Responses to Reviewers

RESPONSE: The authors appreciate the thoughtful feedback provided by the two reviewers. As outlined below, we believe that the revised manuscript has addressed all of the concerns raised, and we have revised the manuscript accordingly. In addition to the specific statements noted below, we have also made minor changes in the manuscript to be consistent with the statements below, as shown in the Tracked Changes version of the manuscript that we submitted. While most of the issues raised were minor and none changed the main conclusions of the paper, the additional explanation and improved wording suggested by the Reviewers makes the revised manuscript a stronger, more focused research article that illustrates the differences between amine measurements with different techniques.

Referee #1

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.

RESPONSE:

We appreciate Referee #1's comments about the issue of the uncertainty of the measurements given the low/clean marine conditions, presumably mostly with respect to the 23-hr FTIR samples. We think the reviewer is suggesting that the lack of correlation (between FTIR and AMS) could result from one or both of the measurements being at or near detection. The reason we did not come to this conclusion is the correlations of both FTIR and AMS to tracers. The correlations summarized in Figure 8 illustrate that the correlations of the two measurement methods are not random, as might be expected if they are driven by detection limit issues.

The reviewer is correct that these issues should be noted, and they are discussed in the methods. They are also noted explicitly in the presentation of tables and figures, showing the small number of FTIR points available. In addition, we show in the table below explicitly the extent to which the lack of agreement between AMS and FTIR is explained by the measurement uncertainty of +/-20%.In terms of time coverage, FTIR NV amine

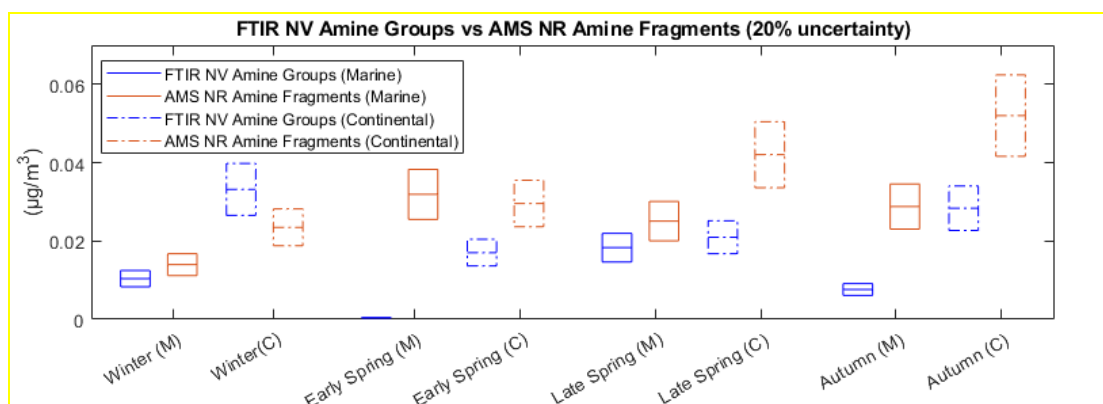
groups and AMS NR amine fragments were both collected during the same 26 days of sampling noted in the Methods for each cruise, and since the overlap was complete it was not discussed. The methods do have different sampling times (FTIR was 1 day and AMS was 5 min), which does make them inherently difficult to compare. The different sampling times also meant that we used different criteria to identify marine air masses, as described in Section 2.2, with 5-min criteria from Saliba et al. (2020), and ~24-hr criteria for filter sampling times matching these if met for 90% of the sampling duration, based on Lewis et al. (2021). The complete time series and categorization of FTIR NV amine groups and AMS NR amine fragments to show the times of overlap are provided in Figure 1.

Correlations of AMS NR amine fragments and tracers were obtained by averaging measurements by the hour, and correlations to IC and FTIR filters were averaged over the filter sampling time. The reviewer is correct also in possibly implying that the greater number of measurements for AMS and some tracers gives these correlations more data points and sometimes p<0.05, whereas this is not true for the IC or FTIR filter sampling.

The estimated 20% uncertainty in the literature is generally based on OM rather than amine measurements, but to show that the FTIR and AMS amine differences exceed this uncertainty we provide this specific comparison (Figure R1 and Table R1 below). Campaign average FTIR NV amine group and AMS NR amine fragment concentrations are within this 20% uncertainty during Winter and for marine air masses in Late Spring. The other campaign averages are not within the 20% uncertainty associated with each instrument. This illustrates that the differences on which our conclusion about AMS and FTIR amine differences are larger than the uncertainties expected for the methods. The reviewer is correct that larger uncertainties in one or both methods could also contribute to the amine differences, but, were that the case, we would expect the differences to be either random or constant rather than associated with tracers. For this reason, we find it likely that the differences are in part driven by chemical and physical differences in amines from different sources.

Table R1. Average concentrations (μg m^{-3}) of FTIR NV amine groups and AMS NR amine fragments ± 20% for marine and continental air masses across all cruises.

	Marine				Continental			
	Winter	Early Spring	Late Spring	Autumn	Winter	Early Spring	Late Spring	Autumn
FTIR	1.04	0.04	1.83	0.76	3.32	1.70	2.10	2.84
FTIR+20%	1.25	0.05	2.20	0.91	3.98	2.04	2.51	3.40
FTIR-20%	0.83	0.03	1.46	0.61	2.65	1.36	1.68	2.27
AMS	1.40	3.19	2.51	2.88	2.35	2.96	4.20	5.20
AMS+20%	1.68	3.83	3.01	3.46	2.82	3.55	5.04	6.24
AMS-20%	1.12	2.55	2.01	2.30	1.88	2.37	3.36	3.36

Figure R1. Average concentrations (μg m^{-3}) of FTIR NV amine groups and AMS NR amine fragments where boxes illustrate ± 20% range of uncertainty for marine and continental air masses for the four NAAMES cruises.

In addition, we find that many trends are consistent regardless of whether air masses are considered marine or continental, indicating that the trends are the same at higher and lower concentrations. As an example, AMS NR amine fragments correlated consistently with AMS NR nitrate (and FTIR NV amine groups correlated consistently with AMS NR chloride) for both marine and continental air masses.

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.

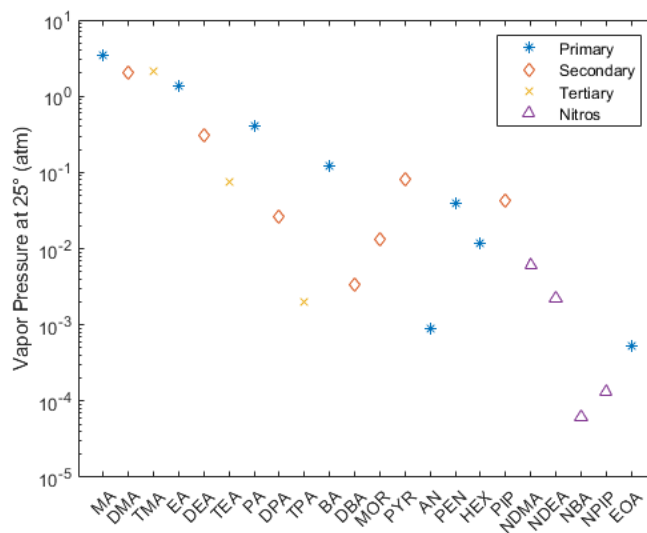
RESPONSE:

The Reviewer is correct that part of this argument is implicit, namely that since AMS has been shown to miss measuring marine organics (because they are mixed with refractory sea salt) then the amines that it is measuring are likely non-marine (which generally do not have substantial refractory material in non-dusty regions). In other words, the lack of reports of AMS missing continental organics suggests that it is not missing continental amines. This argument is supported by reports of amines by AMS for continental sources (Murphy et al., 2007;Ge et al., 2011;Malloy et al., 2009). On the other hand, there are reports that FTIR misses volatile components of continental aerosol in urban conditions (e.g. Liu et al., 2009). Based on this, we have inferred that the reduced amounts of continental amines in the FTIR measurements may be due to their higher volatility (or to their secondary CNH or tertiary CN amine moieties). However, the literature generally lacks quantification of the volatility of relevant marine and continental amines; to assess the properties of observed marine and continental amines, we compiled the volatility of some marine and continental amines in Table R2 and Figure R2 below.

Table R2. Summary of amine compounds identified in aerosols in marine environments, including moiety (primary, secondary, tertiary, nitrosamine), vapor pressure, and source (marine, continental).

