced during 2012-2014, and the VCDs declined by 48% and 31% respectively for the whole region. From a recent unpublished emission study, however, the SO_2 and NO_X emissions were estimated to reduce only 16% and 8% in the YRD region for the two years (personal communication with Cheng Huang from Shanghai Research Academy of Environmental Science). It can be inferred that, the overestimation of SO_2 emissions might enhance their reaction with NH_3 and thereby the formation of $(NH_4)_2SO_4$ in the air quality modeling. The formation of NO_3^-, in contrast, might be suppressed accordingly.

3.4.1 Identification of NH_3-rich/-poor condition in YRD region

To evaluate the non-linear relation between gaseous pollutant emissions (SO_2, NO_X and NH_3) and SIA concentrations for the YRD region, we follow Ansari and Pandis (1998) and calculated the gas ratio (GR) based on the modeling results:

$$GR = \frac{([NH_3]+[NH_4^+]) - 2\times[SO_4^{2-}]}{[NO_3^-]+[HNO_3]} \tag{7}$$

where the species in the bracket indicated the simulated ambient concentration. A negative GR indicates a NH_3-poor condition, and the enhanced NH_3 emissions strengthen the oxidation of SO_2 and lead to increased SO_4^{2-} (Wang et al., 2011). A GR larger than 1 indicates an NH_3-rich condition. Enhanced NH_3 emissions have smaller effects on growth of SO_4^{2-} concentrations, and elevated SO_2 emissions may accelerate the formation of NO_3^- aerosols, as the increased NH_4^+ and SO_4^{2-} reduce the NH_4NO_3 capacity in the liquid phase (Seinfeld and Pandis, 2006). A neutral condition is judged when GR is between 0 and 1.

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Figure 10 illustrates the spatial distribution of simulated GR for the YRD region by month with E1 and E2 NH_3 inventories. Implied by the GR values larger than 1.0 for most of the areas, the YRD region was identified under the NH_3-rich condition when E1 was applied, except southwest Zhejiang. The judgment is consistent with previous studies (Wang et al., 2011; Dong et al., 2014). With the reduced NH_3 emissions in E2, the areas under neutral or NH_3-poor condition expanded particularly for January and April. The common NH_3-rich condition suggested potentially high sensitivity of SIA formation to SO_2 and NO_X emissions.

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3.4.2 Sensitivities of NH_3 and SIA to SO_2 and NOx changes

Three more cases were developed to test the effect of SO_2 and NO_X emission estimates on NH_3 and SIA simulation: Cases 1, 2 and 3 assumed 40% abatement of SO_2 emissions, 40% abatement of NO_X emissions, and 40% abatement of emissions both species, respectively. E1 was applied for NH_3 emission estimates in all the cases. Table 6 summarizes the modeling performance at JSPAES and SHPD for different cases in October. Clear changes in NH_3 and SIA simulation were found with varied SO_2 emissions, while the effect of varied NO_X emissions on air quality modeling was much smaller. The bias between the simulation and observation was partly corrected for most cases, indicated by the smaller NMBs. Indicated by NMEs, however, the modeling performance was less conclusive. NMEs for NH_4^+ and SO_4^{2-} were reduced for Cases 1 and 3, while increased NMEs were found for NH_3 and NO_3^-. Limitation in the mechanisms of SIA formation can be an important reason for the discrepancy. Under NH_3-rich condition, abatement of SO_2 emissions (Case 1) would reduce the formation of $(NH_4)_2SO_4$, and thereby lead to growth of NH_3 concentrations. This is consistent with the situation in North China Plain, another typical region suffering aerosol pollution in China (Liu et al., 2018). The simulated NH_3 were 10.1% and

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11.7% larger than those in base case at JSPAES and SHPD, and the simulated SIA (NH_4^++SO_4^{2-}+NO_3^-) were 7.9% and 11.0% smaller than those in base case at JSPAES and SHPD, respectively. Based on the modeling results in Table 3, as a comparison, the simulated NH_3 concentrations with NH_3 emissions in E2 were calculated 23% and 28% smaller than those with E1 at JSPAES and SHPD for October, respectively, and the analogue number for SIA concentrations were 5% at both sites. While the estimation of NH_3 emissions played an important role on NH_3 simulation, the SO_2 estimation could be more effective on SIA simulation. Abatement of NO_X emissions (Case 2) was much less influential. Less NOx slightly weakened the competition of SIA formation against SO_2, thus enhanced formation of $(NH_4)_2SO_4$ and decreased NH_3 concentration were simulated at both sites, as shown in Table 6. When SO_2 and NO_X were simultaneously reduced in the model (Case 3), similar results were found with Case 1, implying again that SO_2 could be a crucial species in SIA formation in the YRD region. In addition, NO_3^- aerosols were simulated to grow with the 40% abatement of SO_2 and NO_X emissions, and the benefits of SO_2 and NO_X control were partly weakened. To be more effective and efficient on regional air quality improvement, therefore, the control of NH_3 emissions should be strengthened along with other pollutants.

4. Conclusions

We took the YRD region in eastern China as an example and developed two inventories of NH_3 emissions for 2014 based on the constant emission factors (E1) and those characterizing the agricultural processes (E2), respectively. Available information from ground and satellite observation was applied to evaluate the inventories through air quality modeling. Both inventories indicated that agricultural activities (livestock farming and fertilizer use) were the most important sources of NH_3, but clear differences exist in estimates and spatial and seasonal distribution of NH_3 emissions. The total NH_3 emissions in E1 were estimated 60% larger than E2, and the emissions from agriculture in E1 were double of E2. The information on fertilization season and type from local investigation in E2 resulted in discrepancies in monthly distributions of NH_3 emissions from E1, particularly in northern YRD with abundant croplands. Differences in emission estimates lead to varied NH_3 concentrations from CMAQ modeling. At the suburban SHPD site, the overestimation

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in NH_3 concentration from CMAQ with E1 could be largely corrected with E2, implying the improved estimation of NH_3 emissions by E2. At the urban site JSPAES, however, very limited improvement was achieved when E1 was replaced by E2 in the model, indicating that the emission estimation of local urban sources like transportation and residential activities were not improved in E2. Compared to NH_3, the modeling performance for SIA is better for most cases, and differences between the simulated concentrations with E1 and E2 were clearly smaller. Application of E2 improved the simulation of NH_4^+ and SO_4^{2-} moderately. For the comparison with satellite-derived NH_3 column, application of E2 significantly corrected the overestimation in VCD simulation for January and October with E1, but did not improve the model performance for July. Combining the soil distribution, it can be inferred that current method might underestimate the NH_3 volatilization for acidic soil particularly in warm seasons. Judged by the simulated GR, most of the YRD region was identified as an NH_3-rich condition except southwest Zhejiang. Through the sensitivity test in which SO_2 and NOx emissions were solely or simultaneously reduced, estimation of SO_2 emissions was detected to be more effective on SIA simulation compared to NH_3. Reduced SO_2 emissions would suppress the formation of $(NH_4)_2SO_4$, and thereby lead to growth of NH_3 concentrations. The control of NH_3 emissions should be strengthened along with that of SO_2 and NO_X for improving the air quality more effectively and efficiently in the region.

