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

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**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, 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% primary marine amine and 73% secondary continental amine during Early Spring to 53% primary amine and 47% 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 (O₃, OH, NO₃) to nucleate new particles (Tang et al., 2013;Malloy et al., 2009;Bork et al.,
35   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.

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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
45   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).

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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
55   aerosols (SMA) by a variety of reactions. These reactions may be accelerated by airborne oxidants and other pollutants (NOₓ,
O₃, SOₓ) 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
60   biologically-derived marine organic compounds, since they frequently contain a consistent ratio of primary (C-NH₂) 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).

65   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

70 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

### 75 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

80 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.

### 85 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

90 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

95 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

100    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

105    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).

The ET mode of the instrument 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

110    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. The AMS ET methods and results for Autumn and Early Spring are available in the supporting information sections S2-3. Amine fragment contributions were estimated using the unit-mass fragments associated with common amine ion fragments. 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

115    organic signal. These contributions remained largely consistent across particle clusters, showing no notable differences between the particle clusters.

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

120    in 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. Most of the factors identified typically included small amounts of amine; when a factor with higher amine 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).

125    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

130    and sulfate 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

135    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. Quantification of NV organic amine group concentration was accomplished by identifying a primary

140    amine (C-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$_2$-NH) or tertiary (C$_3$-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,

145    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.,

150    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

155    Seawater and atmospheric dimethylsulfide (DMS) concentrations were measured continuously during NAAMES (Bell et al., 2021). 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 were accessed from the SeaBASS archive (Werdell et al., 2003).

## 3 Results

Figure 1 shows AMS NR amine fragments and FTIR NV amine groups for all four NAAMES cruises. 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 $33 \pm 6$ ng m$^{-3}$ during marine periods than during continental periods ($32 \pm 11$ ng m$^{-3}$), but largely similar for both marine and continental air masses (Table 2). 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).

For both marine and continental air masses, 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. 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 $33 \pm 6$ ng m$^{-3}$ in Early Spring and for continental periods $54 \pm 49$ 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 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.

195 AMS NR amine fragments had moderate to strong correlations (0.73 < R < 0.98, Table 3) 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) 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
200 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,
205 and the sea surface microlayer sampled in 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 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. AMS NR amine fragments did not correlate positively to wind
210 speed (Figure 4c,d), consistent with the expectation that primary amines would be mixed with refractory sea salt particles (Hawkins et al., 2010;Frossard et al., 2014b).

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
215 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. 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
220 period, the consistency of their positive correlations contrast with the absence of correlation (-0.15 < R < 0.13, Table 3) 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

225  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

230  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).

The production of methylated amines and sulfurs varies with individual metabolic processes and across different ocean

235  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

240  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

245  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

250  on AMS NR particles rather than sea salt.

Methanesulfonic acid (MSA), an oxidized 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,

255  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

260     supporting a secondary contribution to the FTIR NV amine groups as well, but this result was not significant (p ≥ 0.05). 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

265     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

270     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 source for AMS NR amine fragments that is present during continental and marine periods. The steeper slopes of the linear fits for continental air masses (Y = 0.24-4.28, Table S17) compared to those of marine air masses (Y = 0.08-0.58, Table S17) suggest that these amines have continental sources that are present at low concentrations during the

275     marine periods. 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 ($NH_2$) 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.

280     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

285     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

290    < 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 4) of FTIR NV amine groups with radon, suggesting that FTIR NV amine groups are largely from marine sources.

295    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 and continental seasons except Winter, suggesting an important continental contribution to AMS NR amine fragments. No correlations of FTIR NV
300    amine groups to IC nssK$^+$ were statistically significant (Table 4).

     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
305    (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).

310    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).
315    FTIR NV amine groups weakly correlated (0.28 < r < 0.48, Table 4) 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 AMS ion signal at m/z 44 (CO$_2$$^+$) is a measure of particle oxidation and a tracer for secondary processing (Bahreini et al.,
320    2005). Figures 5e and 5f display largely consistent trends between AMS NR amine fragments and AMS NR m/z 44. Moderate to strong (0.85 < R < 0.94) correlations of AMS NR m/z 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 positively correlated (R = 0.52) with FTIR NV amine group mass

325 concentrations for only the continental period in Early 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

330 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 and ozone, 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

335 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

340 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 and FTIR NV acid groups measured across all four cruises for three different size cut-offs (<1 μm, <0.5 μm, <0.18 μm).

