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.

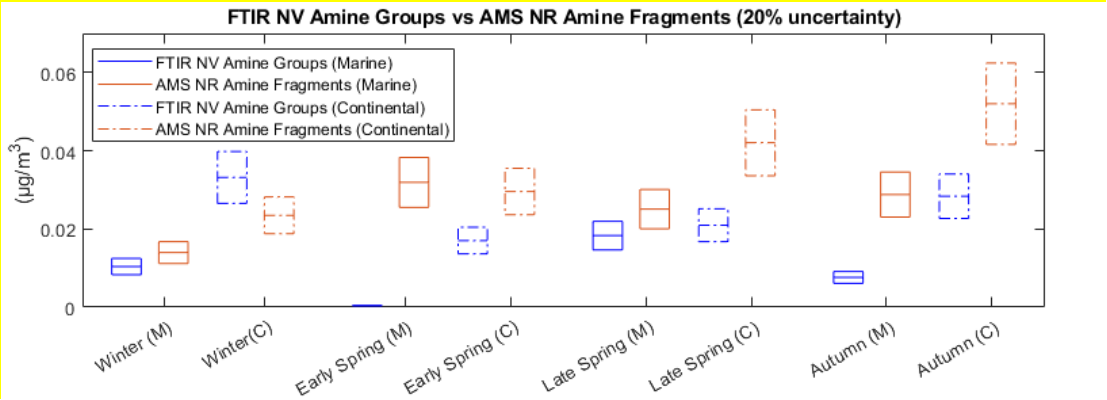
Correlations of AMS NR amine fragments and tracers were obtained by averaging measurements by the hour, and correlations to IC and FTIR filters were averaged over the filter sampling time. The reviewer is correct also in possibly implying that the greater number of measurements for AMS and some tracers 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:

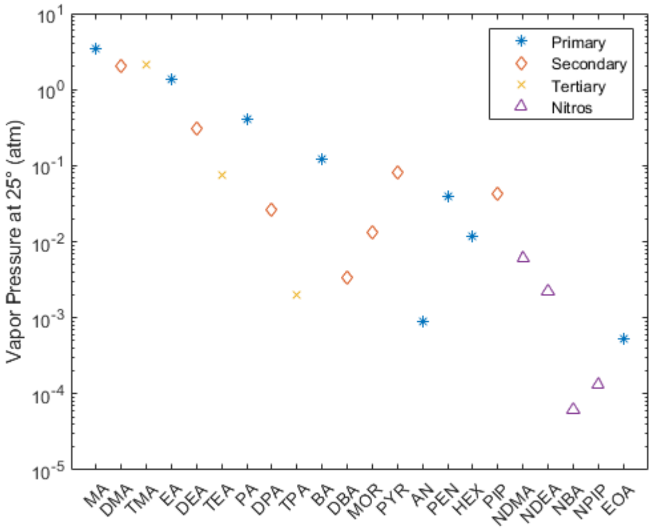
The Reviewer is correct that part of this argument is implicit, namely that since AMS has been shown to miss measuring marine organics (because they are mixed with refractory sea salt) then the amines that it is measuring are likely non-marine (which generally do not have substantial refractory material 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:
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> 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:
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> 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
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> 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."*
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> *New Line 20. "... AMS NR amine fragments were identified by consistent correlations to AMS NR nitrate, AMS NR f44, IC non-sea salt..."*
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> 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:

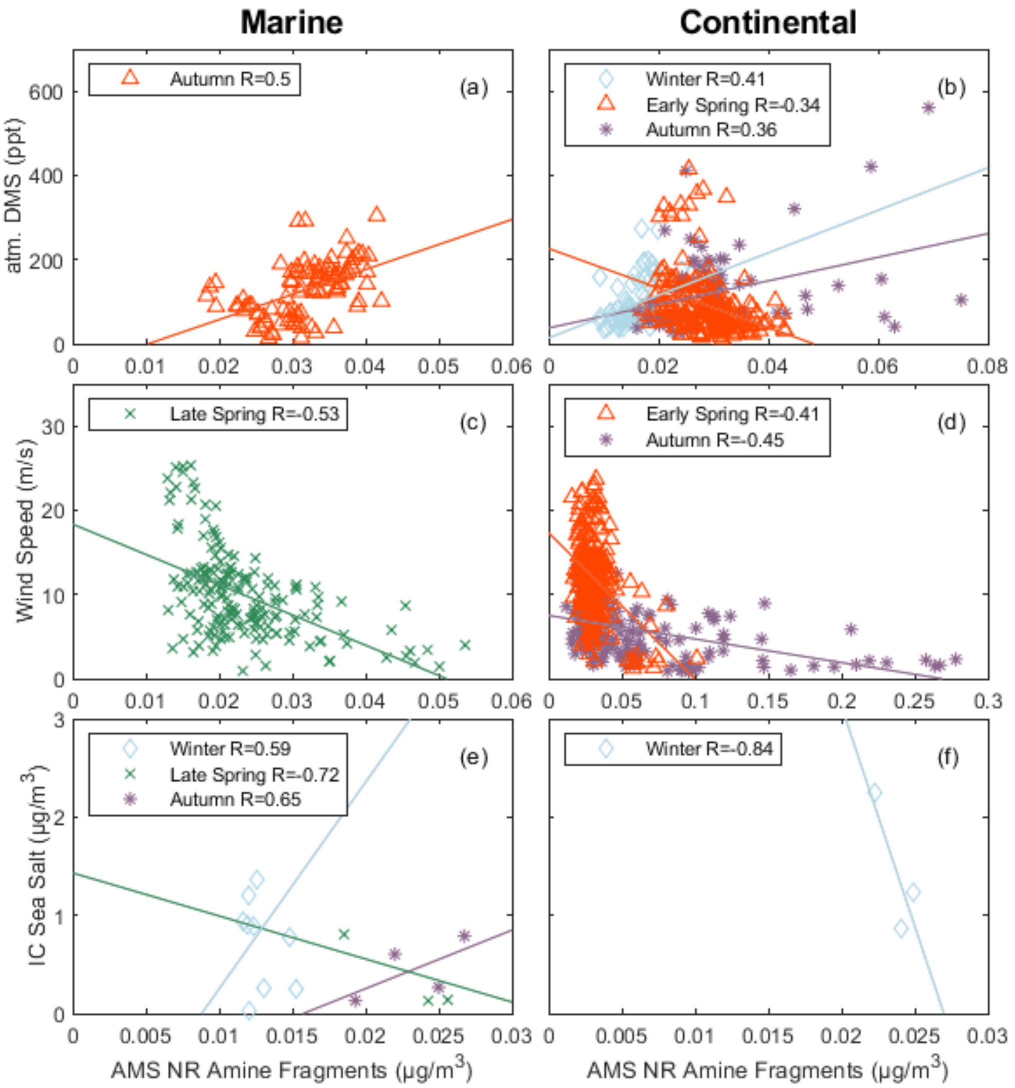


Figure 8. Please, specify which data are represented in the Figure: “Marine” or “Marine+Continental”?

RESPONSE:

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

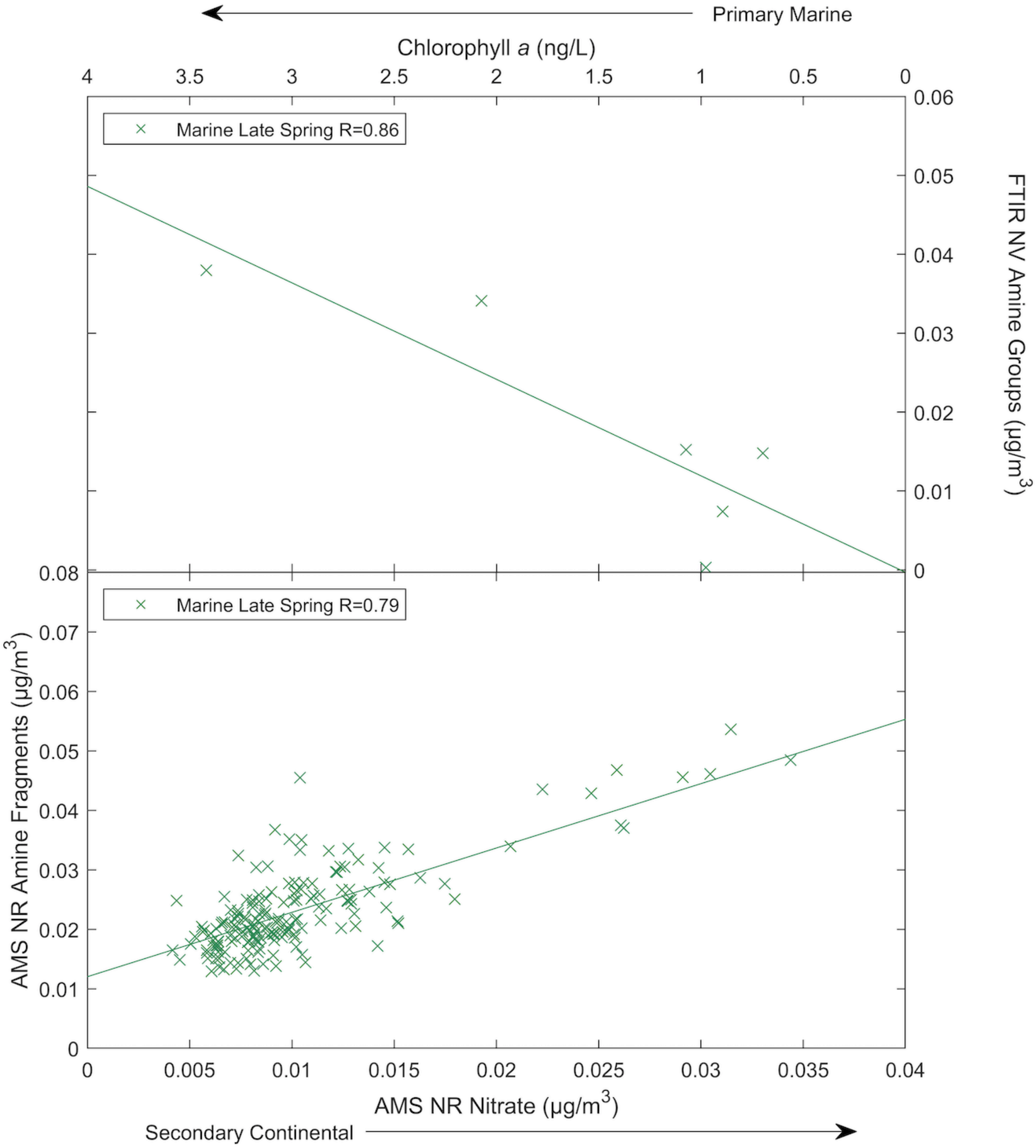
New Line 791-795. *“Figure 8: Plot of Pearson correlation coefficients (R) of AMS NR amine fragments (blue) and FTIR NV amine groups in particles with diameters <1 µm (orange) with selected tracers for both marine and continental air masses averaged over four campaigns. Negative correlations were averaged 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 <u>(chlorophyll a)</u> and (bottom) AMS NR amine fragments versus a secondary continental tracer (AMS NR nitrate) during the <u>marine Late Spring season</u>. 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 <u>chl a in marine Late Spring</u> that exemplify the AMS NR amine fragments correlation to AMS NR nitrate concentrations and the FTIR NV amine groups correlation to <u>chl a</u>."*

<u>Referee #2</u>

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 ($p \geq 0.05$) 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 *($\mu g/m^3$)*	*--* *--*	*--* *(0.00 ± 0.15)*	*0.03 ± 0.04* *(0.06 ± 0.02)*	*0.01 ± 0.01* *(0.01 ± 0.00)*
IC Sea Salt *($\mu g/m^3$)*	*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 $nssK^+$ *($\mu g/m^3$)*	*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:

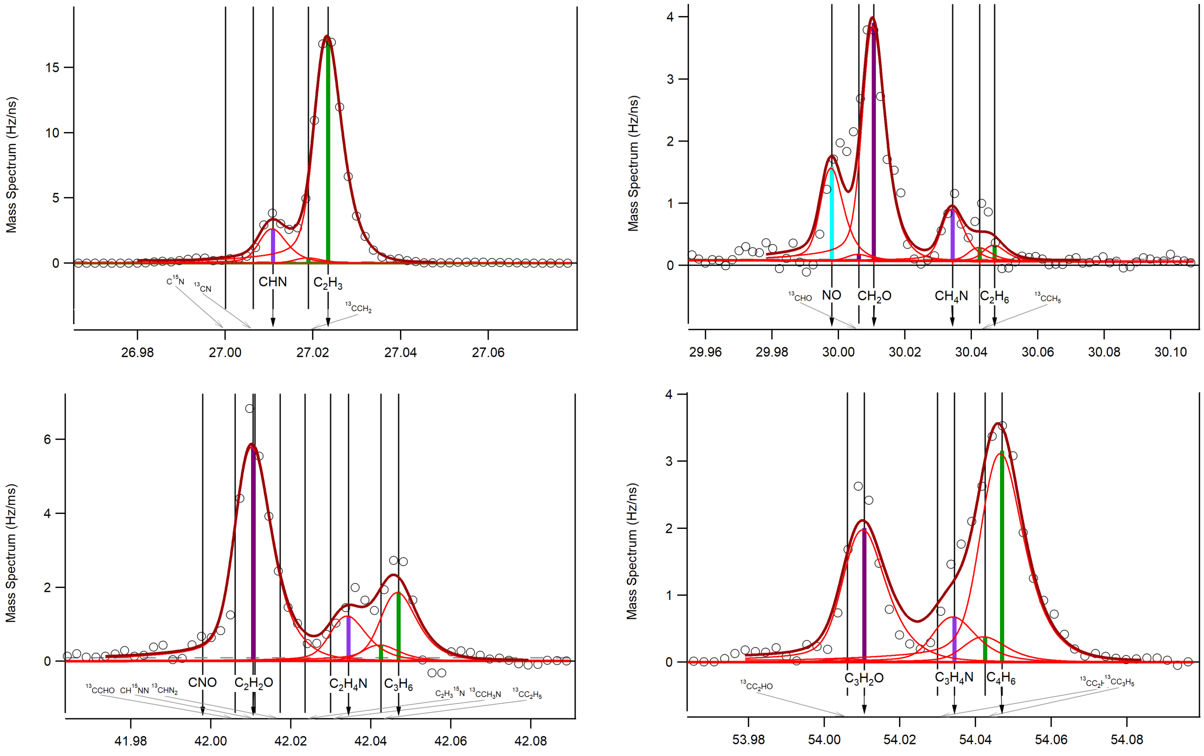
New Line 401-407. *"In general, our results support the expectation that FTIR NV amine groups and AMS NR amine fragments do not measure the same chemical components. Specifically, FTIR measures NV amine groups with primary C-NH*$_2$ *groups that may or may not be refractory. …. In contrast, the AMS measures NR amine fragments with*

> *primary (C-NH_2), secondary (C_2-NH), and tertiary (C_3-N) amine moieties that may be too volatile to be sampled on filters, but the FTIR does not detect secondary and tertiary amines even if they remain on filters.”*

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.



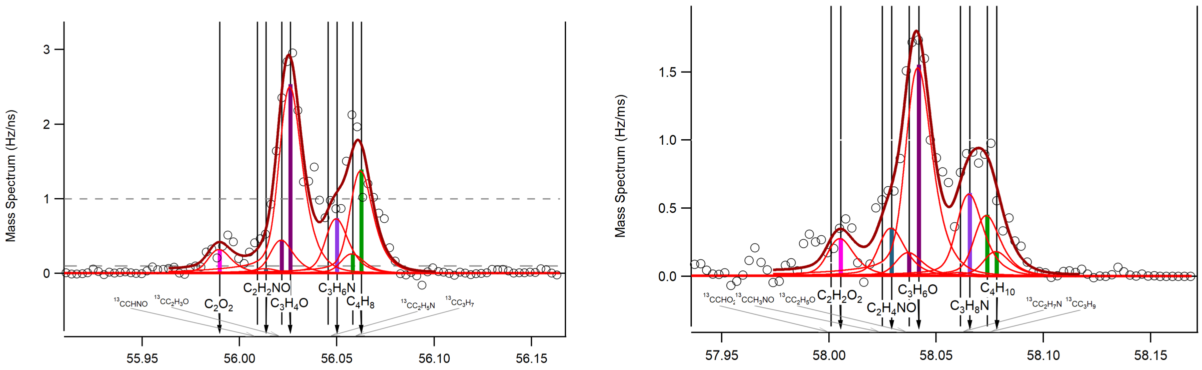


Figure S14. High-resolution mass spectra at dominant $C_xH_yN_p$ m/z ratios taken at Tv = 600 °C.

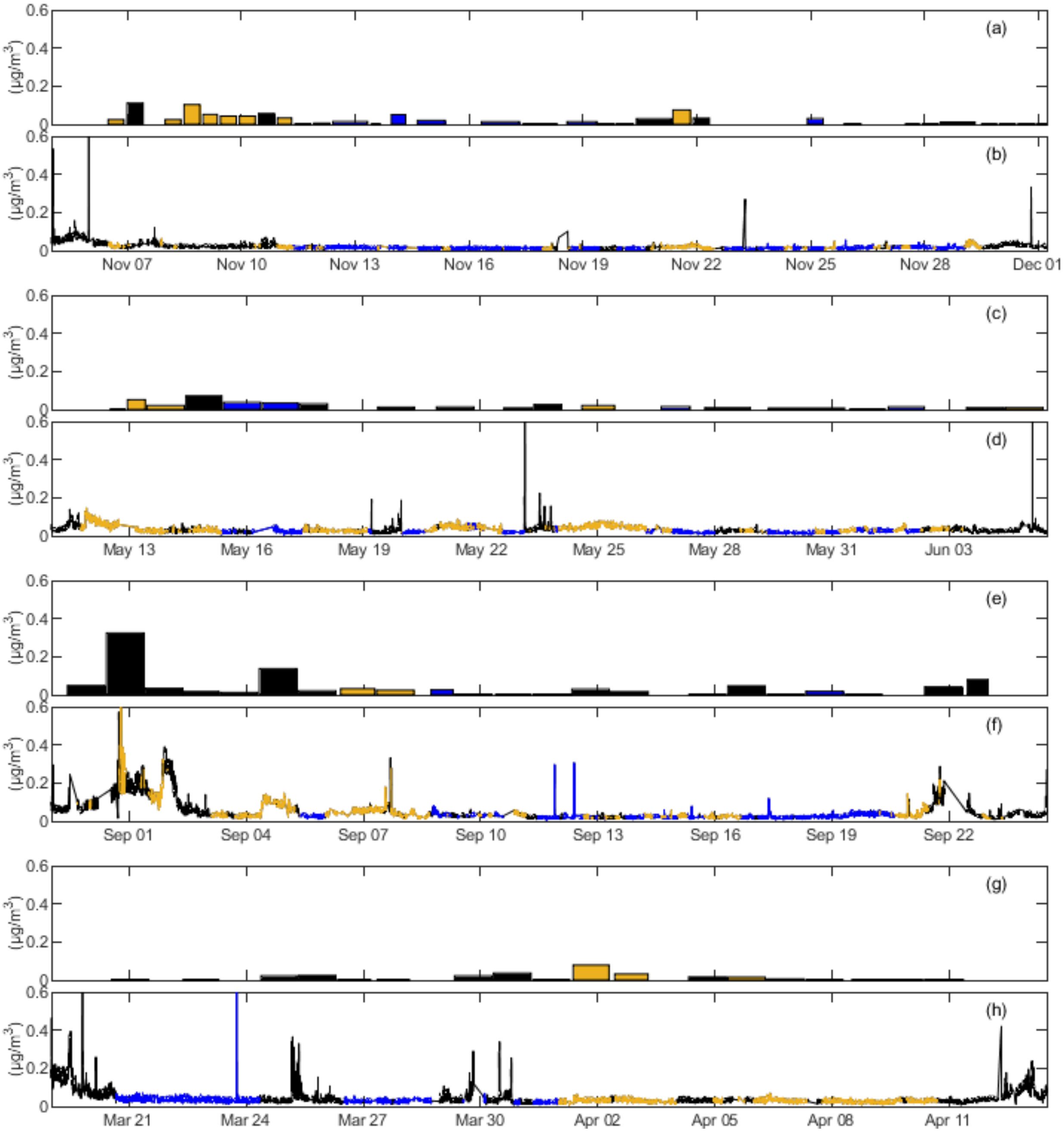
Fig 1. Air mass categorizations (continental vs marine) do not agree between the FTIR and AMS for Nov8-Nov10. Consistent y-axis scaling would help readers better compare seasons.

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 ($0.25 \leq |R| < 0.50$)- light blue/red, moderate correlation ($0.50 \leq |R| < 0.80$)- medium blue/red, strong correlation ($0.80 \leq |R|$)- 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.

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Non-volatile marine and non-refractory continental sources of particle-phase amine during the North Atlantic Aerosols and Marine Ecosystems Study (NAAMES)

Veronica Z. Berta[1], Lynn M. Russell[1], Derek J. Price[1,2], Chia-Li Chen[3], Alex K.Y. Lee[4], Patricia K. Quinn[5], Timothy S. Bates[5,6], Thomas G. Bell[7,8], Mike J. Behrenfeld[9]

[1]Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093, USA
[2]Colorado Department of Public Health and Environment, Air Pollution Control Division, Denver, CO, 80246, USA
[3]California Air Resources Board, Riverside, CA 92507, USA
[4]Air Quality Processes Research Section, Environment and Climate Change Canada, Toronto, ON M3H 5T4, Canada
[5]NOAA Pacific Marine Environmental Laboratory, Seattle, WA 98115, USA
[6]Cooperative Institute for Climate, Ocean and Ecosystems Studies, University of Washington, Seattle, WA 98195, USA
[7]Plymouth Marine Laboratory, Plymouth, PL1 3DH, UK
[8]Department of Earth System Science, University of California, Irvine, CA, USA
[9]Department of Botany and Plant Pathology, Oregon State University, Corvallis, 97331 OR, USA.

Correspondence to: Lynn M. Russell (lmrussell@ucsd.edu)

Abstract. Amines were measured by aerosol mass spectrometry (AMS) and Fourier Transform Infrared (FTIR) spectroscopy during the North Atlantic Aerosols and Marine Ecosystems Study (NAAMES) cruises. Both AMS non-refractory (NR) amine ion fragments comprising the AMS $C_xH_yN_z$ family and FTIR non-volatile (NV)~~ amine measured as~~ primary (C-NH2) amine groups typically had greater concentrations in continental air masses than marine air masses. Secondary continental sources of AMS NR amine fragments were identified by consistent correlations to AMS NR nitrate, AMS NR ~~m/z 44~~f_{44}, IC non-sea salt potassium, and radon for most air masses. FTIR NV amine group mass concentrations for particles with diameters <1 μm showed large contributions from a primary marine source that was identified by significant correlations with measurements of wind speed, chlorophyll *a*, seawater dimethylsulfide (DMS), AMS NR chloride, and ion chromatography (IC) sea salt as well as FTIR NV alcohol groups in both marine and continental air masses. FTIR NV amine group mass concentrations in <0.18 μm and <0.5 μm particle samples in marine air masses likely have a biogenic secondary source associated with strong correlations to FTIR NV acid groups, which are not present for <1 μm particle samples. The average seasonal contribution of AMS NR amine fragments and FTIR NV amine groups ranged from (27~~%~~±57)% amine from primary marine ~~amine~~sources and (73~~%~~±152)% secondary continental amine during Early Spring to (53~~%~~±76)% amine from primary ~~amine~~ marine sources and (47~~%~~±68)% secondary continental amine during Winter. These results demonstrate that AMS NR and FTIR NV amine measurements are complementary and can be used together to investigate the variety and sources of amines in the marine environment.

1 Introduction

Amines are a class of nitrogen-containing organic compounds that have been identified as playing important roles in atmospheric aerosols by reacting with acids (HNO_3, H_2SO_4, MSA) to add organic mass and by acting as precursors that are oxidized by atmospheric radicals (O_3, OH, NO_3) to nucleate new particles (Tang et al., 2013;Malloy et al., 2009;Bork et al., 2014). New particle formation driven by amines can contribute to both the aerosol direct and indirect effects by increasing the number of particles as well as the number of cloud condensation nuclei (CCN) (Yao et al., 2018). Amines may also affect CCN activity by enhancing particle hygroscopicity through the formation of aminium salts or suppressing particle hygroscopicity through photochemical reactions with OH (Tang et al., 2014). The potential for climate impacts associated with amines depends strongly on the magnitude and type of amines in the atmosphere.

While continental sources of amine include animal husbandry, industrial emissions, and biomass burning (Ge et al., 2011), marine sources of aliphatic amines are likely underwater plant, algae, and kelp species, which are found in seawater and sediments (Lee, 1988;King, 1985;Steiner and Hartmann, 1968). These marine sources of amine have also been identified as both primary and secondary contributions to particles (Table 1). Marine amines are estimated to contribute 0.6 TgC/yr to aerosol, and the formation of amine salts have been estimated to comprise 21% of submicron marine secondary organic aerosol (SOA) mass (Myriokefalitakis et al., 2010). Primary marine sources of amines have been identified, showing correlations to sea salt, wind speed, and alcohol groups (Frossard et al., 2014a;Lewis et al., 2022;Russell et al., 2011). Secondary marine sources of amine were identified for diethylamine, dimethylamine, and monomethylamine, which were correlated with primary productivity of phytoplankton (Facchini et al., 2008;Muller et al., 2009).

Fluxes of amine gases from the ocean to the atmosphere are controlled by biological activity because processes including osmoregulation, protein degradation, and subsequent microbial decomposition produce a methylated form of low-molecular-weight aliphatic amine that is concentrated in surface waters (Beale and Airs, 2016;King, 1985). This volatile form allows some amines to enter the atmosphere by air-sea exchange and then partition into the solid phase to form secondary marine aerosols (SMA) by a variety of reactions. These reactions may be accelerated by airborne oxidants and other pollutants (NO_x, O_3, SO_x) that are transported from continental sources or produced by ships locally.

Amines are also included in primary sea spray aerosols (SSA) as jet and film drops of seawater that are ejected into the atmosphere by bursting bubbles formed by breaking waves at the ocean surface. These aerosol types have been associated with biologically-derived marine organic compounds, since they frequently contain a consistent ratio of primary ($C-NH_2$) amine groups to organic mass across multiple oceans including the Arctic, Atlantic, and Pacific (Frossard et al., 2014a). Similar primary amine group contributions have been identified across four seasons in the North Atlantic in seawater, sea surface microlayer, generated primary particles, and atmospheric aerosol particles (Lewis et al., 2021;Lewis et al., 2022).

Here we assess the sources and quantities of amine components sampled in atmospheric aerosol particles during the North Atlantic Aerosols and Marine Ecosystems Study (NAAMES). NAAMES provided unique sampling of the open ocean during distinct seasons that correspond to different periods of the phytoplankton annual biomass cycle. To obtain the most complete picture of open-ocean amines for the region, this study compares online measurements of AMS non-refractory (NR) amine fragments by High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) to non-volatile (NV) primary amine groups by Fourier Transform Infrared Radiation (FTIR) Spectroscopy of size-resolved filters. Chemical and meteorological tracers are used to associate the amine components with both primary and secondary processes and marine or continental sources. Together, the AMS NR amine fragments and FTIR NV amine groups provide a more complete picture of the varied aspects of amine-containing aerosol particles in the North Atlantic.

2 Methods and Materials

2.1 NAAMES Cruises

The North Atlantic Aerosols and Marine Ecosystems Study (NAAMES) was a multi-year campaign that explored the dynamics of ocean ecosystems, atmospheric aerosols, clouds, and climate. The measurements reported here were collected on the R/V *Atlantis* in the western subarctic Atlantic during four separate phases of the phytoplankton annual biomass cycle (Behrenfeld et al., 2019). The first cruise (NAAMES 1) took place during the winter transition in November-December (Winter) 2015. The second cruise (NAAMES 2) took place during the transition in the bloom climax in May-June (Late Spring) 2016. The third cruise (NAAMES 3) took place during the declining biomass in August-September (Autumn) 2017. The final cruise (NAAMES 4) took place during the early accumulation phase of the spring bloom in March-April (Early Spring) 2018. The first three NAAMES cruises departed from Woods Hole, Massachusetts, and the NAAMES 4 cruise sailed from San Juan, Puerto Rico. All four cruises returned to Woods Hole, Massachusetts.

2.2 Marine and Continental Air Mass Periods

Ambient measurements were categorized by air mass origins. Online measurements were considered to be associated with marine air masses if they met the criteria of Saliba et al. (2020), namely (1) particle number concentrations <1,500 cm^{-3}, (2) HYSPLIT 48 hour back trajectories originating from the North or tropical Atlantic that did not pass over land during that time, (3) black carbon (BC) concentrations ~~were~~ <50 ng m^{-3}, (4) radon concentrations <500 mBq m^{-3}, and (5) relative wind direction ~~was~~ within ±90° of the bow of the ship (to avoid ship stack contamination). For the multi-hour filters collected, the classification scheme of Lewis et al. (2021) was used: marine filters were those for which 90% or more of the sampling time met these conditions; air masses were considered to have continental sources when the HYSPLIT 48 hour back trajectories originated from North America; mixed filters were those that did not meet either marine or continental criteria.

2.3 HR-ToF-AMS

A HR-ToF-AMS (Aerodyne Research Inc., Billerica, MA) was deployed to measure non-refractory (AMS NR) components of submicron (approximately 100-800 nm dry aerodynamic diameter) ambient particles (DeCarlo et al., 2006) downstream of a 1 µm cyclone (Russell et al., 2018). The HR-ToF-AMS vaporizer was operated around 600ºC. The instrument alternated periodically between different ion flight modes including a high-resolution W-mode (1-min), a high-sensitivity V-mode (2-min), and an additional single-particle event trigger (ET) mode (2-min). Particle measurements with the W-mode of the AMS instrument were collected for all particles (not separated by size) and were analyzed by the data analysis software packages SQUIRREL (SeQUential Igor data RetRiEvaL) version 1.24 and PIKA (Peak Integration by Key Analysis) version 1.63 on IGOR PRO 8 (Wavemetrics, Inc.). This mode was used instead of the V-mode to obtain better peak separation, which was necessary to identify contributions of amine-containing fragments from other fragments at similar masses. SQUIRREL was used to pre-process data by checking m/z calibration and baselines for each run. PIKA was then utilized for high-resolution analysis of individual ion fragments to be fitted for each mass-to-charge ratio (m/z). AMS NR amine fragments were calculated as the sum of $C_xH_yN_z$ ion fragments (Schurman et al., 2015;Thamban et al., 2021). Figure S14 displays representative peak fittings of selected $CxHyN_z$ ion fragments.

The ET mode of the ~~instrument~~HR-ToF-AMS extracted a mass spectrum for individual particles that had ion signals within a certain range of m/z values that exceeded a threshold established using particle-free air. Single particle analysis of ET mode measurements was previously completed for Winter and Late Spring (Sanchez et al., 2018). This analysis was also performed for Autumn and Early Spring, identifying 5-7 relatively similar clusters for each cruise~~.~~ using criteria listed in Tables S8-S9. The AMS ET methods and results for Autumn and Early Spring are available in the ~~supporting information sections~~Supporting Information Sections S2-3. Amine fragment contributions were estimated using the unit-mass fragments associated with common amine ion fragments~~.~~ (Tables S6-S7). The sum of these fragments was directly compared to the sum of $C_xH_yN_z$ ion fragments in Figure S6. The ten AMS NR single particle amine fragments with the highest mass concentrations were CHN^+, CH_4N^+, $C_2H_3N^+$, $C_2H_4N^+$, $CHNO^+$, $C_2H_5N^+$, $C_2H_6N^+$, C_4HN^+, $C_2H_5N_2O^+$, $C_3H_7NO^+$ (Figure S7). The fraction of amine signal that was associated with the Autumn and Early Spring particle clusters was estimated to be 1.0-3.6% of the total ion signal and for 2.7-8.1% of the total organic signal~~.~~ (Table S10). These contributions remained largely consistent across particle clusters, showing no notable differences between the particle clusters. Correlations of each particle cluster and selected tracers are displayed in Tables S11-S14 and a summary of these results can be found in Section S3. Time series and mass spectra of each single particle cluster are shown in Figures S8-S12.

Positive Matrix Factorization (PMF) Evaluation Tool v3.06B of W-mode data was used for Autumn and Early Spring to compute factors of ion fragments with unique temporal correlations for high-resolution organic mass spectral data, as described in ~~supporting information section S1.~~Supporting Information Section S1. The analysis included selected high-resolution sulfate mass spectral signals that included SO^+, SO_2^+, SO_3^+, HSO^+, $H_2SO_4^+$, HSO_3^+, H_2SO^+, HSO_2^+, and $H_2SO_2^+$ ion fragments. The criteria used to determine the factor solution is listed in Tables S1-S4. Most of the factors identified typically included small amounts of amine; when a factor with higher amine contribution was found, the variability of its mass concentration was largely noise, limiting further source appointment, given the magnitude of twice that of its mean (Table S5). The time series and mass spectra of these factors are shown in Figure S1-S5.

The HR-ToF-AMS ~~used during NAAMES~~ utilizes a multi-slit chopper that obtains efficient Particle Time-of Flight (ePToF) measurements rather than a single-slit chopper that obtains PToF measurements. ePToF ensures high signal-to-noise ratios in the raw spectral bins necessary for marine environments with low aerosol concentrations. ePToF measurements can be analyzed as size distributions of individual unit-mass resolution ion fragments but processing of high-resolution mass spectra for separate size bins has not yet been implemented. Size distributions of cumulative and individual mass fragments for organic and sulfate fragments had low signal-to-noise given the clean marine conditions and low concentrations of AMS NR components. Unit mass resolution did not represent any of the selected amine fragments with sufficiently high signal-to-noise to determine an amine size distribution or size cuts (e.g. <0.5 μm), as the amine fragments comprised less than half of the unit mass resolution peaks in the m/z spectra (Table S7). Consequently size-resolved measurements of AMS NR amine fragments are not available.

2.4 FTIR Spectroscopy

During all four cruises, atmospheric particles were collected after size cuts on pre-scanned 37 mm Teflon filters (Pall Inc., 1 μm) for offline analysis by Fourier Transform Infrared (FTIR) spectroscopy (Tensor 27 spectrometer, Bruker, Billerica, MA) of the NV components that were retained on the filters (Russell et al., 2018). Berner impactors with size cuts of 0.18 μm and 0.5 μm were operated at 30 L min^{-1}, and a 1 μm sharp cut cyclone was operated at 16.7 L min^{-1}. Sampling times for each filter spanned 12 to 23 hours. A sector control was used for filter sampling (Lewis et al., 2021). Quantification of NV organic amine group concentration was accomplished by identifying a primary amine ($C\text{-}NH_2$) peak at an absorption frequency of 1630 cm^{-1} in the FTIR spectrum. Note that the term 'primary' refers to the NH_2 group type that is bonded to the carbon not to the aerosol source type. Specifically, the FTIR absorbance at 1630 cm^{-1} is not sensitive to secondary ($C_2\text{-}NH$) or tertiary ($C_3\text{-}N$) groups in amines, and absorbance peaks for secondary and tertiary amines were not identified in the spectra (Kamruzzaman et al., 2018). The FTIR spectra were quantified by baselining, peak-fitting, and integrating peak areas using calibration standards and an automated algorithm (Maria et al., 2002). Carboxylic acid, alkane, primary amine, and alcohol functional groups were estimated from fitting spectral peaks as described in detail by (Takahama et al., 2013;Lewis et al., 2021).