Compound	Moiety	Vapor Pressure	Marine or Continental Source (Ge et al., 2011)
Monomethylamine (MA)	Primary	304 kPa at 20 °C 2650 mm Hg at 25 °C	Both
Dimethylamine (DMA)	Secondary	203 kPa at 25 °C 1520 mm Hg at 25 °C	Both
Trimethylamine (TMA)	Tertiary	187 kPa at 20 °C 1610 mm Hg at 25 °C	Both
Ethylamine (EA)	Primary	121 kPa at 20 °C 1048 mm Hg at 25 °C	Continental
Diethylamine (DEA)	Secondary	25.9 kPa at 20 °C 237 mm Hg at 25 °C	Both
Triethylamine (TEA)	Tertiary	7.2 kPa at 20 °C 57.07 mm Hg at 25 °C	Both
Propylamine (PA)	Primary	33.9 kPa at 20 °C 310 mm Hg at 25 °C	Continental
Dipropylamine (DPA)	Secondary	7.2 kPa at 20 °C 57.07 mm Hg at 25 °C	Continental
Tripropylamine (TPA)	Tertiary	1.51 mm Hg at 25 °C	Continental
Butylamine (BA)	Primary	10.9 kPa at 20 °C 92.9 mm Hg at 25 °C	Continental
Dibutylamine (DBA)	Secondary	0.27 kPa at 20 °C 2.59 mm Hg at 25 °C	Continental
Morpholine (MOR)	Secondary	1.06 kPa at 20 °C 10.1 mm Hg at 25 °C	Continental
Pyrrolidine (PYR)	Secondary	1.8 kPa at 39 °C 62.7 mm Hg at 25 °C	Continental
Aniline (AN)	Primary	40 kPa at 20 °C 0.67 mm Hg at 25 °C	Continental
Pentylamine (PEN)	Primary	4 kPa at 25 °C 91 mm Hg at 20-25 °C	Continental
Hexylamine (HEX)	Primary	0.87 kPa at 20 °C 7.95 mm Hg at 20 °C	Continental
Piperidine (PIP)	Secondary	75.3 kPa at 29.2 °C 32.1 mm Hg at 25 °C	Continental
Nitrosodimethylamine (NDMA)	Nitrosamine (formed by reactions of secondary or tertiary amines)	0.36 kPa at 20 °C 2.7 mm Hg at 20 °C	Continental
Nitrosodiethylamine (NDEA)	Nitrosamine	0.86 mm Hg at 20 °C	Continental
Nitrosodibutylamine (NBA)	Nitrosamine	0.047 mm Hg at 25 °C	Continental
Nitrosopiperidine (NPIP)	Nitrosamine	0.09 mm Hg at 20 °C	Continental

Ethanolamine (EOA)	Primary	53 kPa at 20 °C 0.40 mm Hg at 25 °C	Continental

Figure R2. Vapor pressures (at 25 °C) of amine compounds identified in aerosols in marine environments. Markers represent amine moiety- blue asterisk: primary amine, orange open diamond: secondary amine, yellow cross: tertiary amine, purple open triangle: nitrosamine.

There are five amines identified as having oceanic sources, only one of which would be detected by FTIR since it is the only one with a primary NH2 group (MA). Since MA is on the high side of the vapor pressures compared to continental amines and if this were a complete set of marine amines, this would suggest that FTIR was able to measure MA despite its high volatility (perhaps because of its presence in a mixture). Unfortunately, this list is not expected to be a complete list of atmospheric amines, and the multiple sources for each amine means that we cannot distinguish which might be better measured by AMS if they are too volatile to be measured by FTIR.

To make the relevant uncertainties more explicit as suggested by the Reviewer, we have revised the first paragraph of Section 4.4 as follows:

New Line 400-414. "*In general, our results support the expectation that FTIR NV amine groups and AMS NR amine fragments do not measure the same chemical components. Specifically, FTIR measures NV amine groups with primary C-NH$_2$ groups that may or may not be refractory. The correlations summarized in Figure 8 show that, in marine air masses, most of the FTIR NV amine groups in <1 μm particles have sources that are primary and marine and that <0.5 μm and <0.18 μm diameter fractions have sources that are secondary and marine. In contrast, the AMS measures NR amine fragments with primary (C-NH$_2$), secondary (C$_2$-NH), and tertiary (C$_3$-N) moieties that may be too volatile to be sampled on filters, although the FTIR does not detect secondary and tertiary amines even if they remain on filters. There is a 20% uncertainty associated with AMS and FTIR OM measurements (Russell et al., 2009a;Russell, 2003). A larger difference between the measurements is seen when there is substantial refractory*

material such as black carbon, mineral dust, and sea salt due to the reduced collection efficiency of the HR-ToF-AMS (Gilardoni et al., 2007) and when there is a high contribution of volatile components as in urban areas (Liu et al., 2009;Chen et al., 2018). The correlations summarized in Figure 8 illustrate that the correlations of the two measurement methods are not random, as might be expected if they are driven by detection limit issues. Specifically, the higher correlations of AMS NR amine fragments to continental and secondary tracers indicate the components measured are largely from continental and secondary sources, although some contribution of primary source emissions from combustion and secondary marine emissions is also possible."

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).

RESPONSE:

We thank Referee #1 for the suggestion. We have revised the manuscript to include two additional tables containing the number of data couples used for the regression (n) in the supporting information as Tables S19 and S20. Tables S15 and S16 contain the p-values corresponding to correlation coefficients displayed in Tables 3 and 4. p < 0.05 was the threshold used to determine significant correlations. We would also like to clarify that the asterisks listed next to the R values in Tables 3 and 4 are indicative of R values that are not significant. All but one correlation of AMS NR amine fragments and AMR NR nitrate are significant. Most of the FTIR correlations are not significant, as the reviewer expected. Nonetheless we have included them because they are the only points available and since each point represents a longer time (a day) so that they are representative of a longer duration event (and subject to less auto-correlation).

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.

RESPONSE:

> We thank Referee #1 for noting this inconsistency. Referee #1 is correct that the p-values reported in the submitted manuscript were not retrieved correctly. We have now corrected the p-values from the standard Student's t-test distribution with (n-2) degrees of freedom within the manuscript and have updated Tables S15 and S16 accordingly.

Specific comments

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

RESPONSE:

> We thank Referee #1 for this suggestion and have corrected the text as suggested.
>
> New Line 128-129. *"when a factor with higher amine contribution was found, the variability of its mass…"*

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)").

RESPONSE:

> We thank the Referee #1 for this comment. We have removed this sentence from the manuscript.

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.

RESPONSE:

> We thank the Referee #1 for this comment. We have used a two-sample t-test using the MATLAB function ttest2 and a threshold of p > 0.05 to determine if the average amine concentrations between marine and continental air masses are statistically different. In all seasons except Early Spring, mean AMS NR amine fragment concentrations in marine and continent air masses were statistically different. Only during Winter (p = 0.03) were the differences in average FTIR NV amine groups concentrations between marine and continental air masses statistically significant. We have updated the manuscript as such:

New Line 177-184: *"Concentrations of AMS NR amine fragments were higher during continental periods (with concentrations ranging from 18 to 54 ng m-3) than during marine periods, when concentrations averaged below 33 ng m-3 (Table 2), except for Early Spring (Table 2). Winter, Late Spring, and Autumn were statistically significant (p < 0.05, two-sample Student's t-test). Similar to AMS NR amine fragments, FTIR NV amine group concentrations were higher overall during continental periods, highlighting that continental transport is a significant source of amines in the North Atlantic. The average FTIR NV amine group concentration ranged from 7 to 18 ng m-3 during marine periods and from 16 to 33 ng m-3 during continental periods (including filters with amine below the detection limit). However, the differences in average FTIR NV amine group concentrations between marine and continental air masses were only statistically significant during Winter.*

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, …".

RESPONSE:

We thank the Referee #1 for this suggestion. We have revised the manuscript as follows:

New Line 186-190. *"Notwithstanding the above consideration on continental transport, concentrations of AMS NR amine fragments were lowest in Winter, when AMS NR organic mass (OM) was also lowest and IC MSA concentrations were below detection, for both marine and continental air masses. These low concentrations of 14 to 18 ng m-3 in Winter may indicate that biologically-derived amine compounds make up a significant fraction of non-refractory amine during other seasons, since primary production has previously been shown to influence amine concentrations in the North Atlantic (Muller et al., 2009)."*

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.

RESPONSE:

We thank the Referee #1 for this comment and agree that this sentence is not clear. We observed consistent, moderate to strong correlations for AMS NR OM and AMS NR amine fragments across all seasons and air masses, suggesting that OM sources had consistent fractions of amine. The exception was in Early Spring for marine air masses which leads us to believe that AMS NR OM and AMS NR amine fragments had sources that were different or that had different amine contributions. The reference to "non

refractory sea salt particles" in this sentence was an error. We have revised the manuscript as follows:

New Line 211-212. *"The weak correlation for the marine period in Early Spring may reflect sources with different contributions of AMS NR amine fragments to AMS NR OM."*

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

RESPONSE:

We thank Referee #1 for this suggestion and have corrected the text as suggested.