345

For <1 μm particle samples, there was a strong correlation (R = 0.87, Figure 7a) between FTIR NV alcohol and amine groups 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

350 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

355 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).

360    In contrast to the weak correlations found for FTIR NV amine groups with FTIR NV alcohol groups for <0.5 μm and <0.18 μm particle samples, strong (0.82 < R < 0.96, Figure 7c,e) correlations of FTIR NV amine to acid groups 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

365    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

370    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

375    were not enough 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$_2$ that may or may not be

380    refractory. The correlations summarized in Figure 8 show that, in marine air masses, most of the FTIR NV amine groups in <1 μm particles are primary and marine and that <0.5 μm and <0.18 μm diameter fractions are secondary and marine. In contrast, the AMS measures NR amine fragments with primary, secondary, and tertiary amine moieties that may be too volatile to be sampled on filters. The correlations summarized in Figure 8 show that AMS NR amine fragments are largely continental and secondary, although some contribution of primary emissions from combustion is also likely.

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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, all of which indicate continental secondary sources. Figure 9 shows similar correlations with AMS NR

390     nitrate and IC sea salt in Autumn that exemplify the AMS NR amine fragments correlation to AMS NR nitrate concentrations and the FTIR NV amine groups correlation to IC sea salt.

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

395     separately. This approach is supported by the poor overall correlation of ρ = 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; 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 primary marine FTIR NV amine group accounts for 53% compared to 47% secondary continental AMS NR

400     amine fragments. For Late Spring and Autumn, primary marine FTIR NV amine group accounts for 34% compared to 66% secondary continental AMS NR amine fragments. And for Early Spring, primary marine FTIR NV amine group accounts for 27% compared to 73% 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

405     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,

410     ozone, AMS NR m/z 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 primary marine tracers such as wind speed, IC sea salt, and seawater DMS, NR chloride, and chlorophyll *a* were higher than for AMS NR amine fragments.

415     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.

420

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 primary marine amine accounting

425    for 53% compared to 47% secondary continental amine in Winter, but primary marine amine accounting for only 27% compared to 73% secondary continental amine for Early Spring.

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## Data Availability

All data collected during NAAMES are available on the NASA data server: https://naames.larc.nasa.gov. Scripps

435    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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670  **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 ($\mu g\ m^{-3}$) 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 ($\mu g\ m^{-3}$) 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) |
| 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]Aµgust-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
675 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/m³) | 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/m³)* | 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/m³)* | 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/m³) | 151 ± 47 (321 ± 309) | 296 ± 107 (422 ± 227) | 373 ± 269 (824 ± 658) | 295 ± 150 (990 ± 1187) |
| FTIR NV OM (ng/m³) | 281 ± 198 (315 ± 220) | 210 ± 156 (209 ± 327) | 220 ± 165 (422 ± 420) | 200 ± 175 (375 ± 431) |
| AMS NR Nitrate (ng/m³) | 6 ± 3 (12 ± 12) | 9 ± 4 (15 ± 5) | 10 ± 6 (45 ± 101) | 8 ± 2 (14 ± 14) |
| AMS NR m/z 44 (ng/m³) | 56 ± 13 (91 ± 55) | 137 ± 33 (192 ± 70) | 123 ± 36 (224 ± 104) | 147 ± 36 (319 ± 241) |
| Black Carbon (ng/m³) | 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) | 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 (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/m³) | -- -- | -- (0.11 ± 0.19) | 0.05 ± 0.05 (0.06 ± 0.03) | 0.01 ± 0.01 (0.01 ± 0.00) |
| IC Sea Salt (µg/m³) | 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⁺ (µg/m³) | 0.01 ± 0.01 (0.02 ± 0.01) | -- (0.02 ± 0.02) | 0.00 ± 0.00 (0.02 ± 0.01) | 0.00 ± 0.00 (0.03 ± 0.02) |

*The average included filters with amine concentration below detection.