This work is a tentative effort on NH_3 emission evaluation at regional scale. The relations between environmental/meteorology conditions and NH_3 volatilization were not fully considered, and the bi-directional surface–atmosphere exchange was not included, resulting in bias in emission estimation. Uncertainties come also from the limitations in ground and satellite observation and incomplete mechanism of SIA formation in current air quality model. For better understanding the role of NH_3 emissions in regional air quality, more measurements on both sources and ambient concentrations are recommended in the future.

Data availability

The Multi-resolution Emission Inventory for China used in this study was obtained at http://www.meicmodel.org/ (last access: 31 July 2019, Tsinghua University, 2012). The high-resolution inventory for Jiangsu province was obtained in

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Zhou et al. (2017) and can be accessed at http://www.airqualitynju.com/ (last access: 31 July 2019). The daily NH_3 VCDs measured through IASI was obtained from ESPRI data center at http://cds-espri.ipsl.upmc.fr/etherTypo/index.php?id=1700&L=1 (last access: 31 July 2019). The two NH_3 emission inventories developed in this work (E1 and E2) will be available with the publication of this paper at http://airquality.nju.com.

Author contributions

YZ developed the strategy and methodology of the work and wrote the draft. MY ran the model and produced the figures. XH revised the method and provided useful comments. FC and JZ conducted ground observation of NH_3 and aerosols.

Competing interests

The authors declare that they have no conflict of interest.

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FIGURE CAPTIONS

Figure 1. Research domain. The blue dots and red triangles indicate the locations of 43 meteorological monitoring sites and 2 air quality monitoring sites, respectively, and the numbers of 1–41 represent the prefectural cities of Fuyang, Bozhou, Huaibei, Suzhou, Liuan, Hefei, Huainan, Bengbu, Chuzhou, Anqing, Tongling, Wuhu, Maanshan, Chizhou, Xuancheng, Huangshan, Xuzhou, Suqian, Lianyungang, Huaian, Yancheng, Yangzhou, Taizhou, Nanjing, Zhenjiang, Changzhou, Wuxi, Suzhou, Nantong, Huzhou, Jiaxing, Hangzhou, Shaoxing, Ningbo, Zhoushan, Quzhou, Jinhua, Taizhou, Lishui, Wenzhou, and Shanghai. The map data provided by Resource and Environment Data Cloud Platform are freely available for academic use (http://www.resdc.cn/data.aspx?DATAID=201).

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Figure 2. Differences of fertilizer application between the two inventories in YRD ($RD = (E_1 - E_2)/(E_1 + E_2)/2$).

Figure 3. The spatial distribution of monthly average of NH_3 vertical columns over YRD region from IASI satellite observation (Unit: 10^{15} molecule/cm^2).

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Figure 4. Monthly NH_3 emissions from fertilizer use and livestock farming in E1 and E2.

Figure 5. Spatial distribution of NH_3 emissions from fertilizer use, livestock farming and all categories in E1 and E2.

Figure 6. Differences of NH_3 emissions from fertilizer use and all categories between the two inventories ($RD = (E_1 - E_2)/(E_1 + E_2)/2$).

Figure 7. Comparison between the estimated NH_3 emissions in this work and other studies by province and source category. "Others" indicate Fang et al. (2015), Liu and Yao (2016), Yu et al. (2016), and Zheng et al. (2016) for Shanghai, Jiangsu, Zhejiang, and Anhui, respectively.

Figure 8. The observed and simulated hourly NH_3 and SIA concentrations with the two inventories at JSPAES and SHPD sites

Figure 9. The NH_3 VCDs in the YRD region simulated with the two inventories by month.

Figure 10. The GR values in the YRD region simulated with the two inventories by month.

TABLES

Table 1. Anthropogenic NH_3 emission source categories

Category	Subcategory	Category	Subcategory
Fertilizer application	urea	Fuel combustion	industrial coal combustion
	ammonium bicarbonate		industrial oil combustion
	ammonium nitrate		industrial gas combustion
	ammonium sulfate		domestic coal combustion
	compound fertilizer		domestic oil combustion
Livestock Farming	beef cattle		domestic gas combustion
	dairy cow	Biomass burning	straw burning
	horse/donkey/mule		domestic firewood
	sow		open
	hog	Transportation	light duty gasoline vehicle
	goat		heavy duty gasoline vehicle
	sheep		light duty diesel vehicle
	layer		heavy duty diesel vehicle
	laying duck		motorcycle
	broiler	Sewage and waste treatment	waste landfill
	duck		waste incineration
	goose		waste compost
	rabbit		sewage treatment
	cattle/buffalo	Industry sources	ammonium synthesis
Human being	human sweat		nitrogenous fertilizer
	human breath		phosphate fertilizer
	human excretion		coking
	baby excretion		

Table 2. Two anthropogenic NH_3 emission inventories in the YRD region in 2014 (Gg)

	Method	Livestock	Fertilizer	Chemical Industry	Biomass Burning	Waste Disposal	Traffic	Fuel Combustion	Human Beings	Total
Shanghai	E_1	14.9	11.9	0.1	0.3	5.0	1.9	5.1	5.5	44.5
	E_2	6.5	9.0							33.2
Jiangsu	E_1	340.8	357.4	14.1	29.1	6.0	8.6	5.2	30.8	791.9
	E_2	145.6	257.1							496.5
Zhejiang	E_1	115.7	93.8	2.4	10.6	6.9	7.7	4.7	28.3	270.1
	E_2	37.4	49.3							147.2
Anhui	E_1	241.5	314.9	14.7	35.9	2.8	3.3	7.3	37.7	658.2
	E_2	102.3	185.9							389.9
Total	E_1	712.7	778.0	31.2	75.9	20.7	21.6	22.3	102.2	1764.7
	E_2	291.8	501.3							1067.0

Table 3. Model performance statistics for the hourly concentrations of NH_3 and SIA from observation and CMAQ simulation with the two inventories at SHPD and JSPAES sites for available months.