2.5 Ion Chromatography

Inorganic ions including SO_4^{2-}, NO_3^-, NH_4^+, Na^+, MSA, Mg^{2+} K^+, Cl^-, Ca^{2+}, and Br^- were collected on a two stage multi-jet impactor with a 1.1 μm size cut filter at 30% RH and subsequently measured using ion chromatography (IC) (Quinn et al., 1998). Sea salt concentrations were estimated as Na^{+} (μg m^{-3}) ×1.47 + Cl^{-} (μg m^{-3}) (Saliba et al., 2020;Frossard et al., 2014a;Bates et al., 2012;Quinn et al., 2019). Non-sea salt (nss) potassium (K^{+}) concentrations were estimated as K^{+} (μg m^{-3}) - Na^{+} (μg m^{-3}) × (ratio of K to Na in seawater), where the latter ratio is constant across major water masses in the ocean (Pilson, 2013).

2.6 Other Measurements

Seawater and atmospheric dimethylsulfide (DMS) concentrations were measured continuously during NAAMES (Bell et al., 2021). Chlorophyll *a* was also measured inline using High Performance Liquid Chromatography (HPLC). A Single Particle Soot Photometer (SP2, DMT, Boulder, CO) measured the mass concentrations of refractory black carbon (BC) in particles with diameters of 60 to 700 nm. Other meteorological properties measured during NAAMES and used in our analysis include sea surface temperature (SST), solar radiation, wind speed, relative humidity, ambient temperature, ozone, and radon and these data, in addition to chlorophyll *a*, were accessed from the SeaBASS archive (Werdell et al., 2003). A thermodenuder Scanning Mobility Particle Sizer (SMPS) measured submicron particle size distributions and a Cloud Condensation Nuclei Counter (CCNC, DMT, Boulder, CO) measured ambient CCN concentrations at 0.1% supersaturation. Aerosol hygroscopicity was estimated from SMPS and CCNC measurements during Autumn and Early Spring (SI Section S5), but the available CCN measurements were too sparse to identify a relationship with composition (Table S21).

3 Results

Figure 1 shows AMS NR amine fragments and FTIR NV amine groups for all four NAAMES cruises. 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. 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). 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 ± 11 ng m^{-3}), but largely similar for both marine and continental air masses (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.

~~For both marine and~~Notwithstanding the above consideration on continental ~~air masses~~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 makes 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). The highest concentration of AMS NR amine fragments for marine periods was 33 ± 6 ng m^{-3} in Early Spring and for continental periods 54 ± 49 ng m^{-3} in Autumn. For marine air masses, FTIR NV amine groups were highest in Late Spring, but, for continental air masses, FTIR NV amine groups were highest in Winter. FTIR NV amine group concentrations were lowest for both marine and continental air masses in Early Spring, when only two filters, both with FTIR NV amine groups below detection, met the marine criteria.

Average concentrations of FTIR NV amine groups were lower than concentrations of AMS NR amine fragments, except for the continental period in Winter. Two campaigns had positive, but not statistically significant, correlations of FTIR NV amine groups with AMS NR amine fragments, with $R = 0.45$ in Winter ~~($p = 0.01$)~~ and $R = 0.87$ in Autumn~~ but not statistically significant ($p = 0.08$).~~. The two Spring campaigns had negative correlations of FTIR NV amine groups and AMS NR amine fragments that were not statistically significant (Fig.2). Consequently, combining the four cruises for both air mass types gives no correlation between FTIR NV amine groups and AMS NR amine fragments ($\rho = 0.02$, where a Spearman's rank correlation coefficient was used for the non-normal distribution of FTIR NV amine groups and AMS NR amine fragments). This result suggests that FTIR and AMS are measuring different amine compounds, likely associated with different source types. In particular, AMS measures non-refractory components and FTIR measures non-volatile components (but some amine compounds are on refractory sea spray particles and some amines volatilize from filters). The inability of AMS to detect ~~non-~~refractory components that are found mixed with sea spray particles is another reason that amine measured by FTIR and AMS are from different sources (Frossard et al., 2014b). The non-zero y-intercepts of AMS NR amine fragments to FTIR NV amine groups in Figures 2b-2e further support the interpretation that AMS and FTIR are measuring different amine compounds.

AMS NR amine fragments had moderate to strong correlations ($0.73 < R < 0.98$, Table ~~3~~4) with AMS NR OM, suggesting that many of the organic sources included a consistent fraction of amines. 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 (Frossard et al., 2014b). FTIR NV amine groups had some weak correlations to AMS NR OM ($-0.66 < R < 0.54$, Table 4~~may reflect sources with different contributions of AMS NR amine fragments to AMS NR OM. FTIR NV amine groups had some weak correlations to AMS NR OM ($-0.66 < R < 0.54$, Table 5) but moderate to strong correlations to FTIR NV OM ($0.69 < R < 0.96$) in all seasons when filters were available (with the exception of Late Spring continental periods). Correlations of FTIR NV amine groups to AMS NR amine fragments in continental and marine air masses were variable across individual seasons.

4 Discussion

4.1 Marine Amine Sources

FTIR NV amine functional groups have been reported in atmospheric aerosol, generated primary marine aerosols, seawater, and the sea surface microlayer sampled ~~in~~during conditions when air masses~~ that~~ were considered clean marine in the North Atlantic, with their presence in both seawater and aerosols supporting that those amines are largely from sources that are both primary and marine (Lewis et al., 2022;Frossard et al., 2014a). FTIR NV amine groups indicate an association with sea spray (Saliba et al., 2019) because of their positive ($0.49 < R < 0.52$, Figure 3h) correlations to wind speed during continental periods in Winter and Early Spring, which included the highest wind speeds during NAAMES. The correlations with FTIR NV amine groups were not significant due to the limited number of samples (Table S16). AMS NR amine fragments did not correlate positively to wind speed (Figure 4c,d), consistent with the expectation that amines from primary ~~amines~~marine sources would be mixed with refractory sea salt particles (Hawkins et al., 2010;Frossard et al., 2014b)~~.~~. 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. 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.

Additional markers for a primary marine source include IC sea salt and AMS NR chloride. While AMS NR amine fragments correlated moderately ($0.59 < R < 0.65$, Figure 4e,f) with IC sea salt for marine air masses in Winter and Autumn, FTIR NV amine groups showed low to moderate correlations ($R = 0.33$-0.64, Figure 3e,f) to IC sea salt during the marine period in Late Spring and Autumn and even a strong correlation ($R = 0.78$) during the continental period in Early Spring. The FTIR NV amine group measurements include some low concentrations and few samples, meaning that these correlations are uncertain and not significant. FTIR NV amine groups correlated moderately ($0.57 < R < 0.76$, Figure 3a,b) with AMS NR chloride during both continental periods (Winter and Early Spring) and two of the three marine periods (Winter and Autumn) for which measurements were available. Although these correlations of FTIR NV amine groups and AMS NR chloride are only significant ($p < 0.05$) for the continental Winter period, the consistency of their positive correlations contrast with the absence of correlation ($-0.15 < R < 0.13$, Table ~~3~~4) between AMS NR chloride and AMS NR amine fragments during all four NAAMES cruises.

Chlorophyll *a* (chl *a*) is a common proxy for phytoplankton productivity that has previously been found to strongly correlate with organic mass in sea spray aerosols in coastal Atlantic regions (O'Dowd et al., 2004), but during NAAMES there was no clear dependence for <1 μm OC samples and a weak dependence for <1 μm OM cruise averages (Bates et al., 2020;Saliba et al., 2020). Consistent with these prior open ocean results for OM during NAAMES, no positive correlations were found for AMS NR amine fragments and chl *a,* or for FTIR NV amine groups in most of the cruises. The exception was a strong (R =

0.85, Figure 3g) correlation for FTIR NV amine groups during the marine period in Late Spring, which is the climax of the annual phytoplankton bloom. This finding is analogous to that of Russell et al. (2010) who attributed a weak, positive correlation of organic mass with chl *a* to particulate organic carbon (POC) in marine particles in bloom regions in the North Atlantic. The lack of correlations of organic mass and chl *a* is consistent with the less variable DOC pool as a carbon source for marine particles, as DOC typically does not correlate to chl *a* (Carlson et al., 1994). Therefore, these correlations with chl *a* support a primary marine source for FTIR NV amine groups.

The production of methylated amines and sulfurs varies with individual metabolic processes and across different ocean phytoplankton species (Keller, 1989;Liu et al., 2022a). Similar to methylated sulfurs, a significant portion of methylated amines are derived from phytoplankton and subsequent biological degradation (Mausz and Chen, 2019). While chlorophyll *a* is produced by various phytoplankton species for photosynthesis, dimethylsulfide (DMS) is primarily produced by coccolithophores (Malin et al., 1993). Therefore, DMS may serve as an alternative tracer for ocean biological production in addition to chl *a*. FTIR NV amine groups correlated positively ($0.54 < R < 0.85$, Figure 3c,d) with seawater DMS during the marine period in Late Spring and the continental period in Winter. During these same periods, correlations of atmospheric DMS and FTIR NV amine groups were weakly positive ($0.26 < R < 0.46$) and lower than the correlations of FTIR NV amine groups to seawater DMS. The weaker correlation with atmospheric than seawater DMS may be explained by the photochemical reactions of atmospheric DMS leading to daytime concentration decreases that are lagged by the peaks in concentration of FTIR NV amine groups. No correlations of seawater DMS to AMS NR amine fragments were observed. This is a distinct difference from FTIR NV amine groups that suggests the seawater DMS is more correlated to seawater organic components (DOC or POC) rather than secondary organic components, and that those seawater organic components are emitted on refractory sea spray particles that are not measured by AMS. Weak to moderate correlations ($0.36 <R < 0.50$, Figure 4a,b) of atmospheric DMS and AMS NR amine fragments were observed during continental periods in Winter and Autumn and during the marine period in Early Spring, consistent with a secondary contribution to the AMS NR amine fragments that is distributed on AMS NR particles rather than sea salt. In summary, correlations of seawater DMS suggest a primary marine source for FTIR NV amine groups but not for AMS NR amine fragments.

Methanesulfonic acid (MSA), an oxidated derivative of DMS, can serve as a reliable indicator of secondary atmospheric processing, since its formation also lags atmospheric DMS concentrations (Sanchez et al., 2018). MSA may also react with alkylamines in acid-base reactions, similar to nitric acid (Chen et al., 2015;Chen et al., 2016;Chen and Finlayson-Pitts, 2017;Perraud et al., 2020). During marine periods, correlations between IC MSA and AMS NR amine fragments were moderate ($R = 0.50$) in Late Spring and strong ($R = 0.90$) in Autumn, indicating that AMS NR amine fragments during marine periods likely included a secondary marine source. IC MSA measurements were below detection during Winter and too few marine air masses were sampled in Early Spring to be able to identify a correlation with any IC inorganic ions. Submicron FTIR NV amine groups were also moderately correlated ($R = 0.74$) with IC MSA for marine air masses in Late Spring supporting a secondary contribution to the FTIR NV amine groups as well~~, but this result was not significant ($p \geq 0.05$).~~. However, correlations with IC MSA of both FTIR NV and AMS NR amine were not significant ($p \geq 0.05$) due to the limited number of simultaneous IC filters available, which indicates that secondary marine source contributions to submicron mass are minor. Additional evidence for secondary contributions of FTIR NV amine groups is considered for <0.5 μm particles in Section 4.3.

4.2 Continental Amine Sources

Anthropogenic nitrogen oxides (NOx) can undergo a variety of reactions that form nitrate-containing secondary organic aerosols. For example, heterogeneous hydrolysis of dinitrogen pentoxide (N_2O_5) can produce nitric acid (HNO_3) that may form aminium nitrate salts though acid-base reactions with amines (Murphy et al., 2007;Price et al., 2016). Aminium salts can also form by the displacement of ammonium by amine in ammonium nitrate. The volatility of these amine-containing compounds is lower than ammonium nitrate such that they are more likely to partition into the particle phase (Smith et al., 2010). The moderate to strong ($0.67 < R < 0.84$, Figure 5b) correlations of AMS NR amine fragments and AMS NR nitrate for the Winter, Late Spring, and Autumn cruises during continental periods provide some evidence that the formation of particle-phase amine is associated with nitrate. To a lesser extent, AMS NR amine fragments and AMS NR nitrate also correlated weakly to moderately ($0.31 < R < 0.79$, Figure 5a) during the marine periods for the Winter, Late Spring, and Autumn cruises. This suggests a secondary continental source for AMS NR amine fragments that is present during continental and marine periods. ~~The steeper slopes~~ Tables S17 and S18 contain the linear fits for AMS NR amine fragments and FTIR NV amine groups, respectively. The zero intercepts (Table S17) of the linear fits for both continental air masses ~~(Y = 0.24-4.28, Table S17) compared to those of~~ in Winter and Autumn and marine air masses ~~(Y = 0.08-0.58, Table S17)~~ in Winter and Late Spring suggest that ~~these amines~~the AMS NR amine fragments largely have continental sources that are present ~~at low concentrations~~ during ~~the~~clean marine periods~~.~~ at lower concentrations. Correlations for FTIR NV amine groups were not available for the continental periods in Autumn and the marine periods in Early Spring due to sampling limitations. No positive correlations ($-0.59 < R < 0.19$, $p > 0.05$) of FTIR NV amine groups and AMS NR nitrate were observed, suggesting that the aminium salts may not have primary amine groups (~~NH_2~~CNH_2) or may be too volatile to remain for filter analysis. ~~Correlations for FTIR NV amine groups were not available for the continental periods in Autumn and the marine periods in Early Spring.~~

Figures 6a and 6b shows the weak to strong ($0.30 < R < 0.86$) correlations of AMS NR amine fragments to black carbon for continental air masses as well as for Autumn marine air masses. This correlation is consistent with the correlation to AMS NR nitrate, as AMS NR nitrate and black carbon are typically produced by combustion. BC is often an indicator of a primary combustion source, suggesting that AMS NR amine fragments may also include some primary sources of amines (Shen et al., 2017;Liu et al., 2022b). BC and AMS NR nitrate could be emitted by ocean-going vessels locally or transported from continents. Two tracers for continental processes are radon (from rocks and soils) and non-sea salt potassium (from biomass burning).

Since radon is a decay product of rocks and soil, it is used as a naturally occurring tracer for continental air masses. The weak correlation ($R = 0.37$, Figure 6c) of AMS NR amine fragments to radon during the marine period in Winter and moderate ($0.55 < R < 0.66$, Figure 6d) correlations during the continental periods in Winter, Autumn, and Late Spring indicate that much of the AMS NR amine fragments are continental. In contrast, all but the Late Spring marine period showed no or negative correlations ($-0.67 < R < -0.01$, Table 45) of FTIR NV amine groups with radon, suggesting that FTIR NV amine groups are largely from marine sources. 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.

Non-sea salt potassium ($nssK^+$) is a widely-used tracer for biomass burning, which also can produce a continental source of methylated amines (Bottenus et al., 2018). Weak to strong correlations ($0.27 < R < 0.95$, Figure 6e,f) of AMS NR amine fragments to IC $nssK^+$ were found for all marine and continental periods when IC measurements of K^+ and sodium (Na^+) were available. The correlations of AMS NR amine fragments and IC $nssK^+$ are significant for ~~all~~ marine air masses in Winter and all continental seasons except Winter, suggesting an important continental contribution to AMS NR amine fragments. No correlations of FTIR NV amine groups to IC $nssK^+$ were statistically significant ~~(Table 4~~due to limited overlap of IC and FTIR filter sampling times (Table 5).

~~During marine periods in Winter and continental periods in Autumn and Early Spring, correlations of AMS NR amine fragments to relative humidity revealed a negative, weak to moderate correlation (-0.55 < R < -0.26). FTIR NV amine groups and relative humidity correlations were also negative (-0.74 < R < -0.45) during Autumn and Early Spring continental periods (Table 4). The partitioning of secondary amine between the particle and gas phase is a strong function of relative humidity (Tang et al., 2014), such that these results provide some support for secondary contributions to both AMS NR amine fragments and FTIR NV amine groups. There was also one positive correlation between relative humidity and FTIR NV amine groups, namely the marine period in Late Spring (R = 0.77, Table 4).~~

Ozone has also been used as a tracer for secondary processes when its availability has limited secondary aerosol formation (Liu et al., 2011;Verma et al., 2017). Some evidence for photochemical formation is observed by positive, weak correlations ($0.41 < R < 0.42$) during continental periods in Late Spring and Autumn (Figure 5d) but marine periods in Late and Early Spring and continental periods in Winter did not show positive correlations. The possible photochemical formation is supported by the weak correlations with solar radiation during continental periods in Autumn ($R = 0.33$) and Early Spring ($R = 0.29$). FTIR NV amine groups weakly correlated ($0.28 < r < 0.48$, Table 45) with ozone during periods when no positive correlations ($-0.94 < R < 0.05$) with solar radiation were observed, providing inconsistent support for a photochemical contribution to FTIR NV amine groups.

The contribution of the AMS ion signal at m/z 44 (CO_2^+) to the total AMS NR OM signal (f_{44}) 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 ~~and~~to the AMS NR ~~m/z 44. Moderate~~OM and f_{44}. Weak to ~~strong~~moderate (0.~~85~~43 < R < 0.~~94~~79) correlations of AMS NR ~~m/z 44~~f_{44} 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 ~~m/z 44~~f_{44} positively correlated (R = 0.~~52~~36) with the contribution of FTIR NV amine group mass concentrations to the FTIR NV OM signal for only the ~~continental~~marine period in ~~Early~~Late Spring, possibly because aminium nitrate salts are too volatile to be retained on filters for FTIR analysis.

The Early Spring cruise began in Puerto Rico rather than Massachusetts and sampled marine air masses at latitudes lower than the other cruises. Few sampled air masses in Early Spring met the criteria for “marine”, in part because black carbon concentrations were high (29 ± 5 ng m^{-3}, Table 2) compared to other cruises. However, AMS NR amine fragments in Early Spring marine air masses did not correlate with continental tracers (black carbon, AMS NR nitrate, radon, or IC nssK^+). AMS NR amine fragments did correlate moderately with atmospheric DMS, ozone, and ~~ozone~~AMS NR f_{44}, which could be consistent with a secondary marine source that was not evident in the other cruises at higher latitudes. For marine air masses in Bermuda, near where marine air masses were sampled in Early Spring, anthropogenic activity is not a large contributor to organic nitrogen compounds, such as amine, despite being downwind of continental pollution sources (Altieri et al., 2016). It is also possible that the lack of correlation with the available tracers could be from sampling shorter durations of marine air masses during Early Spring, which limits the comparison of Early Spring marine periods to marine periods in other seasons.

4.3 Sources for <0.5 and <0.18 µm Amines

Submicron (<1 µm) sampling of marine aerosol over the open ocean and from bubble generators has suggested that alcohol functional groups serve as useful tracers for marine-derived saccharides, amino sugars, and carbohydrates (Frossard et al., 2014a;Gagosian et al., 1982;Leck and Bigg, 2005;Russell et al., 2010;Lewis et al., 2021). Conversely, carboxylic acid groups serve as a tracer for photochemical reaction products of VOCs (Frossard et al., 2014a;Takahama et al., 2010;Russell et al., 2010;Liu et al., 2011;Claflin et al., 2021). Figure 7 shows the correlations of FTIR NV amine groups to FTIR NV alcohol groups and FTIR NV acid groups measured across all four cruises for three different size cut-offs (<1 µm, <0.5 µm, <0.18 µm).

For FTIR NV alcohol and amine groups, <1 µm particle samples~~, there was~~ had a strong correlation (R = 0.87, Figure 7a) ~~between FTIR NV alcohol and amine groups~~s for marine periods and a moderate correlation (R = 0.63, Figure 7b) for continental periods, consistent with a primary source of FTIR NV amine groups. The difference between marine and continental air masses shows that the primary seawater amine source explains more variability for marine air masses than for continental air masses. The correlation of FTIR NV alcohol and amine groups was weaker for marine filters for <0.5 µm and <0.18 µm particle samples, with R = 0.31 for <0.5 µm (Figure 7c) and R = 0.11 for <0.18 µm (Figure 7e). Similarly, there were lower correlations of FTIR NV alcohol and amine groups for continental filters with R = 0.12 for <0.5 µm (Figure 7d) and R = 0.27 for <0.18 µm (Figure 7f). These results show that non-volatile amine groups associated with sea spray are largely found in >0.5 µm particles, where their mass is sufficiently large to control the <1 µm mass variability. 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). ~~The correlations may also be reduced by the higher volatility of combustion-derived aerosols that may be contributed by continental sources (Ni et al., 2019;Silva et al., 2020).~~ No positive correlations of <0.18 and <0.5 size fractions of FTIR NV amine group concentrations and black carbon concentrations were observed for marine or continental air masses, indicating that primary combustion sources were not a major source of amine groups in these small size ranges.

In contrast to the strong correlations found for FTIR NV amine groups with FTIR NV alcohol group for <1 µm samples, no correlations of <1 µm FTIR NV amine to acid groups were found for 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. ~~No correlation of FTIR NV amine to acid groups was found for <1 µm samples.~~ 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). Secondary dimethyl- and diethylaminium salts produced by acid-base reactions with biogenic, gaseous amines have been shown to have mass concentration peaks in similar size ranges of 0.25-0.50 µm (Facchini et al., 2008) and 0.14-0.42 µm (Muller et al., 2009). The strong correlation between FTIR NV amine and acid groups for <0.5 µm and <0.18 µm particle samples indicate that a gas-to-particle reaction mechanism contributes to primary (C-NH_2) amine groups in size ranges that are important for CCN. A secondary marine source of FTIR NV amine groups in aerosols with diameters of <0.18 µm and <0.5 µm is supported by weak to moderate correlations (0.39 < R < 0.73) of MSA and FTIR NV amine groups during marine periods in Late Spring for both size ranges. ~~These correlations for marine periods in two seasons were the only statistically significant correlations among the four cruises that were available for MSA due to the limited number of marine filters.~~ There was no significant correlation between FTIR NV acid and amine groups for any size of the continental FTIR filters~~. There were not enough~~ and too few continental filters with both FTIR NV amine and acid groups above detection to investigate correlations for continental <0.18 µm particle samples.

4.4 Combined AMS NR and FTIR NV Amine Contributions

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) amine moieties that may be too volatile to be sampled on filters~~.~~, but the FTIR does not detect secondary (C$_2$-NH) and tertiary (C$_3$-N) 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 ~~show that~~ 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.

During marine periods in Late Spring, the variability of FTIR NV amine groups was largely explained by correlations with AMS NR chloride, IC sea salt, seawater DMS, and chl *a*, all of which are consistent with primary marine sources. In contrast, the variability of AMS NR amine fragments was largely explained by correlations with AMS NR nitrate, IC nssK$^+$, radon, and AMS NR ~~m/z 44~~f_{44}, all of which indicate continental secondary sources. Figure 9 shows similar correlations with AMS NR nitrate and ~~IC sea salt in Autumn~~chl *a* in marine air masses during Late Spring that exemplify the AMS NR amine fragments correlation to AMS NR nitrate concentrations and the FTIR NV amine groups correlation to ~~IC sea salt.~~ chl *a*. A schematic diagram of amine sources, tracers, and amine-containing particle types in marine environments is shown in Figure S13.

The distinctly different sources of FTIR NV amine groups and AMS NR amine fragments suggest that combining the two measurements is likely to provide a better estimate of particle-phase amines in marine environments than either measurement separately. This approach is supported by the poor overall correlation of $\rho = 0.02$ (Figure 2a) of the two measurements. FTIR NV amine groups provide a good estimate of <1 μm ~~marine primary~~ amine group mass concentration with a primary marine source; AMS NR amine fragments provide a good estimate of continental amine sources that are likely secondary. Results for individual seasons illustrate that the contributions of FTIR NV amine groups and AMS NR amine fragments vary by season (based on Table 2). For Winter, ~~the~~FTIR NV primary (C-NH$_2$) amine groups from primary marine ~~FTIR NV amine group accounts~~sources account 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 ~~FTIR NV amine group accounts~~sources account for (34~~%~~±37)% compared to (66~~%~~±72)% secondary continental AMS NR amine fragments. ~~And for~~For Early Spring, FTIR NV primary (C-NH_2) amine groups from primary marine ~~FTIR NV amine group accounts~~sources account for (27~~%~~±57)% compared to (73~~%~~±152)% secondary continental AMS NR amine fragments.

5 Conclusions

FTIR and AMS amine measurements were used to investigate the sources of submicron aerosol in the North Atlantic during different seasons. Marine and continental air masses were distinguished to separate the different conditions that were measured. Amine concentrations from AMS and FTIR were compared to chemical and meteorological tracers for identification of marine and continental sources and primary and secondary processes. FTIR and AMS measured greater amine concentrations for continental air masses than for marine air masses except for the Early Spring cruise, likely due to its lower latitudes and less pristine marine air masses. AMS NR amine fragments largely correlated with secondary tracers such as AMS NR nitrate, ozone, AMS NR ~~m/z 44~~f_{44} , and IC MSA but did not correlate positively with seawater DMS, AMS NR chloride, chlorophyll *a* or wind speed. Correlations with tracers for secondary particles were lower for <1 μm FTIR NV amine groups than for AMS NR amine fragments, but correlations of FTIR NV amine groups with tracers of primary marine ~~tracers~~sources such as wind speed, IC sea salt, and seawater DMS, NR chloride, and chlorophyll *a* were higher than for AMS NR amine fragments.

FTIR NV amine groups measured during marine periods were found to have largely primary sources for <1 μm particles but secondary sources for <0.5 and <0.18 μm particles. Correlations with FTIR NV alcohol groups show the contribution of a primary source of non-volatile amine for aerosols with diameters <1 μm that had weaker correlations for <0.5 and <0.18 μm. Correlations between FTIR NV amine groups with both FTIR NV acid groups and IC MSA for particles <0.5 and <0.18 μm diameter revealed that secondary processes were a larger contributor for amine groups than in <1 μm particles.

Results presented herein are also consistent with the expectation that FTIR measures the refractory, amine-containing sea salt particles missed by AMS, and that AMS measures the semi-volatile, amine-containing particles missed by FTIR spectroscopy. Therefore, these two techniques offer complementary analyses of amine in marine environments for <1 μm atmospheric particles. Combining them provides a rough source apportionment for marine periods, with amine from primary marine ~~amine~~sources accounting for (53~~%~~±76)% compared to (47~~%~~±68)% secondary continental amine in Winter, but amine from primary marine ~~amine~~sources accounting for only (27~~%~~±57)% compared to (73~~%~~±152)% secondary continental amine for Early Spring.

Acknowledgements

The authors would like to thank the dedicated officers and crew of the R/V Atlantis. The authors would also like to acknowledge Savannah Lewis, Eric Saltzman, Laura Rivellini, Bill Brooks, Tim Onasch, Leah Williams, Raghu Betha, Maryam Askari Lamjiri, Derek Coffman, and Lucia Upchurch for their contributions to collecting and reducing data. This work was funded by NASA NAAMES grant NNX15AE66G, and VB was supported by the UCSD McNair Fellowship Program. This is PMEL contribution number 5413.

Data Availability

All data collected during NAAMES are available on the NASA data server: https://naames.larc.nasa.gov. Scripps measurements: https://library.ucsd.edu/dc/collection/bb34508432; Shipboard measurements: https://seabass.gsfc.nasa.gov/. PMEL measurements: https://saga.pmel.noaa.gov/data/.

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Table 1: Summary of recent measurements of amine concentrations in marine regions.

Sampling Site and Season	Relevant Findings	Citation
Southeast Pacific during October-November	FTIR primary amine groups. The average mass concentration (μg m^{-3}) for campaign: 0.015 ± 0.014; marine air masses: 0.0089 ± 0.0068; mixed air masses: 0.019 ± 0.015; continental air masses: 0.023 ± 0.023.	(Hawkins et al., 2010)
Gulf of Mexico during August- September	FTIR primary amine groups with contributions from oil combustion and wood smoke. The average mass concentration (μg m^{-3}) for campaign: 0.25 ± 0.26; air masses over the Gulf: 0.10 ± 0.07; southerly continental air masses: 0.48 ± 0.33; northerly continental air masses: 0.16 ± 0.13.	(Russell et al., ~~2009~~2009b)
Western Atlantic during August	FTIR primary amine groups. 2% of OM in all ambient aerosols, 13% of OM in generated primary marine aerosols.	(Frossard et al., 2014b)
Tropical East Atlantic during November-January (May-June)	HPLC with ESI-IT-MS secondary marine aliphatic amines (pg m^{-3}~~) .~~). MA: 2-520 (0-30); DMA: 100-1400 (130-360); DEA: 90-760 (5-110).	(Muller et al., 2009)
Gulf of Maine during June-August	FTIR primary amine groups below detection.	(Gilardoni et al., 2007)
Eastern North Atlantic during high biological activity	IC secondary, marine dimethylammonium and diethylammonium salts (ng m^{-3}) in clean air masses: 4-13 and 7-24, respectively. Concentrations peaked in 0.25-0.5 μm size range. Monoalkylammonium, and trialkylammonium salt concentrations below detection.	(Facchini et al., 2008)
Coastal Ireland during low (high) biological activity	IC secondary, marine dimethylammonium and diethylammonium salts (ng m^{-3}): <1-8 (2-24) and <1-12 (4-32), respectively. Monoalkylammonium and trialkylammonium salt concentrations below detection.	(Facchini et al., 2008)
La Jolla in coastal California during August-October	FTIR primary amine groups average mass concentration 0.11 ± 0.09 μg m^{-3}. 1% of combustion (3.0 μg m^{-3}) were amines. 3% of marine (0.97 μg m^{-3}) were amines.	(Liu et al., 2011)
Western North Pacific during Aμgust-September	TOC/TON analyzer secondary, marine DEA: <0.1 to 0.8 ng m^{-3}.	(Miyazaki et al., 2011)
Coastal Northern China during January-February (November-December)	UHPLC-MS amines (MA, DEA, DMA, PA, TMA, MEA, PYR, BA, DEA, MOR, AN, DPA, TEA, DBA, TPA) with averages ranging from 0.1 to 58.7 (0.1 to 86.3) ng m^{-3} from coal combustion activities, industrial emissions, vehicle exhaust, biomass burning, and agricultural and marine emissions.	(Liu et al., 2022b)
Coastal Norway during September-November	GC-MS and LC-MS nitrosamines and alkyl amines (nM) in fog. MEA: BDL-7.1; MA: 0.4-8.9; DMA: 130.3-255; DEA: 1.7-5.8. NDEA, NMOR, NDBA, and NPIP, EA were below detection.	(Wang et al., 2015)
Tropical East Atlantic (2-year average)	IC secondary, aliphatic amines (ng m^{-3}) scavenged in the gas phase by the particle phase. DMA: 5.6; MA: 0.2; DEA: 3.9 .	(van Pinxteren et al., 2019)
Coastal California during July-August	IC and ICP-MS secondary, marine DMA: 2.3-70.3 ng m^{-3}.	(Youn et al., 2015)

East China Sea during June	IC secondary, marine aliphatic amines (nmol m^{-3}). DMA: 0.67 ± 0.21; TMA: 0.20 ± 0.11.	(Xie et al., 2018)
Coastal site near Yellow Sea during August	IC secondary, marine aliphatic amines (nmol m^{-3}). DMA: 0.62 ± 0.50; TMA: 0.15 ± 0.11.	(Xie et al., 2018)
Yellow Sea and Northwest Pacific during March-May	IC secondary, marine aliphatic amines (nmol m^{-3}). DMA: 0.28 ± 0.23; TMA: 0.22 ± 0.23.	(Xie et al., 2018)
Yellow Sea and Bohai Sea during ~~^{1}August~~^{1}August-September ^{2}June-July ^{3}November	IC secondary, marine methylated amines (nmol m^{-3}). ^{1}DMA: 0.52 ± 0.28; TMA: 0.31 ± 0113. ^{2}DMA: 1.1 ± 0.47; TMA: 0.35 ± 0.13. ^{3}DMA: 0.41 ± 0.36; TMA: 0.53 ± 0.32.	(Xie et al., 2018)
High Arctic during July	Single particle laser ablation AMS TMA: 23% of particles 200-1000 nm in diameter.	(Kollner et al., 2017)
Tropical East Atlantic during Winter and Spring	HPLC/ESI-IT-MS aliphatic amines. DMA and DEA: 270 pg m^{-3} (Spring) to 830 pg m^{-3} (Winter).	(Carpenter et al., 2010)
North Atlantic during September, May-June, March-April, November	FTIR primary amine groups. 5-8% of OM in atmospheric primary marine aerosols, 5-12% of OM in generated primary marine aerosols.	(Lewis et al., 2021)
California coast during May	FTIR primary amine groups. 14% of OM in generated primary marine aerosols.	(Bates et al., 2012)
Huaniao Island during January	HPLC/fluorescence alkyl amines (ng m^{-3}). MA: 0.27-7.04~~-~~; EA: 0.37-1.78; PA: 0.76-4.03~~-~~; BA: BDL-0.15; PEN: 0.07–0.40, HEX: BDL; MEA: 0.84–5.62.	(Huang et al., 2018)

*Abbreviations: MA- monomethylamine, DMA- dimethylamine, DEA- diethylamine, TMA- trimethylamine, EA-ethylamine, TEA-triethylamine, PA- propylamine. DPA- dipropylamine, TPA- tripropylamine, BA- butylamine, DBA - dibutylamine, MEA- ethanolamine, MOR-morpholine, PYR- pyrrolidine, AN- aniline, PEN- pentylamine, HEX- hexylamine, PIP- piperidine, NDMA-nitrosodimethylamine, NDEA-nitrosodiethylamine; NBA-nitrosodibutylamine; NPIP- nitrosopiperidine, UHPLC: Ultra High Performance Liquid Chromatography, GC: Gas Chromatography, ESI-IT-MS: Electrospray Ionization Ion Trap Mass Spectrometer, ICP: Inductively Coupled Plasma, TOC/TON: Total Organic Carbon/Total Organic Nitrogen

Table 2: Mean concentrations and standard deviations of amine, tracer, and environmental measurements during NAAMES for marine (first row) and continental (second row, in parentheses) periods. Seasonal mean concentrations and standard deviations are given in in square brackets, which were averaged 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)	14 ± 3 (18 ± 7) [18 ± 6]	33 ± 6 (32 ± 11) [31 ± 6]	23 ± 8 (37 ± 13) [33 ± 12]	26 ± 9 (54 ± 49) [30 ± 11]
FTIR NV Amine Groups (ng/m^3)*	10 ± 15 (33 ± 33) [20 ± 26]	BDL (16 ± 28) [12 ± 23]	18 ± 15 (21 ± 20) [17 ± 14]	7 ± 11 (28 ± 6) [16 ± 15]
Sum of AMS NR Amine Fragments & FTIR NV Amine Groups (ng/m^3)*	24 ± 15 (57 ± 31) [39 ± 27]	32 ± 7 (47 ± 30) [43 ± 25]	43 ± 14 (63 ± 15) [50 ± 16]	36 ± 16 (80 ± 10) [46 ± 21]
AMS NR OM (ng/m^3)	151 ± 47 (321 ± 309)	296 ± 107 (422 ± 227)	373 ± 269 (824 ± 658)	295 ± 150 (990 ± 1187)
FTIR NV OM (ng/m^3)	281 ± 198 (315 ± 220)	210 ± 156 (209 ± 327)	220 ± 165 (422 ± 420)	200 ± 175 (375 ± 431)
AMS NR Nitrate (ng/m^3)	6 ± 3 (12 ± 12)	9 ± 4 (15 ± 5)	10 ± 6 (45 ± 101)	8 ± 2 (14 ± 14)
AMS NR ~~m/z 44~~f_{44} (~~ng/m^3~~unitless)	~~56 ± 13~~ ~~(91 ± 55~~0.39 ± 0.06 (0.35 ± 0.08)	~~137 ± 33~~ ~~(192 ± 70~~0.50 ± 0.09 (0.49 ± 0.08)	~~123 ± 36~~ ~~(224 ± 104~~0.38 ± 0.08 (0.31 ± 0.07)	~~147 ± 36~~ ~~(319 ± 241~~0.56 ± 0.19 (0.45 ± 0.15)
Black Carbon (ng/m^3)	12 ± 14 (220 ± 354)	29 ± 5 (197 ± 62)	21 ± 16 (141 ± 240)	20 ± 17 (148 ± 147)
Ozone (ppb)	41 ± 2 (38 ± 5)	33 ± 14 (47 ± 9)	38 ± 7 (39 ± 6)	29 ± 6 (31 ± 7)
Radon (mBq ~~m^{-3}~~/m^3)	246 ± 109 (472 ± 366)	272 ± 130 (873 ± 333)	298 ± 80 (466 ± 289)	404 ± 202 (876 ± 612)
Wind Speed (m/s)	9.9 ± 3.9 (10.4 ± 3.9)	9.2 ± 3.2 (11.7 ± 4.6)	9.7 ± 5.1 (6.6 ± 3.2)	9.4 ± 4.1 (5.9 ± 3.1)
atm. DMS (ppt)	66 ± 21 (93 ± 51)	129 ± 71 (91 ± 78)	463 ± 293 (214 ± 186)	138 ± 233 (118 ± 87)
sw. DMS (nmol/L)	1.4 ± 0.6 (1.4 ± 0.7)	3.0 ± 1.1 (4.6 ± 3.2)	3.2 ± 2.5 (2.5 ± 2.5)	3.3 ± 0.7 (3.1 ± 1.4)
Temperature (ºC)	10.2 ± 5.8 (11.9 ± 6.5)	19.7 ± 4.3 (13.6 ± 4.5)	8.5 ± 4.3 (9.1 ± 3.8)	13.5 ± 3.4 (16.7 ± 3.1)
Chlorophyll *a* (ng/L)	457 ± 242 (713 ± 774)	643 ± 247 (578 ± 360)	1956 ± 1689 (1647 ± 1396)	379 ± 236 (284 ± 255)
SST (ºC)	13.2 ± 0.~~05~~5 (13.8 ± 5.5)	21.6 ± 3.6 (16.0 ± 3.2)	10.1 ± 5.1 (10.5 ± 4.7)	14.5 ± 2.8 (17.8 ± 4.2)
IC MSA (µg/m^3)	-- --	-- (0.11 ± 0.19)	0.05 ± 0.05 (0.06 ± 0.03)	0.01 ± 0.01 (0.01 ± 0.00)
IC Sea Salt (µg/m^3)	1.01 ± 0.75 (1.45 ± 0.72)	-- (1.28 ± 0.51)	0.30 ± 0.30 (0.06 ± 0.04)	0.45 ± 0.30 (0.43 ± 0.55)
IC nssK$^+$	0.01 ± 0.01	--	0.00 ± 0.00	0.00 ± 0.00

(μg/m^3)	(0.02 ± 0.01)	(0.02 ± 0.02)	(0.02 ± 0.01)	(0.03 ± 0.02)

*The average included filters with amine concentration below detection.