**Table 3: 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 statistically insignificant (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 | 0.77 | 0.18 | 0.85 | 0.55 | 0.85 | 0.62 | 0.89 | 0.94 |
| 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 |

700 **Table 4: 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 ≤ |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 statistically insignificant (p ≥ 0.05) are indicated by \*.**

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| 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 | 0.69 | 0.96* | 0.09* | -- |
| 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 | -0.14 | -- | -0.63 | -0.24 | 0.19 | 0.52 | -0.72 | -- |
| 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* | -- |
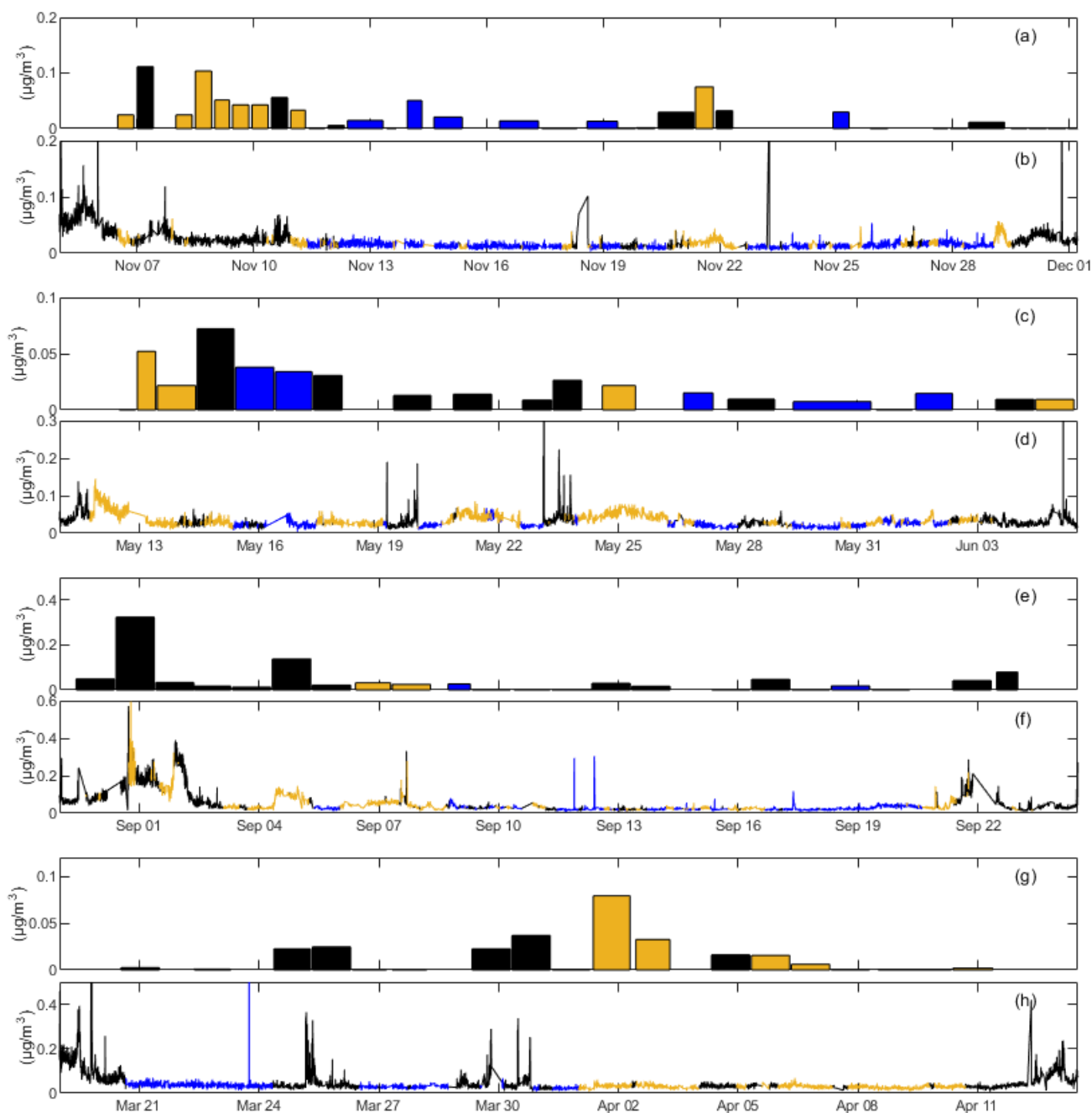
**Figure 1: Time series of AMS NR amine fragments measured by the HR-ToF-AMS (b,d,f,h) and FTIR NV amine groups measured by FTIR spectroscopy in particles with diameters <1 μm (a,c,e,g) for all four cruises. From top to bottom: Winter (a,b), Late Spring (c,d), Autumn (e,f), Early Spring (g,h). Marker colors represent air mass type- blue: marine, yellow: continental, black: winds abaft or mixed.**