New Line 219-220. *"FTIR NV amine functional groups have been reported in atmospheric aerosol, generated primary marine aerosols, seawater, and the sea surface microlayer sampled during conditions when air masses were considered clean marine in the North..."*

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.

RESPONSE:

We thank the Referee #1 for this comment. First, we see that Fig. 4d had a typo for the R values, mistakenly showing R=0.84 for Continental AMS NR amine with wind speed.

This is now corrected to -0.41. The Reviewer is correct that both wind speed and sea salt are imperfect tracers for sea spray. Correlations to local wind speed can be confounded by contributions from upstream areas with different wind speeds. Correlations to sea salt are hampered by the small number of samples and the lack of direct overlap of the IC and FTIR sampling times (Saliba et al., 2020), which makes both FTIR and AMS correlations to IC sea salt not significant. This means that the only significant correlations for marine AMS NR amine are negative with wind speed, strongly in Late Spring and very weakly for other seasons. While the lack of a positive correlation can be explained by differences in upstream wind speeds from the local wind speed, the presence of a strong negative correlation is very difficult to attribute to sea salt. We have revised the manuscript as follows:

New Line 227-231. *"The absence of a positive correlation with wind speed may be attributed to differences in local and upstream wind speeds, but the presence of negative correlations indicates a source of AMS NR amine fragments that is not associated with sea salt. The p-values corresponding to correlations of AMS NR amine fragments are displayed in Table S15. The limited number of points in each correlation of AMS NR amine fragments and FTIR NV amine groups are shown in Tables S19 and S20, respectively."*

New Line 236-238. *"The FTIR NV amine group measurements include some low concentrations and few samples, meaning that these correlations are uncertain and not significant."*

Any observed correlations of FTIR NV amine groups and wind speed with |r| > 0.25 were positive while correlations of AMS NR amine fragments and wind speed with |r| > 0.25 were negative. This highlights a distinct difference in sources of AMS NR amine fragments and FTIR NV amine groups. Overall, average correlations with IC sea salt and wind speed were both higher for FTIR NV amine groups than for AMS NR amine fragments as summarized in Figure 8.

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.

RESPONSE:

We thank Referee #1 for this suggestion. The measured chlorophyll-a is inline and is, therefore, a punctual concentration. We have revised the manuscript as follows:

New Line 164. *"Chlorophyll-a was also measured inline using High Performance Liquid Chromatography (HPLC)."*

Determining the upwind source contributions for air masses reaching a moving ship has limited accuracy and was not attempted here. Satellite chlorophyll-a concentrations have

been shown to serve as a poor proxy for a sea spray aerosol source and has limited interpretation for the relationship between organic components in seawater, including amines, and atmospheric aerosol composition (Quinn et al., 2014).

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).

RESPONSE:

We thank Referee #1 for this suggestion. We would like to clarify that the asterisks indicate correlations that are not significant. Table 3 (now Table 4) initially showed two non-significant positive correlations in continental air masses and only one in marine air masses. However, the corrected p values (see response above) now show that all correlations of AMS NR amine fragments and IC MSA are not significant. Table 3 (now Table 4) and the corresponding table containing p-values for correlations in the supporting information (Table S15) have been updated.

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.

RESPONSE:

We thank Referee #1 for pointing out this inconsistency. We agree that the steeper slope observed for continental air masses is likely due to higher nitrate with largely non-marine sources. We had intended to say that the zero intercept value for the linear fit of AMS NR amine fragments and AMS NR nitrate is indicative of a largely continental and secondary source for AMS NR amine fragments. This was present for periods during which AMS NR amine fragments and AMS NR nitrate were moderately to strongly correlated (Winter and Late Spring marine periods and Winter and Autumn continental periods). The manuscript has been revised as follows:

New Line 299-302. *"The zero intercepts (Table S17) of the linear fits for both continental air masses in Winter and Autumn and marine air masses in Winter and Late Spring suggest that the AMS NR amines largely have continental sources that are present during clean marine periods at lower concentrations."*

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+.

RESPONSE:

> We thank Referee #1 for this comment, and the implication that radon may not be a perfect tracer for all continental sources, especially those that are secondary or associated with urban areas where emissions are disproportionate to land-based emissions of radon. The manuscript has been revised as follows:
>
> New Line 320-321. *"It is possible, however, for weaker correlations to arise from amines associated with secondary or urban emissions that are disproportionate to land-based emissions of radon."*
>
> We would like to add that correlations of AMS NR amine fragments and radon during Late Spring are not significant ($p > 0.05$), largely because of the long sampling time required for low concentrations of radon. Nonetheless, during three of the four seasons, AMS NR amine fragments in continental air masses had a moderate correlation ($0.55 < R < 0.66$) with radon. We agree with the reviewer that these results complement the correlations with IC nssK$^+$, which also indicate a continental source. While we agree that radon is limited as a tracer, we find the correlations during continental periods, and during marine in Early Spring, to be compelling. To summarize all of the evidence for continental sources, we included Figure 8 to show that four other tracers including IC nssK$^+$ also support a secondary or continental source for AMS NR amine fragments.

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.

RESPONSE:

> We thank Referee #1 for this comment. We would like to clarify that the asterisks indicate correlations that are not significant rather than those that are significant; we confirm that Table 4 (now Table 5) initially reported no statistically significant correlation of FTIR NV amine groups to IC nssK$^+$. However, after correcting our p-values, we found that three correlations (out of seven) displayed in Table 4 (now Table 5) are statistically significant. Table 4 (now Table 5) and Table S16 have been updated based on these calculations.

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.

RESPONSE:

We thank the Referee #1 for this comment. We agree that the resolved negative correlations with relative humidity do not support the presence of aminium salts. Instead, these results may suggest that amines with thermodynamic properties similar to trimethylamine (TMA), a tertiary aliphatic amine, are undergoing particle-to-gas partitioning due to an increase in relative humidity and therefore, volatility. Tang et al. (2014) did find that reactions with HNO_3 and TMA produce less aminium salts and instead lower-volatility, organic products with decreasing relative humidity. Although a negative correlation of amines and RH would be consistent with a secondary source, we removed this discussion from the manuscript because of the speculative nature of the explanation.

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.

RESPONSE:

We thank the Referee #1 for this suggestion. We have replaced mz44 with f44 in our main manuscript to compare to the amine fraction

New Line 340-347. *"The contribution of the AMS ion signal at m/z 44 (CO2+) to the total AMS NR OM signal (f44) is a measure of particle oxidation and a tracer for secondary processing (Bahreini et al., 2005). Figures 5e and 5f display largely consistent trends between the contribution of AMS NR amine fragments to the AMS NR OM and f44. Weak to moderate (0.43 < R < 0.79) correlations of AMS NR f44 and AMS NR amine fragments are present across all air masses and seasons, with the exception of marine periods in Early Spring. Murphy et al. (2007) identified large signals of AMS NR m/z 44 in mass spectra of aminium nitrate salts produced by photooxidation, providing further evidence of secondary formation of AMS NR amine fragments. AMS NR f44 positively correlated (R = 0.36) with the contribution of FTIR NV amine group mass concentrations to the FTIR NV OM signal for only the marine period in Late Spring, possibly because aminium nitrate salts are too volatile to be retained on filters for FTIR analysis."*

New Line 20. *"... AMS NR amine fragments were identified by consistent correlations to AMS NR nitrate, AMS NR f44, IC non-sea salt..."*

We have also updated the text regarding the lack of correlation of amine with tracers during Early Spring for marine air masses.

New Line 352-354. *"AMS NR amine fragments did correlate moderately with atmospheric DMS, ozone, and AMS NR f44, which could be consistent with a secondary marine source that was not evident in the other cruises at higher latitudes."*

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.

