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## Reply on RC1

Dihui Chen et al.

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Author comment on "Mapping gaseous dimethylamine, trimethylamine, ammonia, and their particulate counterparts in marine atmospheres of China's marginal seas – Part 1: Differentiating marine emission from continental transport" by Dihui Chen et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-258-AC1>, 2021

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*(1) My major concern lies within the question of the sensitivity of the instrument. Regarding the detection limits of the instruments and partly some time ranges where concentrations were below the LOD, I am wondering how applicable is the method for amine measurements in low concentrated (e.g. remote marine) areas. The concentrations reported here are in part significantly higher than reported in other marine regions and I think with the LODs of the here applied method, the amines would not be detectable. Please comment on the limits of the here presented technique! In this context, please compare the concentration values achieved here with literature data (especially of marine locations).*

**Response:** Thank the comments. The limits of detection (LOD) for ions in AIM-IC are largely adjustable and almost completely determined by the user-chosen volume of the loop installed on the low-pressure injection valve. We adopted the loop volume at 250–2000  $\mu\text{L}$  for measurements in different atmospheres to lower the LOD and gain reasonably accurate concentrations of these species. In this study, 250  $\mu\text{L}$  loop was used by considering that high  $\text{NH}_{3\text{gas}}$  concentrations may occur in the marine atmosphere. The information has been added in the revision. The reviewer's comments are valid by considering measurements made by the use of the deputy loop volume.

In the revision, more comparisons with those values reported in the literature had been added. For example, Gibb et al. (1999) measured  $\text{DMA}_{\text{gas}}$  and  $\text{TMA}_{\text{gas}}$  on November 16 to December 19 in 1994 over Arabian Sea, which were  $8.8 \text{ ng m}^{-3}$  and  $0.48 \text{ ng m}^{-3}$  respectively. The values were approximately one-two orders smaller than the concentrations of  $\text{DMA}_{\text{gas}}$  and  $\text{TMA}_{\text{gas}}$  measured in this work. Including the concentrations of  $\text{DMAH}^+$  and  $\text{TMAH}^+$  in atmospheric particles reported by Gibb et al. (1999), we also made tens of cruise off-line measurements of  $\text{DMAH}^+$  and  $\text{TMAH}^+$  in size-segregated atmospheric particles. Their concentrations varied largely from a few  $\text{ng m}^{-3}$  to  $\sim 1 \mu\text{g m}^{-3}$  in  $\text{PM}_{10}$ . The comparison has also been added in the revision.

*(2) Line 20 "we identified marine emissions of the gas species originating from continental transport..." sounds confusing. Is it marine or continental? Please clarify (and shorten the sentence)*

**Response:** We have changed the word "identified" into "differentiated".

(3) Line 35: please add which numbers (16%, 34%) belong to which species.

**Response:** We have added the corresponding species in the revision.

(4) The introduction mixed amine sources in seawater and in the atmosphere. Please be more correct. For example, the first sentence of the intro states that the atmospheric amines are derived from the degradation of glycine betanine.... But the latter processes happen in the seawater (not in the atmosphere as appears from the sentence).

**Response:** Thank you. The sentence is indeed confusing and corrected in the revision.

(5) Line 57: Please explain, why this is not the case for the continental atmosphere.

**Response:** The sentence has been revised as "However, measuring gaseous amines in real-time simultaneously to their particulate counterparts in the marine atmosphere over the ocean remains challenging because of artifact signals related to self-vessel emissions and amine-contained dew evaporation from outside surfaces of the vessel with sunrise in morning, although this is not the case in the continental atmosphere (VandenBoer et al., 2011)."

(6) Line 82: Do you mean, that 1) higher concentration levels of nutrients result in higher concentrations of amines?

**Response:** This is what we expected prior to the study. Yes. We have added the description for explanation. In the revision, it has been revised as "Winter cruise campaigns provide great opportunities for observational studies due to the 1) higher concentration levels of nutrients in the seas at a lower sea surface water temperature which may emit a large amount of gaseous amines and/or particulate aminium-contained sea spray aerosols from the seas (Guo et al., 2020);"

(7) Line 83: why is 3) "... periodically enhance long-range transport..." an advantage here?

**Response:** In the revision, it has been revised as "periodically enhanced long-range transport of anthropogenic pollutants from continents to the seas which may enhance formation of secondary ammonium and aminium aerosols (Guo et al., 2016; Wang et al., 2019)."

(8) Line 89: unclear expression: "identifying marine sources from continental transport..." do you mean distinguish the sources?

**Response:** Yes. Corrected to "distinguishing" in the revision.

(9) Line 118: in Context with my main comment: please give the LOD converted to the atmospheric measurements (in  $\mu\text{g}/\text{m}^3$ )

**Response:** The limit of detection of  $\text{NH}_4^+$ ,  $\text{DMAH}^+$ , and  $\text{TMAH}^+$  were 0.4, 4 and 2  $\text{ng m}^{-3}$  in ambient air, respectively.

(10) Line 150: is 0.002  $\mu\text{g}/\text{m}^3$  the LOD?

**Response:** Yes. The data of 0.002  $\mu\text{g m}^{-3}$  was the average values of TMA which approached the LOD of TMA.

(11) Line 155: "extremely low" please be more precise here and give numbers. Also, please compare with other published amine measurements in marine regions (see main

comment).

