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Comment on acp-2022-394

Anonymous Referee #1

Referee comment on "Contribution of marine biological emissions to gaseous methylamines in the atmosphere: an emission inventory based on satellite data" by Qi Zhang et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-394-RC1, 2022

In the current study the authors provide a combined satellite and model study to estimate oceanic emissions of methylamine (MMA), dimethylamine (DMA) and trimethylamine (TMA) along the Chinese coastlines. Therefore, sea surface temperature (SST), chlorophyll-a (chl-a), sea surface salinity (SSS) and wind speed data were used. Recent investigations show that satellite data are a useful tool to simulate and understand emissions from the ocean. The study reveals that amine emissions from the ocean can have significant contribution to gas-phase TMA and MMA concentrations, but not to DMA concentrations. Through sensitivity studies wind speed and chl-a concentrations were found to be important drivers of amine emissions. The modeled gas-phase concentrations of MMA, DMA and TMA are compared with measurements in that region and found good matches. Regarding the importance of amines for new particle formation and current limitations the paper addresses relevant scientific questions in the field of atmospheric chemistry.

Nevertheless, emissions from the oceans towards the atmosphere require good established concentration measurements within the sea water. These are not given for the Chinese coastline and thus the authors used an average value derived from different measurements. Here, high uncertainties can exist. Furthermore, the authors do not use established measured physical and chemical parameters for these amines. Besides, it seems that there is a bug in the calculation of the pKa value. Therefore, the simulations have to be reperformed.

The paper needs major revision before publication.

Main Comments

Parameters such as pKa and Henry's Law coefficient are important to calculate the amine flux into the atmosphere. The authors use Henry's Law coefficients obtained for NH_3 as it was done in recent studies. This approach is feasible if such values are not given in literature. However, these values are determined.
Why are the authors not using the Henry's Law coefficients for MMA, DMA and TMA as provided in Sander (2015) and Leng et al. (2015)?
The pKa values used in table 4 from Gibb et al. (1999) are valid for 25°C not 20°C. Why are the temperature dependent pKa values given in the review of Ge et al. (2011b) not used?
The simulations have to be reperformed by using the values for MMA, DMA, and TMA.

The authors use observed values of MMA, DMA and TMA dissolved in sea water from other sea areas and state that "all sites are located in densely populated areas". However, values from Hawaii or the Arabian Sea are used which are obviously not as densely populated areas as the Chinese coastline. Why do the authors use only these values, but neglect other measured values from Yang et al. (1994), Gibb et al. (1999), and van Pinxteren et al. (2019)?

Formula 10
In the publication of Khoo et al. (1977) the formula is different. It is
pKa = pKwa + (0.1552 – 0.0003142T)*I instead of the applied
pKa = pKwa + (0.1552 – 0.003142T)*I
Furthermore, there was a correction of this prediction method by Bell et al. (2007; 2008). This has to be checked and the simulations have to be reperformed.

The authors state that chl-a influences the emission of amines into the atmosphere, but concentrate only on the pH effect. In environments rich of biological activity such as the sea-surface microlayer DMA concentrations can be up to one order of magnitude larger than in the bulk (van Pinxteren et al, 2019). A sensitivity study dealing the possible effect of higher chl-a on dissolved amine concentrations is missing and has to be done.

For anthropogenic emissions the authors use the Amines-to-Ammonia mass emission ratio derived for the Yangtze River Delta region. This ratio will result into lower TMA emissions compared to MMA and DMA. However, in the review of Ge et al. (2011a) animal husbandry TMA emissions dominate MMA and DMA that is not reflected in the current study by the lower agricultural emission ratio. Thus, the high ocean contribution might be coincidence because of the underestimation. The ratio for agricultural emission from Mao et al. (2018) is further 0.00043 instead of the applied 0.0004.
Besides, recently a new source of C2 and C3 amines was detected in China (Chang et al., 2021) that might be a potent TMA source. This is not represented, yet.

Why do the authors not treat uptake on aerosols that was determined to be important for the lifetime of amines by Yu and Luo (2014)?

The authors do refer to a mass ratio of amines with ammonia from Zheng et al. (2015) for the chemical boundary conditions of the model, but there a ratio between amines as well as ammonia with NO_x is given. From the values of Zheng et al. (2015) it is hard to recalculate the ratio presented in this study.

There a two recent measurements campaigns of marine MMA, DMA and TMA in the gas phase at the study area. However, it seems the results are not well discussed. For example, TMA measured is around one order of magnitude higher in Gao et al. (2022), but a discussion is missing. Furthermore, in table 6 the values are sometimes in ng or µg m^{-3} instead of pptv making a comparison difficult. I suggest that the authors include their modeled average values together with pptv also in ng m^{-3} for better comparison. Overall, from the most recent studies it seems that during winter the model overpredict DMA, but underpredict TMA.

Minor Comments

Line 61
Does this refer towards NH_3? Should be better specified.

Line 93
Delete "And"

Line 104
"Multiple"

Lines 108-109
The authors focus only on a very small part of the North Pacific. The sentence should be rephrased.

Line 142
Please provide a reference for the reaction rate coefficients.

Line 145
How long was the spin-up time for the model?

Line 255
From the figure it seems that it is April > October > July > January.

Line 257
"to the at the ocean" rephrase

Line 302
Is this the average of the full area? Has to be mentioned.

Line 303
Is the last part really needed?

Line 311
The referring to MBE is missing for the TMA comparison.

Line 334
Provide a reference for the degradation in sediments.

Line 342
With decreasing SST the emission increases.

Section 3.2
For the reader it would be better when the discussion is structured into (i) MMA, (ii) DMA and (iii) TMA as it is for the figures. Separate figures showing the percentage changes over the ocean will help to better understand and follow the discussion.

Line 364
Table 7 instead of table 6

Line 395
How is the difference of HONO + OH between the simulation with and without MBE?

Line 405
Add that the low agricultural emissions of DMA are related to the contribution.

Line 419
In figure S2 and S3 the distribution of the residential emissions is not shown.

Section 3.3.2
A discussion of DMS when the WS is reduced is missing. Why are there so strong changes in July?

Section 3.3.3
When the Henry's Law coefficient is changed also the emission flux is changed. This discussion is missing.

Line 491
Because of the missing sea water data and the missing uptake on aerosol particles, it could be questionable if the last part of the sentence ("which is more consistent with the reality") is really true. It might be true on global scale, but not necessarily on regional scale.

Table 6
Please add the year of the measurement. Provide also average values.

Figure 4
The figure caption describes MBE and AE contribution different as mentioned in the figure legend.

Figure S2-S6
Give the name of month instead of a number and symbol.

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