RESPONSE:

We thank the Referee #1 for this concern about the FTIR NV amine group source for <0.5 μm and <0.18 μm particle samples in Section 4.3. We agree with the Reviewer that the evidence is insufficient for allocating a combustion source for this particle range. We have added this to our discussion and the manuscript has been revised as follows:

New Line 376-381. *"The weak correlations of FTIR NV alcohol and amine groups for <0.5 μm and <0.18 μm particle samples could result from non-marine sources such as combustion that have different ratios of FTIR NV alcohol and amine groups than those found in sea spray (Liu et al., 2009;Posner and Pandis, 2015;Shen et al., 2017;Liu et al., 2011). No positive correlations of <0.18 and < 0.5 FTIR NV amine group concentrations and black carbon concentrations were observed for marine or continental air masses."*

We also would like to thank Reviewer for the suggestion to reorganize Section 4.3 which is divided into three paragraphs. The first paragraph discusses how FTIR NV acid and alcohol groups are used as tracers for primary marine and secondary aerosol formation, respectively. This paragraph also first introduces Figure 7, which shows correlations of FTIR NV amine groups with alcohol and acid groups across all three filter sizes. The second paragraph discusses the results of FTIR NV amine and alcohol group correlations. The third paragraph discusses the results of FTIR NV amine and acid group correlations. Based on the reviewer's suggestion, we have now included transition sentences to clarify our results.

New Line 383-390. *"In contrast to the strong correlations found for FTIR NV amine groups with FTIR NV alcohol group for <1 μm samples, no correlation of <1 μm FTIR NV amine to acid groups were found during either marine or continental air masses. The weak correlations that were found for FTIR NV amine groups with FTIR NV alcohol groups for <0.5 μm and <0.18 μm particle samples also differ from the strong (0.82 < R < 0.96, Figure 7c,e) correlations of FTIR NV amine to acid groups that were found for <0.5 μm and <0.18 μm during marine periods. The correlations of FTIR NV acid to amine groups for <0.5 μm and <0.18 μm particle samples suggest that secondary amine groups contribute more to particles with diameters smaller than 0.5 μm, which is consistent with expectations for condensing gases having a proportionately larger impact on the mass composition of smaller particles (Maria et al., 2004;Seinfeld and Pandis, 2016)."*

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.

RESPONSE:

We thank the Referee #1 for this comment. First, we note that the updated version of the figure shows that all correlations with IC MSA and sea salt for both FTIR NV amine groups and AMS NR amine fragments were not significant. Second, we consider MSA to be a tracer for secondary rather than primary marine sources, as stated in the text. Secondary particles would be likely to be NR, and hence are likely to be measured by AMS. This highlights an important part of our argument that we have now clarified in the manuscript, namely that it is the primary marine missed by the AMS not the secondary marine. In this sense, we had not intended a "total dismissal" of all natural marine sources, but only the refractory ones – which seem to be the majority in clean marine conditions. In the percentage apportionment, we have not intended to claim that no (secondary) marine amines are measured by the AMS, but that the majority are most often secondary and continental. We have revised the manuscript as follows:

New Line 411-415. *"The correlations summarized in Figure 8 illustrate that the correlations of the two measurement methods are not random, as might be expected if they are driven by detection limit issues. Specifically, the higher correlations of AMS NR amine fragments to continental and secondary tracers indicate the components measured are largely continental and secondary, although some contribution of primary source emissions from combustion and secondary marine emissions is also likely."*

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

Response: See below.

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.

RESPONSE:

We thank the Referee #1 for this comment. We agree with the point and have added standard deviations to the percent contributions based on the variability observed in the seasonal averages of FTIR NV amine groups and AMS NR amine fragments and the concentration of the corresponding sum. The manuscript has been revised as follows:

New Line 26-28. *"The average seasonal contribution of AMS NR amine fragments and FTIR NV amine groups ranged from (27±57)% primary marine amine and (73±152)% secondary continental amine during Early Spring to (53±76)% primary marine amine and (47±68)% secondary continental amine during Winter."*

New Line 431-435. *"For Winter, the FTIR NV primary (C-NH$_2$) amine groups from primary marine sources accounts for (53±76)% compared to (47±68)% secondary continental AMS NR amine fragments. For Late Spring and Autumn, FTIR NV primary (C-NH$_2$) amine groups from primary marine sources account for (34±37)% compared to (66±72)% secondary continental AMS NR amine fragments. For Early Spring, FTIR NV primary (C-NH$_2$) amine groups from primary marine sources account for (27±57)% compared to (73±152)% secondary continental AMS NR amine fragments."*

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.

RESPONSE:

We thank the Referee #1 for pointing out our mistake. We have revised panel d) in Figure 4:

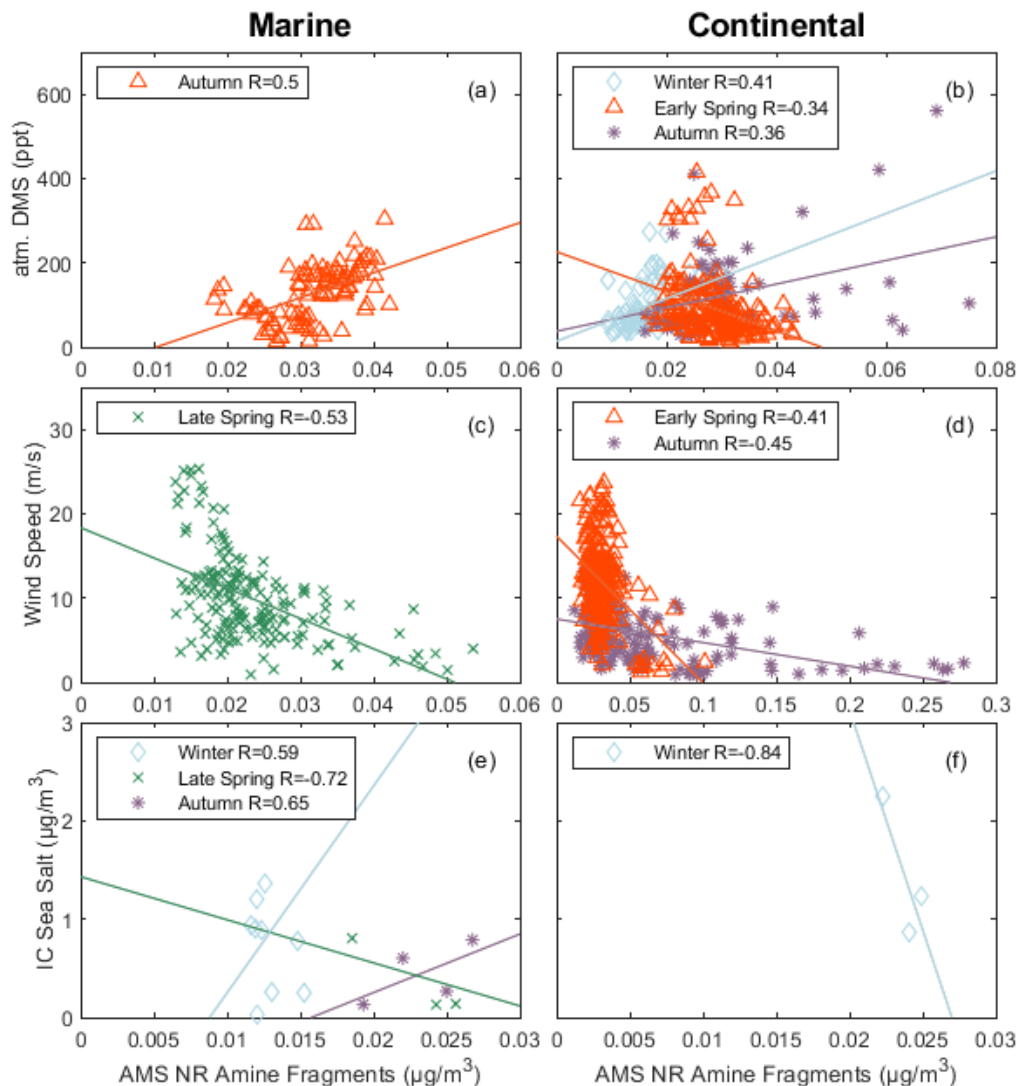



Figure 8. Please, specify which data are represented in the Figure: "Marine" or "Marine+Continental"?