	Indicator	SHPD_ Apr		SHPD_July		SHPD_Oct		JSPAES_Oct	
		E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2
NH_3	NMB（%）	75.11	17.02	15.62	-12.85	32.32	-5.05	1.73	-21.75
	NME（%）	141.08	103.59	88.72	78.00	98.36	76.25	56.94	53.68
	r (p<0.01)	0.23	0.23	0.25	0.23	0.20	0.18	0.35	0.33
	Mean sim.（μg/m^3）	7.12	4.76	10.70	8.06	7.39	5.30	7.75	5.96
	Mean obs.（μg/m^3）	4.58		9.25		5.58		7.62	
NH_4^+	NMB（%）	-8.78	-19.14	12.98	6.11	84.45	74.02	15.01	9.53
	NME（%）	40.07	40.78	64.26	61.76	100.23	91.69	42.27	40.7
	r (p<0.01)	0.66	0.66	0.57	0.56	0.58	0.57	0.57	0.57
	Mean sim.（μg/m^3）	6.91	6.13	7.04	6.61	7.64	7.21	10.97	10.45
	Mean obs.（μg/m^3）	7.58		6.23		4.14		9.54	
SO_4^{2-}	NMB（%）	24.08	14.05	50.86	46.84	91.92	90.41	14.38	12.53
	NME（%）	57.59	51.61	84.63	81.15	110.18	108.61	43.65	42.31
	r (p<0.01)	0.55	0.54	0.46	0.47	0.42	0.44	0.34	0.36
	Mean sim.（μg/m^3）	14.75	13.56	14.60	14.21	14.53	14.41	15.5	15.25
	Mean obs.（μg/m^3）	11.89		9.68		7.57		13.56	
NO_3^-	NMB（%）	-59.13	-65.20	-78.10	-94.24	29.46	12.60	-6.55	-14.18
	NME（%）	65.72	70.16	141.43	142.86	93.69	70.54	44.81	44.94
	r (p<0.01)	0.49	0.50	0.51	0.52	0.53	0.49	0.62	0.61
	Mean sim.（μg/m^3）	4.93	4.19	5.39	4.64	7.32	6.37	17.53	16.1
	Mean obs.（μg/m^3）	12.05		9.01		5.65		18.76	

Note: obs. and sim. indicate the results from observation and simulation, respectively. The NMB and NME were calculated using following equations (P and O indicates the results from modeling prediction and observation, respectively):

$$NMB = \frac{\sum_{i=1}^{n}\left(P_i - O_i\right)}{\sum_{i=1}^{n} O_i} \times 100\% \text{；} \quad NME = \frac{\sum_{i=1}^{n}\left|P_i - O_i\right|}{\sum_{i=1}^{n} O_i} \times 100\%$$

Table 4. Model performance statistics for the daily NH_3 VCDs from IASI observation and CMAQ simulation using the two inventories by month.

	January		April		July		October	
	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2
NMB(%)	77.02	4.29	28.49	-59.12	12.19	-34.12	29.46	-1.77
NME(%)	83.83	37.54	65.8	60.07	43.93	51.91	46.38	43.17
r (p<0.01)	0.38	0.42	0.50	0.51	0.68	0.64	0.50	0.55
Mean sim.	14.09	8.30	9.57	3.40	11.28	6.65	10.00	7.61
IASI obs.	7.96		7.54		10.23		7.72	

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Table 5 The NMBs and NMEs between the simulated and observed daily NH_3 VCDs by soil pH and month

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pH	Statistics (%)	January		April		July		October	
		E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2
pH>7.5	NMB	114.88	28.04	81.41	-38.99	43.3	4.24	67.99	46.95
	NME	117.8	49.27	89.23	44.38	56.11	48.13	71.49	57.44
7.5<=pH<6.5	NMB	92.82	9.19	44.6	-54.14	39.27	-10.78	44.01	11.13
	NME	95.83	34.16	64.13	54.7	52.52	45.54	52.54	37.69
pH<=6.5	NMB	41.61	-11.76	1.30	-67.41	-12.43	-55.81	8.64	-25.48
	NME	54.72	36.76	60.16	68.5	34.78	56.72	35.27	43.68

Table 6 The modeling performance at JSPAES and SHPD in cases with different SO_2 and NO_X emission estimates. The NMBs and NMEs were based on the observed and simulated hourly concentrations.

	Cases	JSPAES			SHPD		
		Increased/ Decreased %	NMB %	NME %	Increased/ Decreased %	NMB %	NME %
NH_3	Base case		1.73	56.94		32.32	98.36
	Case 1	10.14	11.09	59.02	11.67	47.54	102.68
	Case 2	-1.17	-0.59	57.85	-0.83	29.51	96.93
	Case 3	8.48	9.29	59.64	11.12	44.92	100.94
NH_4^+	Base case		15.01	42.27		84.45	100.23
	Case 1	-8.67	5.19	39.24	-10.99	62.53	84.93
	Case 2	1.87	17.55	45.40	1.40	87.40	102.37
	Case 3	-6.95	7.33	41.85	-10.36	65.69	86.27
SO_4^{2-}	Base case		14.38	43.65		91.92	110.18
	Case 1	-17.63	-4.90	40.81	-19.59	54.30	82.62
	Case 2	2.76	18.42	43.7	1.55	94.34	112.30
	Case 3	-14.91	-1.98	39.39	-18.45	55.96	83.67
NO_3^-	Base case		-6.55	44.81		29.46	93.69
	Case 1	1.25	-5.92	44.52	6.30	37.56	92.51
	Case 2	0.86	-5.85	46.71	-0.43	34.61	98.52
	Case 3	1.85	-4.90	46.51	5.78	42.85	97.19