~~Table 3~~**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 in square brackets, which were averaged 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 (ºC)	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 (ºC)	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$^+$ ($\mu g/m^3$)	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)

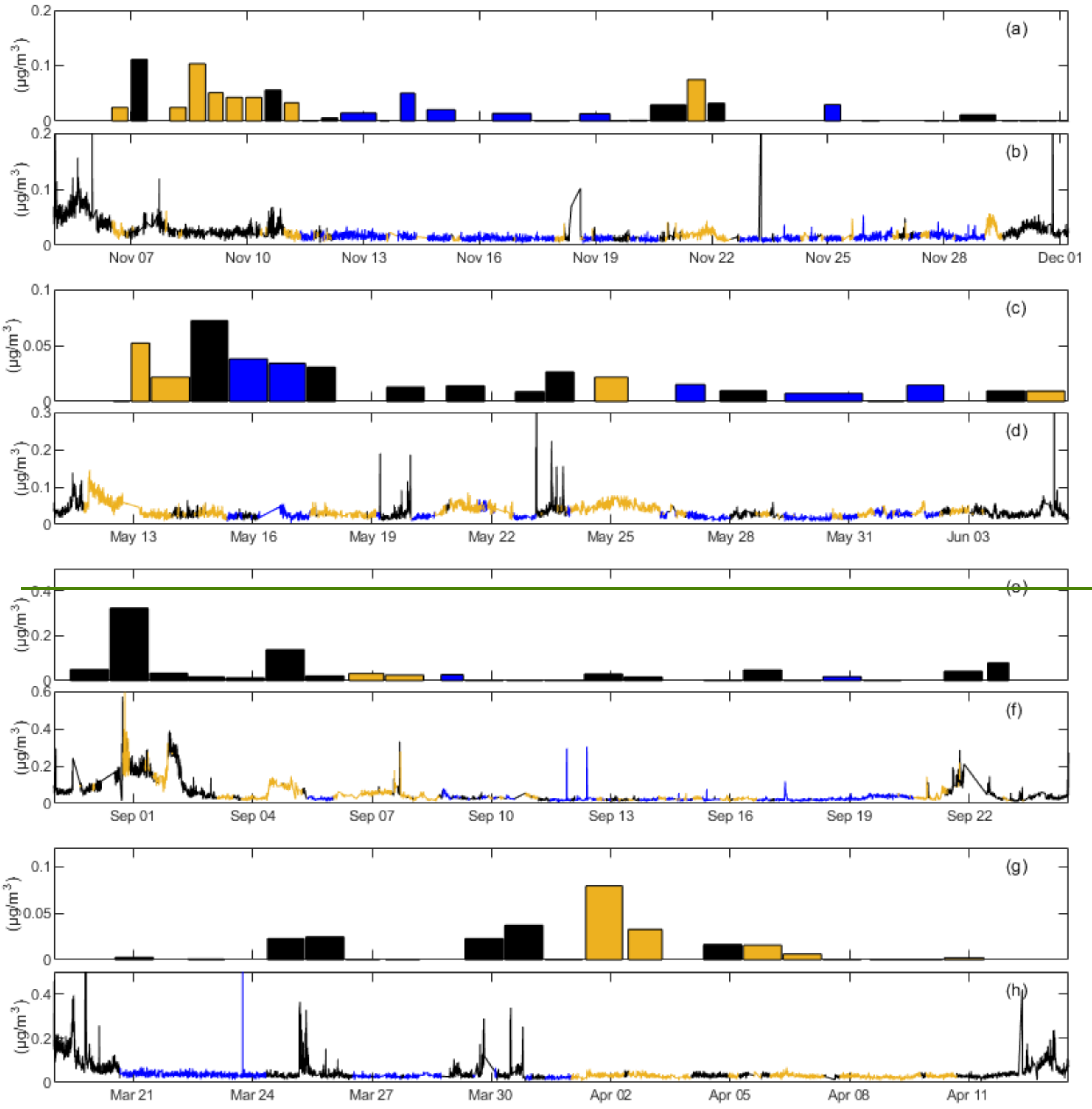
*The median included filters with amine concentration below detection.

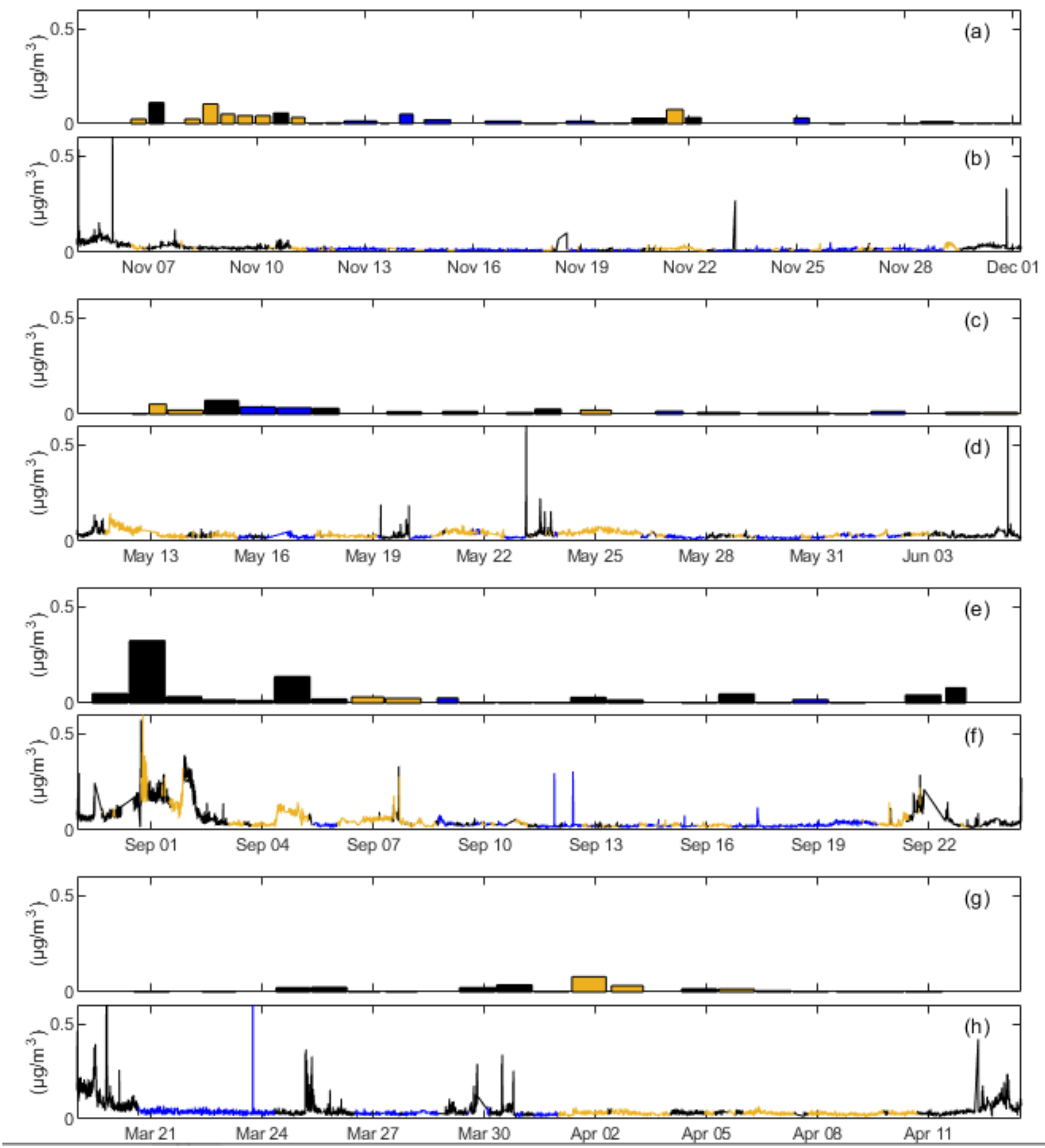
Table 4: Pearson correlation (R) coefficient values between AMS NR amine fragments and various tracers for marine periods (columns 1-4) and continental periods (columns 5-8). Negative correlations are shaded blue and positive correlations are shaded red. The strength of each correlation determines the 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. Correlations that are not statistically ~~insignificant~~significant (p ≥ 0.05) are indicated by *.

Air Masses	Marine				Continental			
Season	Winter	Early Spring	Late Spring	Autumn	Winter	Early Spring	Late Spring	Autumn
AMS NR OM	0.85	0.27	0.80	0.78	0.73	0.83	0.81	0.98
FTIR NV OM	-0.26*	--	-0.07*	0.88*	-0.32*	0.48*	0.45*	--
AMS NR Nitrate	0.59	-0.17	0.79	0.31	0.71	0.10*	0.67*	0.84
AMS NR Sulfate	0.59	0.68	0.52	0.27	0.49	0.14	0.46	0.36
AMS NR Chloride	0.13	-0.09*	-0.08*	-0.07*	0.06*	-0.15	-0.07*	-0.03*
AMS NR ~~m/z 44~~f_{44}	0.~~77~~46	0.~~18~~43	0.~~85~~68	0.~~55~~79	0.85	0.~~62~~51	0.~~89~~76	0.~~94~~76
Black Carbon	0.60*	-0.04*	0.61*	0.33	0.31	0.30	0.30*	0.86
Ozone	0.11*	-0.70	-0.25	-0.22	-0.26	0.02*	0.42	0.41
Radon	0.37	-0.01	-0.17*	0.03	0.66	0.18	0.55*	0.55
Wind Speed	-0.18	-0.09	-0.53*	0.03*	0.00	-0.41	-0.13*	-0.45
sw. DMS	0.08*	-0.06*	-0.09*	0.05*	0.07*	0.05*	-0.23*	-0.08
atm. DMS	-0.20	0.50	-0.20*	0.04	0.41	-0.34	-0.20	0.36
Solar Radiation	-0.03*	0.00*	0.16	0.08*	-0.02*	0.29	-0.05*	0.33
Relative Humidity	-0.55	0.00	-0.08*	-0.04*	0.11*	-0.26	0.04*	-0.49*
Temperature	-0.30	0.77	-0.17	0.34	0.21	0.26	0.41	0.59
Chlorophyll *a*	-0.09*	0.09	0.09	-0.46*	0.21*	-0.07*	-0.01*	-0.26*
SST	-0.15	0.80	-0.23	0.33	0.23	0.29	0.23	0.60
IC MSA	BDL	--	0.50*	0.90*	BDL	0.25*	0.12*	-0.10*
IC Sea Salt	0.59*	--	-0.72*	0.65*	-0.84*	0.15*	-0.17*	-0.05*
IC nssK$^+$	0.78	--	0.27*	0.83*	0.79*	0.59*	0.95	0.89

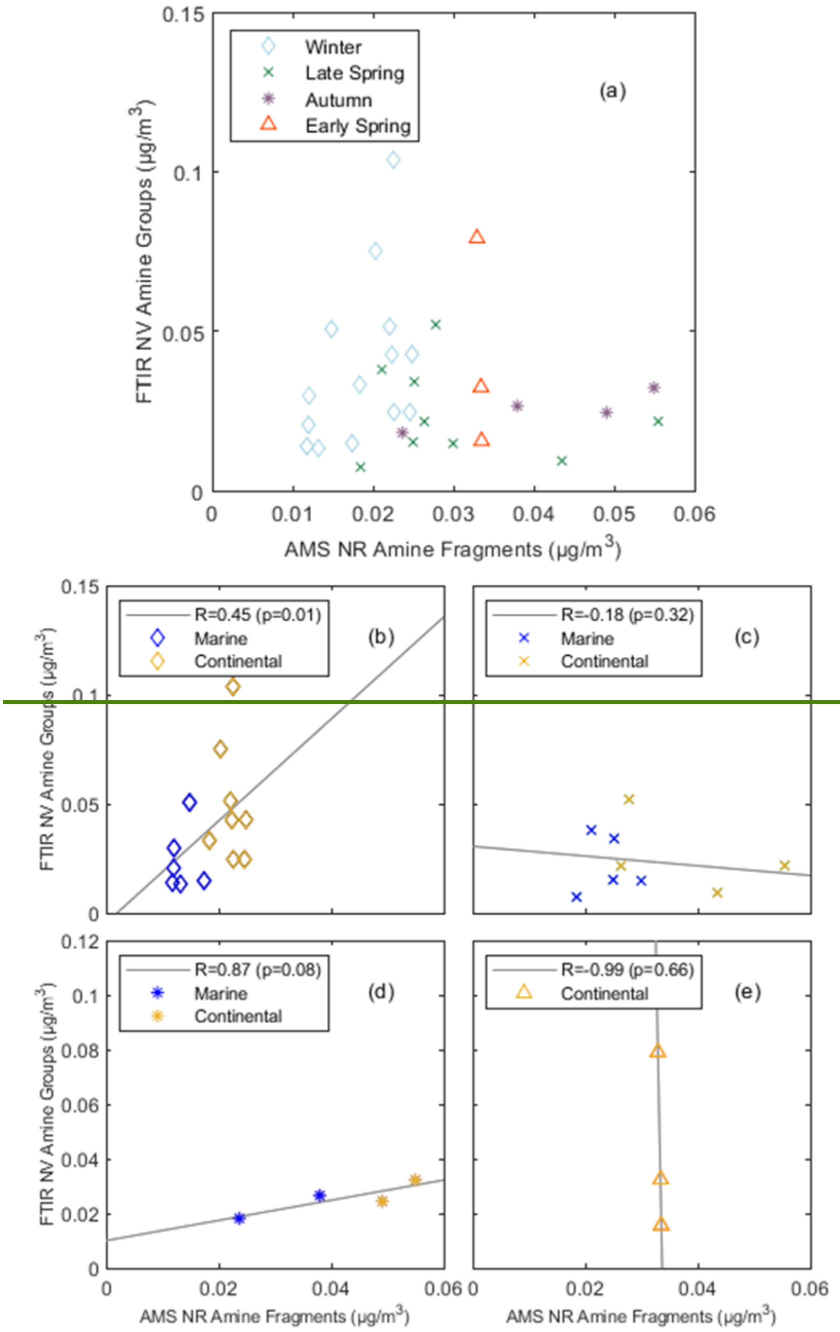
Table ~~4~~5: Pearson correlation (R) coefficient values between FTIR NV amine groups (ADL & BDL) in particles with diameters <1 µm and various tracers for marine periods (columns 1-4) and continental periods (columns 5-8). Negative correlations are shaded blue and positive correlations are shaded red. The strength of each correlation determines the level of saturation for the corresponding shading- no correlation ($|R| < 0.25$)- gray, weak correlation ($0.25 \le |R| < 0.50$)- light blue/red, moderate correlation ($0.50 \le |R| < 0.80$)- medium blue/red, strong correlation ($0.80 \le |R|$)- dark blue/red. Correlations that are not statistically ~~insignificant~~significant ($p \ge 0.05$) are indicated by *.

Air Masses	Marine				Continental			
Season	Winter	Early Spring	Late Spring	Autumn	Winter	Early Spring	Late Spring	Autumn
AMS NR OM	-0.13*	--	0.26*	-0.14*	0.26*	0.54*	-0.66*	--
FTIR NV OM	0.68	--	0.90	0.~~79~~69*	0.69	0.96*	0.~~09~~10*	--
AMS NR Nitrate	-0.16*	--	0.19*	-0.23*	0.01*	0.13*	-0.59*	--
AMS NR Sulfate	-0.19*	--	0.61*	0.27*	0.35*	-0.34*	-0.50*	--
AMS NR Chloride	0.57*	--	0.73*	0.00*	0.67	0.76*	-0.43*	--
AMS NR ~~m/z 44~~f_{44}	-0.~~14~~03*	--	-0.~~63~~36*	-0.~~24~~00*	-0.~~19~~54*	-0.~~52~~67*	-0.~~72~~03*	--
Black Carbon	-0.16*	--	-0.84*	0.14*	0.61*	0.04*	-0.26*	--
Ozone	0.45*	--	0.16*	-0.20*	0.17*	0.28*	0.31*	--
Radon	-0.67	--	0.28*	-0.23*	-0.54*	-0.01*	-0.32*	--
Wind Speed	-0.23*	--	-0.16*	0.04*	0.49*	0.52*	0.02*	--
sw. DMS	-0.30*	--	0.85*	-0.36*	0.54*	-0.26*	--	--
atm. DMS	-0.50*	--	0.46*	-0.15*	0.24*	0.05*	--	--
Solar Radiation	-0.43*	--	0.17*	-0.44*	0.49*	0.05*	-0.94*	--
Relative Humidity	-0.24*	--	0.77*	-0.01*	-0.21*	-0.45*	-0.74*	--
Temperature	-0.25*	--	-0.66*	0.32*	0.08*	-0.05*	-0.14*	--
Chlorophyll *a*	0.24*	--	0.86	-0.33*	-0.36*	0.09*	-0.26*	--
SST	-0.34*	--	-0.70*	0.66*	-0.31*	0.17*	0.02*	--
IC MSA	--	--	0.74*	-0.44*	--	-0.34*	-0.75*	--
IC Sea Salt	0.23*	--	0.33*	0.64*	--	0.78*	-0.25*	--
IC nssK$^+$	0.20*	--	0.35*	0.06*	--	0.72*	-0.31*	--


(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(μg/m^3)
0
0.1
0.2
0.05
0.3
0.4
0.6
Nov 07
Nov 10
Nov 13
Nov 16
Nov 19
Nov 22
Nov 25
Nov 28
Dec 01
May 13
May 16
May 19
May 22
May 25
May 28
May 31
Jun 03
Sep 01
Sep 04
Sep 07
Sep 10
Sep 13
Sep 16
Sep 19
Sep 22
Mar 21
Mar 24
Mar 27
Mar 30
Apr 02
Apr 05
Apr 08
Apr 11



785 **Figure 1: Time series of AMS NR amine fragments measured by the HR-ToF-AMS (b,d,f,h) and FTIR NV amine groups measured by FTIR spectroscopy in particles with diameters <1 µm (a,c,e,g) for all four cruises. From top to bottom: Winter (a,b), Late Spring (c,d), Autumn (e,f), Early Spring (g,h). Marker colors represent air mass type- blue: marine, yellow: continental, black: winds abaft or mixed.**


(a)
Winter
Late Spring
Autumn
Early Spring
FTIR NV Amine Groups (µg/m^3)
AMS NR Amine Fragments (µg/m^3)
0.15
0.1
0.05
0
0.01
0.02
0.03
0.04
0.05
0.06
(b)
R=0.45 (p=0.01)
Marine
Continental
(c)
R=-0.18 (p=0.32)
Marine
Continental
(d)
R=0.87 (p=0.08)
Marine
Continental
(e)
R=-0.99 (p=0.66)
Continental
0.12
0.08
0.06
0.04
0.02

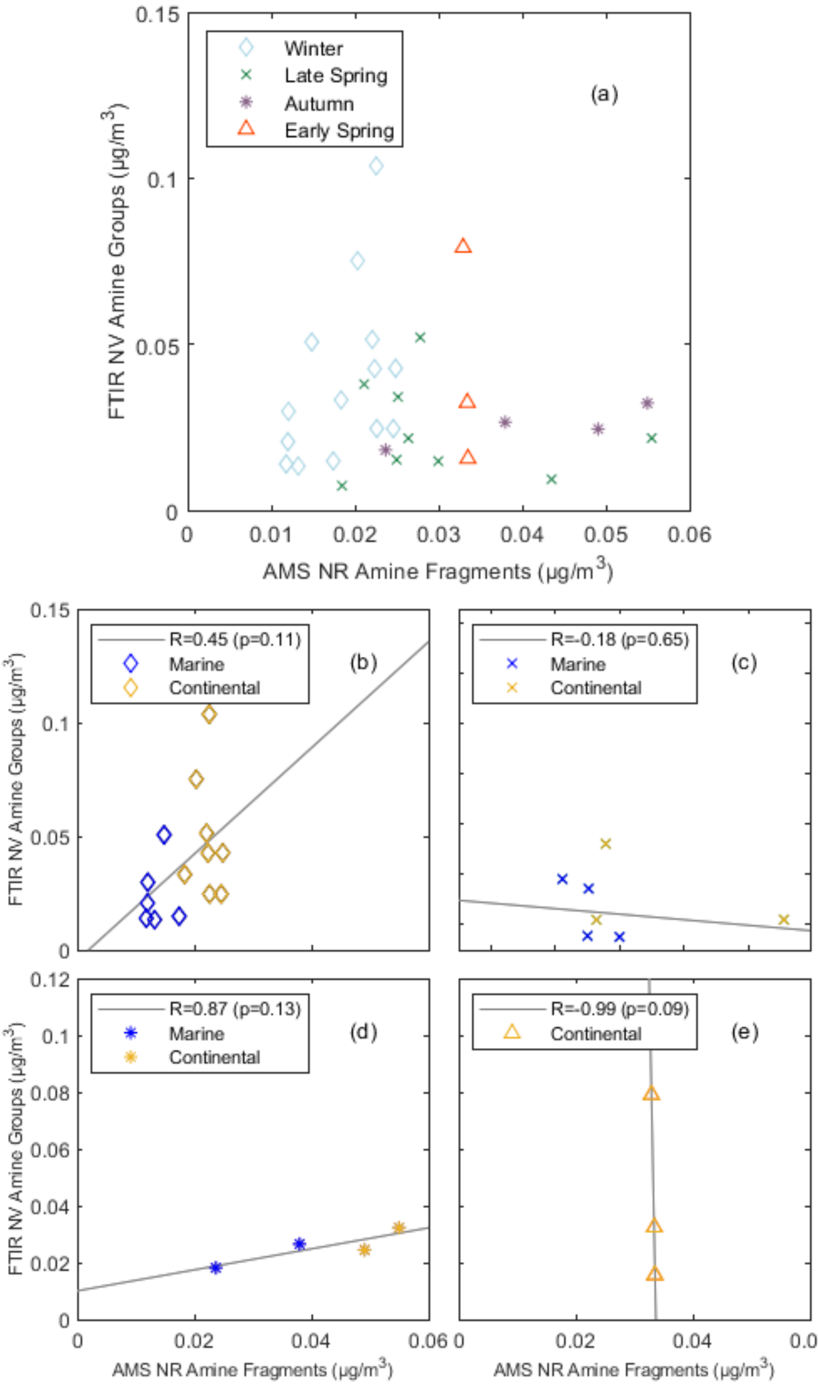


Figure 2: Scatter plot of (ADL) FTIR NV amine groups in particles with diameters <1 µm versus AMS NR amine fragments for (a) all cruises (ρ = 0.02, p = 0.18), (b) Winter, (c) Late Spring, (d) Autumn, and (e) Early Spring. Markers represent each cruise- open diamond: Winter, crosses: Late Spring, asterisk: Autumn, open triangle: Early Spring. Marker colors represent air mass type: blue: marine, yellow: continental. The solid grey lines are the lines of best fit obtained using an ordinary least squares regression. A two-tailed T test is used to estimate p-values.

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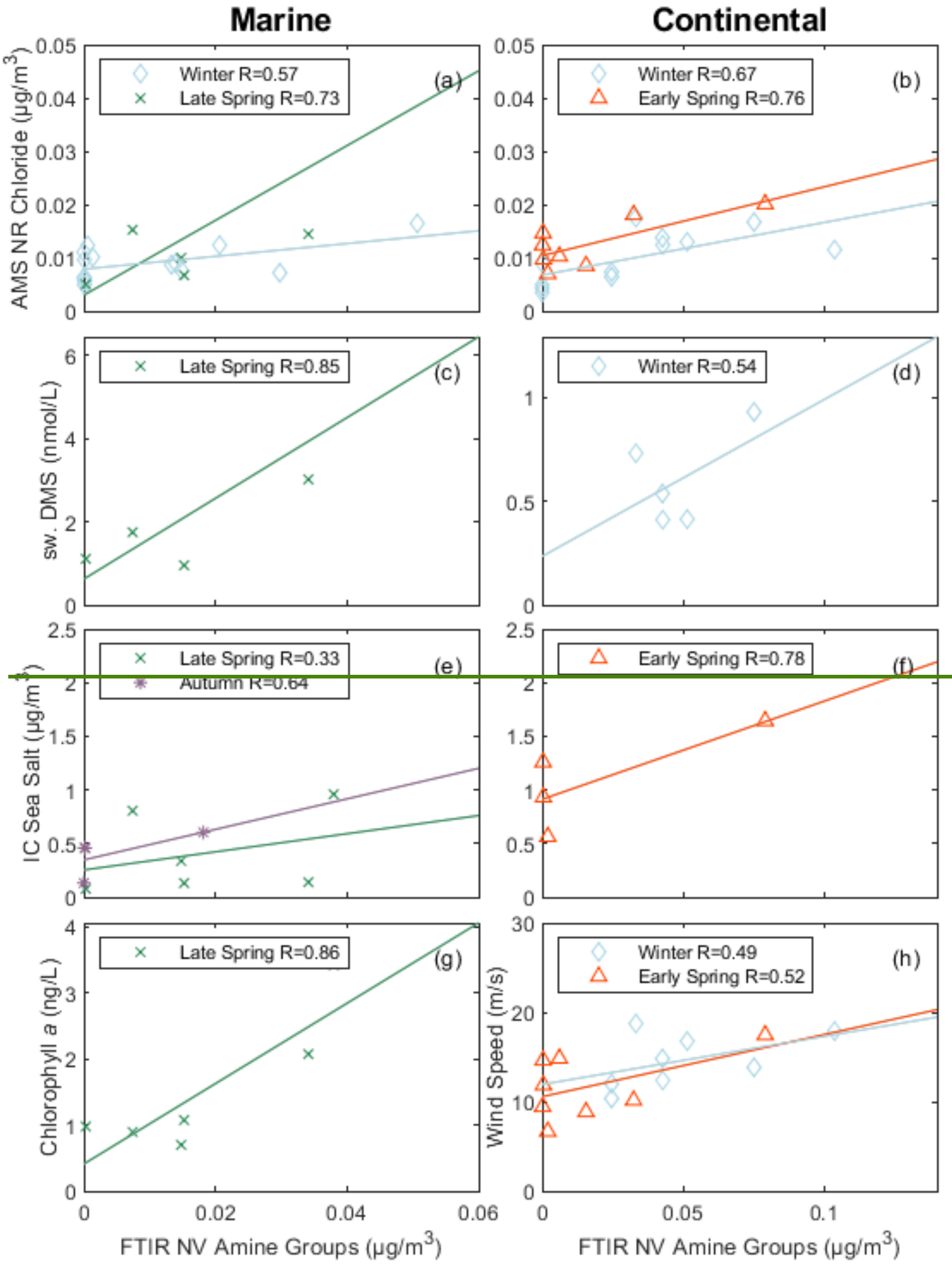

Marine
Continental
AMS NR Chloride (µg/m3)
0.05
0.04
0.03
0.02
0.01
0
Winter R=0.57
Late Spring R=0.73
(a)
Winter R=0.67
Early Spring R=0.76
(b)
sw. DMS (nmol/L)
Late Spring R=0.85
(c)
Winter R=0.54
(d)
IC Sea Salt (µg/m3)
Late Spring R=0.33
Autumn R=0.64
(e)
Early Spring R=0.78
(f)
Chlorophyll a (ng/L)
Late Spring R=0.86
(g)
Wind Speed (m/s)
Winter R=0.49
Early Spring R=0.52
(h)
0
0.02
0.04
0.06
0.05
0.1
FTIR NV Amine Groups (µg/m3)
FTIR NV Amine Groups (µg/m3)

