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Comment on acp-2022-601

Anonymous Referee #1

Referee comment on "Non-volatile marine and non-refractory continental sources of particle-phase amine during the North Atlantic Aerosols and Marine Ecosystems Study (NAAMES)" by Veronica Z. Berta et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-601-RC1>, 2022

The manuscript by V.Z. Berta et al. deals with an interesting topic and contributes to fill the observational gap about particulate phase amines over remote oceanic locations. I believe the manuscript could be beneficial for the scientific community, nevertheless, it would need major revisions before publication. The conclusions are not always adequately supported by the data and sometimes important information are missing to judge their robustness. Furthermore, sometimes the conclusions are presented with too strong assertions, considering the robustness of the data they are based on. Finally, some sections could be better organized to make their message clearer to the reader.

Major comments

One of the main conclusions of the manuscript is that FTIR and HR-ToF-AMS detect different amine types, with different sources. This is based mostly on the lack of correlation between the two datasets, on different correlations with external source/process tracers and by considering well-known limitations of the two techniques (i.e., AMS may have problem with organic species associated to non-refractory particles, like sea-spray particles; FTIR sample handling may determine the loss of volatile species). Although this is a reasonable explanation, it is not the only one. For example, the

discrepancy between FTIR and AMS amine data may derive from a different time coverage of the observations during the cruise; quantitative details about the overlapping of the two measurements during the different cruises were not provided. Most importantly, the lack of correlation may derive from the uncertainties associated to the two measurement techniques. Being the measurements performed in a very clean environment, one could guess that uncertainties may be large. This aspect is never discussed in detail in the manuscript.

The motivation for which FTIR tends to detect more primary biogenic amines from the ocean than the AMS is quite convincing, being based on well-known characteristics of the AMS (difficulty in measuring quantitatively primary sea-spray particles) and on previously published multi-technique studies in the marine environment. Conversely, the authors do not provide a clear motivation for the fact that AMS would be more representative of continental SOA, while FTIR data would be more related to biogenic SOA (in sizes not dominated by the marine POA signal: <0.18 , <0.5 μm). Some reference to the volatility is made in the manuscript but this is not addressed quantitatively. The authors should discuss this issue, providing support from the literature to motivate the apparently different sensitivity of the two techniques to different amine sources. Otherwise, a much simpler explanation for the observed differences would be the analytical uncertainty of one or both techniques, due to the low concentrations.

The manuscript bases some of the conclusions on statistically non-significant correlations. To make such conclusions more trustworthy, the authors should provide more information in Tables 3 and 4 (besides those provided in the insets of Figures 3-6). To judge how far one R value is from the significance threshold one needs at least the number of data couples used for the regression (n) and/or the corresponding P value (confidence interval). For instance, in Lines 268-275 the authors compare the different correlations between AMS NR amine and AMS NO₃ between continental and marine air masses, concluding that the correlation is stronger in continental ones. Considering that only one R value is significant (late spring - continental) it is difficult to understand if the interpretation given by the authors is supported by the results or not. In winter, they got $R=0.59$ for marine and $R=0.71$ for continental air masses (both non-significant), nevertheless, without knowing the P value associated to each R it is not possible to judge properly. This is particularly important for FTIR results, which are based on a lower number of samples than AMS data. I also invite the authors to be more consistent and quantitative in the evaluation of the regressions, for instance choosing a maximum P value threshold over which the correlation is dismissed (too low confidence on the result).

I have noted something strange with the evaluation of the significance of the linear regressions through the manuscript. For instance, in Figure 7e, it is reported that the P value for FTIR alcohol group vs FTIR NV amines is 0.03 (significant correlation!): the regression has $n = 8$ and $R = 0.11$; according to any table of Pearson critical values these cannot result in a significant correlation. Other similar examples can be found in Figure 7d ($n = 11$, $R = 0.12$, $P = 0.00???$), Figure 7f ($n = 9$, $R = 0.27$, $P = 0.03???$), Figure 2b. Please double check the significance tests. This supports the previous request for more information in Tables 3 and 4.

Specific comments

L122. "when a factor with higher amine..." CONTRIBUTION, maybe?

L165. "but largely similar for both marine and continental air masses": I do not understand what this sentence adds with respect to the previous one ("The exception to this trend was the Early Spring cruise when concentrations were slightly higher at 33 ± 6 ng m⁻³ during marine periods than during continental periods (32 ± 165 11 ng m⁻³)").

L160-169. Are the discussed differences in amines concentration between marine and continental air masses statistically significant? They may be not, particularly in the case of FTIR data, which are based on a limited number of samples. In any case, this would be an important information to provide to the reader.

L171-175. This sentence seems to contradict what stated above about "continental transport" being "a significant source of amines in the North Atlantic". Reading further on, the position of the authors is made clearer, nevertheless I would invite the authors to modify this sentence in order to make it less contrasting with the previous statements. For instance, they could just start the sentence with something like "Notwithstanding the above consideration on continental transport, ...".

L196-198. Please provide some more details to explain why the "weak correlation for the marine period in Early Spring is likely evidence of the AMS not measuring components including amine on refractory sea salt particles". The logical path is not straightforward.

L204-205. Please revise this sentence: stating that seawater and sea-surface-microlayer samples were collected in clean air masses does not make sense.