RESPONSE:

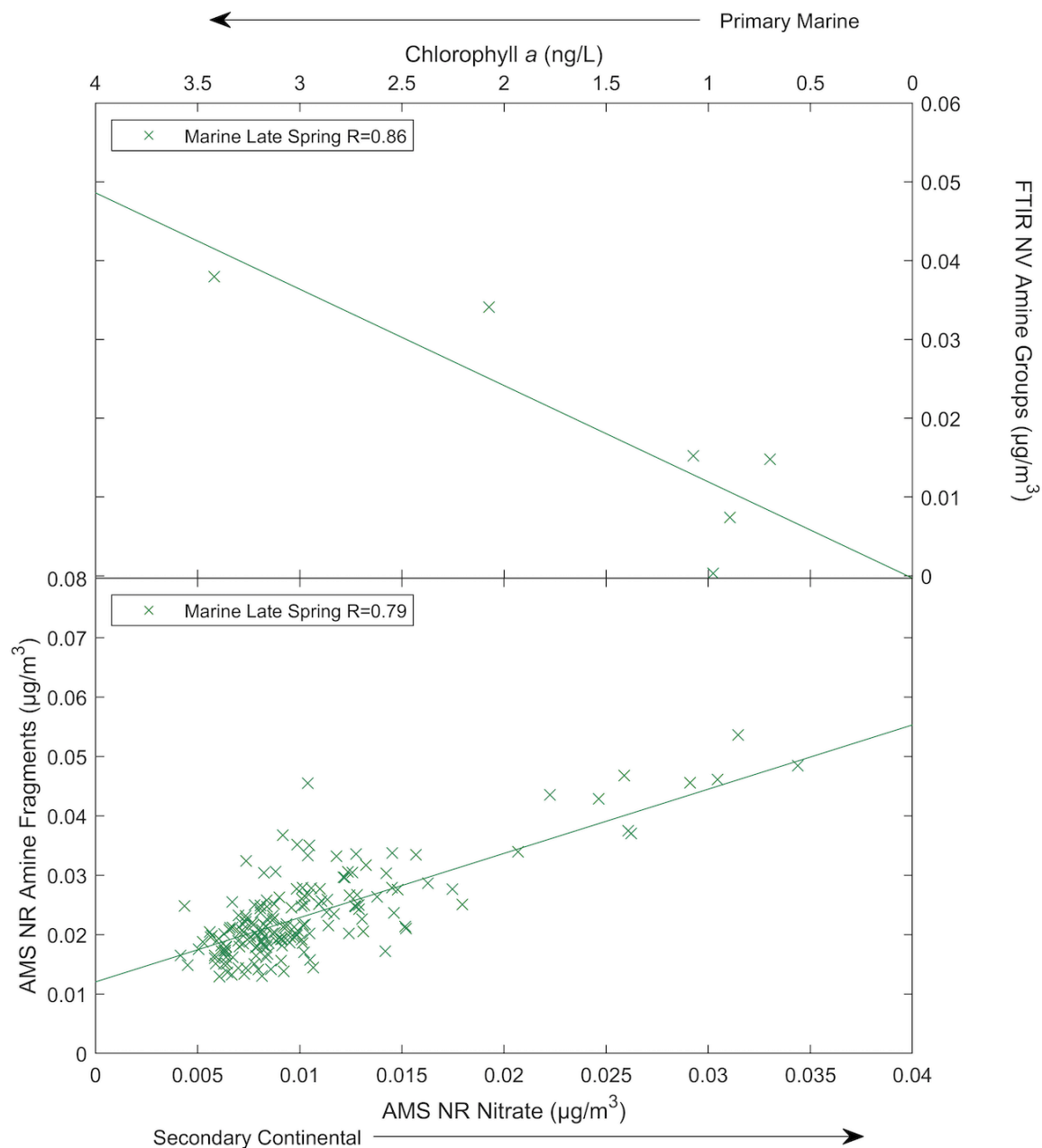
We thank the Referee #1 for this suggestion. We have revised the Figure 8 caption in the manuscript:

New Line 791-795. *"Figure 8: Plot of Pearson correlation coefficients (R) of AMS NR amine fragments (blue) and FTIR NV amine groups in particles with diameters <1 μm (orange) with selected tracers for both marine and continental air masses averaged over four campaigns. Negative correlations were averaged as 0 and only statistically significant (p < 0.05) correlations were included, except for markers shown as solid red (which were not significant correlations). No statistically significant correlations were available for AMS NR amine fragments and IC MSA and sea salt, and for FTIR NV*

amine groups and all tracers with exception of black carbon, radon, AMS NR chloride, and chlorophyll a."

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.

RESPONSE:

We thank the Referee #1 for this comment. This correlation was chosen because IC sea salt is the most widely accepted tracer for a primary marine aerosol source in current literature, despite the very low sample numbers. We also point out that there are actually four data points in this correlation, rather than three, as two points are overlapping. However, we have revised the figure to instead include a significant ($p < 0.05$) correlation with chlorophyll *a* rather than IC sea salt during marine Late Spring which contains six points rather than four. The manuscript has been revised as follows:

New Line 798-801. *"**Figure 9: Scatter plot of (top) FTIR NV amine groups in particles with diameters <1 µm versus a tracer of a primary marine source (chlorophyll a) and (bottom) AMS NR amine fragments versus a secondary continental tracer (AMS NR nitrate) during the marine Late Spring season. The solid lines are the lines of best fit obtained using an ordinary least squares regression and a two-tailed T test is used to estimate p-values.**"*

New Line 420-422. *"Figure 9 shows similar correlations with AMS NR nitrate and chl a in marine Late Spring that exemplify the AMS NR amine fragments correlation to AMS NR nitrate concentrations and the FTIR NV amine groups correlation to chl a."*

Referee #2

This paper combines FTIR and AMS measurements to characterize marine and continental sources of and atmospheric processing resulting in particulate amines. However, the analysis is severely hindered by the scant FTIR data points and insignificant correlations, so that the conclusions of the analysis are not strongly supported by the evidence presented. A major interpretation is that the FTIR and AMS see different, but complementary, amine components, but additional discussion is needed to further explain the lack of correlation between these two measurements.

RESPONSE:

> We thank the Referee #2 for this comment. We acknowledge that FTIR data points are very limited, in part due to the 24-hr sampling time and in part due to our strict criteria for marine and continental air masses that excluded a number of mixed samples. However, we find that there is sufficient evidence of correlations with multiple tracers across four seasons to offer the most likely explanation of the results. Specifically, correlations with wind speed, AMS NR chloride, seawater DMS, and chlorophyll a were quite high for FTIR NV amine groups. In contrast, correlations with AMS NR nitrate, black carbon, radon, f44, and IC nssK+ were identified for AMS NR amine fragments. The discussion of Figure 2 highlights the non-correlation of FTIR NV amine groups and AMS NR amine fragments provides further evidence of two distinct sources.

Readability would improve with consistent treatment of significant vs non-significant correlations including complete set of statistics **(**including number of points**)** and adding implications at the end of each paragraph. Long descriptions of numbers from a table without consistent interpretations are not effective.

RESPONSE:

> We thank Reviewer #2 for this comment. We have added two tables, Tables S19 and S20, containing the number of points in each correlation displayed in old Tables 3 and 4 (new Tables 4 and 5) in the updated main manuscript. We have updated Tables S15 and S16, which contain p-values for these correlations. Tables S21 and S22 provide the linear regressions for each pair of measurements. We have also reviewed the text for readability and added implications near the end of paragraphs as noted below.
>
> New Line 227-229. *"The absence of a positive correlation with wind speed may be attributed to differences in local and upwind wind speeds, but the presence of negative correlations indicates a source of AMS NR amine fragments that is not associated with sea salt."*
>
> New Line 254-255. *"Therefore, these correlations with chl a support a primary marine source for FTIR NV amine groups."*
>
> New Line 273-274. *"In summary, correlations of seawater DMS suggest a primary marine source for FTIR NV amine groups but not for AMS NR amine fragments."*

New Line 284-286. "*However, correlations with IC MSA with both measurements of amine were not significant (p ≥ 0.05) due to the limited number of IC filters available, which indicates that secondary marine source contributions to submicron mass are minor.*"

Specific comments:

176: The time series in Fig1 shows dynamic changes in amine concentrations, but I wonder what an average over a dynamic period really means. The authors claim that the highest concentration for continental periods was Autumn with a mean of 54 ± 49 ng m-3. Fig 1f shows that the concentration during this cruise is particularly dynamic and the large standard deviation here suggests that is the case. There are separate time periods of high concentrations (around Sept 1 and Sept 5) while other periods remain quite low. I suggest considering a different metric – median – or analysis (back trajectories during specific periods of strong amine enhancement) – to characterize the variability here.

RESPONSE:

The Reviewer's point is well taken . We have added an additional table containing medians of our measurements (Table 3), similar to Table 2. Generally, the trends mirror those of the means, which we have now stated in the manuscript.