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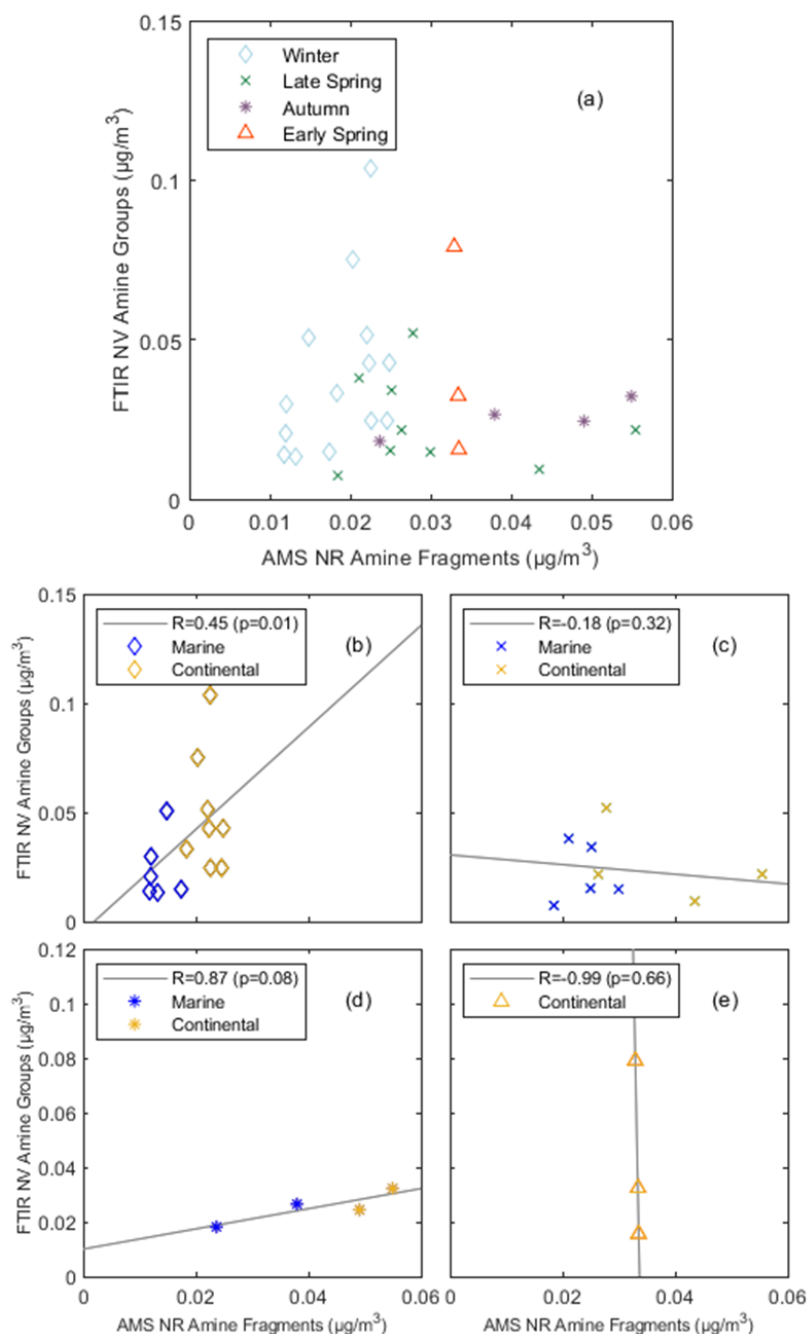
**Figure 2: Scatter plot of (ADL) FTIR NV amine groups in particles with diameters <1 μm versus AMS NR amine fragments for (a) all cruises (ρ = 0.02, p = 0.18), (b) Winter, (c) Late Spring, (d) Autumn, and (e) Early Spring. Markers represent each cruise- open diamond: Winter, crosses: Late Spring, asterisk: 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-**
720    **tailed T test is used to estimate p-values.**