Figure 1

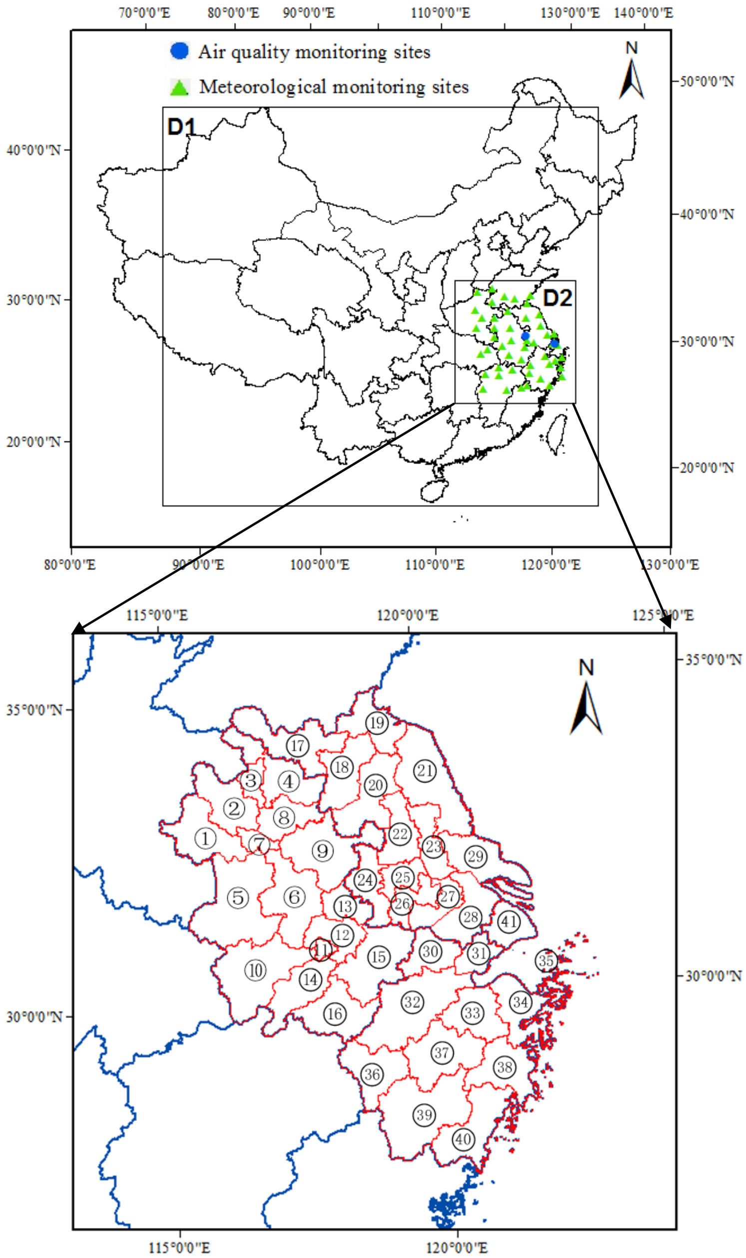
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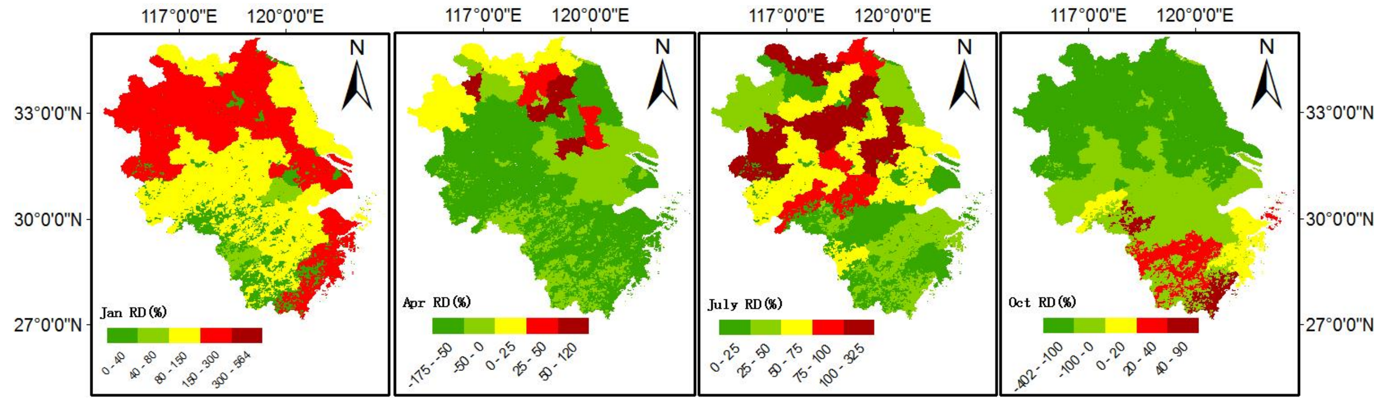
Figure 2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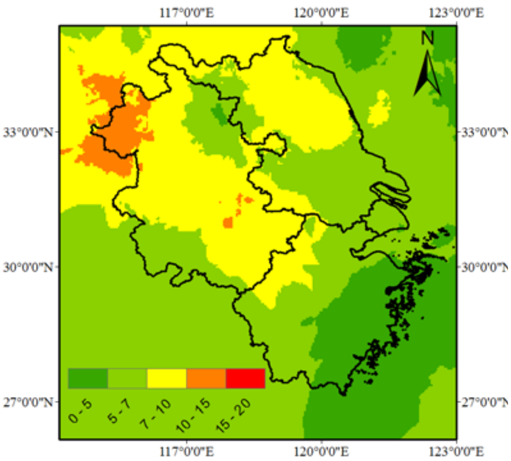
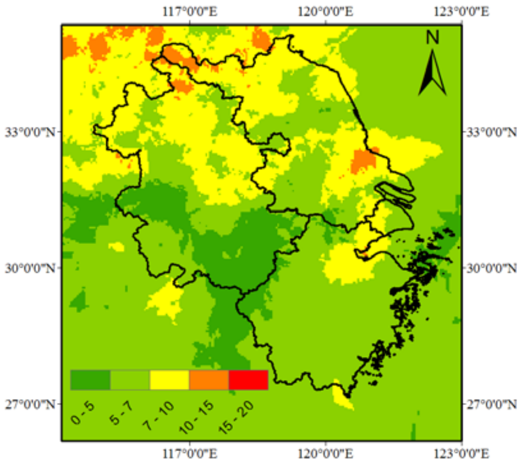
40 - 80
80 - 150
150 - 300
300 - 564
Apr RD(%)
-175 - -50
-50 - 0
0 - 25
25 - 50
50 - 120
July RD(%)
0 - 25
25 - 50
50 - 75
75 - 100
100 - 325
Oct RD(%)
-402 - -100
-100 - 0
0 - 20
20 - 40
40 - 90