New Line 719-722. *"Table 3: Median concentrations and median absolute deviations of amine, tracer, and environmental measurements during NAAMES for marine (first row) and continental (second row, in parentheses) periods. Seasonal median concentrations and median absolute deviations are given in square brackets, which were calculated over the sampling times of filters categorized as marine, continental, or mixed."*

Season	Winter	Early Spring	Late Spring	Autumn
AMS NR Amine Fragments (ng/m^3)	13 ± 2 (17 ± 5) [18 ± 4]	33 ± 5 (30 ± 7) [30 ± 4]	21 ± 6 (34 ± 12) [27 ± 10]	23 ± 7 (32 ± 33) [26 ± 9]
FTIR NV Amine Groups (ng/m^3)*	1 ± 12 (29 ± 25) [13 ± 20]	BDL (4 ± 19) [1 ± 25]	15 ± 12 (22 ± 13) [14 ± 11]	0 ± 10 (28 ±47) [17 ± 13]
Sum of AMS NR Amine Fragments & FTIR NV Amine Groups (ng/m^3)*	18 ± 11 (50 ± 24) [32 ± 21]	32 ± 5 (34 ± 22) [34 ± 17]	42 ± 11 (57 ± 12) [48 ± 13]	35 ± 12 (80 ± 7) [40 ± 17]
AMS NR OM (ng/m^3)	136 ± 38 (204 ± 205)	271 ± 61 (375 ± 142)	299 ± 151 (623 ± 403)	247 ± 114 (480 ± 806)
FTIR NV OM (ng/m^3)	260 ± 135 (295 ± 172)	210 ± 110 (80 ± 208)	180 ± 143 (260 ± 299)	145 ± 133 (375 ± 305)
AMS NR Nitrate (ng/m^3)	6 ± 2 (9 ± 7)	8 ± 2 (15 ± 4)	9 ± 3 (16 ± 49)	8 ± 2 (10 ±8)
AMS NR f_{44} (unitless)	0.39 ± 0.45 (0.36 ± 0.06)	0.50 ± 0.06 (0.49 ± 0.06)	0.39 ± 0.06 (0.33 ± 0.06)	0.57 ± 0.13 (0.43 ± 0.11)
Black Carbon (ng/m^3)	6 ± 11 (74 ± 24)	23 ± 19 (120 ± 159)	15 ± 15 (77 ± 113)	16 ± 37 (76 ± 121)
Ozone (ppb)	41 ± 2 (39 ± 4)	27 ± 13 (50 ± 7)	40 ± 6 (39 ± 5)	30 ± 5 (34 ± 6)

Radon (mBq/m^3)	219 ± 78 (308 ± 281)	253 ± 80 (914 ± 253)	282 ± 61 (383 ± 191)	358 ± 202 (735 ± 460)
Wind Speed (m/s)	10.1 ± 3.3 (10.2 ± 3.1)	9.4 ± 2.7 (11.9 ± 3.5)	8.9 ± 4.0 (6.2 ± 2.3)	9.0 ± 3.1 (5.8 ± 2.5)
atm. DMS (ppt)	63 ± 15 75 ± 40)	134 ± 58 (68 ± 53)	373 ± 220 (173 ± 149)	63 ± 119 (98 ± 62)
sw. DMS (nmol/L)	1.3 ± 0.4 (1.2 ± 0.5)	2.7 ± 0.8 (3.7 ± 2.6)	2.4 ± 1.9 (1.56 ± 1.9)	3.3 ± 0.5 (2.7 ± 0.9)
Temperature (°C)	10.2 ± 5.2 (13.9 ± 5.9)	22.1 ± 4.1 (12.6 ± 3.5)	7.7 ± 3.8 (9.1 ± 3.2)	12.6 ± 3.0 (17.2 ± 2.3)
Chlorophyll a (ng/L)	396 ± 180 (457 ± 519)	642 ± 206 (489 ± 259)	1246 ± 1267 (1212 ± 1098)	282 ± 210 (133 ± 219)
SST (°C)	15.2 ± 4.7 (16.2 ± 4.9)	21.4 ± 3.3 (16.4 ± 2.4)	9.0 ± 4.7 (10.0 ± 4.1)	14.1 ± 2.2 (18.2 ± 3.4)
IC MSA (µg/m^3)	-- --	-- (0.00 ± 0.15)	0.03 ± 0.04 (0.06 ± 0.02)	0.01 ± 0.01 (0.01 ± 0.00)
IC Sea Salt (µg/m^3)	0.90 ± 0.55 (1.23 ± 0.53)	-- (1.26 ± 0.42)	0.14 ± 0.22 (0.05 ± 0.03)	0.44 ± 0.25 (0.23 ± 0.37)
IC nssK$^+$ (µg/m^3)	0.00 ± 0.01 (0.02 ± 0.01)	-- (0.01 ± 0.01)	0.00 ± 0.00 (0.02 ± 0.01)	0.00 ± 0.00 (0.02 ± 0.02)

*The median included filters with amine concentration below detection.

Comparing the mean concentrations of AMS NR amine fragments and FTIR NV amine groups in continental air masses to marine air masses the mean concentration AMS NR amine fragments are higher during continental periods than during marine periods, except in Early Spring, for both mean and median concentration of AMS NR amine fragments. We also see that the mean and median concentrations of FTIR NV amine groups are both higher during continental periods than during marine periods. We have revised the manuscript to note the reviewer's point about the dynamic changes in concentration while noting the same trends remain across both metrics.

New Line 174-176. *"Concentrations of both amine measurements varied substantially during each cruise, but median and mean amine concentrations (Tables 2 and 3, respectively) had similar differences between air masses for AMS NR amine fragments and FTIR amine groups."*

190 The "inability of AMS to detect non-refractory components" should be the "inability of the AMS to detect refractory" components. The AMS measures non-refractory components. Generally, the discussion of the lack of correlation between the AMS and FTIR is insufficient, and a few questions remain. If the issue was that the AMS does not detect the amines on refractory NaCl, we would expect the FTIR amines to be higher than the AMS CxHyN, so this hypothesis is inconsistent with the relationship between FTIR and AMS data.

RESPONSE:

We thank Referee #2 for correcting the typo of non-refractory. The reviewer is correct that if this were the only difference between the methods then the AMS would be lower than FTIR. However, as discussed in section 2.4, the FTIR also misses volatile amine

groups (that are not retained on the filter) and secondary/tertiary amine groups (since it only detects C-NH2). In this sense, the two methods are largely (but not perfectly) complementary, with one measuring what the other cannot.

New Line 205. *"The inability of AMS to detect refractory components"*

Other potential sources of the discrepancy: What is the size distribution of submicron particles during these cruises, and how does the size transmission of particles for the AMS and FTIR compare? Could transmission to the sampler affect the relative measurements of amines?

RESPONSE:

We thank Referee #2 for this comment. The size distribution of submicron particles during each cruise has been previously reported in Saliba et al. (2020): "Campaign-averaged submicron number size distributions were mostly bimodal with one peak at dry mobility diameter <0.05μm and the second peak in the 0.1 to 0.2μm accumulation mode range." As stated in the methods sections 2.3 and 2.4, a 1 μm sharp cut cyclone was used to sample particles with diameters less for analysis by both FTIR and HR-ToF-AMS, respectively. Since both used the same sampling device, the transmission of both are nominally <1μm for FTIR NV amine groups and AMS NR amine fragments. However, the AMS is most efficient for particles with a dry aerodynamic diameter of 100-800 nm (DeCarlo et al., 2006), and the Teflon filters may allow some losses below 50 nm given the 1 um pore size. However, past comparisons of OM for the same sample setup have had better agreement, generally within the nominal +/-20% uncertainty of both measurements (Russell et al., 2010), with exceptions for marine conditions associated with sea salt (Frossard et al. 2014).

In Section 2.4, it is noted that FTIR absorbance is not sensitive to secondary or tertiary groups in amines – those that are more likely to form particles. (e.g. Murphy et al., 2007; https://doi.org/10.5194/acp-7-2313-2007). If the particles consist of secondary or tertiary amines, the AMS mass would be higher than the FTIR mass. In line 381, add that the FTIR is not sensitive to the secondary and tertiary amines even if they do remain on the filter for analysis. Further discussion in the differences and similarities between the measurement methods and sensitivities would strengthen the argument that these two measurements are indeed complementary, rather than inconsistent.

RESPONSE:

We thank Referee #2 for the suggestion. We also appreciate the reference, which reports on the likelihood of secondary and tertiary amine groups from continental but not marine sources. We have revised the manuscript (first paragraph of section 4.4) as follows:

New Line 401-407. *"In general, our results support the expectation that FTIR NV amine groups and AMS NR amine fragments do not measure the same chemical components. Specifically, FTIR measures NV amine groups with primary C-NH₂ groups that may or may not be refractory. .... In contrast, the AMS measures NR amine fragments with*

195 CxHyN fragments are typically sandwiched between more common ion fragments containing carbon, hydrogen, and oxygen atoms, so if the CxHyN peaks are not well separated, one might expect the OM and CxHyN to be correlated for this reason. The analysis was done using mass spectra from W-mode in the TOF with higher resolution and diminished sensitivity compared to the typically-used V-mode. Could you include a representative peak fitting (in the supplement) to convince the readers that W-mode captured the CHN ion fragments with minimal interference from other ions?