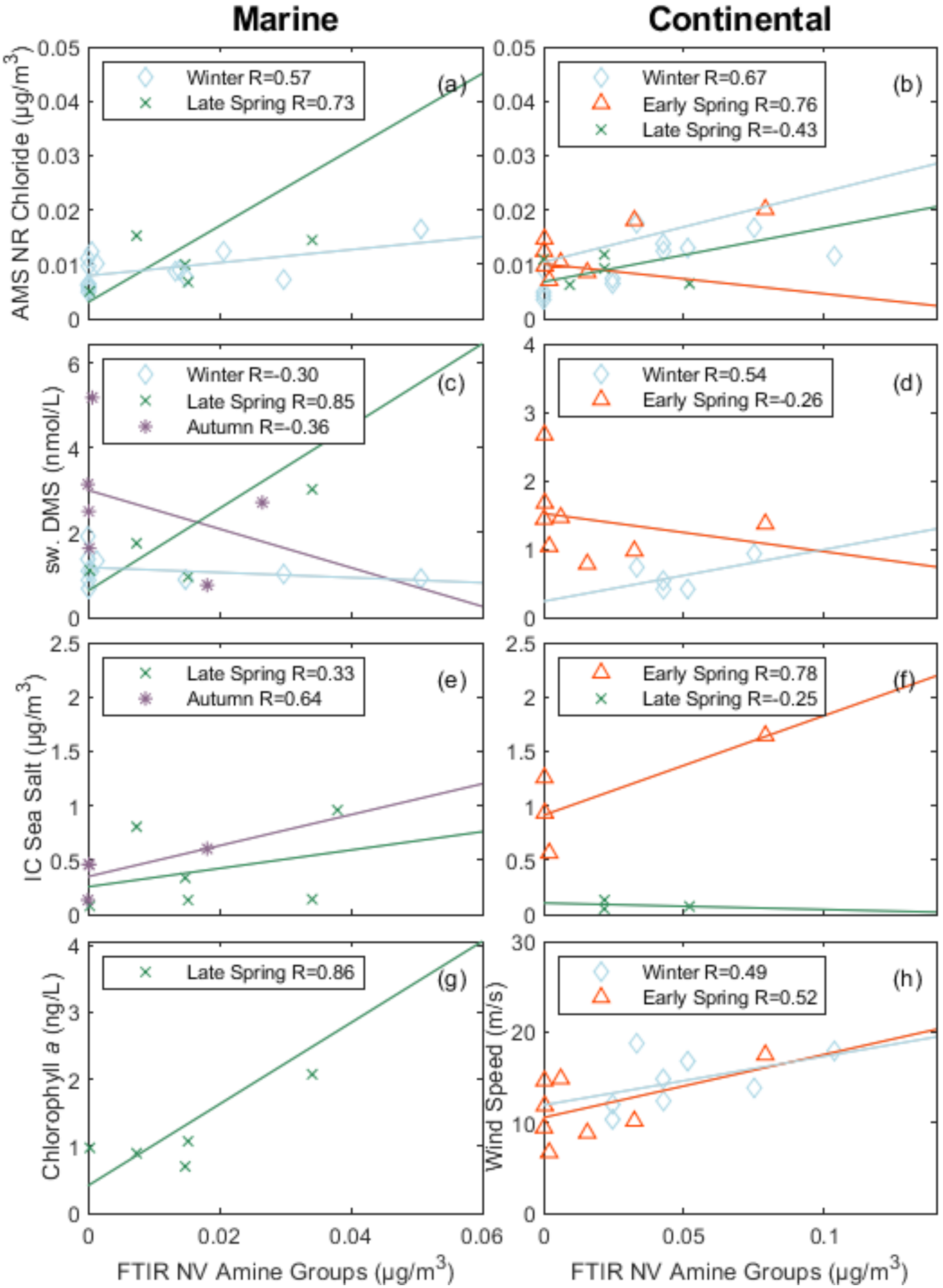
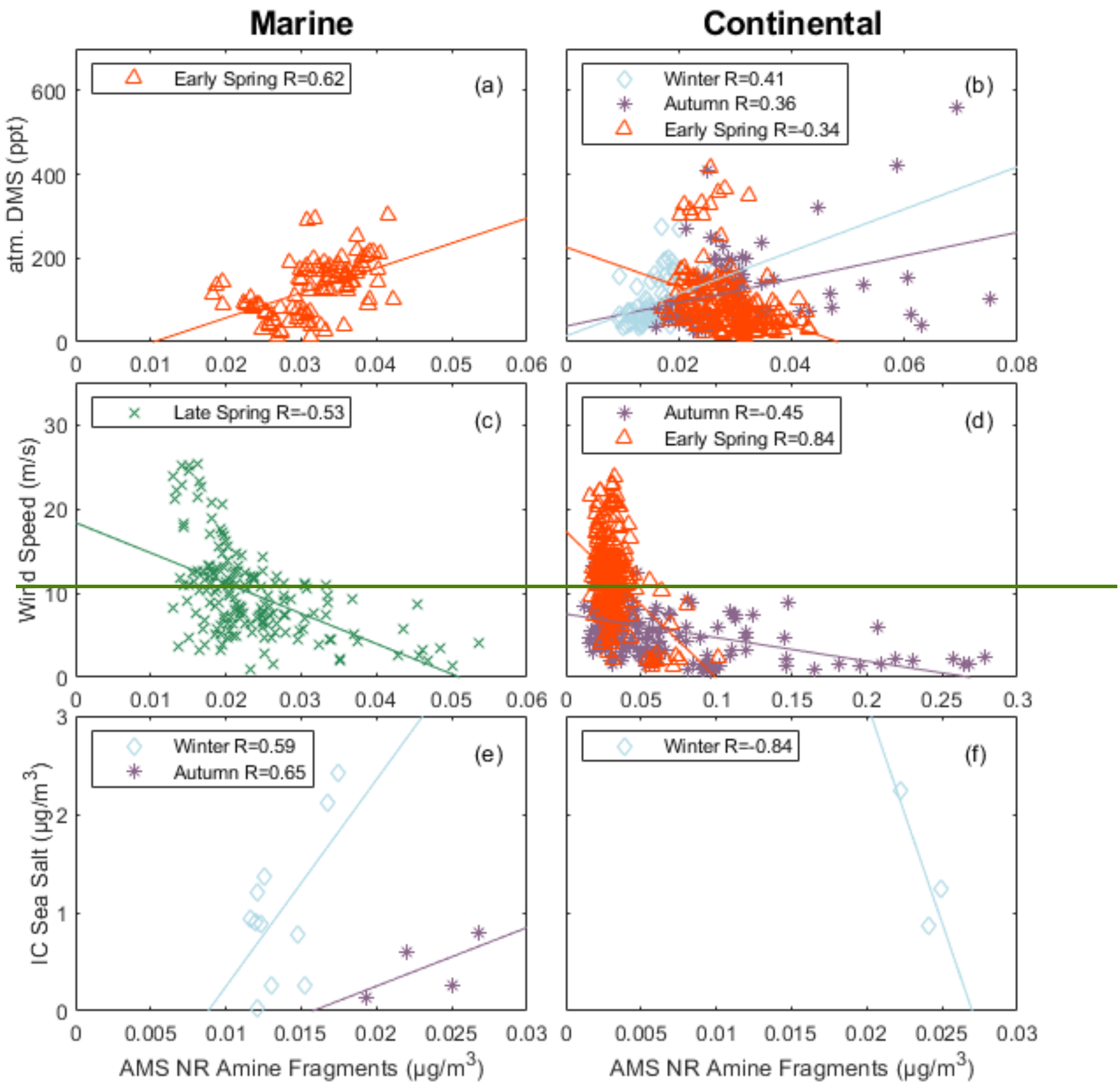


Figure 3: Scatter plot of marine tracers versus FTIR NV amine groups in particles with diameters <1 µm for marine periods (a,c,e,g) and continental periods (b,d,f,h). The panels include AMS NR chloride (a,b), seawater DMS (c,d), IC sea salt (e,f), chlorophyll *a* (g), wind speed (h). Markers represent each cruise- blue open diamond: Winter, green cross: Late Spring, purple asterisk: Autumn, red open triangle: Early Spring. ~~All correlations shown are statistically significant ($p < 0.05$) with the exception of AMS NR chloride.~~ The solid lines are the lines of best fit obtained using an ordinary least squares regression ~~and~~for $|R| \geq 0.25$ with the exception of chlorophyll *a* ~~two-tailed T test is used to estimate p-values~~which displays a fit only for $R \geq 0.25$.


Marine
Continental
atm. DMS (ppt)
600
400
200
0
Early Spring R=0.62
(a)
0
0.01
0.02
0.03
0.04
0.05
0.06
Winter R=0.41
Autumn R=0.36
Early Spring R=-0.34
(b)
0
0.02
0.04
0.06
0.08
Wind Speed (m/s)
30
20
10
0
Late Spring R=-0.53
(c)
0
0.01
0.02
0.03
0.04
0.05
0.06
Autumn R=-0.45
Early Spring R=0.84
(d)
0
0.05
0.1
0.15
0.2
0.25
0.3
IC Sea Salt (μg/m3)
3
2
1
0
Winter R=0.59
Autumn R=0.65
(e)
0
0.005
0.01
0.015
0.02
0.025
0.03
AMS NR Amine Fragments (μg/m3)
Winter R=-0.84
(f)
0
0.005
0.01
0.015
0.02
0.025
0.03
AMS NR Amine Fragments (μg/m3)

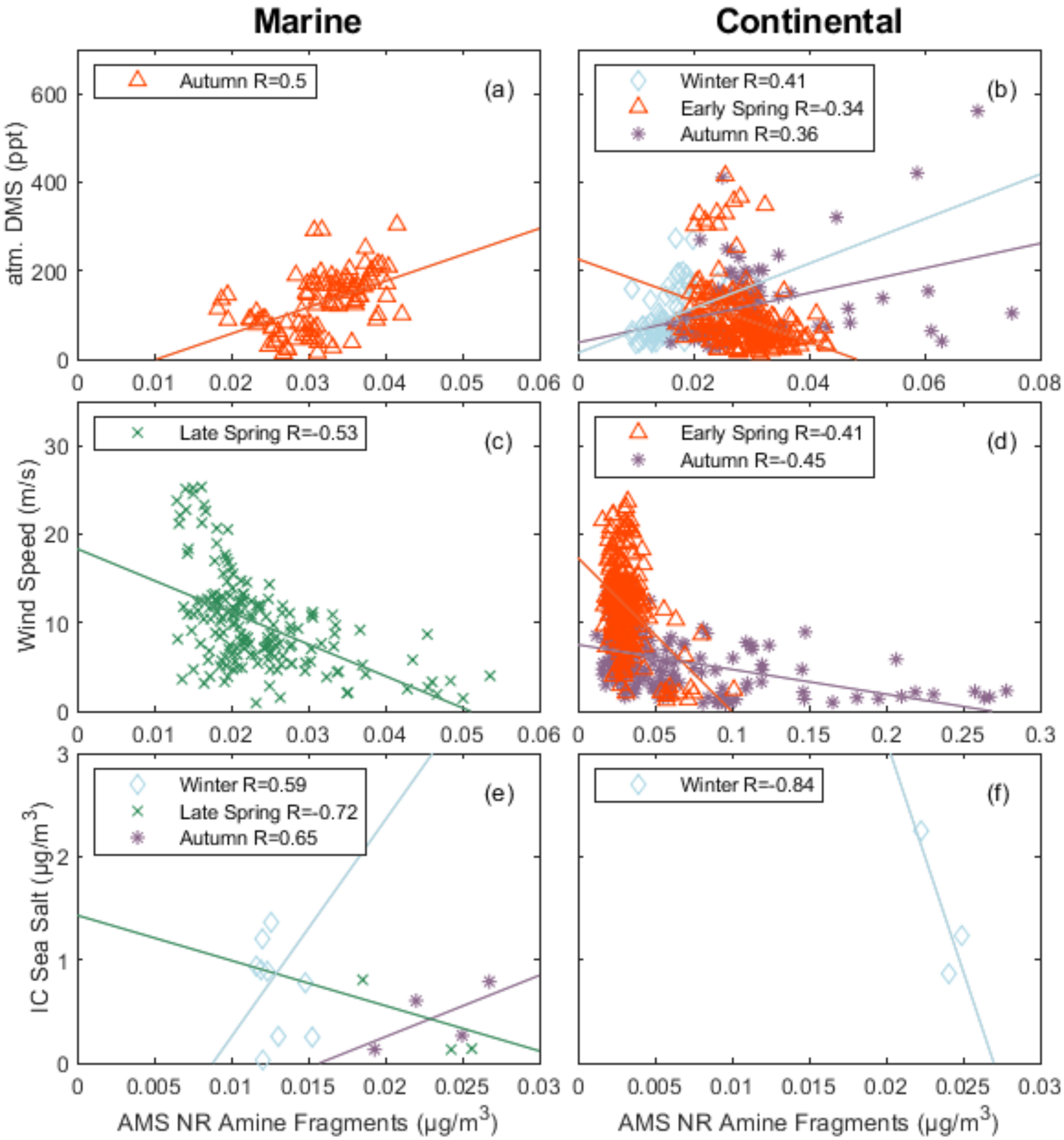
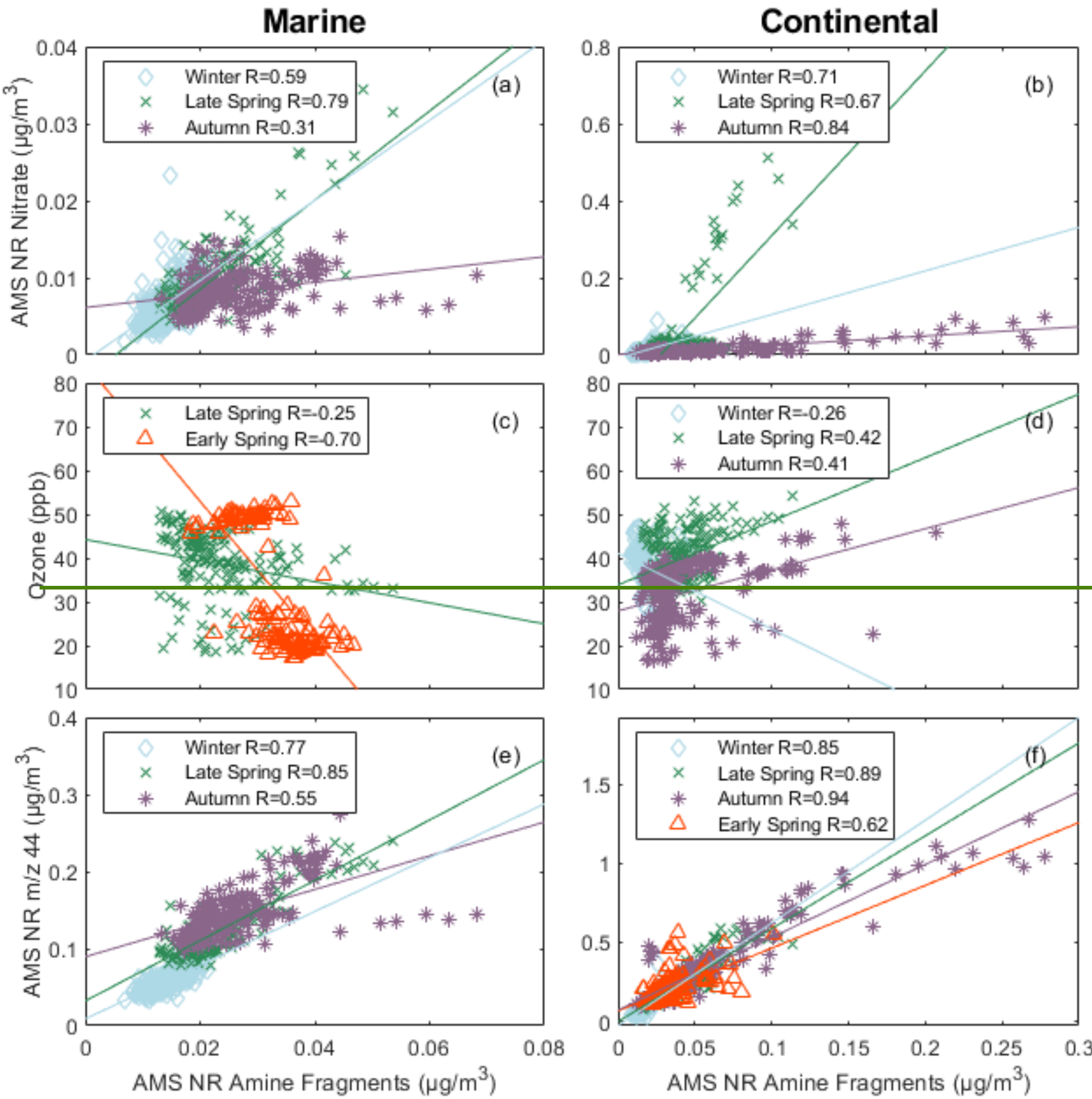


Figure 4: Scatter plot of marine tracers versus AMS NR amine fragments for marine periods (a,c,e) and continental periods (b,d,f). The panels include atmospheric DMS (a,b), wind speed (c,d), IC sea salt (e,f). Markers represent each cruise- blue open diamond: Winter, green cross: Late Spring, purple asterisk: Autumn, red open triangle: Early Spring. ~~All correlations shown are statistically significant ($p < 0.05$).~~ 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~~for R| ≥ 0.25.


Marine
Continental
AMS NR Nitrate (µg/m^3)
Ozone (ppb)
AMS NR m/z 44 (µg/m^3)
AMS NR Amine Fragments (µg/m^3)
AMS NR Amine Fragments (µg/m^3)
(a)
Winter R=0.59
Late Spring R=0.79
Autumn R=0.31
(b)
Winter R=0.71
Late Spring R=0.67
Autumn R=0.84
(c)
Late Spring R=-0.25
Early Spring R=-0.70
(d)
Winter R=-0.26
Late Spring R=0.42
Autumn R=0.41
(e)
Winter R=0.77
Late Spring R=0.85
Autumn R=0.55
(f)
Winter R=0.85
Late Spring R=0.89
Autumn R=0.94
Early Spring R=0.62
0
0.01
0.02
0.03
0.04
0
0.2
0.4
0.6
0.8
10
20
30
40
50
60
70
80
0
0.1
0.2
0.3
0.4
0
0.5
1
1.5
0
0.02
0.04
0.06
0.08
0
0.05
0.1
0.15
0.2
0.25
0.3

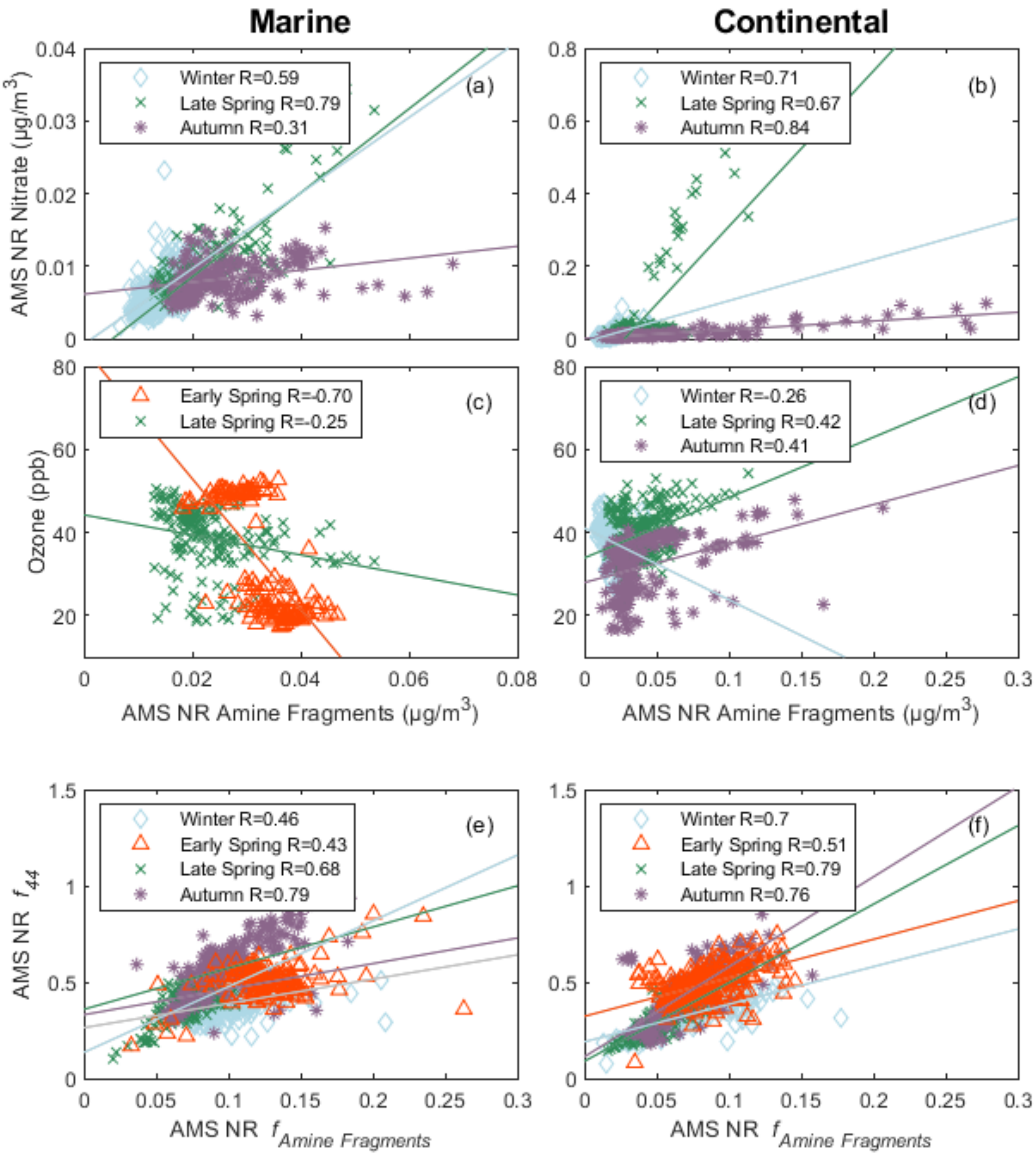
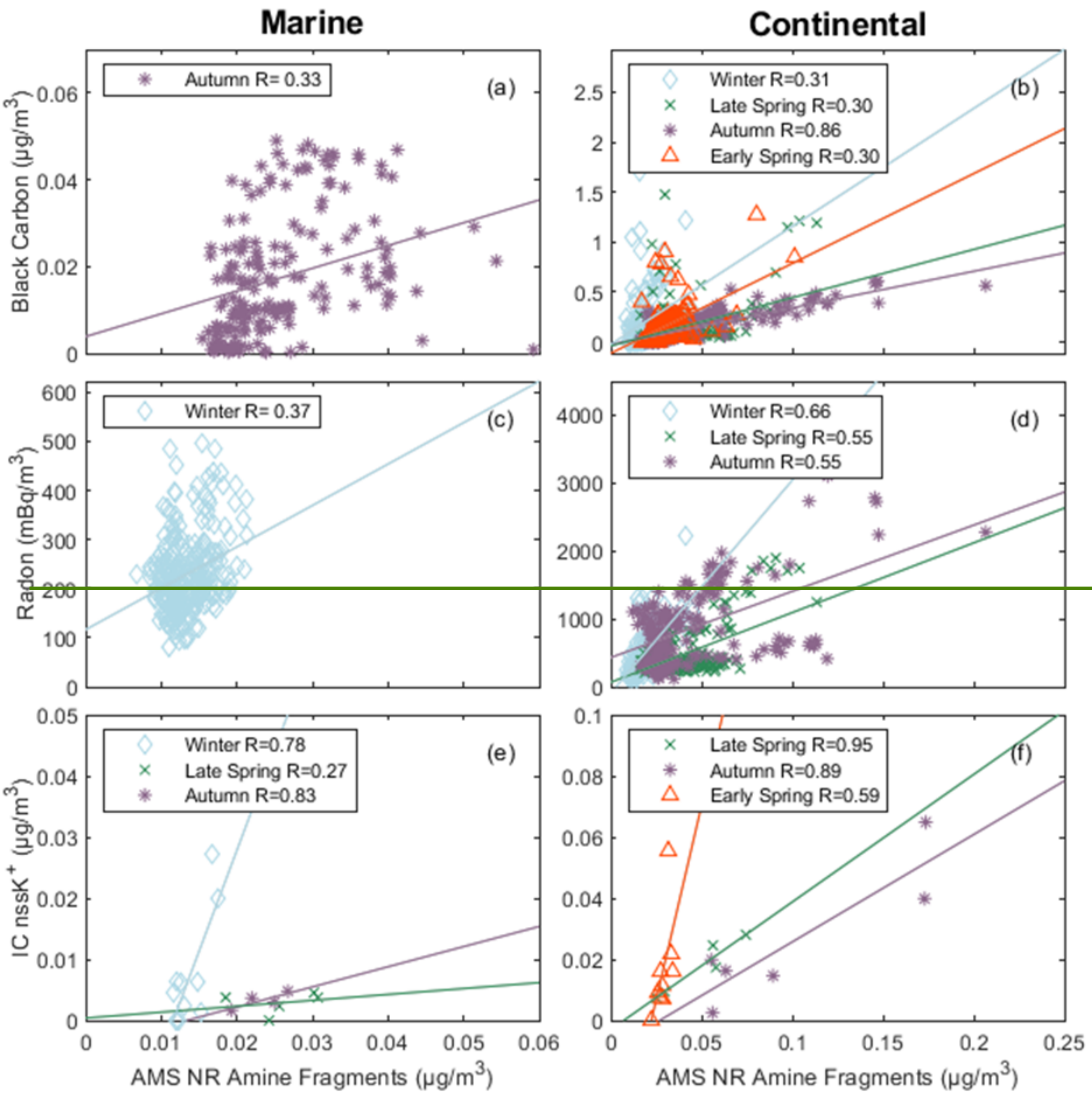


Figure 5: Scatter plot of secondary tracers versus AMS NR amine fragments for marine periods (a,c,e) and continental periods (b,d,f). The panels include submicron AMS NR nitrate (a,b), ozone (c,d), and AMS NR m/z 44 (e,f). Markers represent each cruise-blue open diamond: Winter, green cross: Late Spring, purple asterisk: Autumn, red open triangle: Early Spring. ~~All correlations shown are statistically significant (p < 0.05) except for AMS NR nitrate during the Late Spring continental period (p = 0.27).~~ 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~~for R| ≥ 0.25.


Marine
Continental
Black Carbon (μg/m^3)
Autumn R= 0.33
(a)
Winter R=0.31
Late Spring R=0.30
Autumn R=0.86
Early Spring R=0.30
(b)
Radon (mBq/m^3)
Winter R= 0.37
(c)
Winter R=0.66
Late Spring R=0.55
Autumn R=0.55
(d)
IC nssK$^+$ (μg/m^3)
Winter R=0.78
Late Spring R=0.27
Autumn R=0.83
(e)
Late Spring R=0.95
Autumn R=0.89
Early Spring R=0.59
(f)
AMS NR Amine Fragments (μg/m^3)
AMS NR Amine Fragments (μg/m^3)

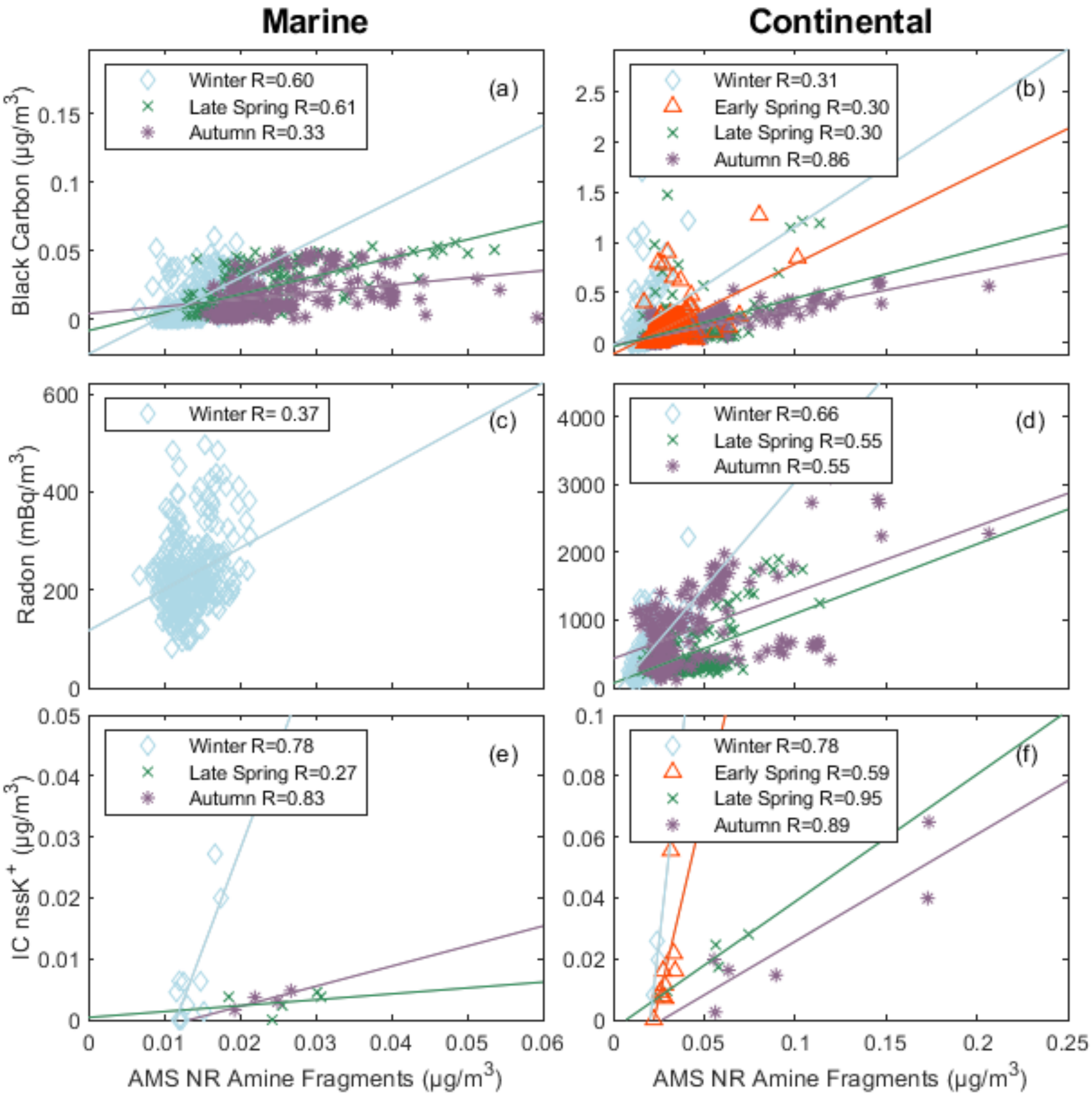
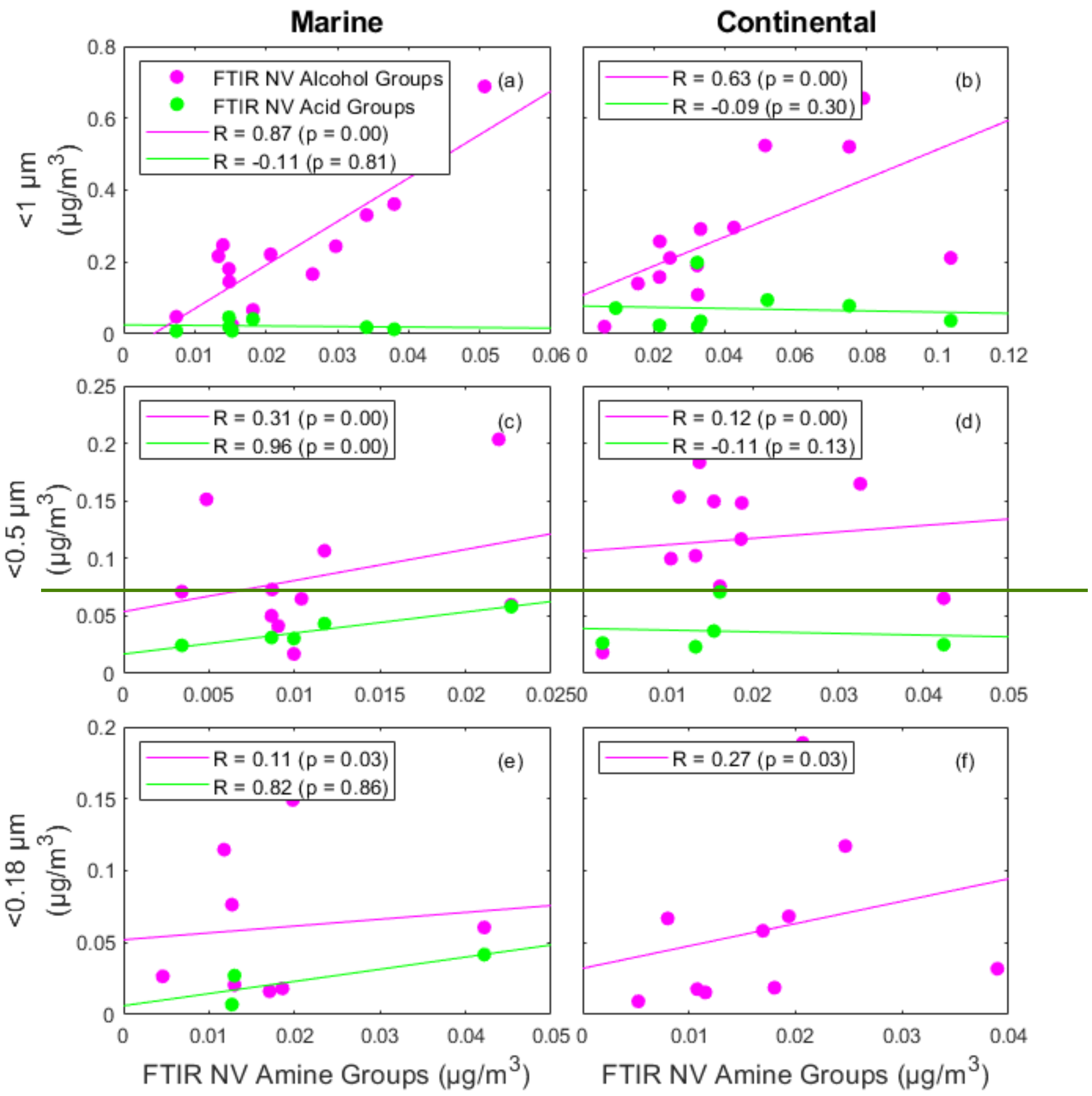


Figure 6: Scatter plot of non-marine tracers versus AMS NR amine fragments for marine periods (a,c,e) and continental periods (b,d,f). The panels include black carbon (a,b), radon (c,d), IC nssK$^+$ (e,f). Markers represent each cruise- blue open diamond: Winter, green cross: Late Spring, purple asterisk: Autumn, red open triangle: Early Spring. ~~All correlations shown are statistically significant ($p < 0.05$).~~ 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~~for R| ≥ 0.25.