Figure 3

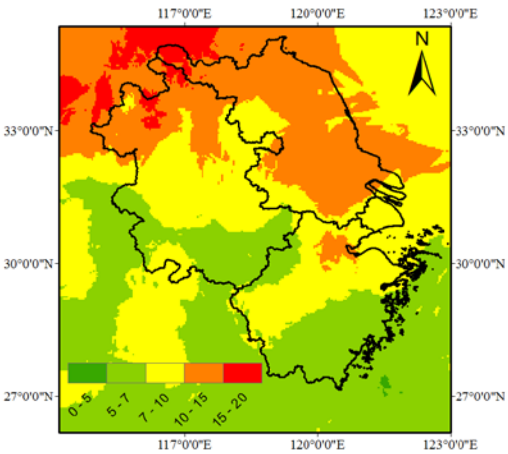


(a) January

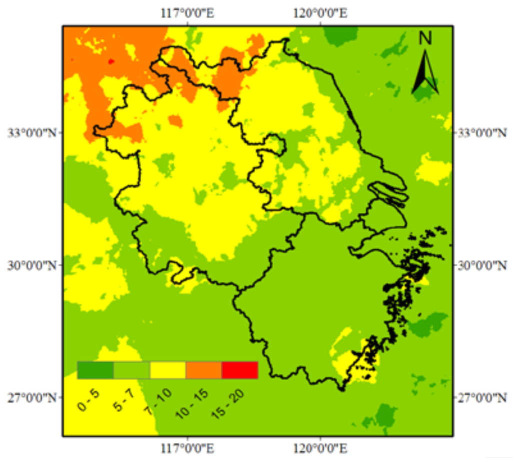


(b) April

删除的内容: a



(c) July



(d) October

Figure 4

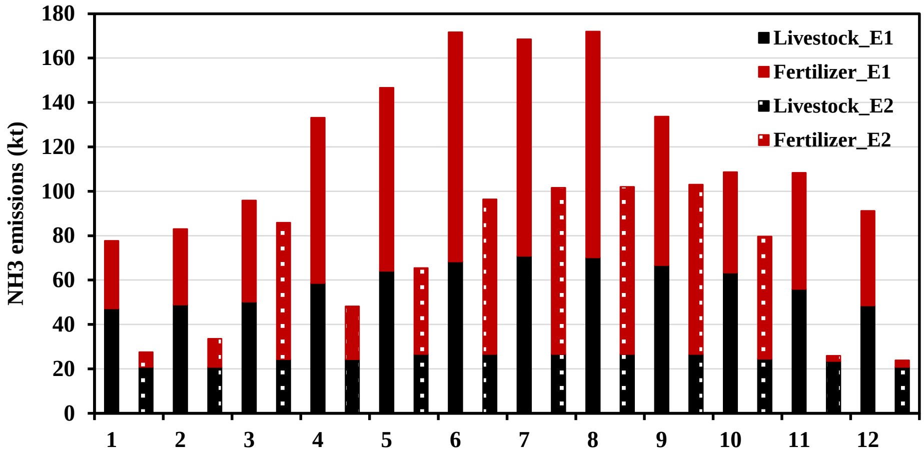
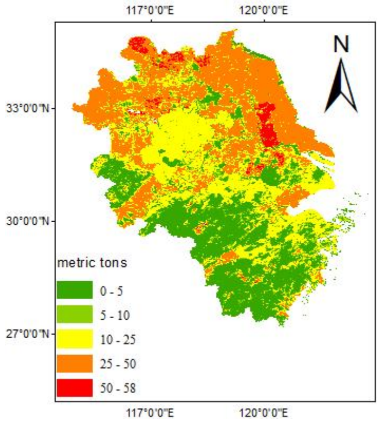
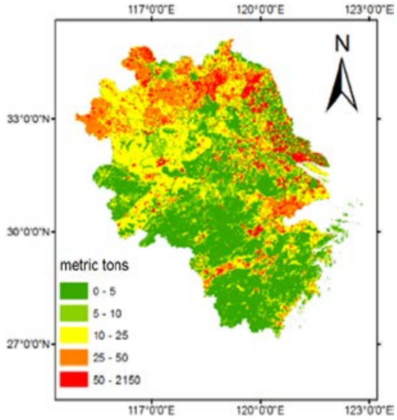

NH3 emissions (kt)
0
20
40
60
80
100
120
140
160
180
1
2
3
4
5
6
7
8
9
10
11
12
Livestock_E1
Fertilizer_E1
Livestock_E2
Fertilizer_E2