RESPONSE:

We thank Referee #2 for this recommendation. We agree that CxHyNz are often occluded by other ion fragments. This issue is especially pertinent for ambient measurements of aerosols with diverse particle sources and composition in comparison to a controlled laboratory environment. We have added representative peak fittings of CxHyN ion fragments as Figure S14 in the supporting information. These peak fits show that for the six largest CxHyN ion signals the average fraction of that peak that was fitted as amine fragments. It is evident that the amine fragment peaks can be clearly distinguished in the W mode, and hence the need for the higher resolution and lower sensitivity approach.

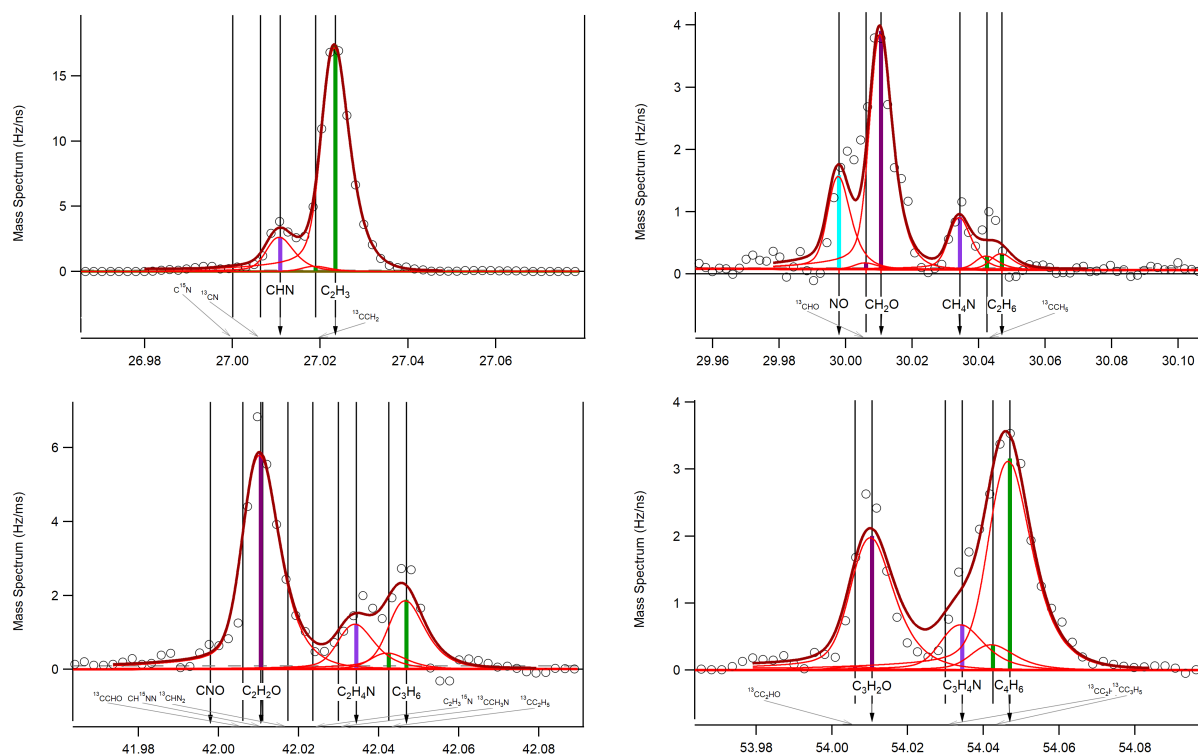
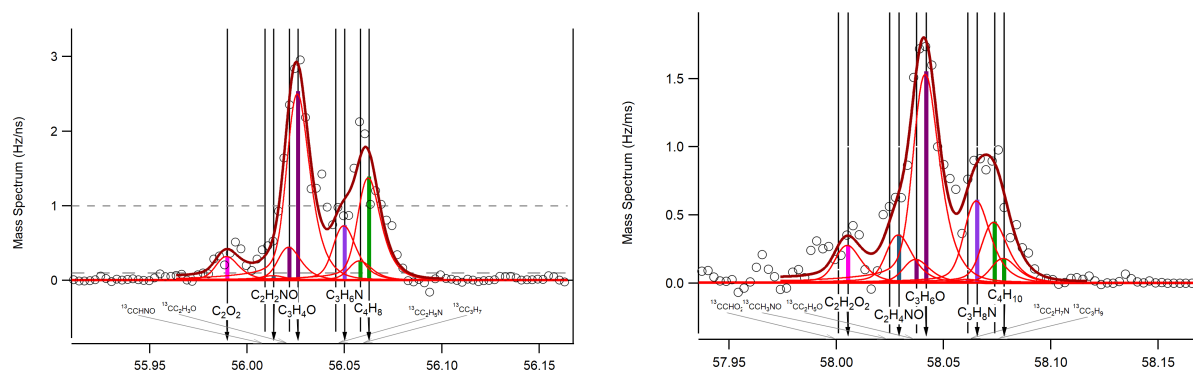



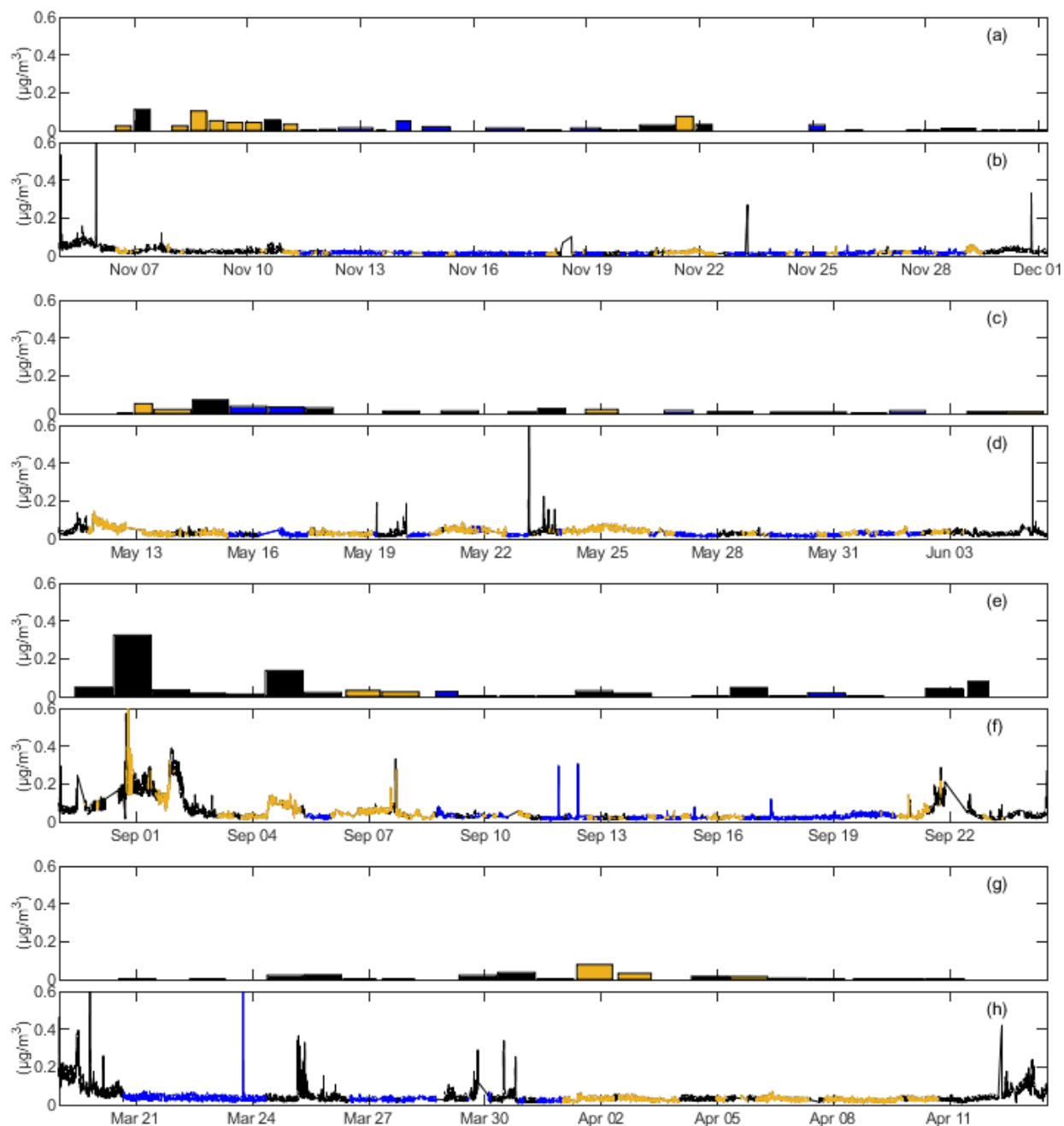
Figure S14. High-resolution mass spectra at dominant $C_xH_yN_p$ m∕z ratios taken at Tv = 600 °C.