Marine
Continental
<1 μm ($\mu g/m^3$)
<0.5 μm ($\mu g/m^3$)
<0.18 μm ($\mu g/m^3$)
FTIR NV Alcohol Groups
FTIR NV Acid Groups
R = 0.87 (p = 0.00)
R = -0.11 (p = 0.81)
(a)
R = 0.63 (p = 0.00)
R = -0.09 (p = 0.30)
(b)
R = 0.31 (p = 0.00)
R = 0.96 (p = 0.00)
(c)
R = 0.12 (p = 0.00)
R = -0.11 (p = 0.13)
(d)
R = 0.11 (p = 0.03)
R = 0.82 (p = 0.86)
(e)
R = 0.27 (p = 0.03)
(f)
0.8
0.6
0.4
0.2
0
0.25
0.2
0.15
0.1
0.05
0
0.2
0.15
0.1
0.05
0
0
0.01
0.02
0.03
0.04
0.05
0.06
0.02
0.04
0.06
0.08
0.1
0.12
0.005
0.01
0.015
0.02
0.025
0.01
0.02
0.03
0.04
0.05
0.01
0.02
0.03
0.04
0.05
0.01
0.02
0.03
0.04
FTIR NV Amine Groups ($\mu g/m^3$)
FTIR NV Amine Groups ($\mu g/m^3$)

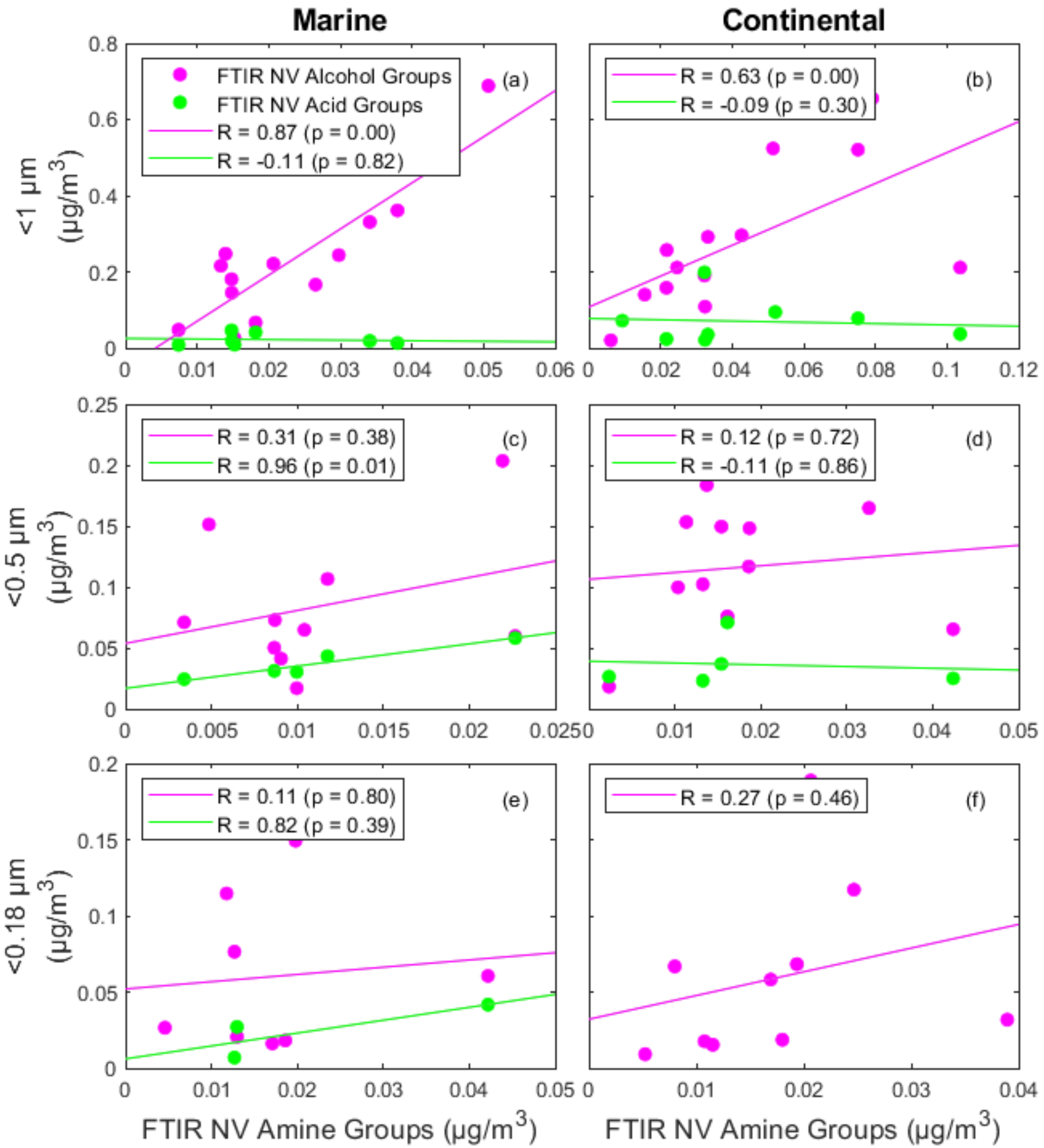
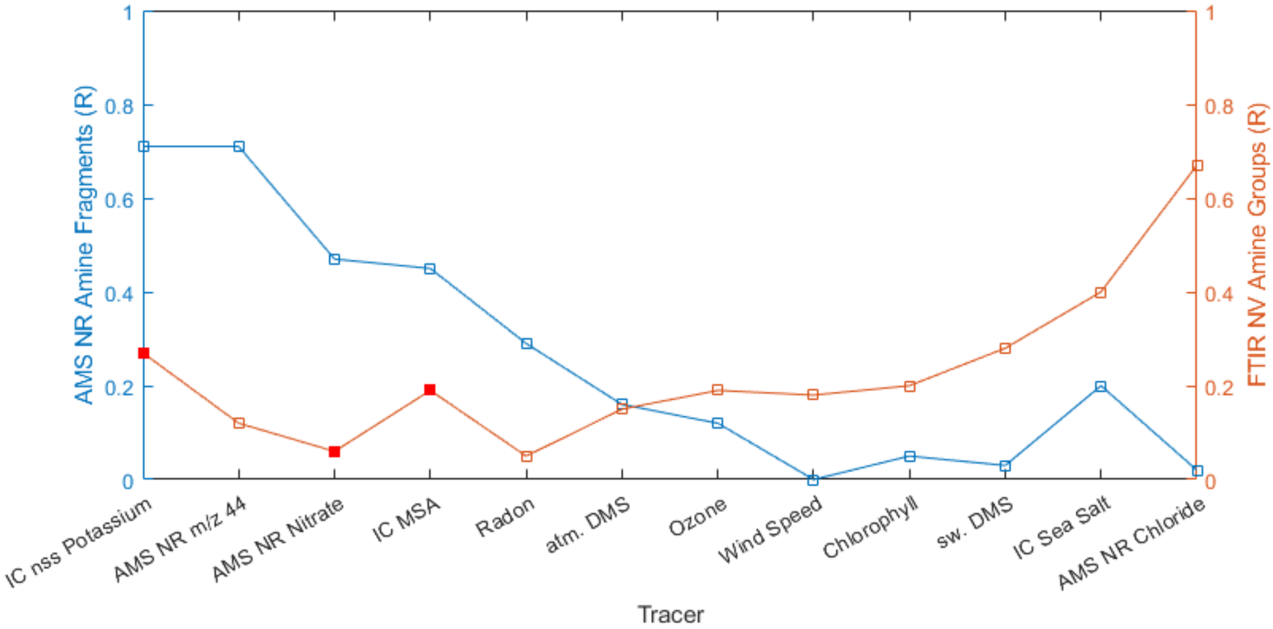


Figure 7: Scatter plot of FTIR primary (FTIR NV alcohol group: pink) and secondary (FTIR NV carboxylic acid group: green) tracers versus FTIR NV amine groups for marine filters (a,c,e) and continental filters (b,d,f) with functional group concentrations twice the standard deviation. The panels show the three filter size cut-offs: 1 µm (a,b), 0.5 µm (c,d), and 0.18 µm (e,f). The solid lines are the lines of best fit obtained using an ordinary least squares regression. ~~All correlations with FTIR NV alcohol groups and only~~

~~one correlation (<0.5 μm, marine) with FTIR NV acid groups were statistically significant (p < 0.05).~~ A two-tailed T test is used to estimate p-values.



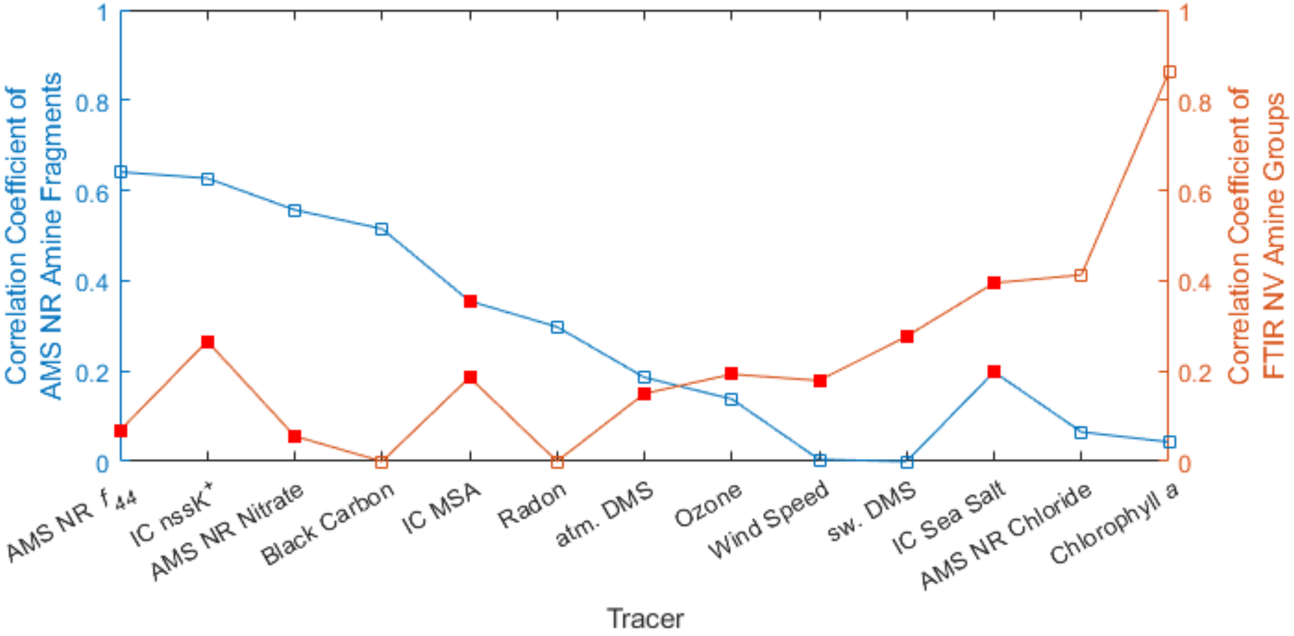
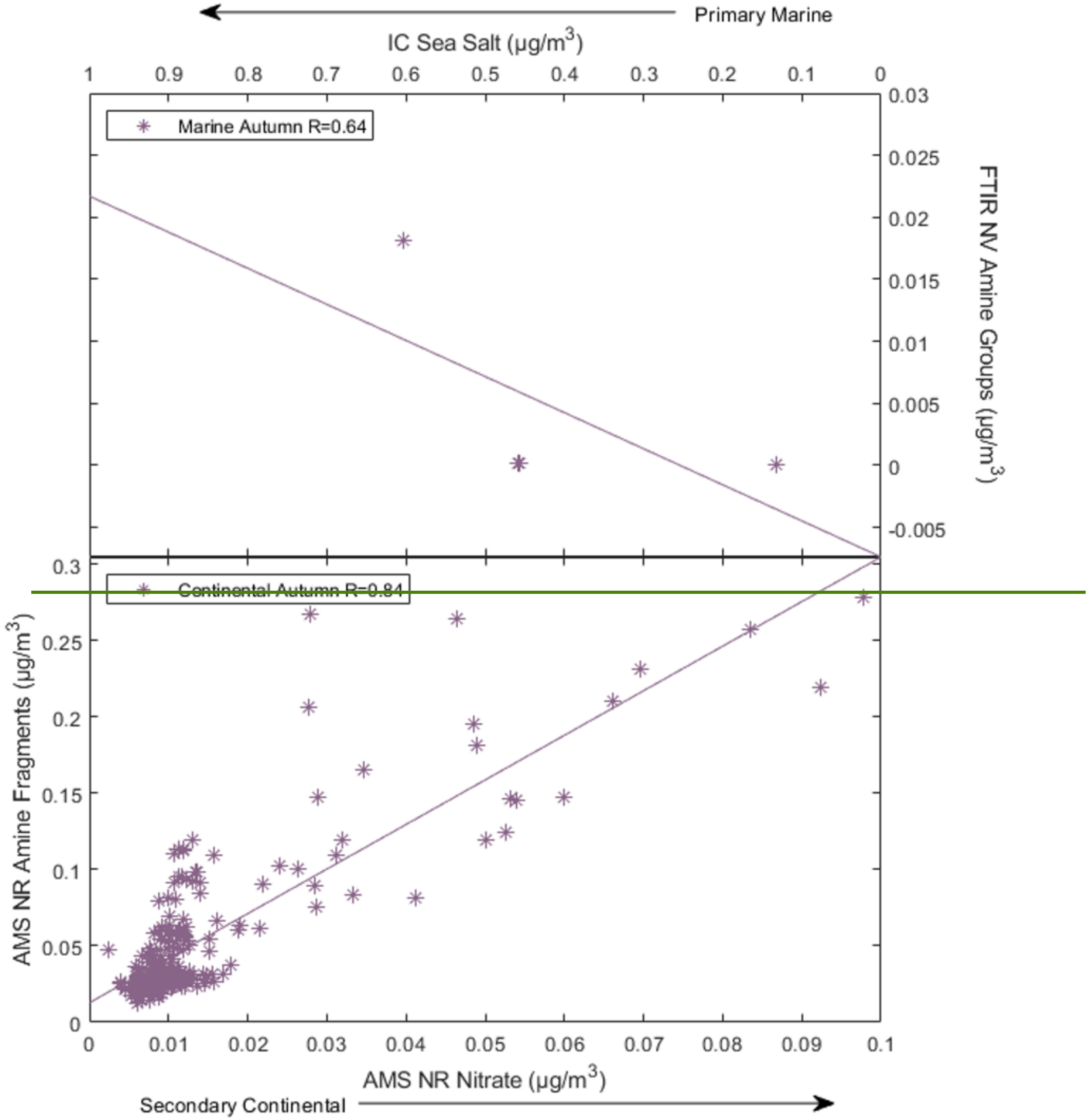


Figure 8: Plot of average Pearson correlation coefficients (R) of AMS NR amine fragments (blue) and FTIR NV amine groups in particles with diameters <1 μm (orange) with selected tracers~~.~~ for both marine and continental air masses. Negative correlations

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). 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*.


Primary Marine
IC Sea Salt (μg/m^3)
1 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0
Marine Autumn R=0.64
FTIR NV Amine Groups (μg/m^3)
0.03 0.025 0.02 0.015 0.01 0.005 0 -0.005
Continental Autumn R=0.84
AMS NR Amine Fragments (μg/m^3)
0.3 0.25 0.2 0.15 0.1 0.05 0
0 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.1
AMS NR Nitrate (μg/m^3)
Secondary Continental

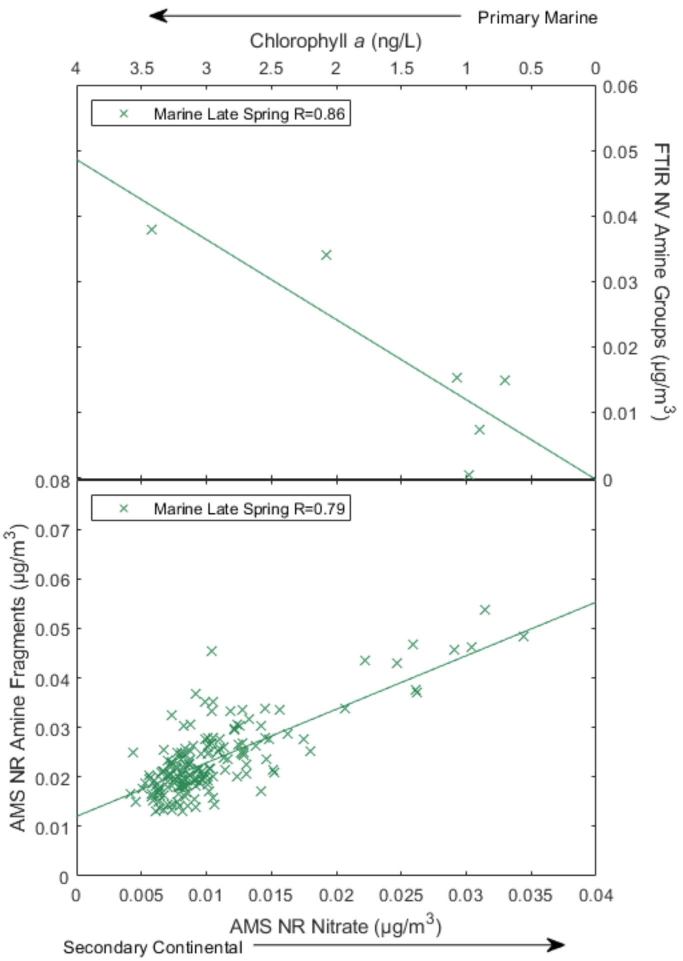


Figure 9: Scatter plot of (top) FTIR NV amine groups in particles with diameters <1 µm versus a tracer of a primary marine ~~tracer~~ 845 ~~(IC sea salt~~source (chlorophyll *a*) and (bottom) AMS NR amine fragments versus a secondary continental tracer (AMS NR nitrate) during the ~~Autumn season. Both correlations are statistically significant ($p < 0.05$).~~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.

S1. PMF Analysis of AMS NR HR-Org and AMS NR HR-SO_4

Positive matrix factorization of high resolution (HR) organic (Org) and sulfate (SO_4) AMS data was performed using the PMF Evaluation Tool, PET (Ulbrich et al., 2009). Ion fragments with low signal-to-noise (SNR) were downweighted ($0.2 < SNR < 2$) by a factor of 2 or removed ($SNR < 0.2$). Ion fragments associated with m/z 44 (CO_2^+, CO^+, H_2O^+, HO^+, O^+) were also downweighted by a factor of 2. No data smoothing or spike removal was applied to the matrices.

Fit quality (Q/Q_{exp}) and uncentered correlations were used to identify the best number of factors. Q/Q_{exp} decreases with an increasing number of factors as each factor introduces an additional degree of freedom. Solutions with numbers of factors that resolve Q/Q_{exp} near a value of 1 is ideal such that an increased distance of Q/Q_{exp} from 1 is used as one of the criteria for rejecting a solution.

The 1 to 7 factor solutions and criteria of PMF analysis are summarized in Tables S1-4. Both “OminusC” and “Diff” data types were used for PMF analysis. The Diff data type is obtained by fitting the raw difference spectra while the OminusC data type is obtained by subtracting the “Open” ion sticks from the “Closed” ion sticks after peak fitting. The HR Diff Sticks data type was chosen due to its low absolute residual when compared to the HR OminusC Sticks data type. The OminusC data type had also produced solutions with high Q/Q_{exp} values, indicating that the errors associated with the input data have been underestimated.

The highest number of factors with no temporal nor spectral correlations was the final number of factors chosen as a solution for each period. A 3-factor solution with a Q/Q_{exp} value of 0.73 was chosen for marine periods during Autumn as the 4-factor solution produced an additional factor with a very similar spectrum ($R > 0.8$) to a factor identified in both the 3- & 4-factor solutions. A 2-factor solution with a Q/Q_{exp} value of 2.41 was selected for continental periods during Autumn. A 2-factor solution with a Q/Q_{exp} value of 0.51 was selected for marine periods during Early Spring. A 2-factor solution with a Q/Q_{exp} value of 0.34 was selected for continental periods during Early Spring. Only 1 factor in the 3-factor solution made up less than 10% of the total mass for marine periods during Autumn. For all other time periods, each factor made up more than 10% of the total mass.

The 2-3 resulting factors included a combination of a low-volatility oxidized organic aerosol (LVOOA) factor, a Sulfate factor, and an Amine factor. The mass spectra and time series of each factor are available in Figures S1-S5, and Table S5 shows the average mass concentrations.

The mass spectrum of the LVOOA factor shows prominent peaks at m/z 28 (CO^+), m/z 43 ($C_2H_3O^+$) and m/z 44 (CO_2^+), which are attributed to oxidized organic fragments (CHO1 and CHOgt1 AMS families). A high ratio of m/z 44/43, also evident of SOA oxidation, is used to identify the LVOOA factor as well as comparisons to previously reported LVOOA factors (Crippa et al., 2013;Hu et al., 2013;Ng et al., 2010;Hayes et al., 2013). This factor was present throughout Autumn but absent during Early Spring when there was also less continental transport of AMS NR amine fragments. During continental periods in Autumn, this factor had the highest mass concentration but also the most variability (995 ± 1602 ng m^{-3}).

The Sulfate factor was found within all air masses and seasons and contained sulfate peaks at m/z 48 (SO^+), m/z 64 ($SO2^+$), m/z 80 (SO_3^+), m/z 81 (HSO_3^+), m/z 96 (SO_4^+), and m/z 98 ($H_2SO_4^+$) as well as organic peaks that are characteristic of particle aging at m/z 28 (CO^+) and m/z 44 (CO_2^+) in its mass spectrum. Larger organic peaks were present in continental air masses and during Autumn. Mass concentrations of the Sulfate factor were higher during continental periods than during marine periods and in Early Spring than in Autumn. The highest mass concentration of the Sulfate factor was observed during continental periods in Early Spring (609 ± 376 ng m^{-3}). With the exception of continental periods in Autumn, the Sulfate factor had the highest mass concentration among all the factors.

The final factor resolved during NAAMES was the Amine factor. This factor's mass spectrum consisted of both sulfate (m/z 48, m/z 64) and organic fragments, namely m/z 28 (CO^+) and m/z 44 (CO_2^+) which were of similar intensities. This factor is further characterized by a large, peak at m/z 73 ($C_3H_7NO^+$, $C_2H_5N_2O^+$), analogous to an oxidized amine ion fragment. This peak had the highest intensity for marine air masses in Autumn. Alternatively, oxidized organic peaks (m/z 28, m/z 44) had higher intensities during Early Spring. An unoxidized peak of a parent amine is seen at m/z 63 (C_4HN^+) for only marine air masses in Autumn (Qi et al., 2022). Interestingly, this factor was not observed during continental periods in Autumn. The highest mass concentration observed for the Amine factor was during continental periods in Early Spring (51 ± 90 ng m^{-3}). Overall, the Amine factor accounted for the lowest observed mass concentrations among all factors.

It is likely that a lack of organic mass during Early Spring resulted in no LVOOA factor and a smaller organic ion signal for the Sulfate factor for both marine and continental air masses. The Amine factor was very noisy, exhibiting high variability in mass concentration (±34-90 ng m^{-3}) that was nearly twice that of its mean (±17-51 ng m^{-3}). The noisiness of the time series of the Amine factor meant that it did not yield any useful source information for AMS NR amine fragments.

S2. AMS NR Single Particle Amine Fragments

AMS NR single particle amine fragments were estimated from the sum of 29 ions ($\Sigma CHN = CHN^+ + CH_3N^+ + CH_4N^+ + C_2H_3N^+ + C_2H_4N^+ + CHNO^+ + C_2H_5N^+ + C_2H_6N^+ + C_2H_4NO^+\ C_3H_8N^+ + C_2H_5NO^+ + C_3H_9N^+ + CH_4N^+ + C_3H_6NO^+ + C_4H_{10}N^+ + C_2H_3NO_2^+ + C_2H_5N_2O^+ + C_3H_7NO^+ + C_4H_{11}N^+ + C_4H_6NO^+ + C_5H_{10}N^+ + C_4H_7NO^+ + C_5H_{11}N^+ + C_4H_8NO^+ + C_5H_{12}N^+ + C_4H_8N_2O^+ + C_5H_{10}NO^+ + C_6H_{14}N^+ + C_6H_{15}N^+$) to approximate amine within ET single particle measurements. Both unoxidized and oxidized amine ion fragments and ion fragments of parent amines are included. The average mass concentration and standard deviation of AMS NR single particle amine fragments in both marine and continental air masses during Autumn and Early Spring are shown in Table S6. Mass concentrations of AMS NR single particle amine fragments during marine periods were equivalent for both seasons but higher in Autumn than in Early Spring for continental air masses. The average mass concentration was also higher during marine periods in Early Spring but lower during marine periods in Autumn, similar to the trend in mass concentrations seen for AMS NR amine fragments estimated by $C_xH_yN_z$ ion fragments.

Figure S6 displays the differences and similarities in the selection of AMS NR single particle amine fragments compared to the selection of AMS NR amine fragments. Both AMS NR single particle amine fragments and AMS NR amine fragments have little variability when regressed against FTIR NV amine groups in Early Spring and display a nearly vertical slope with p-values of 0.26 and 0.66, respectively. During Autumn, AMS NR single particle amine fragments and AMS NR amine fragments both display a strong correlation ($R = 0.87$, $p = 0.13$) to FTIR NV amine groups. While each of the four correlations is not statistically significant ($p > 0.05$), the overall p-value is lower when using AMS NR amine fragments rather than AMS NR single particle amine fragments. This shows that the sum of AMS NR amine fragments is less variable than the sum of AMS NR single particle amine fragments. Therefore, AMS NR amine fragments likely have more similarity to FTIR NV amine groups than the AMS NR single particle amine fragments, consistent with the expectation that the single particle signals are less accurate because of their lower m/z resolution and lower fragment specificity.

The ten AMS NR single particle amine fragments with the highest mass concentrations were CHN^+, CH_4N^+, $C_2H_3N^+$, $C_2H_4N^+$, $CHNO^+$, $C_2H_5N^+$, $C_2H_6N^+$, C_4HN^+, $C_2H_5N_2O^+$, $C_3H_7NO^+$. The presence of m/z 73 ($C_2H_5N_2O^+$, $C_3H_7NO^+$) in a mass spectrum is indicative of biomass burning, yet the concentration of these fragments remained largely constant across all periods. This either suggests that these fragments may come from a non-continental source or that a continental influence is present even for marine air masses. Figure S7 shows the variability of these low-molecular-weight ion fragments across marine and continental periods in Autumn and Early Spring. The average mass was highest during continental periods in Autumn for CHN^+, CH_4N^+, $C_2H_3N^+$, $C_2H_4N^+$, $CHNO^+$, $C_2H_5N^+$, $C_2H_6N^+$, $C_2H_5N_2O^+$, and $C_3H_7NO^+$. For C_4HN^+, the highest mass concentration was recorded during marine periods in Autumn. The average mass was lowest during marine periods in Autumn for CHN^+, $C_2H_4N^+$, $CHNO^+$, $C_2H_5N^+$, and $C_2H_6N^+$, during marine periods in Early Spring for $C_2H_3N^+$ and C_4HN^+, and during continental periods in Early Spring for CH_4N^+, $C_2H_5N_2O^+$, and $C_3H_7NO^+$.

The average fraction of total ion signal that each AMS NR single particle amine fragment contributes to its respective m/z is given in Table S7. While some AMS NR single particle fragments accounted for a greater portion of the average mass concentration, additional non-AMS NR single particle amine fragments that were fitted to the same m/z had dominated the signal, leading to a smaller fraction of the signal being apportioned to AMS NR single particle amine fragments. In Autumn, the fractions of AMS NR single particle amine fragments during marine periods were greater than during continental periods. In Early Spring, 8 of the 29 AMS NR single particle amine fragments accounted for a lower fraction of the ion signal in continental air masses than in marine air masses.

S3. ET Single Particle Analysis

The event trigger (ET) mode of the HR-ToF-AMS used three regions of interest (ROI) corresponding to a range of m/z to identify a single particle event and extract a mass spectrum. These regions were set to m/z 43 (ROI1) with an event trigger level of 3.5 ions/extraction, m/z

55–79 (ROI2) with an event trigger level of 8 ions/extraction, and m/z 48-150 (ROI3) with an event trigger level of 9 ions/extraction. ROI1 could be triggered by rBC- and organic-containing particles hydrocarbon while ROI2 and ROI3 was set to identify aerosol components including nitrate, sulfate and organic. The single particle measurements were initially pre-processed using Tofware version 2.5.10 to generate input data for Cluster Input Preparation Panel (CIPP) version 2.1b which is used to identify real particles. Cluster Analysis Panel (CAP) version 2.1a (developed by Alex Lee and Megan Willis) then uses a k-means clustering algorithm to compute an initial 10 clusters containing particles with similar spectra (Lee et al., 2019;Lee et al., 2015).

Temporal correlations and cosine similarity for different solutions of the single particle k-means clustering analysis were determined. The number of clusters for each solution was chosen using a threshold of 10% for the average fraction of total particles for each cluster. Tables S8-9 summarizes the 2 to 10 cluster solutions and criteria of single particle analysis. A 5-cluster solution was selected for Autumn and Early Spring marine periods, a 6-cluster solution was selected for the Autumn continental period, and a 7-cluster solution was selected for the Early Spring continental period.

Each cluster was categorized as oxidized organic aerosol (OOA), hydrocarbon-like organic aerosol (HOA), partially sulfate (PS), or mostly sulfate (MS) particle types. Clusters were considered organic (OOA, HOA) when 70% or more of the ion signal was organic (fORG > 70%). Organic clusters were further categorized as HOA when the highest ion signal was observed at m/z 43 ($C_3H_7^+$) and as OOA when highest ion signal was observed at m/z 44 (CO_2^+). The HOA cluster also required a larger fraction (>10%) of the ion signal from the sum of peaks in the alkane series $C_xH_{2y-1}^+$ and $C_xH_{2y+1}^+$, namely m/z 41 ($C_3H_5^+$), m/z 55 ($C_4H_7^+$), and m/z 57 ($C_4H_9^+$), than the OOA particle type (<10%). The peak at m/z 43 was not considered in this calculation since m/z 43 in OOA's mass spectrum is likely from $C_2H_3O^+$ rather than $C_3H_7^+$. Clusters were considered sulfate (PS, MS) when 40% or more of the ion signal was sulfate (fSO_4 > 40%). The MS particle type additionally required 65% of the ion signal to be sulfate ($fSO_4 \geq$ 65%). The mass spectra of PS particle type also met the criteria of attributing 30% or more of the ion signal to organics (fORG > 30%).

For each period, MS and PS clusters were further combined into a single MS cluster and a single PS cluster. One OOA cluster was resolved for all periods except during continental periods in Autumn when there were two OOA clusters (OOA-I, OOA-II). A single HOA cluster was resolved for continental air masses in Autumn. The mass spectra and time series of each particle type are found in Figures S8-12. The normalized UMR mass spectrum is used to find the signal from AMS NR single particle amine fragments by summing the product of the total ion signal fraction of each m/z in the spectrum and the average fraction of AMS NR single particle amine fragments attributed to the same m/z (estimated in Table S7). These results, along with a summary of the single particle measurements and particle types, are found in Table S10.

The mass spectra of the OOA particle type shows prominent peaks at m/z 29 (CHO^+), m/z 43 ($C_2H_3O^+$), and m/z 44 (CO_2^+). During continental Autumn periods, when two separate OOA clusters were resolved, the sum of these oxidized organic peaks was greater in the mass spectrum of OOA-II than that of OOA-I, indicating different magnitudes of particle aging. In Early Spring, OOA particles contained larger contributions from sulfate fragments identified from peaks at m/z 48 (SO^+), m/z 64 ($SO2^+$), m/z 80 (SO_3^+), m/z 81 (HSO_3^+), m/z 96 (SO_4^+), and m/z 98 ($H_2SO_4^+$). These sulfate peaks were most prominent in the mass spectrum of the OOA particle type during the continental periods in Early Spring. Additionally, the OOA particle type was more abundant relative to other particle types within continental air masses in Autumn. OOA particles made up a greater fraction of the total particle count during continental periods than during marine periods. The signal attributed to AMS NR single particle amine fragments for the OOA particle type was greater when air masses were marine. Specifically, the AMS NR single particle amine fragment fraction of the OOA mass spectrum's ion signal was 3.6% and 3.2% for marine periods and 2.3-2.8% and 2.8% for continental periods during Autumn and Early Spring, respectively. The OOA particle type had the largest contributions from AMS NR single particle amine fragments among all particle types except during continental periods in Autumn.

The HOA particle type contained substantial contributions from m/z 29 (CHO^+), m/z 43 (C_3H_7), and m/z 44 (CO_2^+) as well as m/z 55 ($C_4H_7^+$) and m/z 57 ($C_4H_9^+$) within its mass spectrum. Unlike the OOA particle type, the peaks at m/z 43 and m/z 55 are larger than the peak at m/z 44. The highest contribution from AMS NR single particle amine fragments observed in continental air masses during Autumn was for the HOA particle type with AMS NR single particle amine fragments accounting for 2.9% of the total ion signal. However, the HOA particle type made up only 15.3% of the total particle count during this period.

The MS particle type contained large peaks at m/z 48 (SO^+), m/z 64 ($SO2^+$), m/z 80 (SO_3^+), m/z 81 (HSO_3^+), m/z 96 (SO_4^+), and m/z 98 ($H_2SO_4^+$) within its mass spectra. This particle type had the smallest contributions from AMS NR single particle amine fragments (1.0-1.4% of the ion signal) but was the most abundant across all air masses except for continental Autumn air masses. The mass spectrum of the PS particle type contained both sulfate (m/z 48, m/z 64, m/z 80, m/z 81, and m/z 96) and organic (m/z 29, m/z 43, m/z 44) contributions. In Early Spring, the oxidized organic peaks were less significant in the MS mass spectra than in Autumn. The signal apportioned to AMS NR single particle amine fragments for the PS particle type ranged from 1.1-1.9% of the total ion signal.

Correlations of particle types with various tracers are shown in Tables S11-14. The organic (OOA & HOA) particle types had a moderate to strong correlation ($0.50 < R < 0.80$) to the LVOOA factor that was resolved in Autumn. Similarly, the sulfate (PS & MS) particle types had a weak to strong correlation ($0.68 < R < 0.86$) to the Sulfate factor for both air masses and seasons. This correlation was weakest for marine air masses in Early Spring and strongest for marine air masses in Autumn. No particle type had correlated with the Amine factor during any period.

Non-refractory AMS species used to identify sources of single particle clusters included AMS NR OM, AMS NR nitrate, AMS NR sulfate, AMS NR ammonium, and AMS NR chloride. Moderate correlations ($0.57 < R < 0.75$) of organic particle types and AMS NR OM were observed during Autumn. However, no correlation was found during Early Spring. The PS cluster resolved for marine air masses in Autumn is the only other particle type to correlate weakly ($R = 0.38$) to AMS NR OM during both seasons. Weak to moderate correlations ($0.38 < R < 0.69$) of the organic particle types to AMS NR nitrate were observed for all periods except during continental periods in Early Spring. The strongest correlation with AMS NR nitrate was with the HOA particle type, suggesting an anthropogenic source. A weak correlation was also observed for the MS particle type during continental periods in Early Spring. Weak to strong correlations ($0.28 < R < 0.85$) of the sulfate particle types to AMS NR sulfate were observed during both seasons and periods. This correlation was weakest during marine periods in Early Spring and strongest during continental periods in Autumn. Weak to moderate correlations ($0.32 < R < 0.64$) of all particle types and AMS NR ammonium were observed throughout different seasons and were largely inconsistent. No particle type had correlated with AMS NR chloride.

IC inorganic ions included SO_4^{2-}, NO_3^-, NH_4^+, Na^+, MSA, Mg^{2+} K^+, Cl^-, Ca^{2+}, Br^-. Correlations with IC inorganic ions were not significant for OOA particle types during marine periods in Early Spring and for MS particle types during continental periods in Autumn. Limited marine air mass sampling resulted in too few marine IC filters to retrieve correlation coefficients for marine air masses in Early Spring. Sulfate particle types had moderate to strong correlations with IC SO_4^{2-} ($0.54 < R < 0.88$) and IC NH_4^+ ($0.50 < R < 0.95$), and weak to strong correlations ($0.30 < R < 0.94$) with IC MSA when IC measurements were available. Weak to strong ($0.27 < R < 0.84$) correlations of IC NO_3^- and organic particle types were seen in Autumn. No correlations of any particle types with IC Br^- were observed.