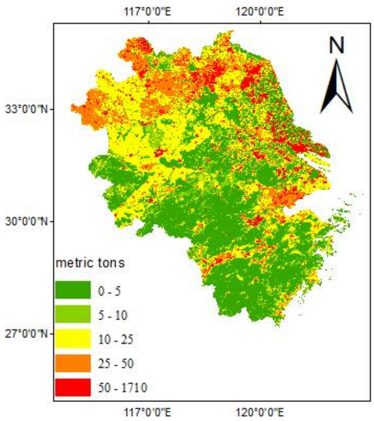
Figure 5



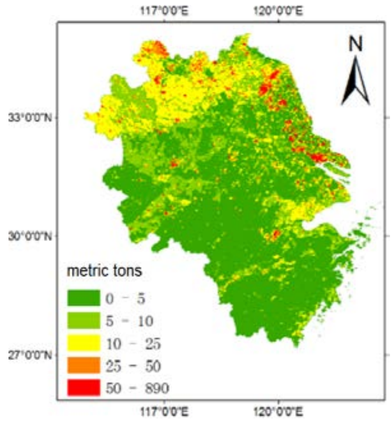
(a) Fertilizer use in E1



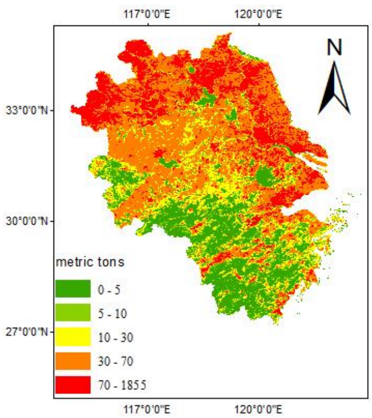
(b) Fertilizer use in E2



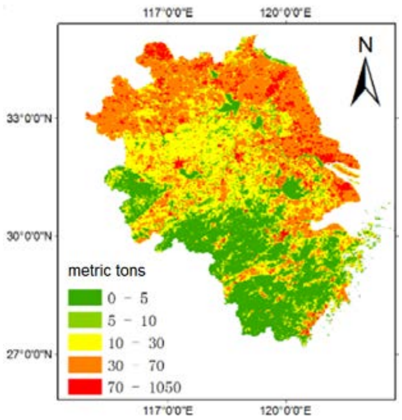
(c) Livestock farming in E1



(d) Livestock farming in E2

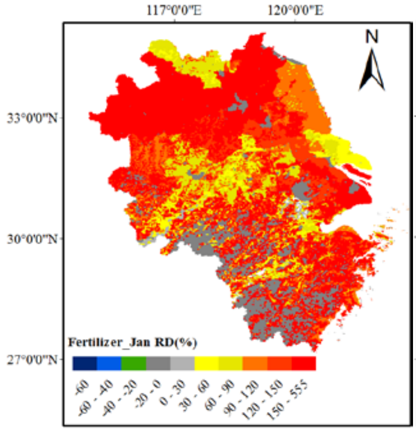


(e) Total emissions in E1

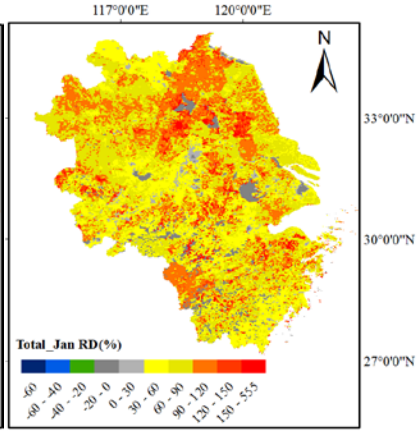


(f) Total emissions in E2

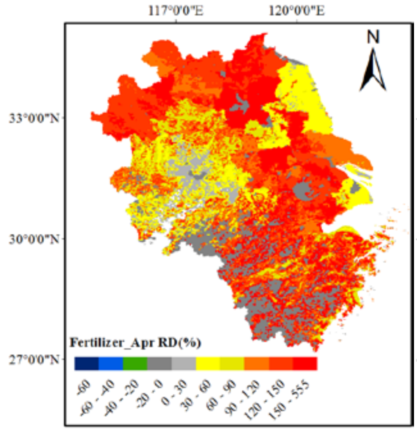
Figure 6



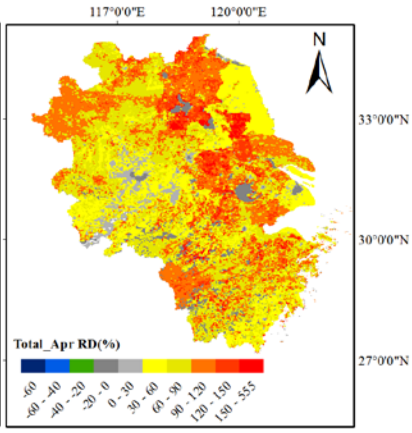
(a) Fertilizer_January



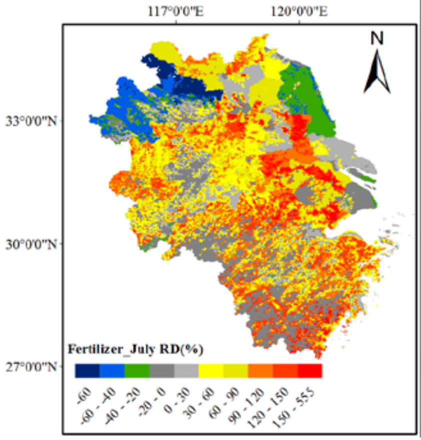
(b) Total_January



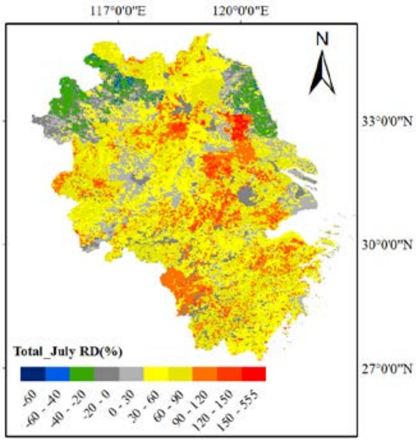
(c) Fertilizer_April



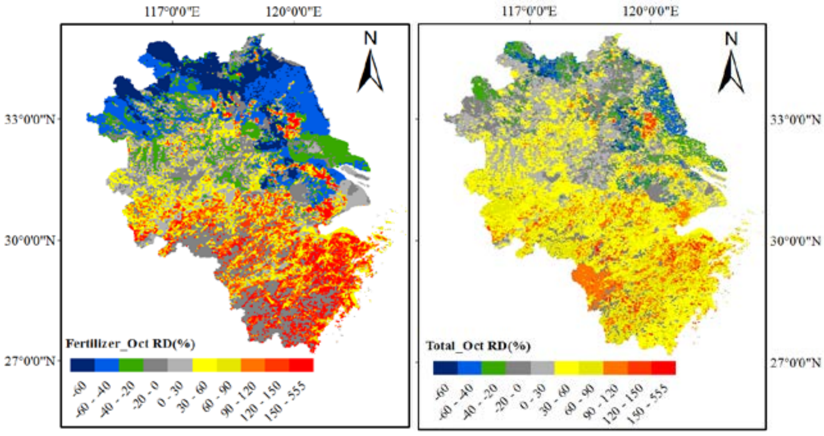
(d) Total_ April



(e) Fertilizer_July

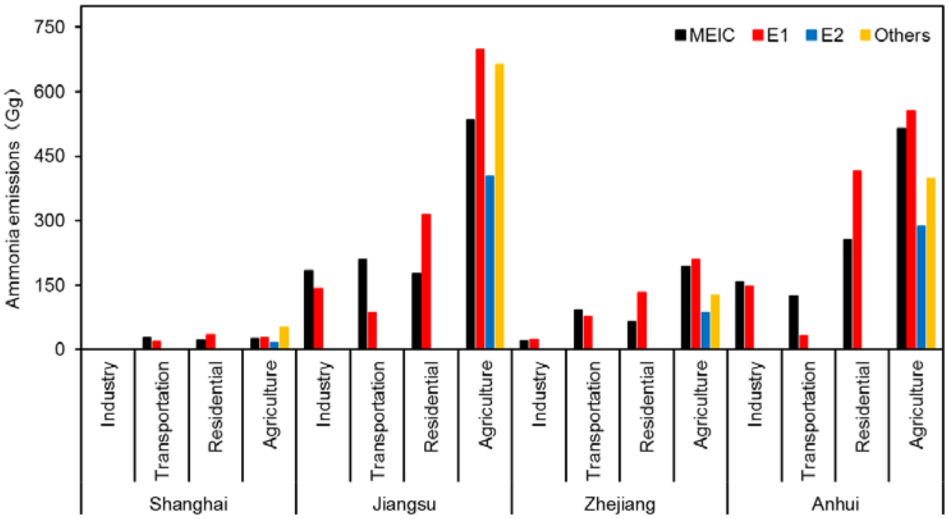


(f) Total_ July



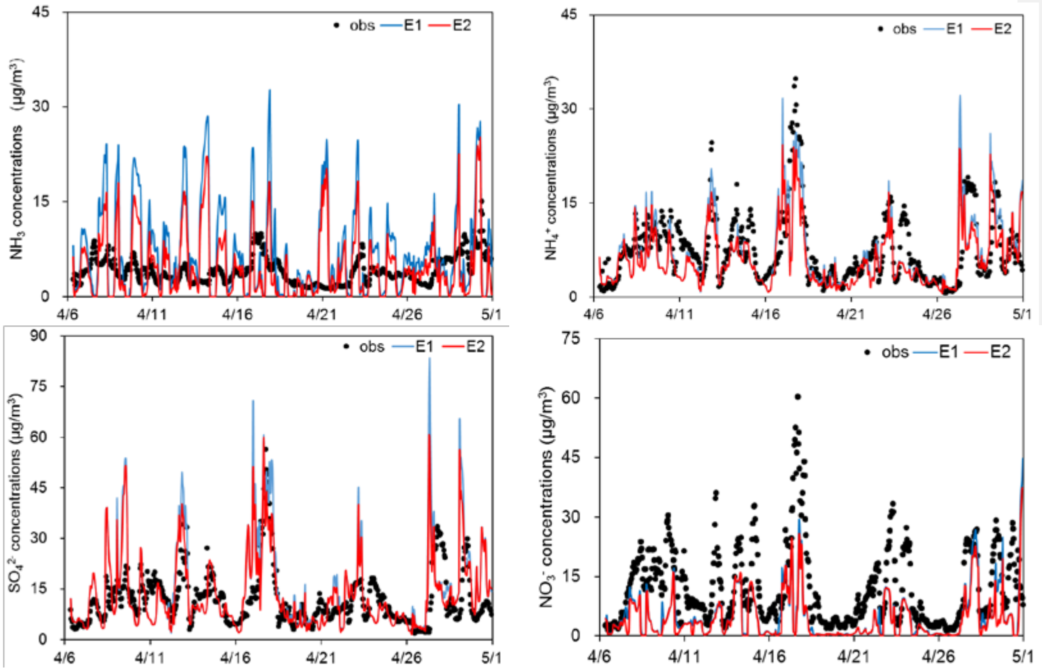
(g) Fertilizer_October (h) Total_ October