**Response:** In the revision, it reads as "The TMA<sub>gas</sub> and TMAH<sup>+</sup> concentrations at 0.002±0.001 µg m<sup>-3</sup> in the upwind continental and coastal atmospheres were much lower than most of observed values over tens of ng m<sup>-3</sup> reported in the literature. However, Gibb et al. (1999) reported even lower values of TMA<sub>gas</sub> (0.5 ng m<sup>-3</sup>) and particulate TMAH<sup>+</sup> (0.5 ng m<sup>-3</sup>) in the marine atmosphere over Arabian Sea on November 16 to December 19 in 1994."

(12) Line 161: Explain the amines in relation to "onshore" and "offshore" winds more detailed and refer to the corresponding Figures.

**Response:** To be clear, the sentence has been changed to "The DMA<sub>gas</sub> and DMAH<sup>+</sup> in PM<sub>2.5</sub> concentrations with north offshore winds were substantially higher than those with south or southeast onshore winds (Fig 1), suggesting that their continental emissions and related secondary sources were stronger." in the revision.

(13) Line 175: I am wondering if the times when the concentrations were below LOD are included in the given average values (e.g. for example setting the concentration to ½ LOD for times when the analytes could not be detected). Otherwise the mean data represent too high concentrations. A Table listing the mean (min-max) values for the gas and particulate amines for the different "campaigns" would help.

**Response:** The concentrations below LOD are included in the given average values. The min-max values have been added in the revision.

(14) Line 185: From Fig.1 it looks as if DMA<sub>gas</sub> shows a similar behaviour as TMA<sub>gas</sub>. Please show the correlations reported in this passage (e.g in the supporting information). Otherwise, the differences between TMA<sub>gas</sub> and DMA<sub>gas</sub> are not easily understandable.

**Response:** In the revised SI, the correlations between TMA<sub>gas</sub> and DMA<sub>gas</sub> were added in SI, in which three periods such as Peak 1, Peak 2 and Peak 3 were highlighted in different markers.

(15) Line 192: Please define "campaign A" and "campaign B" and the "costal station" more concise. Use the same descriptions concerning these separate "campaigns" consistently in the text and in the Figures. 20-22. Dec is "campaign B" = "port-anchoring period"?

**Response:** Agree. Revised accordingly. Campaign A was conducted on 9-19 December, 2019. Port-anchoring occurred on December 19-22. Campaign B started from 27 December, 2019 to 17 January, 2020, organized by another research team.

(16) Line 227/228: Do these references state that the amines (or TMA) are transferred via primary sea spray? Please state this more clear. Connected to this: has a primary sea spray transfer (Line 236) been shown for (gaseous and/or particulate) amines?

**Response:** The sentence has been revised as "This suggests that the observed TMAH<sup>+</sup> may not be derived from the neutralization reactions of TMA<sub>gas</sub> with acids in the marine atmosphere, and may have been derived from primary sea-spray organic aerosols (Hu et al., 2015, 2018). Primary sea-spray organic aerosols mainly contained primary and degraded organics (Ault et al., 2013; Prather et al., 2013; Quinn et al., 2015; Dall'Osto et al., 2019)."

(17) Line 256: It is highly speculative to comment on changing amine concentrations in the seawater, if such values were not measured. What means not "directly"? Same for line 265

**Response:** Agree. The regression equation can allow to argue the emission potential, but it is highly speculated to argue the concentrations of TMAH<sup>+</sup> concentrations. In the revision, the sentence has been revised as "However, the measured concentrations of TMAH<sup>+</sup> and seawater pH in the surface seawater were needed to confirm this".

*(18) Line 270: What is meant with "scenarios"? Do you mean "hypothesis"? Please explain.*

**Response:** Hypothesis is better and used in the revision.

*(19) Line 278: What is meant with "increasing" and "decreasing" period?*

**Response:** The sentence has been clarified as "The purple-red and dark-green markers represent the data obtained at 10:00 on 14 December - 22:59 on 16 December with increasing concentrations and at 23:00 on 16 December -19:59 on 17 December with decreasing concentrations of the species during Peak 3, respectively, which were analyzed separately."

*(20) Line 276 and following (chapter 4.2 and 4.3): I find it difficult to follow and understand the estimations and conclusions from the given information. I suggest adding some more details. Why is it justified to estimate the DMA<sub>gas</sub> in this way? This part is very descriptive and little explanatory. For example: The good correlation is mentioned (Line 280) but what can be concluded from that and why? What is the explanation that TMAH<sup>+</sup> decomposed into DMAH<sup>+</sup> (Line 283)? I have the feeling that the interrelationships and conclusion in 4.2 and 4.3 should be elaborated more strongly. The connections were much better illustrated in chapter 4.4.*

**Response:** We had revised two parts accordingly to clarify our approaches and findings.

*(21) Line 360: Did you exclude emissions of seabirds because the peaks were persistent for a long time under strong winds? Or what else is the reason? If so, maybe add ".. were therefore unlikely to be derived..." (Line 361)*

**Response:** Agree and revised accordingly.

*(22) Line 362: why "alternatively"?*

**Response:** The word has been removed.

*(23) Line 369: undetectable chemical conversion? What is meant by that?*

**Response:** It has been revised "Chemical conversion of particulate TMAH<sup>+</sup> by AIM-IC likely occurred and the products were undetectable by the AIM-IC. This requires further investigation."