Additional source associated tracers included atmospheric and seawater DMS, chlorophyll *a*, ozone, and radon. No positive correlations were observed for atmospheric DMS and any of the identified particle types. Positive correlations ($R = 0.38$-0.41) of seawater DMS and sulfate particle types were seen for marine air masses in Early Spring. Negative correlations ($-0.34 < R < -0.25$) of chlorophyll *a* and the PS particle type during Autumn and the OOA-II and MS particle types in continental air masses during Autumn were observed. The only positive correlation of chlorophyll *a* and a particle type was seen for the HOA particle type ($R = 0.29$). No particle type had correlated with chlorophyll *a* during Early Spring. A weak, positive correlation was observed for ozone and the OOA-I particle type during continental periods in Autumn and the OOA particle type in marine air masses during Early Spring. Alternatively, sulfate particle types in marine air masses in Autumn and continental air masses in Early Spring were shown to negatively correlate ($-0.54 < R < -0.45$) to ozone. Weak to moderate correlations ($0.32 < R < 0.68$) of radon and organic particle types during continental periods in Autumn and all particle types during marine periods in Early Spring were observed. However, the sulfate particle types had a negative correlation ($-0.37 < R < -0.27$) with radon within marine air masses in Autumn and continental air masses in Early Spring, indicating a local marine source.

Correlations of sea surface temperature (SST) did not display a consistent trend among particle types. Weak, positive correlations of photosynthetic activated radiation (PAR) and the HOA particle type ($R = 0.35$) and all particle types during marine periods in Early Spring ($0.29 < R < 0.39$) were found. Positive correlations ($0.31 < R < 0.49$) of sulfate particle types and relative humidity (RH) could indicate secondary organic aerosol formation in all periods except during marine periods in Early Spring. A weak, positive correlation ($0.26 < R < 0.29$) of wind speed and the sulfate particle types during continental Early Spring periods suggests a primary marine origin. Conversely, negative correlations are seen with the PS particle type during marine Early Spring periods, and the MS particle type during marine Autumn periods. No particle types had correlated with CCN number concentration but the PS particle type during marine periods in

Autumn weakly correlated to CCN/CN (R = 0.25). No positive correlations with atmospheric temperature were observed. Only weak, negative correlations (-0.38 < R < -0.27) were seen for the OOA-I and PS particle types during continental periods in Autumn and for the OOA particle type during marine periods in Early Spring.

S4. Linear Regressions and p-values for AMS NR Amine Fragments and FTIR NV Amine Groups

Pearson correlation (R) coefficients retrieved for AMS NR amine fragments and FTIR NV amine groups during all four seasons and both air mass types are available in Table 2 and 3, respectively. The corresponding p-values for correlation coefficients pertaining to AMS NR amine fragments are shown in Table S15. Table S16 contains the p-values of correlations with FTIR NV amine groups. Correlations with black carbon and IC inorganic ions (nssK^+ and MSA) were typically not statistically significant for both AMS NR amine fragments and FTIR NV amine groups. For FTIR NV amine groups, correlations with AMS NR chloride and AMS NR nitrate were also mostly not significant. Linear regressions for AMS NR amine fragments and numerous tracers are displayed in Table S17. Table S18 contains the linear regressions for FTIR NV amine groups.

S5. CCN Activity

The extent to which amine affects CCN activity is explored by determining particle hygroscopicity using SMPS and CCNC measurements made during the Autumn and Early Spring seasons. A thermodenuder Scanning Mobility Particle Sizer (SMPS) system was used to measure the number of particles with geometric mean diameters between ~0.02 and 0.5 µm. Unheated samples produced measurements with a time resolution of 2 minutes (Quinn et al., 2019). Measurements from the SMPS system and a Cloud Condensation Nuclei Counter (CCNC, DMT, Boulder, CO) measuring ambient CCN concentrations at 0.1% supersaturation were used to determine aerosol hygroscopicity. CCN measurements were taken every 10 seconds. Data from these two instruments were synchronized into 2-minute averaged data for further analysis.

The critical diameter is found by summing the number of particles from the bin with the largest diameter down to the bin with the diameter by which the following equation is satisfied:

1. $\frac{N_{CCN}}{N_{CN}} = 1$.

Hygroscopicity parameters (κ) are determined using SMPS and CCN counter data by the following equations:

2. $\kappa = \frac{4A^3}{27\, D_{crit}^3 \ln^2 Sc}$
3. $A = \frac{\sigma_{s/a} M_w}{RT\rho_w}$

where $\sigma_{s/a}$ is the surface tension of pure water (0.073 J m^{-2}), Sc is the ratio of supersaturation (for SS = 0.1%, $Sc = 1.01$), M_w is the molecular weight of water (18.016 g mol^{-1}), ρ_w is the density of water (1000 kg mol^{-1}), R is the universal gas constant (8.3145 J mol^{-1} K^{-1}), T is the ambient temperature (298.15 K) , and D_{crit} is the diameter by which 100% of particles have activated to CCN (Petters and Kreidenweis, 2007).

Measurements when CCN/CN >1 and when the CCN count was less than 100 cm^{-3} were excluded from the dataset. Table S19 contains a summary of the remaining measurements. The low duty cycle of ambient sampling coupled with low CCN concentrations resulted in only a finite number of κ estimates that limited further interpretation.

S6. Tracer and Amine Sources

Figure S13 displays the sources of tracers and amine in marine environments. Continental sources of gaseous amine and tracers such as nssK$^+$, black carbon, AMS NR nitrate, ozone, carboxylic acid, and radon include combustion (vehicular, industrial), agriculture, and biomass burning. Marine sources of amine in primary and secondary aerosols and tracers such as AMS NR chloride, IC sea salt, chlorophyll *a*, FTIR NV alcohol groups, IC MSA, as well as atmospheric and seawater DMS are linked to biological (microbial decomposition) and mechanical (wave breaking, bubble bursting) processes.

S7. AMS Peak Fittings

Figure S14 displays representative peak fittings of $C_xH_yN_z$ ion fragments at m/z with dominant signals.

Table S1**.** Summary of solutions and criteria used for PMF analysis of AMS NR HR-Org and AMS NR HR-SO_4 for marine air masses in Autumn. Criteria that are not applicable for one factor are indicated by N/A. Paired clusters that do not have uncentered correlation coefficients (UC) higher than 0.8 are indicated by None.

Criteria	Factor number (p)	1	2	3	4	5	6	7
Diff	Q/Q_{exp}	1.00	0.79	0.73	0.71	0.69	0.66	0.65
	Absolute residual	40.0	19.8	19.2	14.3	12.1	12.6	13.3
	Temporal correlation factors strength ($R > 0.8$)	N/A	None	None	None	None	None	None
	Similarity of factor spectra ($R > 0.8$)	N/A	None	None	2 pairs	3 pairs	2 pairs	5 pairs
	Factors with less than 10% total mass	None	None	1 factor	1 factor	2 factors	3 factors	5 factors
OminusC	Q/Q_{exp}	2.39	2.15	2.12	2.11	2.11	2.09	2.09
	Absolute residual	46.0	28.0	33.6	32.8	29.5	28.6	28.0
	Temporal correlation factors strength ($R >0.8$)	N/A	None	None	None	None	1 pair	3 pairs
	Similarity of factor spectra ($R > 0.8$)	N/A	None	1 pair	1 pair	3 pairs	3 pairs	2 pairs
	Factors with less than 10% total mass	None	None	None	1 factor	1 factor	2 factors	2 factors

Table S2**.** Summary of solutions and criteria used for PMF analysis of AMS NR HR-Org and AMS NR HR-SO_4 for continental air masses in Autumn. Criteria that are not applicable for one factor are indicated by N/A. Paired clusters that do not have uncentered correlation coefficients (UC) higher than 0.8 are indicated by None.

Criteria	Factor number (p)	1	2	3	4	5	6	7
Diff	Q/Q_{exp}	2.74	2.14	2.05	1.93	1.88	1.82	1.79
	Absolute residual	30.8	16.9	14.5	12.7	8.92	10.3	8.67
	Temporal correlation factors strength ($R > 0.8$)	N/A	None	None	None	None	None	None
	Similarity of factor spectra ($R > 0.8$)	N/A	None	1 pair	1 pair	2 pairs	6 pairs	5 pairs
	Factors with less than 10% total mass	None	None	None	1 factor	1 factor	3 factors	3 factors
OminusC	Q/Q_{exp}	3.37	2.82	2.71	2.58	2.55	2.53	2.51
	Absolute residual	81.9	97.9	70.6	71.4	69.8	63.9	64.0
	Temporal correlation factors strength ($R >0.8$)	N/A	None	None	None	None	2 pairs	1 pair
	Similarity of factor spectra ($R > 0.8$)	N/A	None	None	1 pair	1 pair	1 pair	3 pairs
	Factors with less than 10% total mass	None	None	1 factor	2 factors	3 factors	4 factors	5 factors

Table S3**.** Summary of solutions and criteria used for PMF analysis of AMS NR HR-Org and AMS NR HR-SO_4 for marine air masses in Early Spring. Criteria that are not applicable for one factor are indicated by N/A. Paired clusters that do not have uncentered correlation coefficients (UC) higher than 0.8 are indicated by None.

Criteria	Factor number (p)	1	2	3	4	5	6	7
Diff	Q/Q_{exp}	0.55	0.51	0.48	0.48	0.45	0.43	0.41
	Absolute residual	30.2	28.4	23.3	22.7	20.9	19.5	19.4
	Temporal correlation factors strength (R > 0.8)	N/A	None	None	None	None	None	None
	Similarity of factor spectra (R > 0.8)	N/A	None	1 pair	3 pairs	None	None	15 pairs
	Factors with less than 10% total mass	None	1 factor	1 factor	2 factors	2 factors	3 factors	4 factors
OminusC	Q/Q_{exp}	0.88	0.88	0.87	0.86	0.86	0.85	0.85
	Absolute residual	34.6	28.7	29.0	31.3	31.0	31.8	32.3
	Temporal correlation factors strength (R >0.8)	N/A	None	None	1 pair	None	None	None
	Similarity of factor spectra (R > 0.8)	N/A	None	1 pair	1 pair	1 pair	1 pair	2 pairs
	Factors with less than 10% total mass	None	None	None	None	1 factor	2 factors	2 factors

Table S4. Summary of solutions and criteria used for PMF analysis of AMS NR HR-Org and AMS NR HR-SO_4 for continental air masses in Early Spring. Criteria that are not applicable for one factor are indicated by N/A. Paired clusters that do not have uncentered correlation coefficients (UC) higher than 0.8 are indicated by None.

Criteria	Factor number (p)	1	2	3	4	5	6	7
Diff	Q/Q_{exp}	0.38	0.34	0.31	0.29	0.28	0.28	0.26
	Absolute residual	29.8	28.3	8.45	8.40	8.38	7.71	7.64
	Temporal correlation factors strength (R > 0.8)	N/A	None	None	None	None	None	None
	Similarity of factor spectra (R > 0.8)	N/A	None	1 pair	None	None	None	1 pair
	Factors with less than 10% total mass	None	1 factor	1 factor	2 factors	3 factors	3 factors	4 factors
OminusC	Q/Q_{exp}	0.88	0.88	0.87	0.86	0.86	0.85	0.85
	Absolute residual	30.3	11.8	9.55	10.4	10.4	10.5	10.8
	Temporal correlation factors strength (R >0.8)	N/A	None	None	None	None	None	None
	Similarity of factor spectra (R > 0.8)	N/A	None	1 pair	1 pair	1 pair	2 pairs	4 pairs
	Factors with less than 10% total mass	None	None	None	None	None	1 factor	2 factors

Table S5. Mean mass concentrations and standard deviations (ng m^{-3}) of each PMF factor resolved for marine and continental air masses in Autumn and Early Spring.

Factor Air Mass/Season	LVOOA	Sulfate	Amine
Marine Autumn	184 ± 216	281 ± 224	17 ± 34
Marine Early Spring	--	493 ± 314	39 ± 70
Continental Autumn	995 ± 1602	590 ± 400	--
Continental Early Spring	--	609 ± 376	51 ± 90

Table S6. Mean mass concentrations and standard deviations (µg m^{-3}) of AMS NR single particle amine fragments for marine and continental air masses in Autumn and Early Spring.

		Autumn		Early Spring	
m/z	Ion Fragment	Marine	Continental	Marine	Continental
27	CHN^+	0.0017 ± 0.0006	0.0045 ± 0.0041	0.0022 ± 0.0011	0.0021 ± 0.0006
29	CH_3N^+	0.0002 ± 0.0004	0.0001 ± 0.0001	0.0004 ± 0.0004	0.0002 ± 0.0001
30	CH_4N^+	0.0015 ± 0.0004	0.0024 ± 0.0022	0.0011 ± 0.0005	0.0008 ± 0.0003
41	$C_2H_3N^+$	0.0011 ± 0.0005	0.0029 ± 0.0027	0.0010 ± 0.0004	0.0012 ± 0.0004
42	$C_2H_4N^+$	0.0008 ± 0.0006	0.0016 ± 0.0014	0.0010 ± 0.0003	0.0009 ± 0.0002
43	$CHNO^+$	0.0012 ± 0.0004	0.0029 ± 0.0023	0.0014 ± 0.0009	0.0013 ± 0.0004
	$C_2H_5N^+$	0.0007 ± 0.0004	0.0011 ± 0.0008	0.0008 ± 0.0002	0.0008 ± 0.0002
44	$C_2H_6N^+$	0.0005 ± 0.0002	0.0012 ± 0.0011	0.0010 ± 0.0005	0.0003 ± 0.0011
58	$C_2H_4NO^+$	0.0005 ± 0.0001	0.0007 ± 0.0003	0.0006 ± 0.0003	0.0004 ± 0.0001
	$C_3H_8N^+$	0.0002 ± 0.0001	0.0004 ± 0.0003	0.0004 ± 0.0002	0.0003 ± 0.0001
59	$C_2H_5NO^+$	0.0004 ± 0.0001	0.0006 ± 0.0004	0.0004 ± 0.0002	0.0003 ± 0.0001
	$C_3H_9N^+$	0.0001 ± 0.0001	0.0001 ± 0.0001	0.0001 ± 0.0002	0.0001 ± 0.0001
63	C_4HN^+	0.0031 ± 0.0003	0.0030 ± 0.0005	0.0010 ± 0.0004	0.0013 ± 0.0003
72	$C_3H_6NO^+$	0.0002 ± 0.0001	0.0004 ± 0.0002	0.0005 ± 0.0006	0.0002 ± 0.0001
	$C_4H_{10}N^+$	0.0001 ± 0.0001	0.0001 ± 0.0001	0.0002 ± 0.0001	0.0001 ± 0.0001
73	$C_2H_3NO_2^+$	0.0003 ± 0.0001	0.0007 ± 0.0005	0.0003 ± 0.0001	0.0002 ± 0.0001
	$C_2H_5N_2O^+$	0.0022 ± 0.0008	0.0024 ± 0.0009	0.0021 ± 0.0009	0.0016 ± 0.0006
	$C_3H_7NO^+$	0.0019 ± 0.0005	0.0019 ± 0.0003	0.0019 ± 0.0010	0.0016 ± 0.0005
	$C_4H_{11}N^+$	0.0002 ± 0.0001	0.0002 ± 0.0001	0.0002 ± 0.0001	0.0001 ± 0.0001
84	$C_4H_6NO^+$	0.0001 ± 0.0001	0.0003 ± 0.0003	0.0001 ± 0.0001	0.0002 ± 0.0001
	$C_5H_{10}N^+$	0.0001 ± 0.0001	0.0002 ± 0.0002	0.0003 ± 0.0003	0.0002 ± 0.0001
85	$C_4H_7NO^+$	0.0003 ± 0.0003	0.0003 ± 0.0002	0.0002 ± 0.0001	0.0002 ± 0.0001
	$C_5H_{11}N^+$	0.0002 ± 0.0001	0.0003 ± 0.0005	0.0003 ± 0.0001	0.0003 ± 0.0001
86	$C_4H_8NO^+$	0.0001 ± 0.0001	0.0001 ± 0.0001	0.0001 ± 0.0001	0.0001 ± 0.0001
	$C_5H_{12}N^+$	0.0001 ± 0.0001	0.0001 ± 0.0001	0.0001 ± 0.0001	0.0001 ± 0.0001
100	$C_4H_8N_2O^+$	0.0001 ± 0.0001	0.0001 ± 0.0001	0.0001 ± 0.0001	0.0001 ± 0.0001
	$C_5H_{10}NO^+$	0.0001 ± 0.0001	0.0001 ± 0.0001	0.0001 ± 0.0001	0.0001 ± 0.0001
	$C_6H_{14}N^+$	0.0001 ± 0.0001	0.0001 ± 0.0001	0.0001 ± 0.0001	0.0001 ± 0.0001
101	$C_6H_{15}N^+$	0.0001 ± 0.0001	0.0001 ± 0.0001	0.0001 ± 0.0001	0.0001 ± 0.0001
Total	----	0.0180 ± 0.0056	0.0288 ± 0.0174	0.0180 ± 0.0040	0.0155± 0.0018

Table S7. Mean ion signal fractions and standard deviations of AMS NR single particle amine fragments for marine and continental air masses in Autumn and Early Spring.

		Autumn		Early Spring	
m/z	Ion Fragment	Marine	Continental	Marine	Continental
27	CHN^+	0.211 ± 0.064	0.160 ± 0.064	0.318 ± 0.156	0.238 ± 0.062
29	CH_3N^+	0.001 ± 0.001[a]	0.001 ± 0.001	0.001 ± 0.001	0.001 ± 0.001
30	CH_4N^+	0.099 ± 0.088	0.074 ± 0.032	0.084 ± 0.042	0.039 ± 0.008
41	$C_2H_3N^+$	0.123 ± 0.033	0.097 ± 0.036	0.194 ± 0.076	0.196 ± 0.061
42	$C_2H_4N^+$	0.104 ± 0.049	0.076 ± 0.040	0.168 ± 0.047	0.112 ± 0.044
43	$CHNO^+$ $C_2H_5N^+$	0.090 ± 0.023 0.052 ± 0.020	0.062 ± 0.027 0.029 ± 0.017	0.139 ± 0.042 0.108 ± 0.028	0.106 ± 0.053 0.057 ± 0.021
44	$C_2H_6N^+$	0.004 ± 0.003	0.003 ± 0.001	0.008 ± 0.006	0.004 ± 0.001
58	$C_2H_4NO^+$ $C_3H_8N^+$	0.204 ± 0.042 0.110 ± 0.037	0.149 ± 0.057 0.072 ± 0.031	0.199 ± 0.041 0.136 ± 0.047	0.174 ± 0.037 0.107 ± 0.037
59	$C_2H_5NO^+$ $C_3H_9N^+$	0.126 ± 0.020 0.051 ± 0.018	0.112 ± 0.035 0.040 ± 0.018	0.118 ± 0.062 0.064 ± 0.030	0.109 ± 0.045 0.060 ± 0.019
63	C_4HN^+	0.405 ± 0.030	0.321 ± 0.097	0.217 ± 0.071	0.334 ± 0.067
72	$C_3H_6NO^+$ $C_4H_{10}N^+$	0.083 ± 0.020 0.040 ± 0.010	0.081 ± 0.019 0.034 ± 0.015	0.149 ± 0.129 0.078 ± 0.030	0.102 ± 0.038 0.062 ± 0.019
73	$C_2H_3NO_2^+$ $C_2H_5N_2O^+$ $C_3H_7NO^+$ $C_4H_{11}N^+$	0.050 ± 0.018 0.186 ± 0.042 0.160 ± 0.030 0.042 ± 0.022	0.066 ± 0.028 0.173 ± 0.051 0.141 ± 0.041 0.032 ± 0.017	0.171 ± 0.373 0.157 ± 0.049 0.152 ± 0.066 0.046 ± 0.029	0.050 ± 0.024 0.176 ± 0.063 0.164 ± 0.053 0.038 ± 0.013
84	$C_4H_6NO^+$ $C_5H_{10}N^+$	0.101 ± 0.022 0.096 ± 0.021	0.086 ± 0.025 0.080 ± 0.040	0.079 ± 0.033 0.132 ± 0.106	0.083 ± 0.023 0.116 ± 0.057
85	$C_4H_7NO^+$ $C_5H_{11}N^+$	0.146 ± 0.056 0.086 ±0.022	0.092 ± 0.050 0.059 ± 0.029	0.108 ± 0.043 0.118 ± 0.037	0.119 ± 0.045 0.099 ± 0.031
86	$C_4H_8NO^+$ $C_5H_{12}N^+$	0.105 ± 0.155 0.088 ± 0.033	0.061 ± 0.021 0.054 ± 0.026	0.108 ± 0.034 0.084 ± 0.029	0.111 ± 0.036 0.084 ± 0.024
100	$C_4H_8N_2O^+$ $C_5H_{10}NO^+$ $C_6H_{14}N^+$	0.075 ± 0.022 0.038 ± 0.016 0.061 ± 0.023	0.037 ± 0.019 0.034 ± 0.030 0.046 ± 0.027	0.032 ± 0.016 0.035 ± 0.023 0.082 ± 0.044	0.038 ± 0.015 0.034 ± 0.025 0.067 ± 0.063
101	$C_6H_{15}N^+$	0.066 ± 0.024	0.027 ± 0.021	0.092 ± 0.027	0.058 ± 0.026

Table S8. Summary of criteria used for cluster analysis of single particle ET measurements taken in Autumn. Paired clusters that do not have uncentered correlation coefficients (UC) higher than 0.8 are indicated by None.

Cluster number (p) Criteria		2	3	4	5	6	7	8	9	10
Marine	Temporal correlation clusters strength (R > 0.8)	None	1 pair	2 pairs	4 pairs	7 pairs	11 pairs	10 pairs	12 pairs	16 pairs
	Similarity of cluster spectra (R > 0.8)	None	1 pair	2 pairs	4 pairs	7 pairs	11 pairs	10 pairs	12 pairs	15 pairs
	Clusters with less than 10% total count	None	None	None	None	2 clusters	3 clusters	4 clusters	4 clusters	6 clusters
Continental	Temporal correlation clusters strength (R > 0.8)	None	1 pair	1 pair	3 pairs	5 pairs	8 pairs	9 pairs	10 pairs	15 pairs
	Similarity of cluster spectra (R > 0.8)	None	1 pair	2 pairs	3 pairs	5 pairs	9 pairs	9 pairs	10 pairs	15 pairs
	Clusters with less than 10% total count	None	None	None	None	None	4 clusters	5 clusters	5 clusters	7 clusters

Table S9. Summary of criteria used for cluster analysis of single particle ET measurements taken in Early Spring. Paired clusters that do not have uncentered correlation coefficients (UC) higher than 0.8 are indicated by None.

Cluster number (p) Criteria		2	3	4	5	6	7	8	9	10
Marine	Temporal correlation clusters strength (R > 0.8)	1 pair	2 pairs	4 pairs	4 pairs	8 pairs	7 pairs	12 pairs	14 pairs	20 pairs
	Similarity of cluster spectra (R > 0.8)	1 pair	2 pairs	4 pairs	4 pairs	8 pairs	7 pairs	12 pairs	14 pairs	20 pairs
	Clusters with less than 10% total count	None	None	None	None	1 cluster	1 cluster	2 clusters	8 clusters	9 clusters
Continental	Temporal correlation clusters strength (R > 0.8)	1 pair	3 pairs	3 pairs	4 pairs	7 pairs	9 pairs	16 pairs	18 pairs	20 pairs
	Similarity of cluster spectra (R > 0.8)	1 pair	3 pairs	3 pairs	4 pairs	8 pairs	9 pairs	16 pairs	18 pairs	21 pairs
	Clusters with less than 10% total count	None	None	None	None	None	None	1 cluster	3 clusters	3 clusters

Table S10. Summary of single particle measurements and aerosol types and identified by ET mode for marine and continental air masses in Autumn and Early Spring.

Statistic \ Particle Type		OOA	OOA-I	OOA-II	HOA	PS	MS
Marine Autumn	Particle count	15121	--	--	--	17849	19715
	Fraction of total particle count	28.7%	--	--	--	33.9%	37.4%
	Signal from AMS NR single particle amine fragments relative to the total ion signal	3.6%	--	--	--	1.9%	1.4%
	Signal from AMS NR single particle amine fragments relative to the total organic ion signal	4.6%	--	--	--	4.4%	7.5%
Marine Early Spring	Particle count	1098	--	--	--	1934	6489
	Fraction of total particle count	11.5%	--	--	--	20.3%	68.2%
	Signal from AMS NR single particle amine fragments relative to the total ion signal	3.2%	--	--	--	1.4%	1.3%
	Signal from AMS NR single particle amine fragments relative to the total organic ion signal	3.8%	--	--	--	3.7%	8.1%
Continental Autumn	Particle count	--	8522	5525	5448	10390	5709
	Fraction of total particle count	--	23.9%	15.5%	15.3%	29.2%	16.0%
	Signal from AMS NR single particle amine fragments relative to the total ion signal	--	2.8%	2.3%	2.9%	1.7%	1.1%
	Signal from AMS NR single particle amine fragments relative to the total organic ion signal	--	3.3%	2.7%	3.2%	3.8%	5.9%
Continental Early Spring	Particle count	8412	--	--	--	7851	40771
	Fraction of total particle count	14.7%	--	--	--	13.7%	71.5%
	Signal from AMS NR single particle amine fragments relative to the total ion signal	2.8%	--	--	--	1.1%	1.0%
	Signal from AMS NR single particle amine fragments relative to the total organic signal	3.9%	--	--	--	3.4%	7.1%

Table S11. Pearson correlation (R) coefficient values between ET single particle types and other measured properties for marine air masses in Autumn. 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 ($0.25 \leq |R| < 0.50$)- light blue/red, moderate correlation ($0.50 \leq |R| < 0.80$)- medium blue/red, strong correlation ($0.80 \leq |R|$)- dark blue/red. All correlations shown are statistically significant ($p < 0.05$).

Particle Type Tracer	OOA	PS	MS
LVOOA Factor	0.80	-0.09	-0.29
Sulfate Factor	-0.09	0.83	0.86
Amine Factor	-0.17	0.03	0.10
CCN/CN	-0.06	0.25	0.24
CCN Count	-0.18	0.08	0.04
atm. DMS	-0.10	0.38	0.32
sw. DMS	0.16	-0.14	-0.19
AMS NR OM	0.75	0.31	0.13
AMS NR Nitrate	0.38	0.16	0.05
AMS NR Sulfate	-0.07	0.83	0.85
AMS NR Ammonium	-0.04	0.37	0.45
AMS NR Chloride	-0.14	-0.09	-0.05
IC SO_4^{2-}	0.12	0.85	0.88
IC NO_3^-	0.84	0.22	0.22
IC NH_4^+	0.00	0.95	0.95
IC Na^+	0.63	-0.01	0.03
IC MSA	0.64	0.41	0.49
IC Mg^{2+}	0.65	-0.02	0.02
IC K^+	0.37	0.14	0.19
IC Cl^-	0.60	-0.12	-0.08
IC Ca^{2+}	0.67	-0.20	-0.16
IC Br^-	-0.18	-0.15	-0.24
IC Sea salt	0.62	-0.06	-0.02
Chlorophyll *a*	-0.23	-0.27	-0.17
Ozone	0.02	-0.47	-0.54
Radon	0.18	-0.37	-0.36
Sea Surface Temperature	-0.12	0.45	0.45
Photosynthetically Activated Radiation	0.13	-0.10	-0.11
Relative Humidity	-0.21	0.42	0.46
Wind Speed	0.09	-0.24	-0.37
Atmospheric Temperature	0.01	0.14	0.13

Table S12. Pearson correlation (R) coefficient values between ET single particle types and other measured properties for continental air masses in Autumn. 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 ($0.25 \leq |R| < 0.50$)- light blue/red, moderate correlation ($0.50 \leq |R| < 0.80$)- medium blue/red, strong correlation ($0.80 \leq |R|$)- dark blue/red.

Particle Type Tracer	OOA-I	OOA-II	HOA	PS	MS
LVOOA Factor	0.69	0.50	0.61	-0.33	-0.31
Sulfate Factor	-0.08	0.29	-0.16	0.69	0.68
CCN Measurements	--	--	--	--	--
atm. DMS	-0.07	-0.35	-0.06	-0.46	-0.22
sw. DMS	-0.03	-0.16	-0.03	-0.16	-0.08
AMS NR OM	0.68	0.57	0.64	-0.24	-0.23
AMS NR Nitrate	0.58	0.38	0.69	-0.26	-0.24
AMS NR Sulfate	0.17	0.46	0.07	0.56	0.57
AMS NR Ammonium	0.49	0.64	0.32	0.24	0.21
AMS NR Chloride	-0.07	-0.04	-0.03	-0.04	-0.01
IC SO_4^{2-}	-0.18	0.61	-0.20	0.81	0.81
IC NO_3^-	0.14	0.27	0.66	0.11	0.10
IC NH_4^+	-0.21	0.56	-0.31	0.83	0.83
IC Na^+	0.17	-0.65	0.51	-0.71	-0.71
IC MSA	-0.65	-0.27	0.11	0.30	0.30
IC Mg^{2+}	0.35	-0.48	0.65	-0.81	-0.81
IC K^+	0.97	0.62	0.60	-0.60	-0.61
IC Cl^-	-0.18	-0.87	0.21	-0.57	-0.57
IC Ca^{2+}	0.48	-0.20	0.87	-0.79	-0.80
IC Br^-	--	--	--	--	--
IC Sea salt	0.01	-0.78	0.39	-0.68	-0.68
Chlorophyll *a*	0.13	-0.25	0.29	-0.32	-0.34
Ozone	0.24	0.44	-0.09	0.07	-0.01
Radon	0.49	0.44	0.36	0.11	-0.03
Sea Surface Temperature	0.27	0.34	0.11	-0.05	-0.05
Photosynthetically Activated Radiation	0.18	0.16	0.35	-0.22	-0.20
Relative Humidity	-0.25	-0.16	-0.16	0.49	0.46
Wind Speed	0.07	0.05	0.05	0.03	0.00
Atmospheric Temperature	-0.07	-0.27	-0.04	-0.29	-0.15

Table S13. Pearson correlation (R) coefficient values between ET single particle types and other measured properties for marine air masses in Early Spring. 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.

Particle Type Tracer	OOA	PS	MS
Sulfate Factor	-0.20	0.29	0.28
Amine Factor	0.18	-0.05	-0.01
CCN Measurements	--	--	--
atm. DMS	-0.26	0.03	-0.04
sw. DMS	-0.04	0.41	0.38
AMS NR OM	-0.03	-0.05	-0.05
AMS NR Nitrate	0.52	0.18	0.28
AMS NR Sulfate	-0.19	0.29	0.28
AMS NR Ammonium	-0.24	0.13	0.04
AMS NR Chloride	0.37	0.28	0.29
IC Measurements	--	--	--
Chlorophyll *a*	-0.09	-0.03	0.01
Ozone	0.30	0.03	0.08
Radon	0.68	0.25	0.48
Sea Surface Temperature	-0.50	-0.25	-0.31
Photosynthetically Activated Radiation	0.29	0.39	0.36
Relative Humidity	-0.14	0.19	0.17
Wind Speed	0.04	-0.26	-0.24
Atmospheric Temperature	-0.38	-0.14	-0.19

Table S14. Pearson correlation (R) coefficient values between ET single particle types and other measured properties for continental air masses in Early Spring. 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 ($0.25 \leq |R| < 0.50$)- light blue/red, moderate correlation ($0.50 \leq |R| < 0.80$)- medium blue/red, strong correlation ($0.80 \leq |R|$)- dark blue/red.

Particle Type Tracer	OOA	PS	MS
Sulfate Factor	0.14	0.69	0.79
Amine Factor	-0.05	-0.23	-0.17
CCN/CN	0.02	0.17	0.17
CCN Count	-0.07	0.09	0.10
atm. DMS	-0.42	-0.10	-0.16
sw. DMS	-0.25	-0.38	-0.35
AMS NR OM	0.16	-0.10	0.08
AMS NR Nitrate	0.07	-0.28	-0.19
AMS NR Sulfate	0.14	0.70	0.80
AMS NR Ammonium	0.18	0.15	0.38
AMS NR Chloride	-0.11	0.21	0.13
IC SO_4^{2-}	-0.31	0.54	0.58
IC NO_3^-	-0.28	-0.52	-0.48
IC NH_4^+	-0.30	0.50	0.55
IC Na^+	-0.28	0.26	0.25
IC MSA	0.34	0.89	0.94
IC Mg^{2+}	-0.29	0.33	0.32
IC K^+	-0.30	0.52	0.55
IC Cl^-	-0.20	0.12	0.09
IC Ca^{2+}	-0.40	0.41	0.43
IC Br^-	--	--	--
IC Sea salt	-0.24	0.20	0.18
Chlorophyll *a*	-0.02	-0.01	-0.04
Ozone	0.20	-0.45	-0.23
Radon	0.02	-0.27	-0.27
Sea Surface Temperature	0.11	-0.36	-0.12
Photosynthetically Activated Radiation	0.02	0.10	0.16
Relative Humidity	-0.08	0.40	0.31
Wind Speed	0.04	0.29	0.26
Atmospheric Temperature	0.01	0.12	0.14

Table S15. p-values retrieved for correlations of AMS NR amine fragments and various tracers for marine periods (columns 1-4) and continental periods (columns 5-8). p-values that are greater than 0.05 are not statistically significant and are shaded in red. p-values that are less than 0.05 are statistically significant and are shaded in green. A two-tailed T test is used to estimate p-values.

Air Masses	Marine				Continental			
Season	Winter	Early Spring	Late Spring	Autumn	Winter	Early Spring	Late Spring	Autumn
AMS NR OM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FTIR NV OM	0.36	--	0.89	0.02	0.31	0.23	0.45	--
AMS NR Nitrate	0.00	0.00	0.00	0.00	0.00	0.11	0.05	0.00
AMS NR Sulfate	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00
AMS NR Chloride	0.03	0.61	0.35	0.45	0.31	0.02	0.28	0.26
AMS NR f_{44}	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00
Black Carbon	0.00	0.00	0.00	0.00	0.00	0.00	0.64	0.00
Ozone	0.05	0.00	0.00	0.00	0.00	0.75	0.00	0.00
Radon	0.00	0.00	0.73	0.00	0.03	0.01	0.87	0.00
Wind Speed	0.00	0.00	0.68	0.99	0.00	0.00	0.34	0.03
sw. DMS	0.17	0.33	0.56	0.43	0.24	0.54	0.56	0.00
atm. DMS	0.01	0.00	0.64	0.00	0.02	0.00	0.00	0.01
Solar Radiation	0.58	0.97	0.03	0.25	0.81	0.00	0.43	0.00
Relative Humidity	0.00	0.00	0.62	0.19	0.27	0.00	0.97	0.48
Temperature	0.00	0.00	0.00	0.01	0.02	0.00	0.00	0.00
Chlorophyll *a*	0.23	0.00	0.00	0.10	0.27	0.33	0.57	0.93
SST	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00
IC MSA			0.39	0.10		0.52	0.84	0.85
IC Sea Salt	0.06		0.17	0.35	0.37	0.71	0.78	0.93
IC nssK$^+$	0.00		0.66	0.17	0.42	0.09	0.01	0.02

Table S16. p-values retrieved for correlations of FTIR NV amine groups (ADL & BDL) in particles with diameters <1 μm and various tracers for marine periods (columns 1-4) and continental periods (columns 5-8). p-values that are greater than 0.05 are not statistically significant and are shaded in red. p-values that are less than 0.05 are statistically significant and are shaded in green. A two-tailed T test is used to estimate p-values.