Figure 7

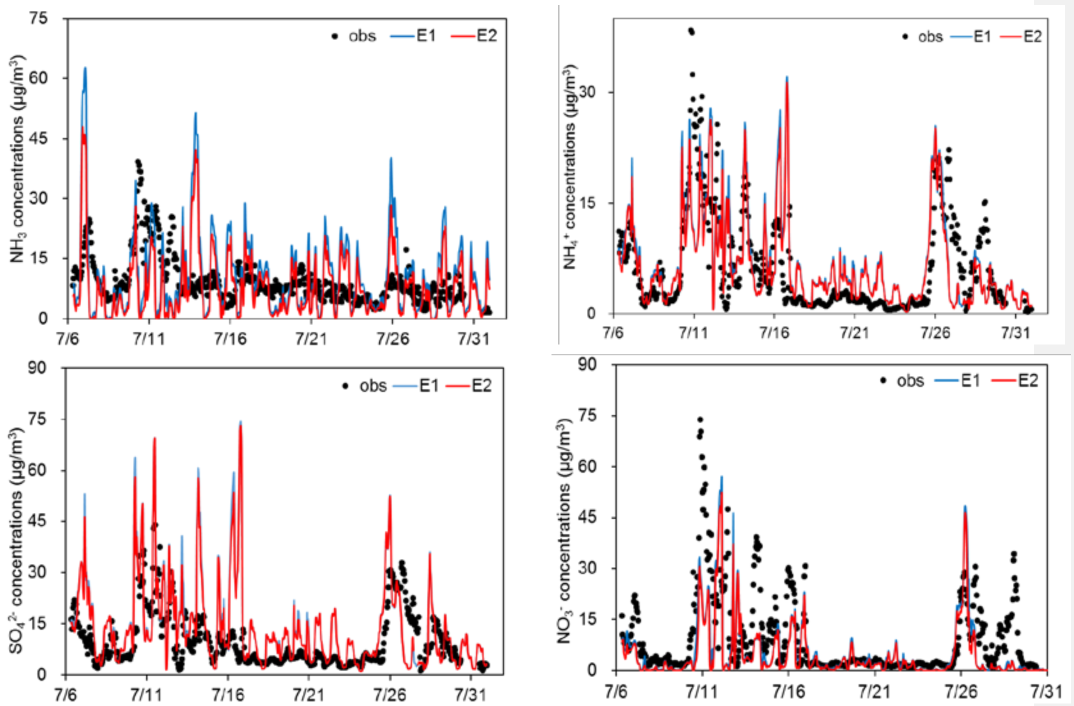


MEIC
E1
E2
Others
Ammonia emissions (Gg)
750
600
450
300
150
0
Industry
Transportation
Residential
Agriculture
Shanghai
Jiangsu
Zhejiang
Anhui