Fig 1. Air mass categorizations (continental vs marine) do not agree between the FTIR and AMS for Nov8-Nov10. Consistent y-axis scaling would help readers better compare seasons.

RESPONSE:

We thank Referee #2 for the comments. The reviewer is correct that FTIR and AMS categorizations vary given different criteria set forth in the Methods, and this is necessary because of the different durations of the sampling times for the two methods. For November 8-10, FTIR filters were categorized as continental while AMS measurements were categorized as winds abaft. For a FTIR filter to be categorized as either marine or continental, 90% of the sampling time must follow the criteria described in Sections 2.

Categorization of FTIR filters excluded sampling times when filter sampling was shut off by the solenoid valve, as described by Lewis et al. (2021). This occurs during periods of high particle concentrations. These conditions are likely to occur when there is influence of ship exhaust (also called winds abaft), resulting in non-continental categorizations for AMS NR amine fragments and continental categorization for FTIR NV amine groups. For the time spanning November 8th through 10th, the solenoid was open for only a few hours of the total sampling duration. For this reason, the FTIR samples are characterized as Continental during the 2-3 hr time period sampled during the 24-hr period, even though the AMS measurements were categorized as Winds Abaft.

We have updated the y-axis of Figure 1 to address the reviewer's point:

210: These are not strong correlations. In Fig 3h, for example, FTIR amine groups = 0 for almost the full range of observed wind speeds for early spring.   With so few data points for the FTIR, these correlations are weak, and the R values should not be overinterpreted.

RESPONSE:

We thank Referee #2 for the comment. We have revised to manuscript to make clear to the reader that these datapoints contained concentrations that are near zero for FTIR NV amine groups:

New Line 224-225. *"The correlations with FTIR NV amine groups were not significant due to the limited number of samples (Table S16)."*

To assess the importance of low concentrations for the correlations reported here (which were included to represent the conditions more fully), we repeated the correlations with measurements below detection excluded (Table R1 below). The results show similar correlations with primary marine tracers for FTIR NV amine groups above detection only as for correlations of FTIR NV amine groups when below detection values were included. Specifically, there are positive, weak to strong correlations of AMS NR chloride and FTIR NV amine groups for all air masses except continental air masses in Late Spring. Moderate to strong correlations with seawater DMS are present for all air masses except marine air masses in Winter. Specifically for the concern for the correlations of wind speed and FTIR NV amine groups for Winter and Early Spring continental air masses, these correlations remain positive and are stronger for Early Spring continental air masses when excluding FTIR NV amine group concentrations below detection. Therefore, including FTIR NV amine groups below detection results in weaker correlations but with more measurement points, which we believe is a more accurate representation of the data set.

Table R3. Pearson correlation (R) coefficient values between FTIR NV amine groups (ADL) in particles with diameters <1 μm and various tracers for marine periods (columns 1-4) and continental periods (columns 5-8). Negative correlations are shaded blue and positive correlations are shaded red. The strength of each correlation determines the level of saturation for the corresponding shading- no correlation (|R| < 0.25)- gray, weak correlation (0.25 ≤ |R| < 0.50)- light blue/red, moderate correlation (0.50 ≤ |R| < 0.80)- medium blue/red, strong correlation (0.80 ≤ |R|)- dark blue/red.

Air Masses	Marine				Continental			
Season	Winter	Early Spring	Late Spring	Autumn	Winter	Early Spring	Late Spring	Autumn
AMS NR OM	-0.11	--	0.31	--	-0.09	-0.83	-0.46	--
FTIR NV OM	0.94	--	0.90	--	0.42	0.94	-0.14	--
AMS NR Nitrate	0.01	--	0.09	--	-0.09	-0.34	0.11	--
AMS NR Sulfate	-0.15	--	0.52	--	0.31	-1.00	-0.15	--
AMS NR Chloride	0.75	--	0.69	--	0.33	0.81	-0.23	--
AMS NR f_{44}	-0.04	--	0.61	--	-0.36	-0.98	-0.86	--
Black Carbon	0.01	--	-0.79	--	0.48	-0.67	-0.61	--
Ozone	-0.04	--	0.19	--	0.17	-0.81	0.36	--
Radon	-0.50	--	0.18	--	-0.54	-0.66	0.85	--
Wind Speed	-0.47	--	-0.45	--	0.49	0.99	-0.86	--
sw. DMS	0.09	--	0.84	--	0.54	--	--	--
atm. DMS	-0.54	--	0.42	--	--	-0.74	--	--
Solar Radiation	-0.74	--	0.71	--	0.49	-0.74	-0.90	--
Relative Humidity	-0.27	--	0.64	--	-0.21	0.67	-0.66	--
Temperature	-0.16	--	-0.80	--	0.08	-0.95	-0.16	--
Chlorophyll *a*	-0.06	--	0.91	--	-0.36	-0.82	0.56	--

SST	-0.27	--	-0.82	--	0.36	-0.70	-0.33	--
IC MSA	--	--	0.73	--	--	--	-0.75	--
IC Sea Salt	--	--	0.10	--	--	--	-0.25	--
IC nssK$^+$	--	--	0.44	--	--	--	-0.31	--

PMF analysis (described in methods section) does not appear in the main text.
CCN measurements (described in supplement) does not appear in the main text.
Many supplementary figures and tables are not referenced in the main text.

RESPONSE:

> We thank Referee #2 for the comment. We have revised the main manuscript and now reference each table and figure that is available in the supporting information.

DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer, Analytical Chemistry, 78, 8281-8289, 10.1021/ac061249n, 2006.

Facchini, M. C., Decesari, S., Rinaldi, M., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Moretti, F., Tagliavini, E., Ceburnis, D., and O'Dowd, C. D.: Important Source of Marine Secondary Organic Aerosol from Biogenic Amines, Environmental Science & Technology, 42, 9116-9121, 10.1021/es8018385, 2008.

Ge, X., Wexler, A. S., and Clegg, S. L.: Atmospheric amines - Part I. A review, Atmospheric Environment, 45, 524-546, 2011.

Lewis, S. L., Saliba, G., Russell, L. M., Quinn, P. K., Bates, T. S., and Behrenfeld, M. J.: Seasonal Differences in Submicron Marine Aerosol Particle Organic Composition in the North Atlantic, Frontiers in Marine Science, 8, 13, 10.3389/fmars.2021.720208, 2021.

Malloy, Q. G. J., Qi, L., Warren, B., Cocker, D. R., Erupe, M. E., and Silva, P. J.: Secondary organic aerosol formation from primary aliphatic amines with NO3 radical, Atmospheric Chemistry and Physics, 9, 2051-2060, 10.5194/acp-9-2051-2009, 2009.

Muller, C., Iinuma, Y., Karstensen, J., van Pinxteren, D., Lehmann, S., Gnauk, T., and Herrmann, H.: Seasonal variation of aliphatic amines in marine sub-micrometer particles at the Cape Verde islands, Atmospheric Chemistry and Physics, 9, 9587-9597, 2009.

Murphy, S. M., Sorooshian, A., Kroll, J. H., Ng, N. L., Chhabra, P., Tong, C., Surratt, J. D., Knipping, E., Flagan, R. C., and Seinfeld, J. H.: Secondary aerosol formation from atmospheric reactions of aliphatic amines, Atmospheric Chemistry and Physics, 7, 2313-2337, 10.5194/acp-7-2313-2007, 2007.

Quinn, P. K., Bates, T. S., Schulz, K. S., Coffman, D. J., Frossard, A. A., Russell, L. M., Keene, W. C., and Kieber, D. J.: Contribution of sea surface carbon pool to organic matter enrichment in sea spray aerosol, Nature Geoscience, 7, 228-232, 10.1038/ngeo2092, 2014.

Saliba, G., Chen, C. L., Lewis, S., Russell, L. M., Quinn, P. K., Bates, T. S., Bell, T. G., Lawler, M. J., Saltzman, E. S., Sanchez, K. J., Moore, R., Shook, M., Rivellini, L. H., Lee, A., Baetge, N., Carlson, C. A., and Behrenfeld, M. J.: Seasonal Differences and Variability of Concentrations, Chemical Composition, and Cloud Condensation Nuclei of Marine Aerosol Over the North Atlantic, Journal of Geophysical Research-Atmospheres, 125, 10.1029/2020JD033145, 2020.