L214-221. This paragraphs evidence some inconsistencies in the data correlations.

- FTIR NV amine groups show a clear correlation with wind speed in continental air masses. This suggests that the source of primary marine amines is so strong as to influence the total amine signal even when mixed with land sources. Nevertheless, this correlation disappears in marine air masses, where primary marine amines should be dominant (at least following the manuscript conclusions). This should be better addressed in the manuscript and the apparent inconsistency clarified.
- Furthermore, it is showed that AMS NR amines does not correlate with wind speed. This is taken in strong considerations by the authors to state that amines present in sea-spray particles are not detected by AMS and to, therefore, justify the lack of correlation between the two datasets (AMS vs FTIR). Nevertheless, some moderate correlations are showed between AMS NR amines and the other chosen sea-spray tracer (i.e., IC sea-salt), which suggests that some primary marine amines should contribute to the AMS signal. This is a clear inconsistency, apparently not taken into account in deriving the conclusions of the study. If the authors have reasons to consider the lack of correlation with wind speed as more robust/reliable than the correlation with IC sea-salt, they should provide evidence for it.

To me, the inconsistencies evidenced here suggest that the relations between amines and tracers are affected by some degree of randomness, as it can derive from large casual errors (uncertainty) associated to the measurements.

L223-232. Please provide information on how chlorophyll-a concentration was calculated. It is measured on board or estimated from satellite data? In this case, is it the punctual concentration? Or is it back-trajectory-weighted in order to consider the air mass history? According to the chosen approach the result may vary strongly.

L255-257. Actually, Table 3 shows two significant positive correlations (AMS NR amine vs IC MSA) in continental air masses against only one in marine air masses. Maybe, the authors want to double check the correlations significance of the continental-Early Spring and Late Spring cases (see also the above comment on the P values).

L273-275. Please explain better how the steeper slope in continental air masses suggests a continental source for AMS NR amines. To me, this just demonstrates that NO₃ is enhanced in continental air masses with respect to marine ones relatively more than amines. This is expected as NO₃ sources are almost entirely continental, while amines have potentially both marine and continental sources.

L288-290. In marine air masses, only one cruise over four presents a positive correlation (weak and non-significant) between AMS NR amines and Radon. Based on this, the authors should make a less strong statement about the continental origin of AMS NR amines. I am not saying that I do not believe amines can have continental sources, I am only saying that, in this particular case, the correlation with Radon does not seem to allow a strong confidence on this. Other traces allow for stronger statements as for instance IC nssK+.

L299-300. "No correlations of FTIR NV amine groups to IC nssK+ were statistically significant (Table 4)": actually, Table 4 reports all the correlations in that line as significant (presence of *). Please double check the Table entries or modify the text.

L301-308. Please explain better the logic pathway for the conclusion highlighted here. Tang et al (2014) report that increasing RH increases the production of secondary aminium salts. This should result in a positive relation between RH and secondary amines concentration.

L319. I do not think that the absolute concentration of the ion signal at mz44 is a good proxy for particle oxidation. According to my experience, the mz44 signal generally increases when Org increases. Therefore, the correlation observed with mz44 just replicates the relation with AMS Org. I would suggest, instead, to use what the AMS community calls the "f44" parameter (i.e., the relative contribution of mz44 to the whole Org spectrum), which would better trace chemical processes adding oxidized functionalities to the organic aerosol mixture.

L354-356. This conclusion is not supported by evidence and is in contrast with the following paragraphs, where a potential source of secondary biogenic marine amines is considered (correlation between FTIR NV amines and acid groups or AMS). To me, Section 3.4 could be better organized for major clarity.

L383-384. From Figure 8 I see that, for AMS NR amines, the most correlating tracers are IC nssK+ and AMS NR mz44, followed by AMS NR Nitrate. This is clearly consistent with a major continental source. Nevertheless, the fourth most correlating tracer is MSA, with a significant R value close to that of AMS NR Nitrate. I think this does not provide support for a total dismissal of natural marine sources. Furthermore, also a significant correlation with IC sea-salt is evidenced in Figure 8 (even though with lower R): this should allow for less peremptory conclusions about the source of AMS NR amines.

L399-402. Please refer to the following comment regarding the Conclusions Section.

L424-426. The authors themselves admit that the "source apportionment" obtained by merging FTIR and AMS amine data is "rough". Nevertheless, they report it as sharp percent contributions (e.g., 53% vs 47% or 27% vs 73%). This does not reflect at all the roughness of the apportionment. I am not against providing a tentative apportionment of the amine sources during the cruises, but it should reflect the uncertainties in the measurements, the variability of the observations and the limitations of the apportionment approach. Contributions of marine and continental sources should be provided as ranges or associated with appropriated uncertainty bars.

Figure 4. The insert of panel d) reports a wrong correlation coefficient for the Early Spring case: it should be negative (-0.41, according to the Table), while it is reported as 0.84.

Figure 8. Please, specify which data are represented in the Figure: "Marine" or "Marine+Continental"?

Figure 9. I think the authors should select a better cruise to represent the relation between FTIR NV amines and IC sea-salt. Figure 9a presents a correlation which is based on only 3 data points, of which two present concentrations so close to zero as to be probably affected by a huge uncertainty. If this is the most robust correlation they can select to summarize their findings, one can be legitimated to question the robustness of the manuscript conclusions.