Air Masses	Marine				Continental			
Season	Winter	Early Spring	Late Spring	Autumn	Winter	Early Spring	Late Spring	Autumn
AMS NR OM	0.66	--	0.62	0.80	0.42	0.17	0.23	--
FTIR NV OM	0.01	--	0.01	0.13	0.01	0.00	0.88	--
AMS NR Nitrate	0.60	--	0.72	0.66	0.97	0.75	0.30	--
AMS NR Sulfate	0.52	--	0.20	0.61	0.27	0.41	0.39	--
AMS NR Chloride	0.03	--	0.10	0.99	0.02	0.03	0.47	--
AMS NR f_{44}	0.93	--	0.48	0.99	0.07	0.07	0.96	--
Black Carbon	0.60	--	0.04	0.80	0.06	0.93	0.68	--
Ozone	0.11	--	0.77	0.71	0.70	0.50	0.69	--
Radon	0.01	--	0.59	0.66	0.17	0.97	0.68	--
Wind Speed	0.43	--	0.76	0.94	0.22	0.18	0.98	--
sw. DMS	0.07	--	0.36	0.78	0.84	0.90	--	--
atm. DMS	0.40	--	0.07	0.49	0.35	0.53	--	--
Solar Radiation	0.12	--	0.75	0.38	0.22	0.94	0.06	--
Relative Humidity	0.40	--	0.07	0.98	0.63	0.26	0.26	--
Temperature	0.39	--	0.16	0.53	0.85	0.90	0.86	--
Chlorophyll *a*	0.50	--	0.03	0.52	0.43	0.83	0.74	--
SST	0.23	--	0.12	0.15	0.42	0.68	0.98	--
IC MSA	--	--	0.09	0.56	--	0.66	0.46	--
IC Sea Salt	0.71	--	0.52	0.36	--	0.22	0.84	--
IC nssK$^+$	0.75	--	0.50	0.94	--	0.28	0.80	--

Table S17. Linear regressions (Y = mX + b) for various tracers versus AMS NR amine fragments for marine periods (columns 1-4) and continental periods (columns 5-8).

Air Masses	Marine				Continental			
Season	Winter	Early Spring	Late Spring	Autumn	Winter	Early Spring	Late Spring	Autumn
AMS NR OM	14X	4.8X + 0.1	28X	13X	31X	17X	34X	24X
FTIR NV OM	-21X	--	-2.4X + 0.3	19X	-17X + 1	39X -1	13X	--
AMS NR Nitrate	0.52X	-0.12X + 0.01	0.58X	0.08X + 0.01	1.1X	0.04X + 0.01	4.3X - 0.1	0.24X
AMS NR Sulfate	18X	26X	8.7X	5.0X + 0.1	22X	4.0X + 0.3	4.8X + 0.1	1.5X + 0.3
AMS NR Chloride	0.17X + 0.01	-0.04X + 0.01	-0.12X + 0.02	-0.04 + 0.01	0.16X + 0.01	-0.09X + 0.01	-0.08X + 0.02	-0.01X + 0.01
AMS NR m/z 44	3.5X	1.0X + 0.01	3.9X	2.2X + 0.1	6.5X	4.0X + 0.1	5.9X	4.6X + 0.1
Black Carbon	2.8X	-0.31X + 0.04	1.3X - 0.01	0.59X	12X	9.0X - 0.1	4.8X	3.7X
Ozone	91X + 40	-1568X + 84	-241X + 44	-142X + 33	-172X + 41	30X + 46	145X + 34	94X + 28
Radon	13811X + 60	-315X + 386	-1860X + 341	580X + 397	31344X + 34	7090X	10264X + 34	9747X
Wind Speed	-247X	-47X	-359X	14X	-0.43X	-174X	-28X	-28X
sw. DMS	15X + 1	-12X + 3	-34X + 4	3.7X + 3.2	7.1X + 1.3	27X + 4	-48X + 4	-7X + 3
atm. DMS	-1326X + 85	5945X -61	-6285X + 570	995X + 111	5049X + 14	-4689X + 226	-2971X + 331	2800X + 38
Solar Radiation	-891X + 65	163X + 3	3677X + 4	1656X + 3	-257X +1	7562X + 4	-902X + 4	1414X + 3
Relative Humidity	-2074X + 103	-2.5X + 78	-89X + 86	-46X + 83	174X + 74	-336X +79	28X + 77	-126X + 89
Temperature	-592X +18	572X + 2	-96X + 11	132X + 10	183X +9	132X +9	100X + 5	37X + 15
Chlorophyll *a*	-7.5X + 0.6	4.5X + 0.5	19X + 1	-12X + 1	16X	-3.9X + 0.7	-0.5X + 1.6	-2.0X + 0.4
SST	-265X + 17	465X + 6	-153X + 14	102X + 12	181X + 11	139X + 12	83X + 7	52X + 15
IC MSA	--	--	4.9X – 0.1	1.8X	--	13X	0.16X + 0.06	0X
IC Sea Salt	210X – 2	--	-44X + 1	60X – 1	-447X	20X + 1	-0.40X + 0.08	-0.47X + 0.48
IC nssK^+	3.3X	--	0.10X	0.33X	5.3X – 0.1	2.5X – 0.1	0.41X	0.35X -0.01

Table S18. Linear regressions (Y = mX + b) for various tracers versus FTIR NV amine groups (ADL & BDL) in particles with diameters <1 µm for marine periods (columns 1-4) and continental periods (columns 5-8).

Air Masses	Marine				Continental			
Season	Winter	Early Spring	Late Spring	Autumn	Winter	Early Spring	Late Spring	Autumn
AMS NR OM	-0.36X + 0.20	--	2.0X + 0.4	-1.7X + 0.3	1.6X + 0.5	2.2X + 0.4	33X + 2	--
FTIR NV OM	8.9X + 0.2	--	10X	10X	4.6X + 0.2	11.4X	2.1X + 0.4	--
AMS NR Nitrate	-0.02X	--	0.04X	-0.04X	0X	-0.02X	-3.0X + 0.1	--
AMS NR Sulfate	-0.93X + 0.01	--	3.2X + 0.2	3.7X + 0.2	2.6X + 0.3	-3.0X + 0.5	-4.9X + 0.4	--
AMS NR Chloride	0.12X	--	0.70X	0X	0.10X	0.13X	-0.05X	--
AMS NR m/z 44	-0.10X + 0.06	--	-0.82X + 0.15	-0.66X + 0.15	0.18X + 0.11	0.76X + 0.18	-5.1X + 0.4	--
Black Carbon	-32X + 1	--	-1.1X + 0.1	0.18X + 0.02	2.5X + 0.04	0.15X + 0.19	-1.3X + 0.1	--
Ozone	41X + 41	--	57X + 37	-94X + 28	19X +33	47X + 48	71X + 40	--
Radon	-3698X + 304	--	993X + 277	-1904X + 446	-4413X + 855	-67X + 886	-3048X + 616	--
Wind Speed	-62X + 11	--	-37X + 10	14X + 10	54X + 12	70X + 10.6	1.1X + 6.1	--
sw. DMS	-6.0X + 1.2	--	97X + 0.62	-46X + 3	7.6X + 0.2	-5.6X + 1.5	--	--
atm. DMS	-405X + 79	--	21137X + 135	-1216X + 80	1532X + 47	-235X + 64	--	--
Solar Radiation	-1848X + 73	--	621X + 147	-2647X + 149	1745X + 1	105X + 181	-13163X + 642	--
Relative Humidity	-145X + 75	--	314X + 79	-12X + 82	-114X + 1	-104X + 69	-156X + 642	--
Temperature	-98X + 11	--	-216X + 12	103X + 13	16X + 9	-5.6X + 12	-21X + 10	--
Chlorophyll *a*	1.7X + 0.4	--	61X	-5.2X + 0.3	-15X + 2	0.45X + 0.50	-7.9X + 1.4	--
SST	-110X + 14	--	-252X + 14	143X + 14	-46X +16	13X + 15	2.9X + 10.7	--
IC MSA	--	--	4X	-0.13X	--	-0.95X + 0.07	-1.1X + 0.1	--
IC Sea Salt	10X + 1	--	8.4X + 0.3	14X	--	9.2X + 0.9	-0.60X + 0.10	--
IC nssK$^+$	0.08X	--	0X + 0.06	0.003X + 0.009	--	0.13X + 0.01	-0.09X + 0.01	--

Table S19. Number of available samples for correlations of AMS NR amine fragments and various tracers for marine periods (columns 1-4) and continental periods (columns 5-8).

Air Masses	Marine				Continental			
Season	Winter	Early Spring	Late Spring	Autumn	Winter	Early Spring	Late Spring	Autumn
AMS NR OM	134	122	273	166	405	289	271	352
FTIR NV OM	14	2	6	6	12	8	5	2
AMS NR Nitrate	134	122	273	166	405	289	271	352
AMS NR Sulfate	134	122	273	166	405	289	271	352
AMS NR Chloride	134	122	273	166	405	289	271	352
AMS NR f_{44}	134	122	273	166	405	289	271	352
Black Carbon	128	108	247	146	381	270	237	324
Ozone	127	108	245	146	380	270	239	321
Radon	129	114	247	146	376	272	240	325
Wind Speed	126	112	245	146	375	270	236	319
sw. DMS	130	111	248	151	384	273	251	330
atm. DMS	131	110	248	152	387	275	250	339
Solar Radiation	126	108	245	146	376	271	236	317
Relative Humidity	126	108	245	146	375	268	236	317
Temperature	126	108	245	146	375	268	236	317
Chlorophyll *a*	129	112	247	153	394	274	237	326
SST	127	108	249	147	382	268	240	319
IC MSA	0	2	5	4	0	9	5	6
IC Sea Salt	11	2	5	4	3	9	5	6
IC nssK^+	11	2	5	4	3	9	5	6

Table S20. Number of available samples for correlations of FTIR NV amine groups (ADL & BDL) in particles with diameters <1 µm and various tracers for marine periods (columns 1-4) and continental periods (columns 5-8).

Air Masses	Marine				Continental			
Season	Winter	Early Spring	Late Spring	Autumn	Winter	Early Spring	Late Spring	Autumn
AMS NR OM	14	2	6	6	12	8	5	2
FTIR NV OM	14	2	6	6	12	8	5	2
AMS NR Nitrate	14	2	6	6	12	8	5	2
AMS NR Sulfate	14	2	6	6	12	8	5	2
AMS NR Chloride	14	2	6	6	12	8	5	2
AMS NR f_{44}	14	2	6	6	12	8	5	2
Black Carbon	13	2	6	6	10	8	5	2
Ozone	14	2	6	6	8	8	4	2
Radon	14	2	6	6	8	8	4	2
Wind Speed	14	2	6	6	8	8	4	2
sw. DMS	14	2	5	6	3	8	1	2
atm. DMS	14	2	6	6	5	8	1	2
Solar Radiation	14	2	6	6	8	5	4	2
Relative Humidity	14	2	6	6	8	8	4	2
Temperature	14	2	6	6	8	8	4	2
Chlorophyll *a*	14	2	6	6	7	8	4	2
SST	14	2	6	6	10	8	4	2
IC MSA	0	1	6	4	0	4	3	0
IC Sea Salt	5	1	6	4	0	4	3	0
IC nssK$^+$	5	1	6	4	0	4	3	0

Table S21. Critical Diameters and Hygroscopicity Estimates, Continued

Time	Cruise	Air Mass	CCN (cm^{-3})	CN (cm^{-3})	CCN/CN	D_{crit} (μm)	κ
09/09/2017 04:08	3	M	104	282	0.37	0.14	0.57
09/09/2017 04:16	3	M	109	289	0.38	0.13	0.63
09/09/2017 04:18	3	M	110	289	0.38	0.13	0.70
09/15/2017 01:58	3	C	171	342	0.50	0.11	1.21
09/15/2017 06:28	3	C	140	295	0.48	0.10	1.34
09/15/2017 06:34	3	C	132	291	0.45	0.04	22.14
09/15/2017 06:36	3	C	138	290	0.47	0.11	1.21
09/15/2017 06:38	3	C	135	291	0.46	0.11	1.21
03/23/2018 11:24	4	M	109	206	0.53	0.02	112.04
03/23/2018 11:26	4	M	109	204	0.54	0.12	0.78
03/23/2018 11:28	4	M	109	205	0.53	0.11	1.08
03/23/2018 11:34	4	M	108	203	0.53	0.03	42.45
03/23/2018 11:36	4	M	107	204	0.52	0.11	0.97
03/23/2018 11:38	4	M	111	204	0.54	0.10	1.34
04/01/2018 17:44	4	C	150	506	0.30	0.07	3.54
04/01/2018 17:46	4	C	188	507	0.37	0.10	1.50
04/01/2018 17:48	4	C	199	515	0.39	0.10	1.34
04/01/2018 22:14	4	C	157	478	0.33	0.07	3.96
04/01/2018 22:16	4	C	180	480	0.37	0.11	1.08
04/01/2018 22:18	4	C	209	474	0.44	0.10	1.50
04/01/2018 22:24	4	C	205	477	0.43	0.05	9.36
04/01/2018 22:26	4	C	195	480	0.41	0.10	1.50
04/01/2018 22:28	4	C	173	500	0.35	0.11	1.08
04/02/2018 02:54	4	C	167	567	0.29	0.07	3.54
04/02/2018 02:56	4	C	195	562	0.35	0.11	1.21
04/02/2018 02:58	4	C	191	544	0.35	0.11	1.21
04/02/2018 03:04	4	C	181	532	0.34	0.06	6.76
04/02/2018 03:06	4	C	185	534	0.35	0.11	1.21
04/02/2018 03:08	4	C	178	532	0.34	0.11	1.08
04/03/2018 00:08	4	C	180	585	0.31	0.07	3.96
04/03/2018 04:34	4	C	159	506	0.31	0.05	10.44
04/03/2018 04:36	4	C	158	505	0.31	0.12	0.78
04/03/2018 04:38	4	C	158	502	0.31	0.12	0.78
04/03/2018 04:44	4	C	152	502	0.30	0.05	11.61
04/03/2018 04:46	4	C	154	501	0.31	0.12	0.87
04/03/2018 04:48	4	C	150	498	0.30	0.13	0.70
04/03/2018 09:18	4	C	101	427	0.24	0.13	0.70
04/03/2018 09:28	4	C	100	458	0.22	0.13	0.70
04/05/2018 03:24	4	C	105	201	0.52	0.10	1.34
04/05/2018 03:26	4	C	102	199	0.51	0.12	0.87
04/05/2018 03:28	4	C	101	202	0.50	0.10	1.50
04/07/2018 02:38	4	C	158	333	0.47	0.12	0.87
04/07/2018 02:44	4	C	165	336	0.49	0.11	1.08
04/07/2018 02:46	4	C	161	339	0.48	0.11	0.97
04/07/2018 02:48	4	C	163	340	0.48	0.11	1.08
04/07/2018 22:48	4	C	161	449	0.36	0.14	0.51
04/08/2018 03:18	4	C	208	423	0.49	0.11	0.97
04/08/2018 03:24	4	C	177	425	0.42	0.06	7.53
04/08/2018 03:26	4	C	221	425	0.52	0.11	1.21

04/08/2018 03:28	4	C	221	426	0.52	0.11	1.21
04/08/2018 07:58	4	C	156	285	0.55	0.09	2.07
04/08/2018 08:04	4	C	144	279	0.52	0.03	42.45
04/08/2018 08:06	4	C	150	279	0.54	0.10	1.50
04/08/2018 08:08	4	C	152	278	0.55	0.09	2.07
04/08/2018 12:36	4	C	114	282	0.41	0.11	1.21
04/08/2018 12:38	4	C	114	282	0.40	0.10	1.50
04/08/2018 12:44	4	C	111	282	0.39	0.03	38.04
04/08/2018 12:46	4	C	114	280	0.41	0.09	1.67
04/08/2018 12:48	4	C	115	281	0.41	0.10	1.50
04/09/2018 04:06	4	C	236	499	0.47	0.09	1.86
04/09/2018 04:08	4	C	241	502	0.48	0.09	1.86
04/09/2018 04:14	4	C	235	503	0.47	0.02	213.29
04/09/2018 04:16	4	C	255	517	0.49	0.09	2.30
04/09/2018 04:18	4	C	247	501	0.49	0.09	1.67
04/09/2018 16:34	4	C	203	687	0.29	0.11	1.08
04/09/2018 16:36	4	C	192	666	0.29	0.12	0.87
04/09/2018 16:38	4	C	192	666	0.29	0.05	14.47
04/10/2018 01:44	4	C	137	748	0.18	0.03	34.21
04/10/2018 01:46	4	C	157	744	0.21	0.08	2.57
04/10/2018 01:48	4	C	158	767	0.21	0.09	1.67
04/10/2018 01:54	4	C	163	752	0.22	0.02	101.25
04/10/2018 01:56	4	C	144	720	0.20	0.10	1.34
04/10/2018 01:58	4	C	137	697	0.20	0.10	1.50
04/10/2018 06:24	4	C	157	673	0.23	0.02	191.13
04/10/2018 06:26	4	C	136	678	0.20	0.11	1.21
04/10/2018 06:28	4	C	135	663	0.20	0.11	1.08
04/10/2018 06:34	4	C	156	696	0.22	0.02	112.04
04/10/2018 06:36	4	C	169	699	0.24	0.10	1.50
04/10/2018 06:38	4	C	156	714	0.22	0.11	1.21
04/10/2018 11:04	4	C	211	840	0.25	0.03	38.04
04/10/2018 11:06	4	C	215	841	0.26	0.11	1.08
04/10/2018 11:08	4	C	228	839	0.27	0.10	1.34
04/10/2018 11:14	4	C	250	885	0.28	0.02	191.13
04/10/2018 11:16	4	C	200	872	0.23	0.12	0.87
04/10/2018 11:18	4	C	217	863	0.25	0.11	1.21

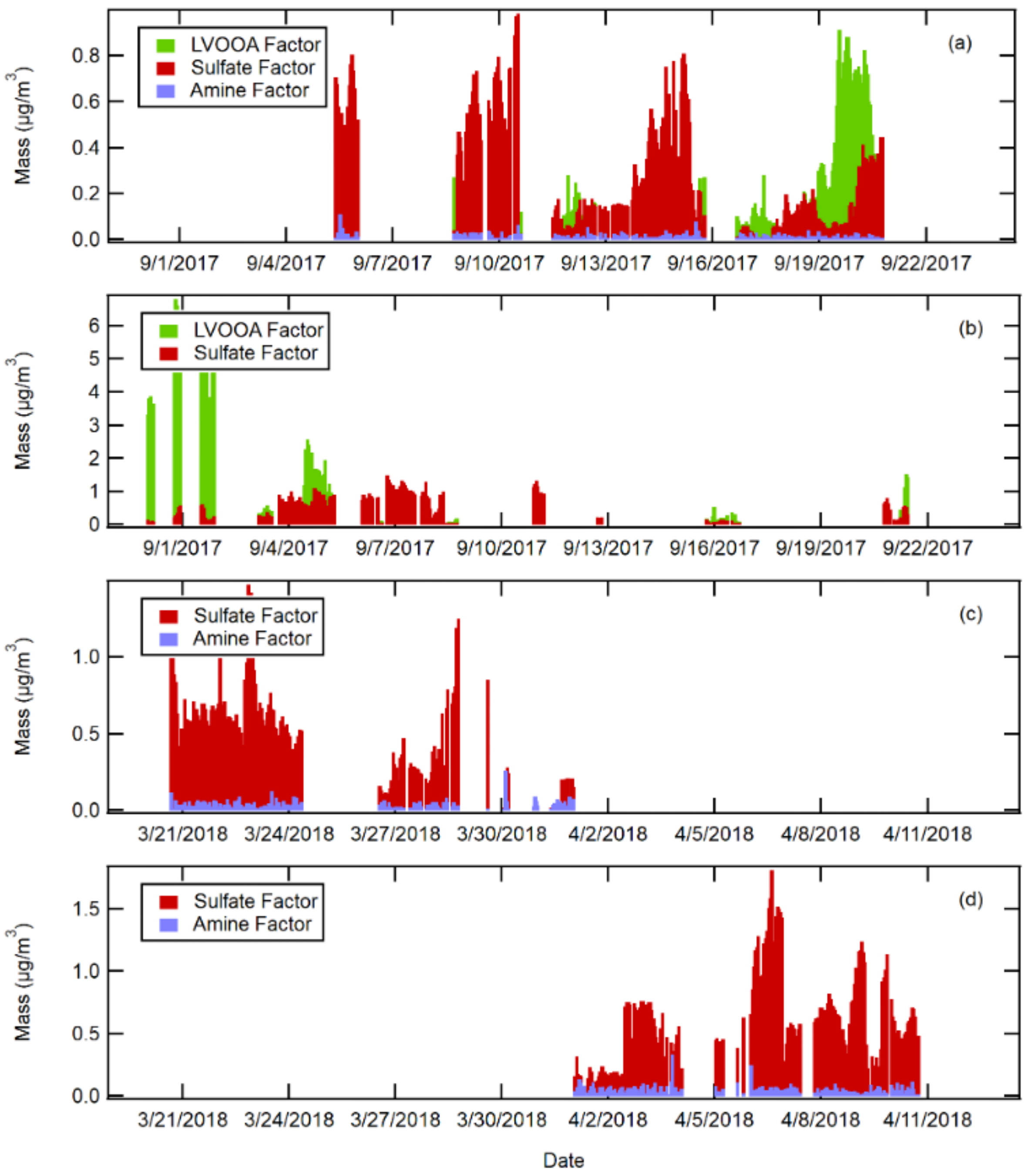


Figure S1. Time series (bottom right) of factors resolved from PMF analysis of AMS NR HR-Org and AMS NR HR-SO_4 for (a) marine air masses in Autumn, (b) continental air masses in Autumn, (c) marine air masses in Early Spring, and (d) continental air masses in Early Spring.

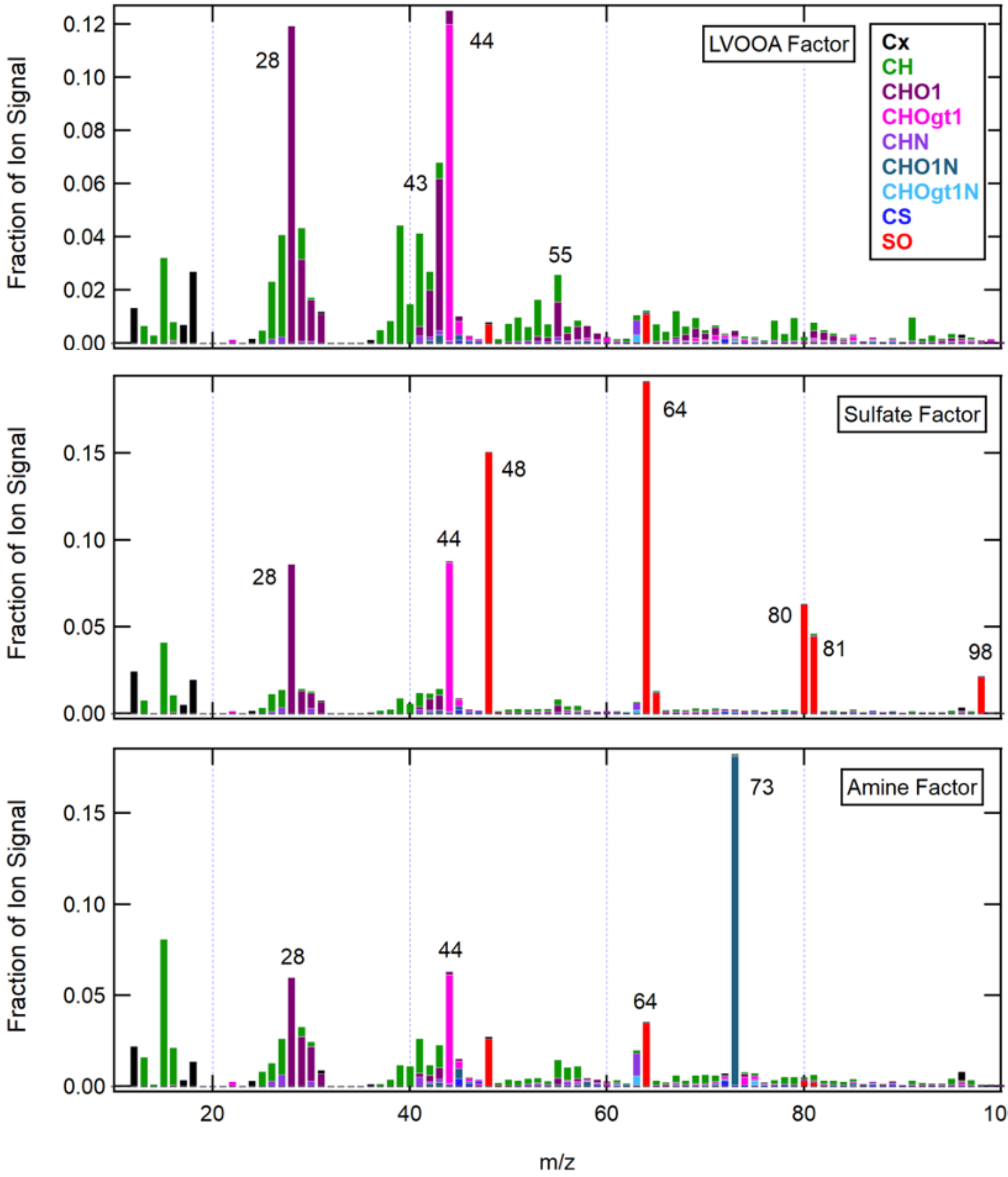


Figure S2. Mass spectra of factors resolved from PMF analysis of AMS NR HR-Org and AMS NR HR-SO_4 for marine air masses in Autumn. The factors shown include the LVOOA factor (top), the Sulfate factor (middle), and the Amine factor (bottom).

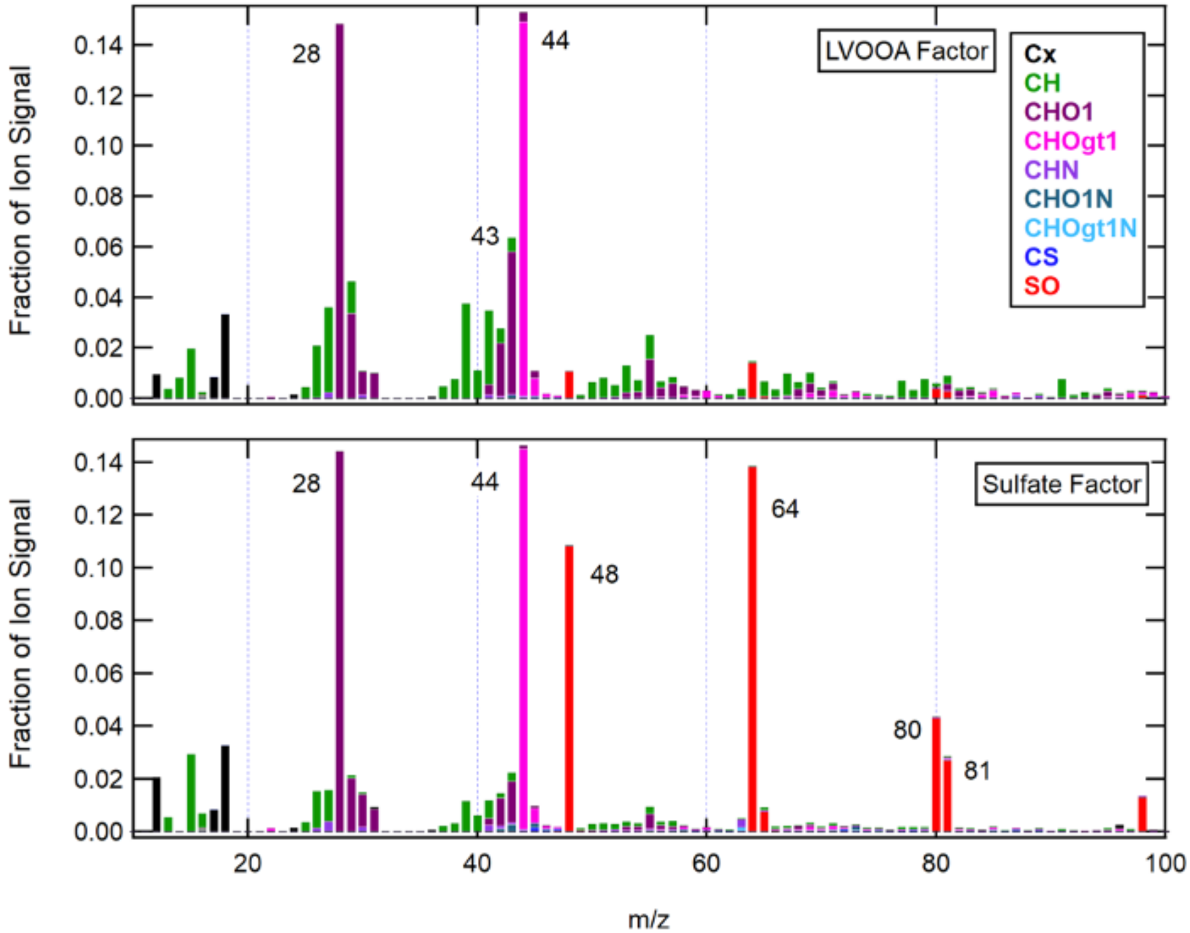


Figure S3. Mass spectra of factors resolved from PMF analysis of AMS NR HR-Org and AMS NR HR-SO_4 for continental air masses in Autumn. The factors shown include the LVOOA factor (top) and the Sulfate factor (bottom).

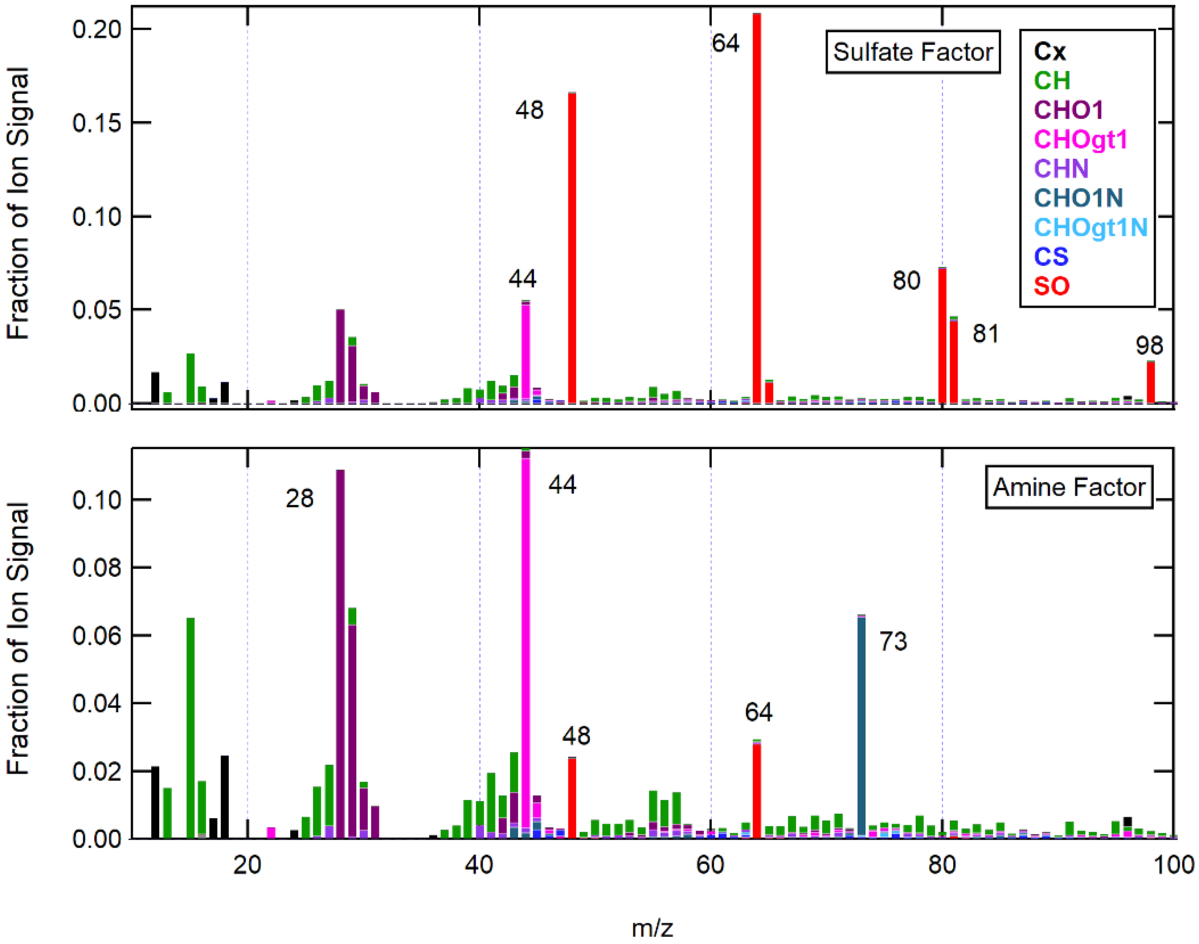


Figure S4. Mass spectra of factors resolved from AMS NR HR-Org and AMS NR HR-SO_4 for marine air masses in Early Spring. The factors shown include the Sulfate factor (top) and the Amine factor (bottom).

