

Interactive comment on “High resolution modeling of gaseous methylamines over a polluted region in China: Source-dependent emissions and implications to spatial variations” by Jingbo Mao et al.

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We would like to thank the referee for his/her constructive comments which help to improve our manuscript. Our point-to-point replies (in blue) to the comments are given below (the original comments are copied here in black). The manuscript has been revised accordingly. All the changes to the manuscript have been highlighted using the Microsoft word “track-changes” tool in one version of the submitted revised manuscript.

Anonymous Referee 2

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Gas-phase amines can influence the new particle formation and growth in the atmosphere. Although their concentrations in the ambient air are clearly lower than ammonia they play an important role in the particle formation and growth due to higher reactivity compared ammonia. Largely due to the lower concentrations and higher reactivity they will only affect the processes near the source regions. Due to lack measurements of amines previously the emissions of amines have been modelled using fixed ratios (FR) between ammonia and amines. This paper presents a simulation study over the Yangtze River Delta Region to produce and test source dependent amine-to-ammonia ratios (SDR) in order to improve future model simulations of amines in the atmosphere. The idea is worthy and can produce a significant contribution to the field.

We appreciate the positive comments confirming the importance of this study.

However, there several things that need to be improved before publication. In the following I detail the changes by sections that are needed before publication.

Methods

- please state the emission frequency (daily, hourly, more frequent?), what is available in the dataset and what is used in this study.

The emission frequency in present study is hourly with a daily cycle. The dataset contains emissions of five source types: residential, agriculture, transportation, chemical industry, and other industry. This has been clarified in the revised manuscript.

- Is the emission data available online, and/or how to get it?

We derived methylamines emissions based on ammonia emissions for different sources, causing the emission frequency is the same as ammonia. In our study, for ammonia emissions, the dataset for MEIC is available online, and we download it from <http://www.meicmodel.org>, while we get the refined emission data for ammonia in YRD from the Shanghai Academy of Environmental Sciences (SAES). Interested reader can use the amines to ammonia ratios presented in this manuscript to calculate amines

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emissions.

- What is the reasoning behind the emission sectors?

In various emission inventories such as MEIC and INTEX-B, emission sources are generally separated into different types like residential, agriculture, transportation, industry, and power. Considering that emission rates of amines from organic synthesis may differ significantly with those from power generation and heavy industries using selective catalytic reduction (Zheng et al., 2015), we divided industrial sources into chemical industry and other industry in the present study.

- In Zheng et al. (2015) and current study, the times for observations are different, why? I don't see any other than "other industry" sector in Zheng et al. (2015), where are the other emission factors coming? The numbers do not match with Zheng et al. (e.g. 31.8. [C1/NO_x]/[NH₃/NO_x]:0.000076/0.037=0.0021 and current works states 0.0032) or am I misunderstanding something? And please describe the calculation in the text.

We chose a one-week period (26 August to 31 August 2012) instead of all the observation period because plumes with high concentrations of amines and ammonia were measured only during this period.

For the source types: residential, agriculture, transportation, and other industry, we derived the ratios according to the peak values of amines and ammonia in the plumes identified by and as shown in Fig. 6 of Zheng et al. (2015). As described in the manuscript, the source of ratio for the chemical industry is based on the direct measurement of amines in the ammonia water solution used as absorbent during flue gas treatment.

Numbers in our manuscript are peak values of plumes shown in Fig.6 of Zheng et al. (2015) while the ratios of NH₃ and amines to NO_x given in Table 2 of Zheng et al. (2015) (for five industrial plumes only) were acquired by using orthogonal distance regression analyses. The table below shows the ratios in the five plumes in Zheng et

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al. and present study, respectively. We used the averaged peak values of five plumes in present study. The slight difference in the ratios does not affect the main conclusions of this study. The table please see the pdf file shown in Supplement.

- SDR is based on NUIST, but main study on Fudan, why not do two simulations with the finest resolution for both stations?

Considering the complex underlying surface in urban Shanghai, we applied 4-domain-nested simulations to further study the Shanghai urban area, and the simulated results showed that there is no significant difference in the variations of amines. For the NUIST site which is located in a suburban area without complex underlying surface, 3-domain-nested simulations appear to be adequate.

- Model description must be improved, now the authors only say they follow Yu Luo (2014), but this is the first time of implementing amine compounds in WRF-Chem, it needs to be explained in detail. Absolutely necessary information: - What is the particle uptake mechanism for amines? - What are the oxidation coefficients? and which oxidants? - other removal mechanisms? wet deposition for example?

More detailed model description and references have been added to Section 2.3.

- NMBs in Table 4 are not correct, it looks like that they are only bias of the total mean

$$\frac{(\bar{C}_m - \bar{C}_o)}{\bar{C}_o}$$

. Correct way to calculate NMB is

$$\frac{\sum_{i=1}^N (C_m - C_o)}{\sum_{i=1}^N C_o}$$

C4

, check Boylan Russell (2006) for more information. As it is now, it can give a wrong impression of model ability to reproduce observations.

We calculated the NMBs according to the equation:

$$\frac{\sum_{i=1}^n (S_i - O_i)}{\sum_{i=1}^n O_i} \times 100\%$$

- It would be reasonable to focus on NUIST since the emission (SDR) factors are based on this station, so could you make run with the domain4 also for NUIST

Please see our reply to a similar comment earlier.

- Please add domain 3 for Fudan in Table 5 also, to facilitate comparing to NUIST site
Added.

- Please analyse the discrepancy between model and observations more carefully, now the reasons for discrepancies are vague

The analysis has been improved and expanded by including the impact of uptake coefficients ($\gamma=0.001, 0.01, 0.03$) on the results.

- in addition to separating Fudan by agricultural/residential sector, add separation by land/sea also. This would allow evaluating non-pollution sector concentrations.

In the present study, the emission of amines over ocean is limited to ships and has already been included in the transport sector (Figs. 2-4e). The simulated concentrations of amines over ocean are generally quite lower.

- The sensitivity test is doubling/halving SDRs only. Can you use the uncertainty from observations to create uncertainty range in SDR and do sensitivity test with max/min
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range for that, could you do different particle uptake coefficients, this would be interesting. This way we could have an idea to which of the uncertainties are in most urgent need of new research.

This is a good point, but the number of plumes for different sources is too limited to derive uncertainty range from observations. To look into impact of different particle uptake coefficients is a good suggestion. We have added two additional uptake coefficients ($\gamma=0.03, 0.01$), and relevant discussion has been given in Section 3.2 of the revised manuscript.

- Authors refer to short lifetime for amine many times without a reference or calculation of lifetime of amines, please add reference and/or calculation from your model

Two references have been added.

- Can you compare the particle size distributions with observations to evaluate the particle sink for amine?

Particle size distributions were not observed at the two sites during the periods when amines were measured.

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2017-1184/acp-2017-1184-AC2-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-1184>, 2018.