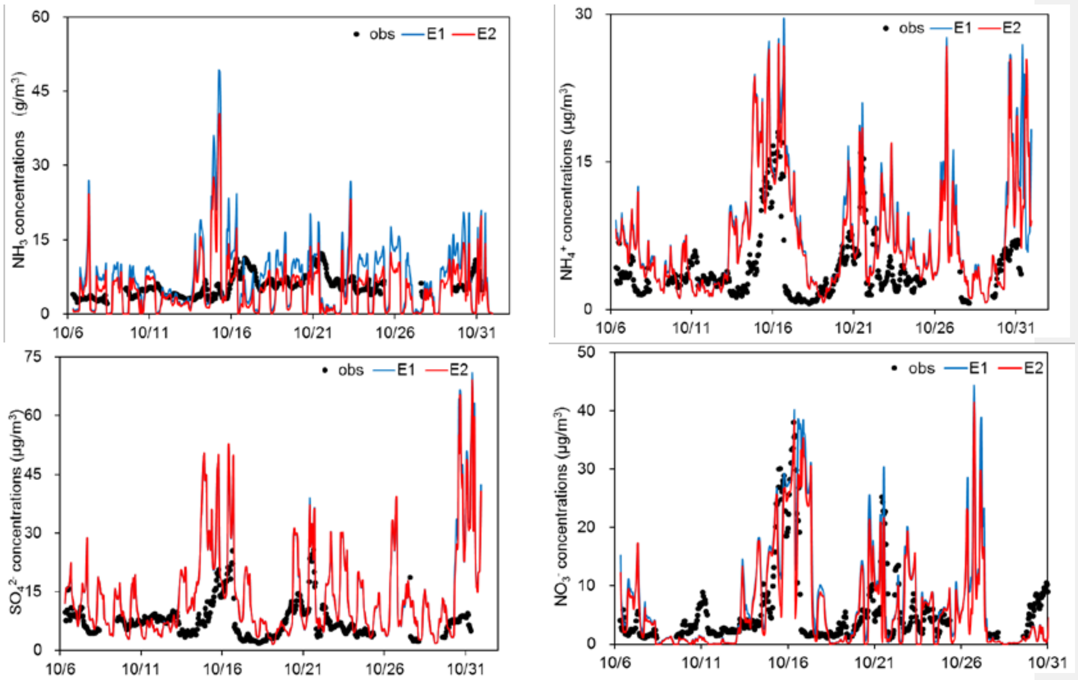
Figure 8



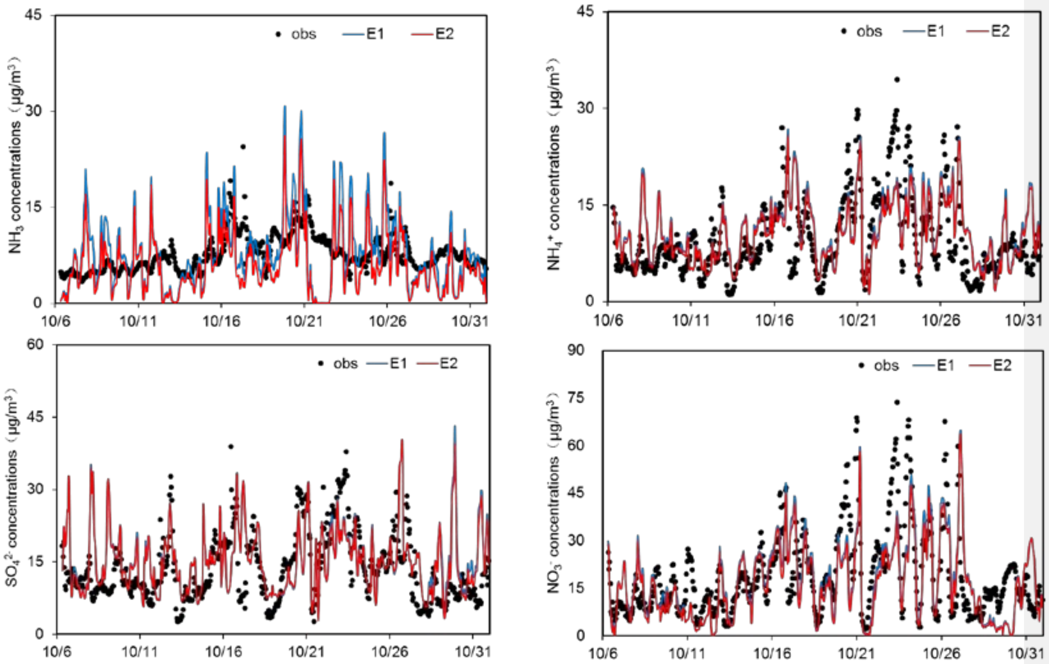
(a) SHPD_April



(b) SHPD_July

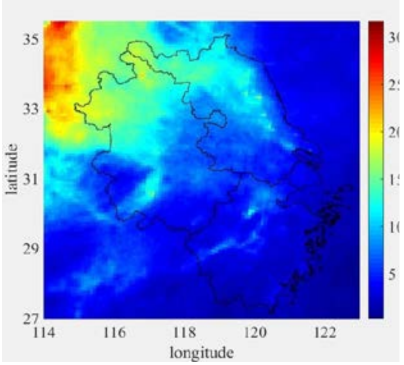


(c) SHPD_October

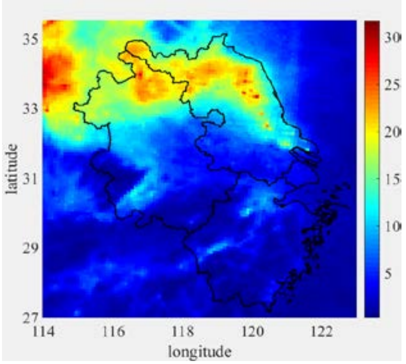


(d) JSPAES_October

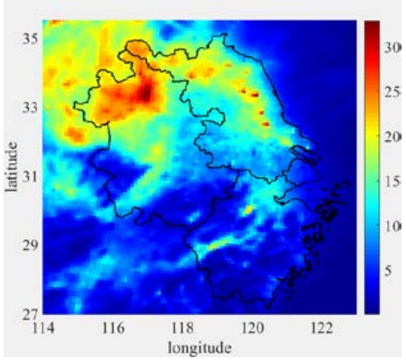
Figure 9



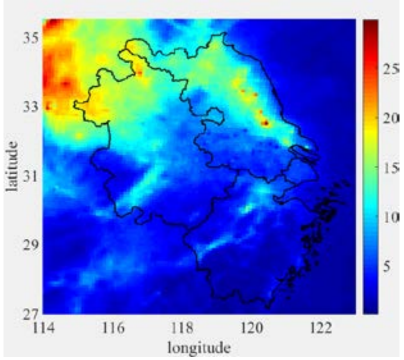
(a) E1 January



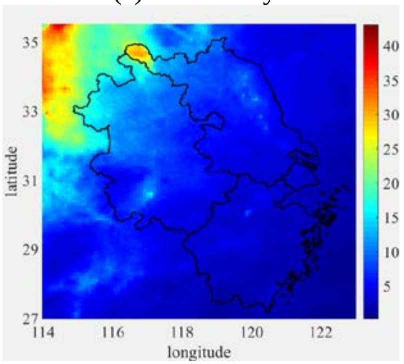
(b) E1 April



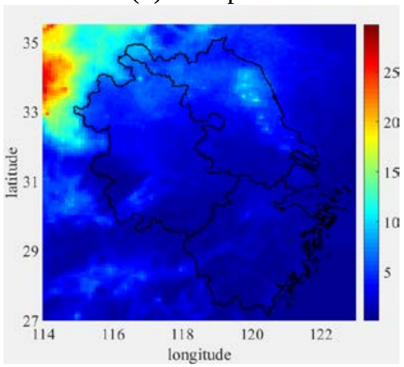
(c) E1 July



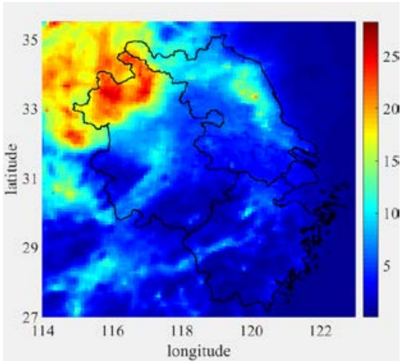
(d) E1 October



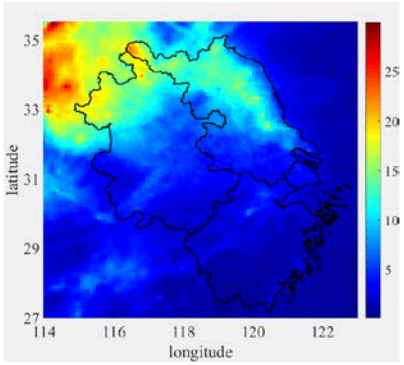
(e) E2 January



(f) E2 April

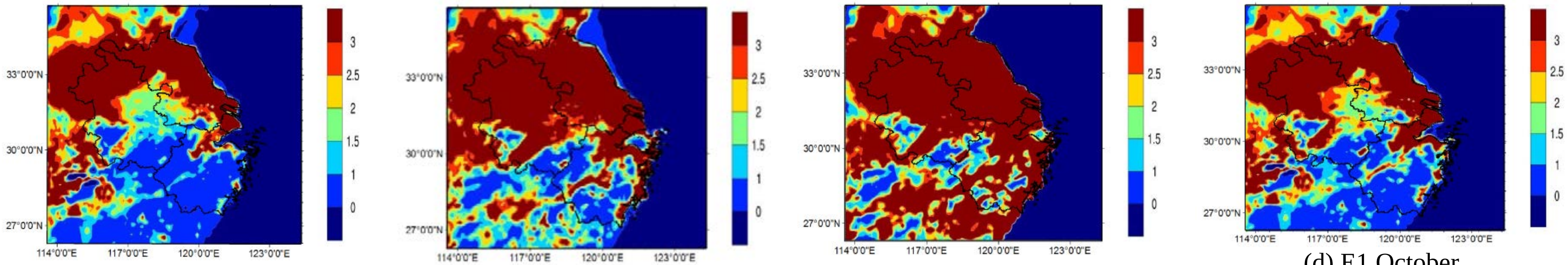


(g) E2 July

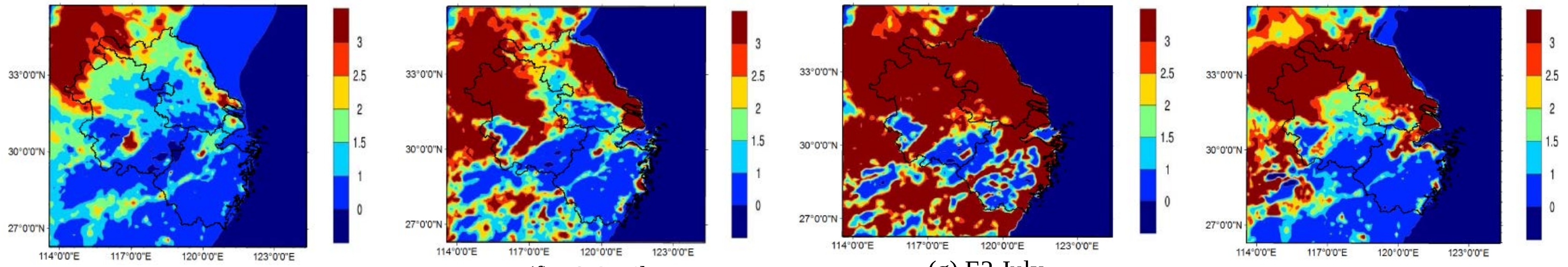


(h) E2 October

Figure 10



(a) E1 January (b) E1 April (c) E1 July (d) E1 October



(e) E2 January (f) E2 April (g) E2 July (h) E2 October