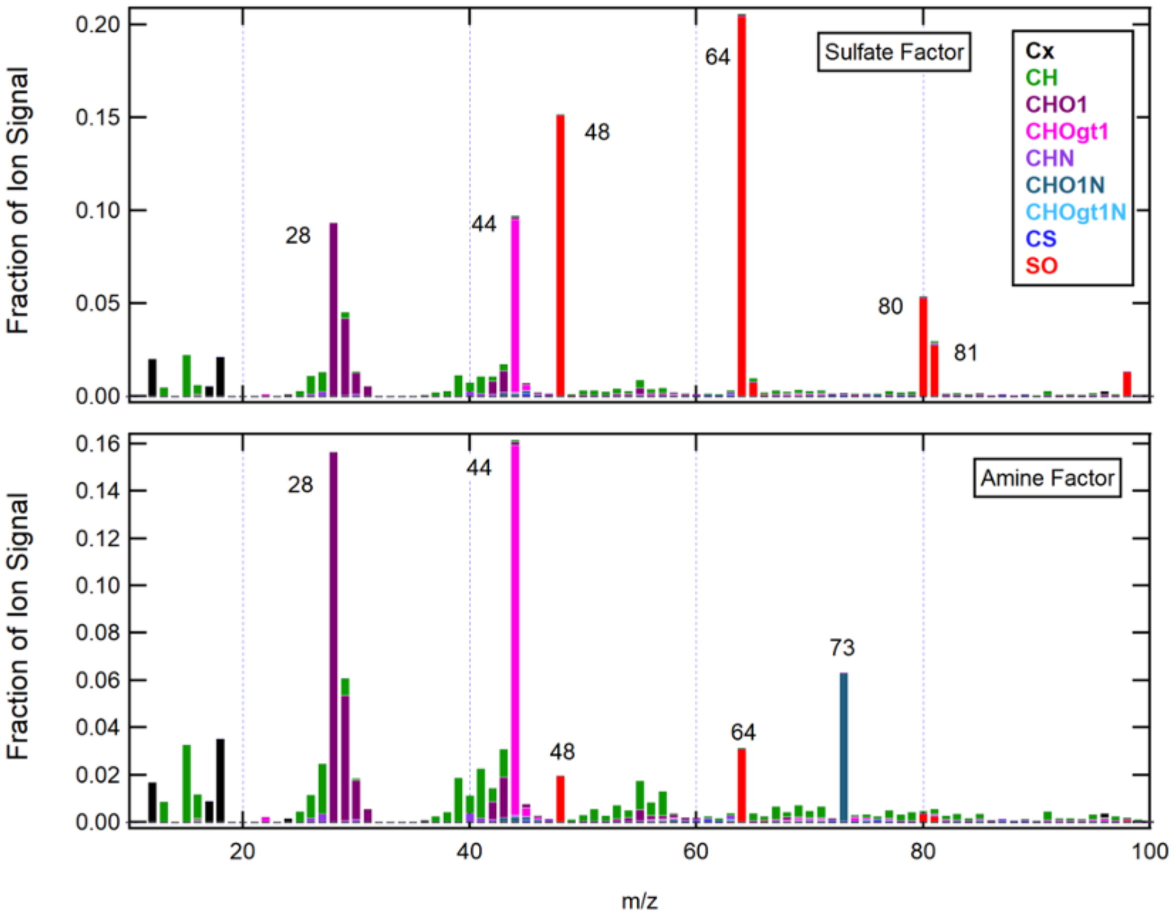


Figure S5. Mass spectra of factors resolved from PMF analysis of AMS NR HR-Org and AMS NR HR-SO_4 for continental air masses in Early Spring. The factors shown include the Sulfate factor (top) and the Amine factor (bottom).

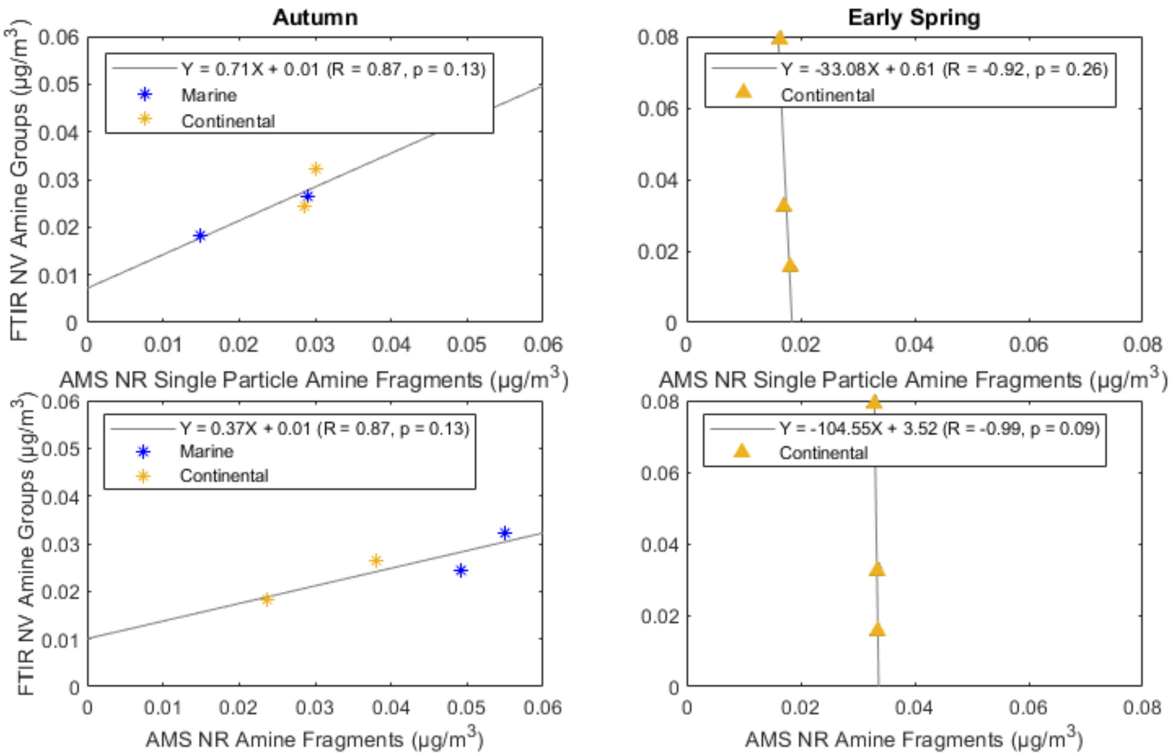


Figure S6. Scatter plot of FTIR (ADL) NV amine groups in particles with diameters <1 µm versus (top row) AMS NR single particle amine fragments and (bottom row) AMS NR amine fragments during (left column) Autumn and (right column) Early Spring. Marker colors represent air mass type (b,c): blue: marine, yellow: continental. The solid grey lines are the lines of best fit obtained using an ordinary least squares regression. A two-tailed T test is used to estimate p-values.

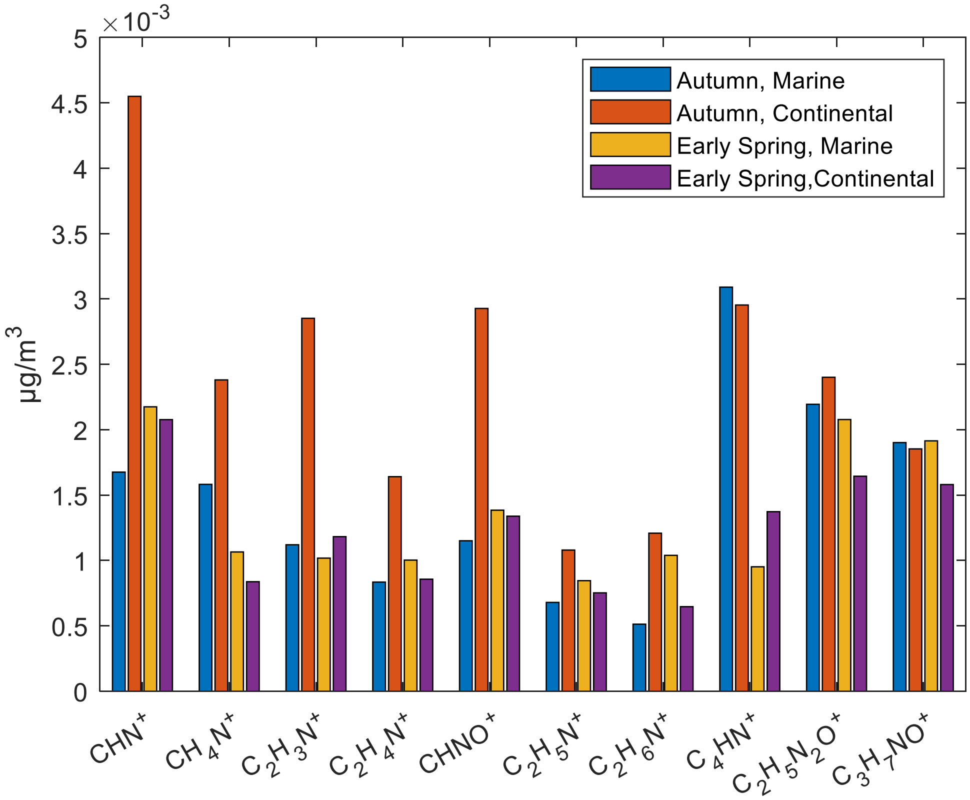


Figure S7. Bar graph of the 10 highest mass concentrations among AMS NR single particle amine fragments for marine air masses in Autumn (blue), continental air masses in Autumn (orange), marine air masses in Early Spring (yellow), and continental air masses in Early Spring (purple).

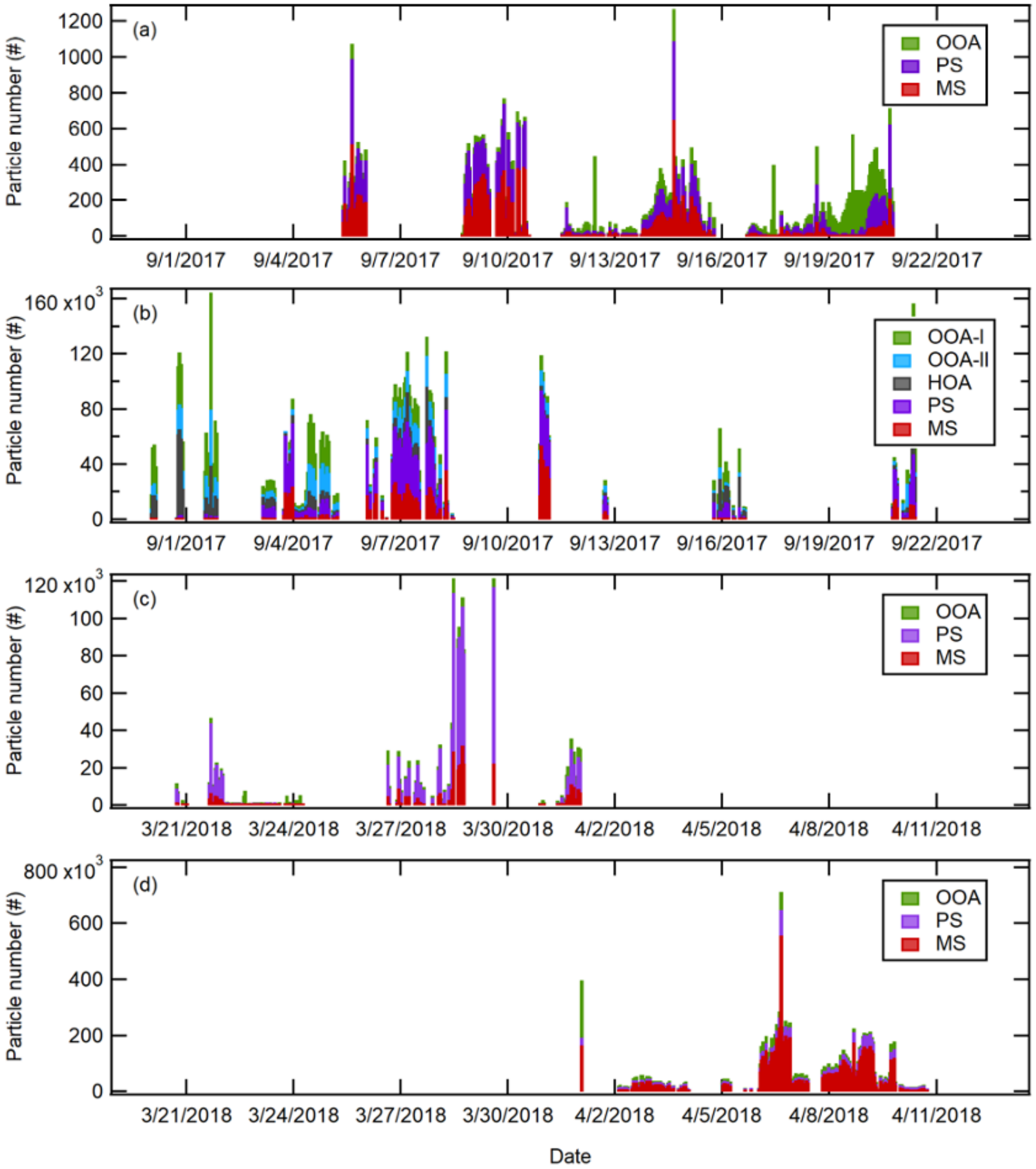


Figure S8. Time series of single particle clusters resolved from the ET mode for (a) marine air masses in Autumn, (b) continental air masses in Autumn, (c) marine air masses in Early Spring, and (d) continental air masses in Early Spring.

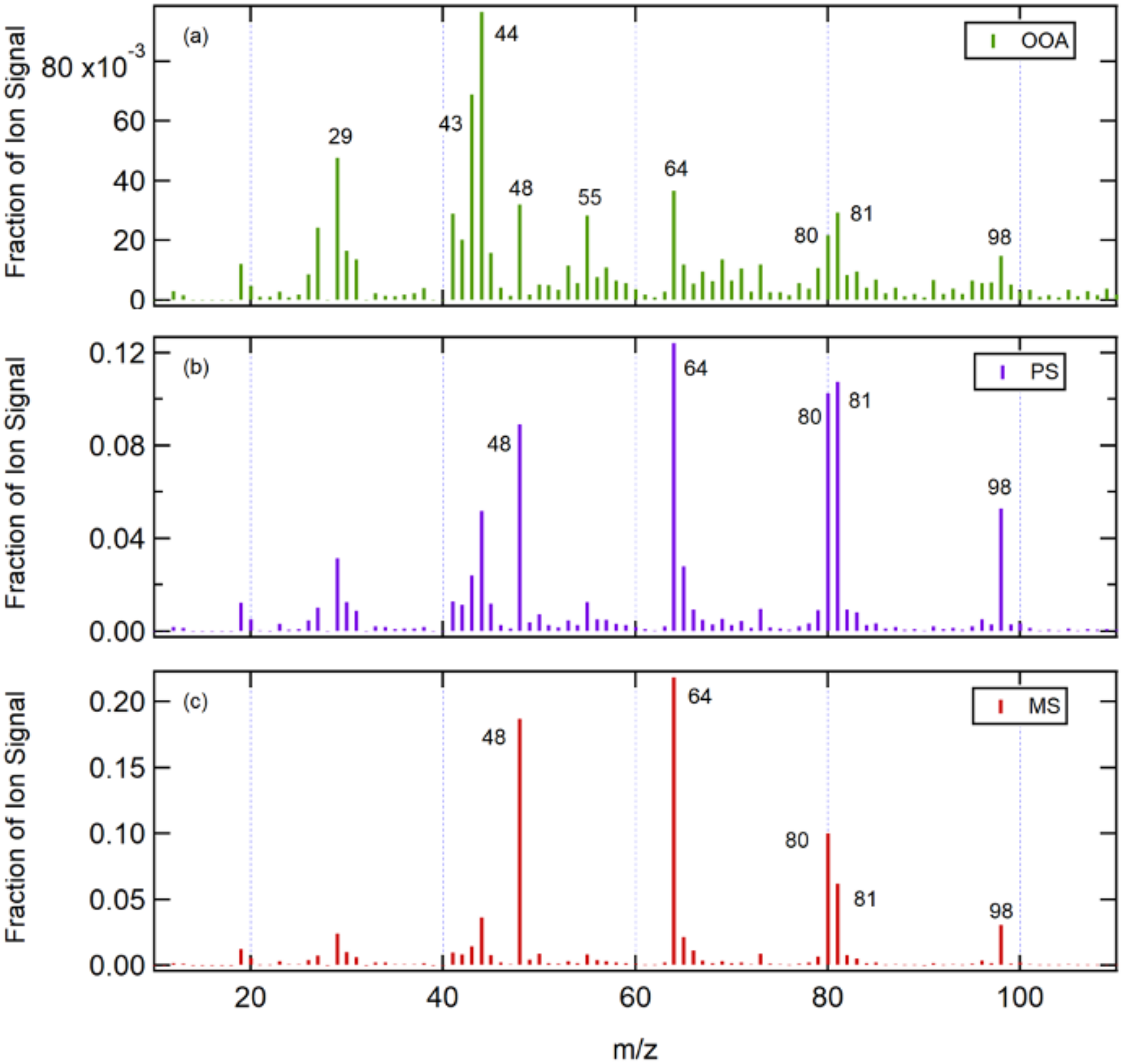


Figure S9. Mass spectra of single particle clusters resolved from the ET mode for marine air masses in Autumn. The particle types shown include (a) OOA, (b) PS, and (c) MS.

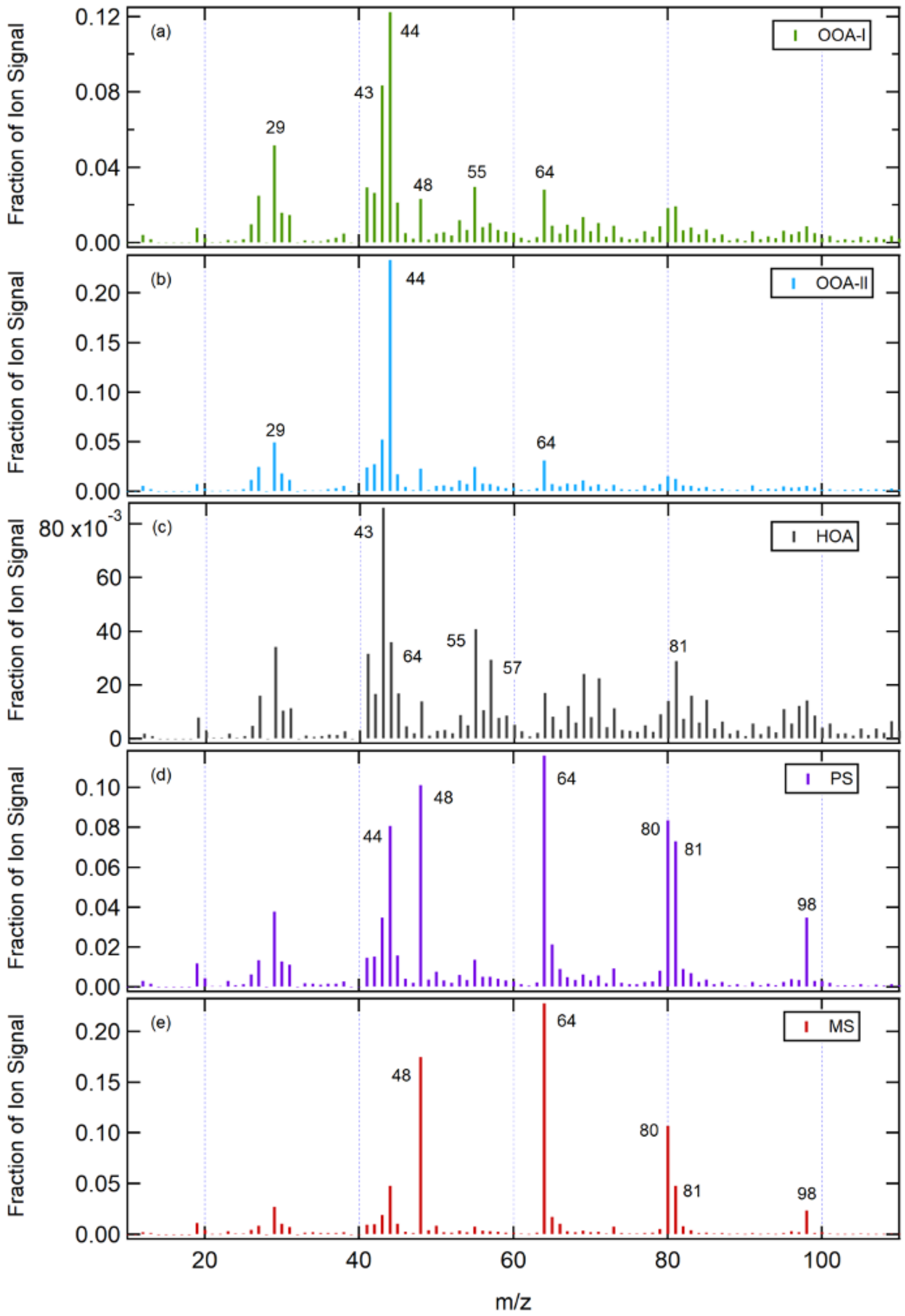


Figure S10. Mass spectra of single particle clusters resolved from the ET mode for continental air masses in Autumn. The particle types shown include (a) OOA-I, (b) OOA-II, (c) HOA, (d) PS, and (e) MS.

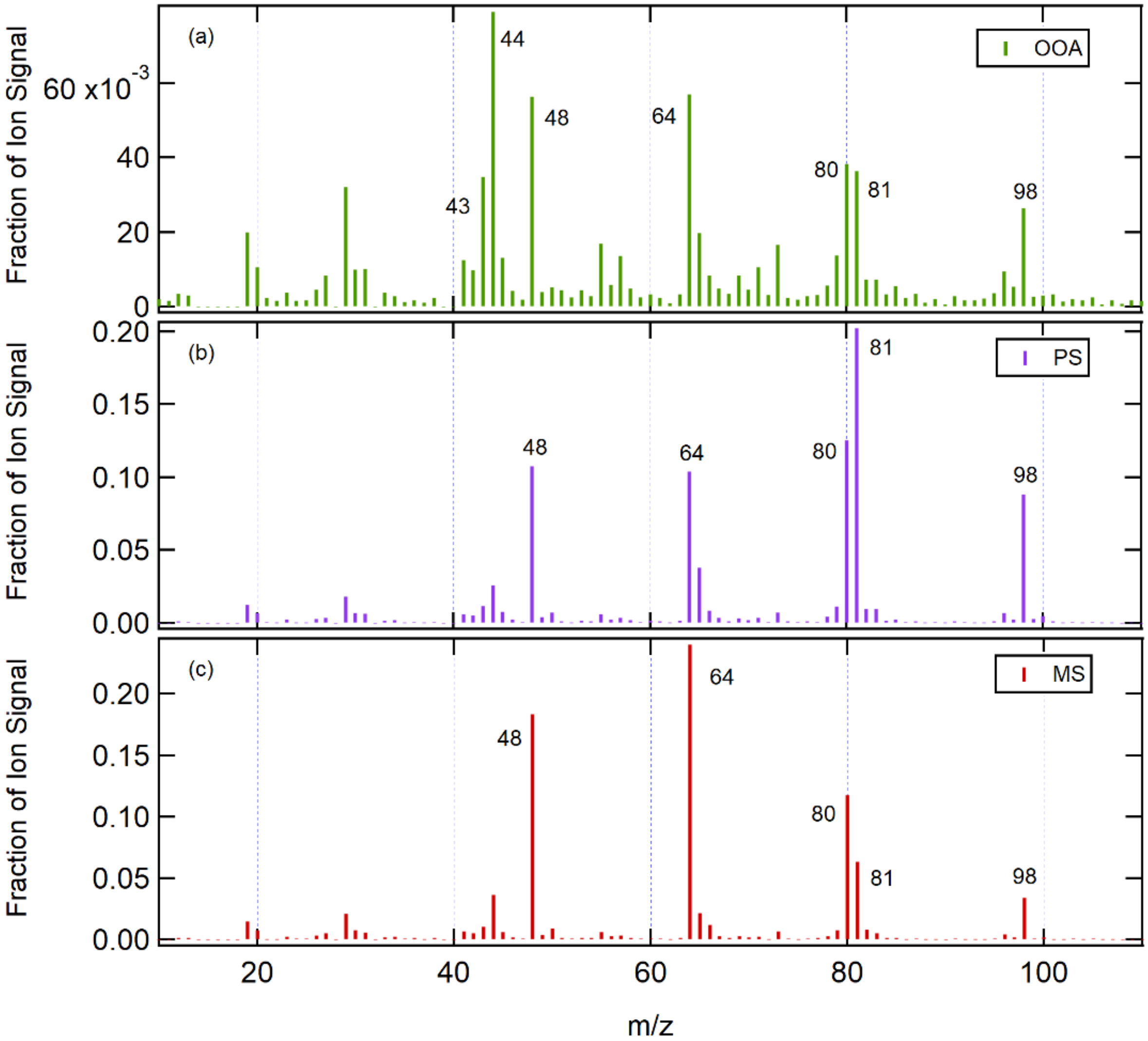


Figure S11. Mass spectra of single particle clusters resolved from the ET mode for marine air masses in Early Spring. The particle types shown include (a) OOA, (b) PS, and (c) MS.

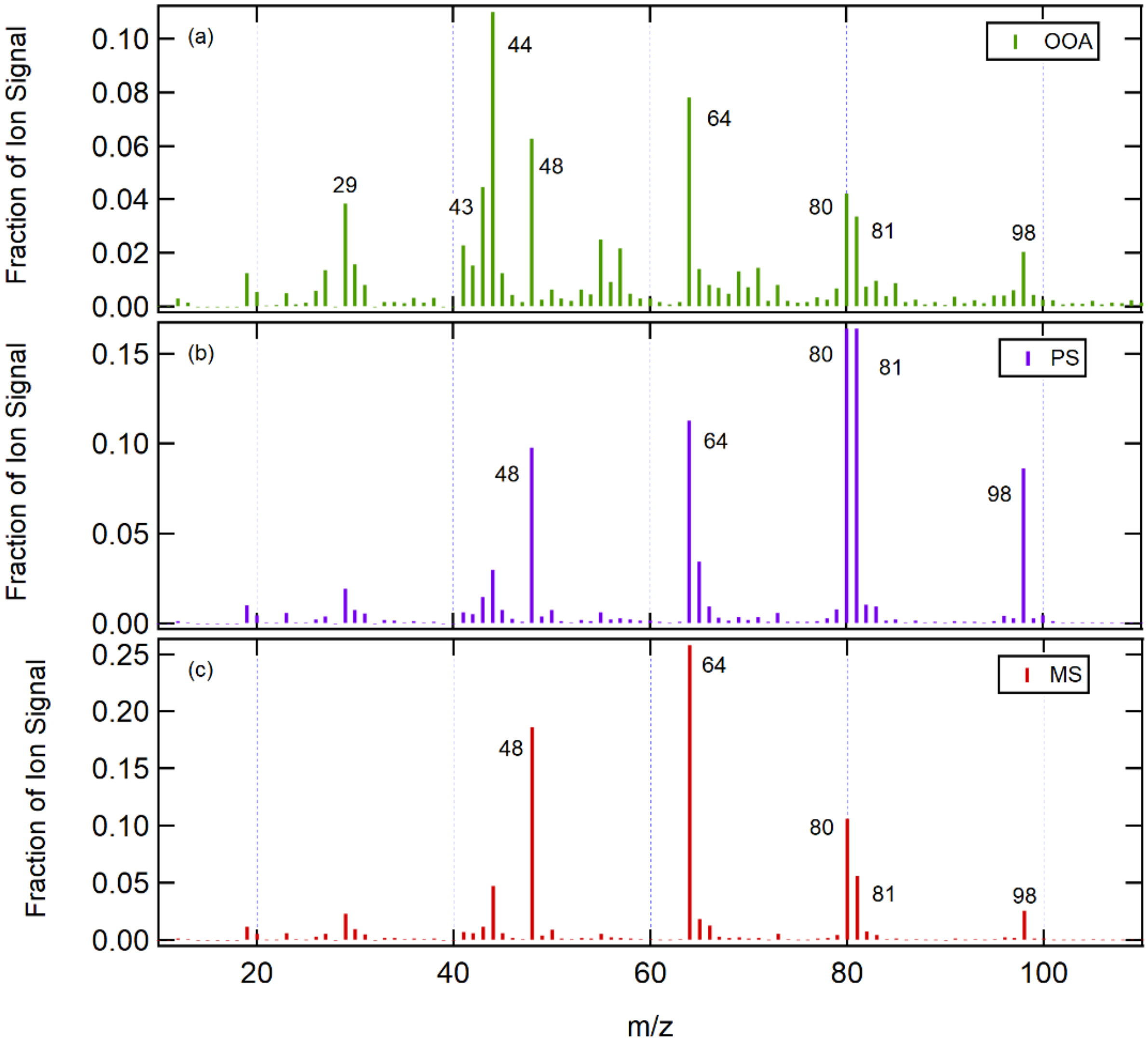


Figure S12. Mass spectra of single particle clusters resolved from the ET mode for continental air masses in Early Spring. The particle types shown include (a) OOA, (b) PS, and (c) MS.

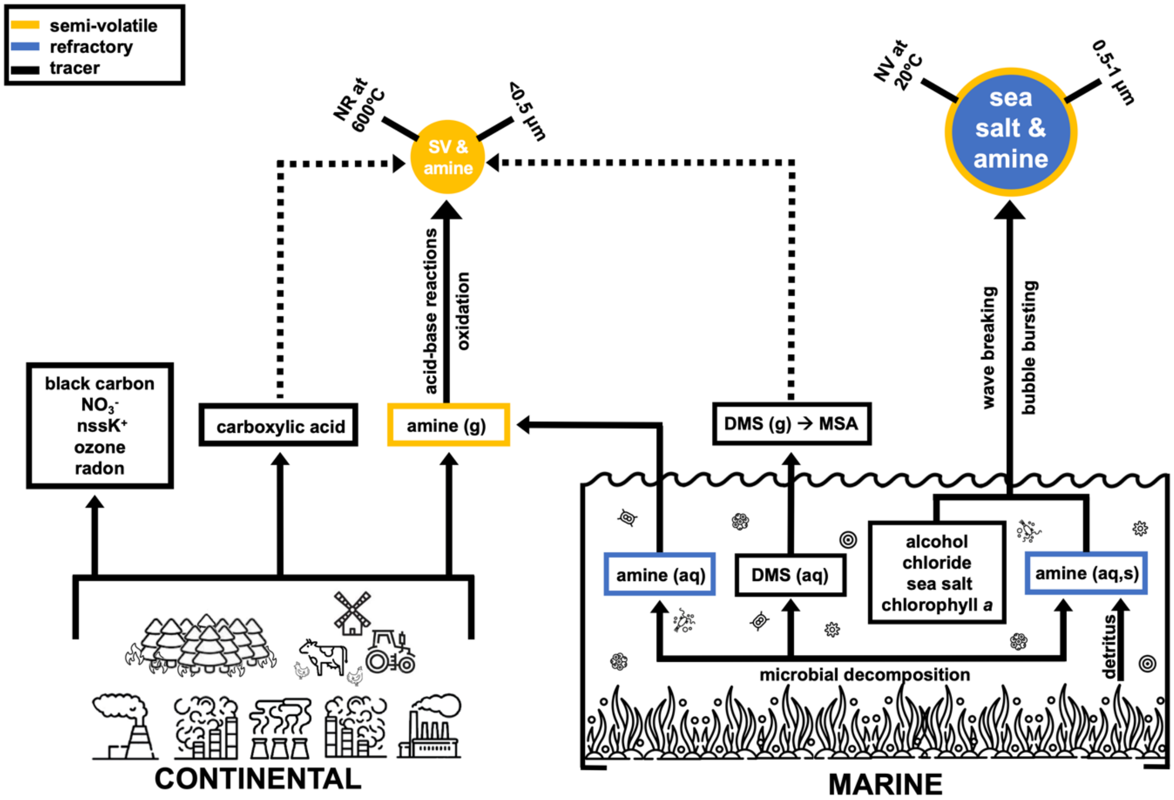


Figure S13. Diagram of tracers and amine sources in aerosols found in marine environments.

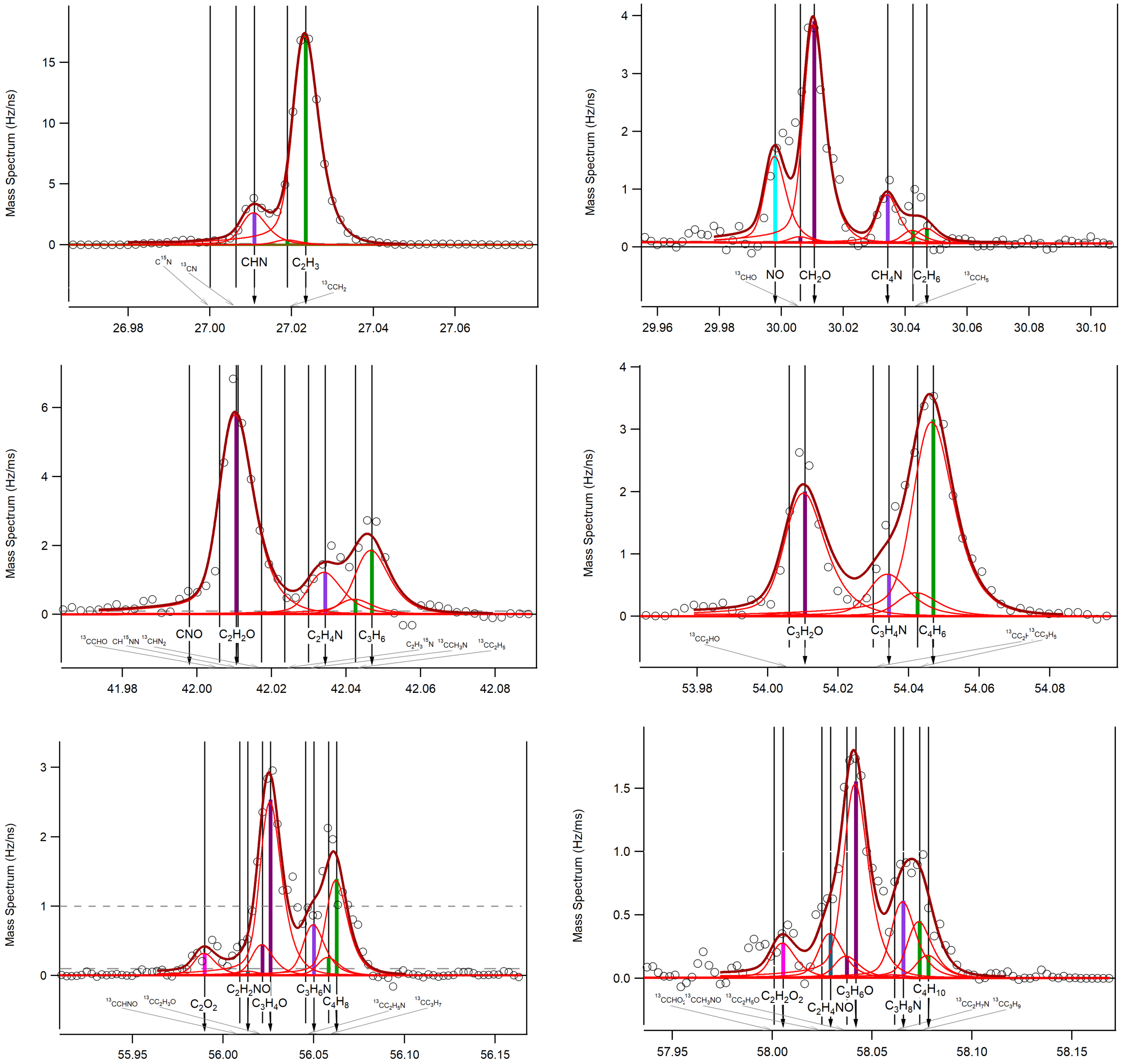


Figure S14. High-resolution mass spectra at dominant $C_xH_yN_z$ m/z ratios taken at T_v = 600 °C.

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