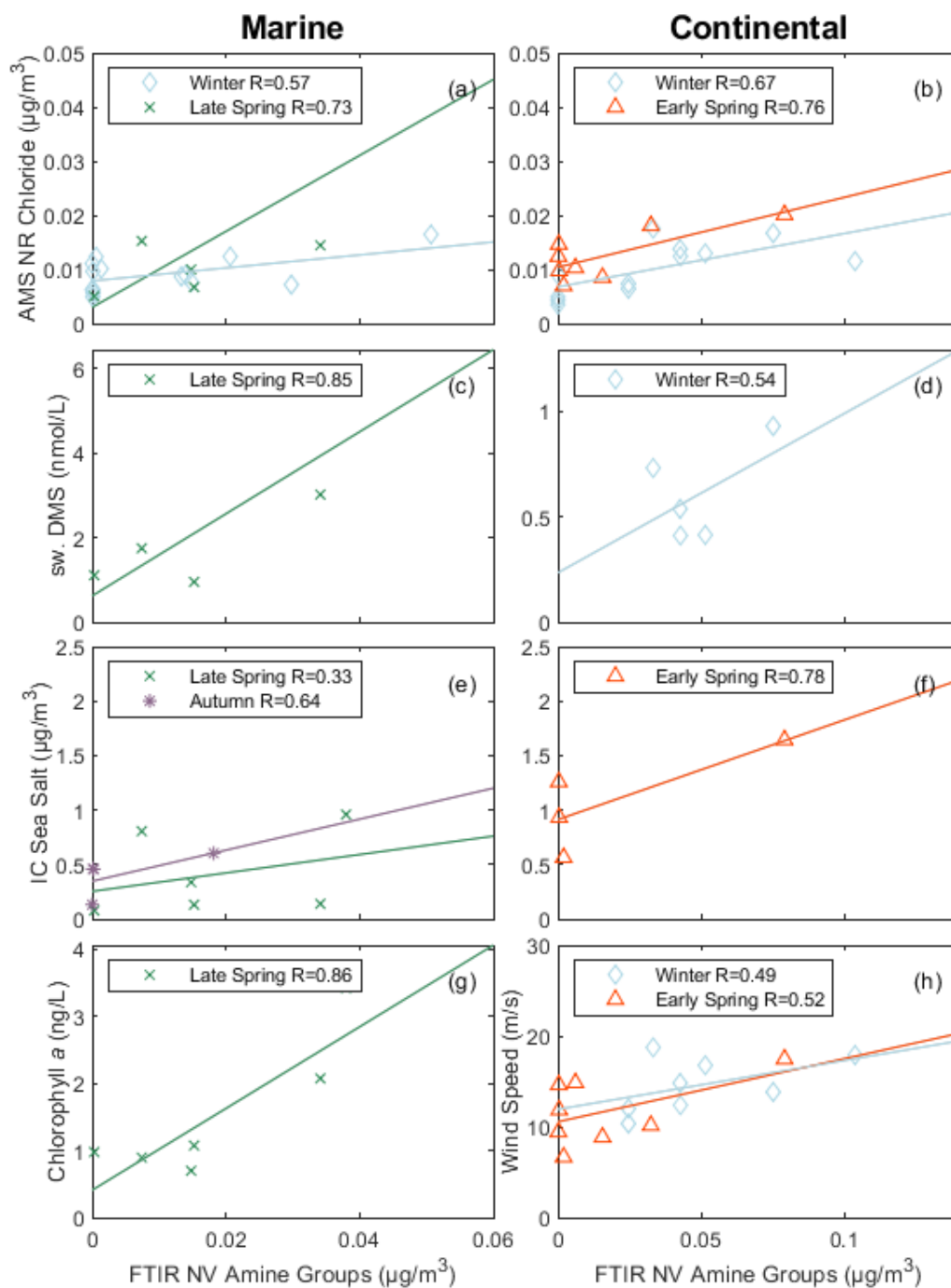
**Figure 3: Scatter plot of marine tracers versus FTIR NV amine groups in particles with diameters <1 µm for marine periods (a,c,e,g) and continental periods (b,d,f,h). The panels include AMS NR chloride (a,b), seawater DMS (c,d), IC sea salt (e,f), chlorophyll *a* (g), wind speed (h). Markers represent 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 a two-tailed T test is used to estimate p-values.**
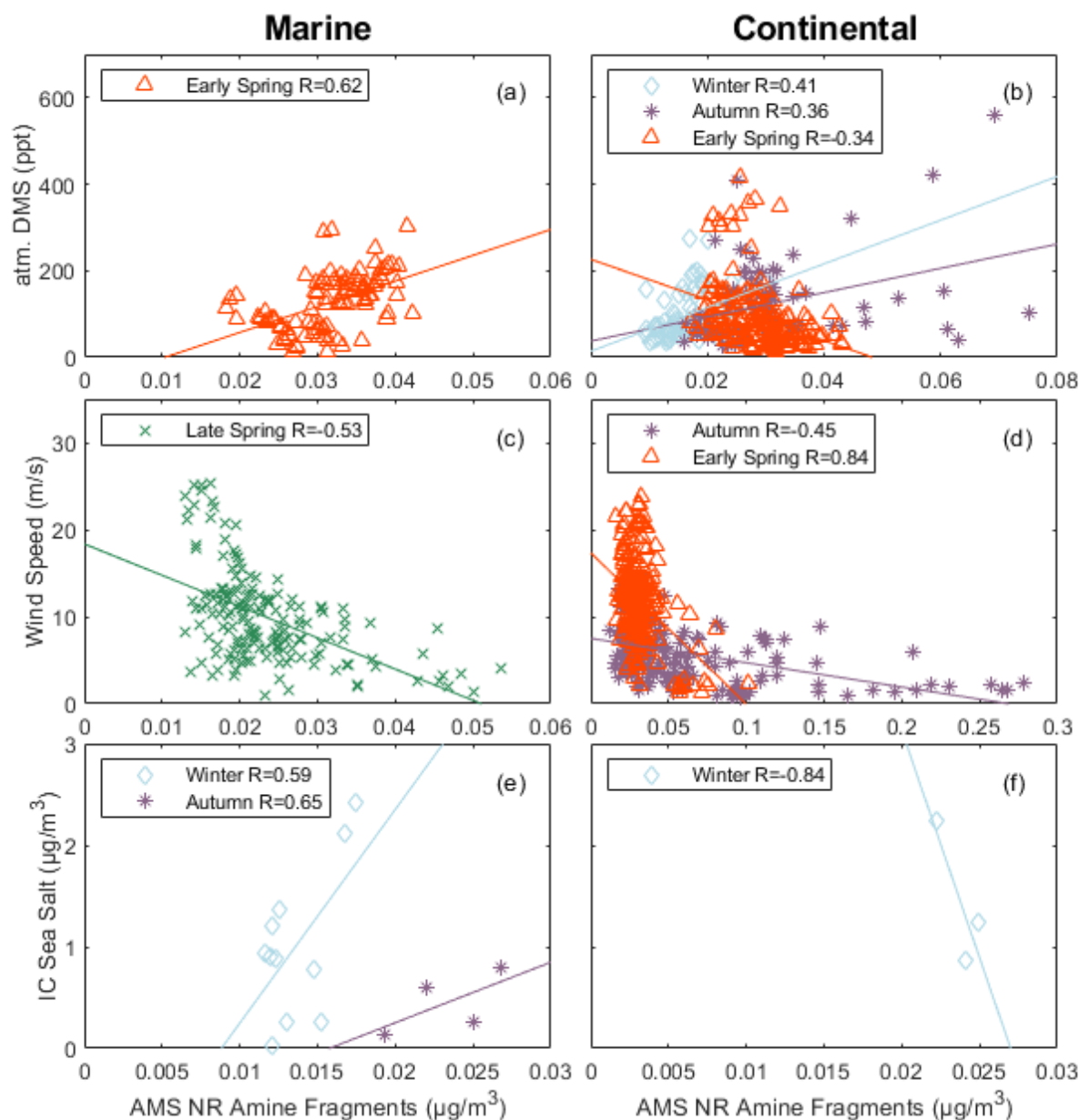
**Figure 4: Scatter plot of marine tracers versus AMS NR amine fragments for marine periods (a,c,e) and continental periods (b,d,f).** The panels include atmospheric DMS (a,b), wind speed (c,d), IC sea salt (e,f). Markers represent each cruise- blue open diamond: Winter, green cross: Late Spring, purple 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.

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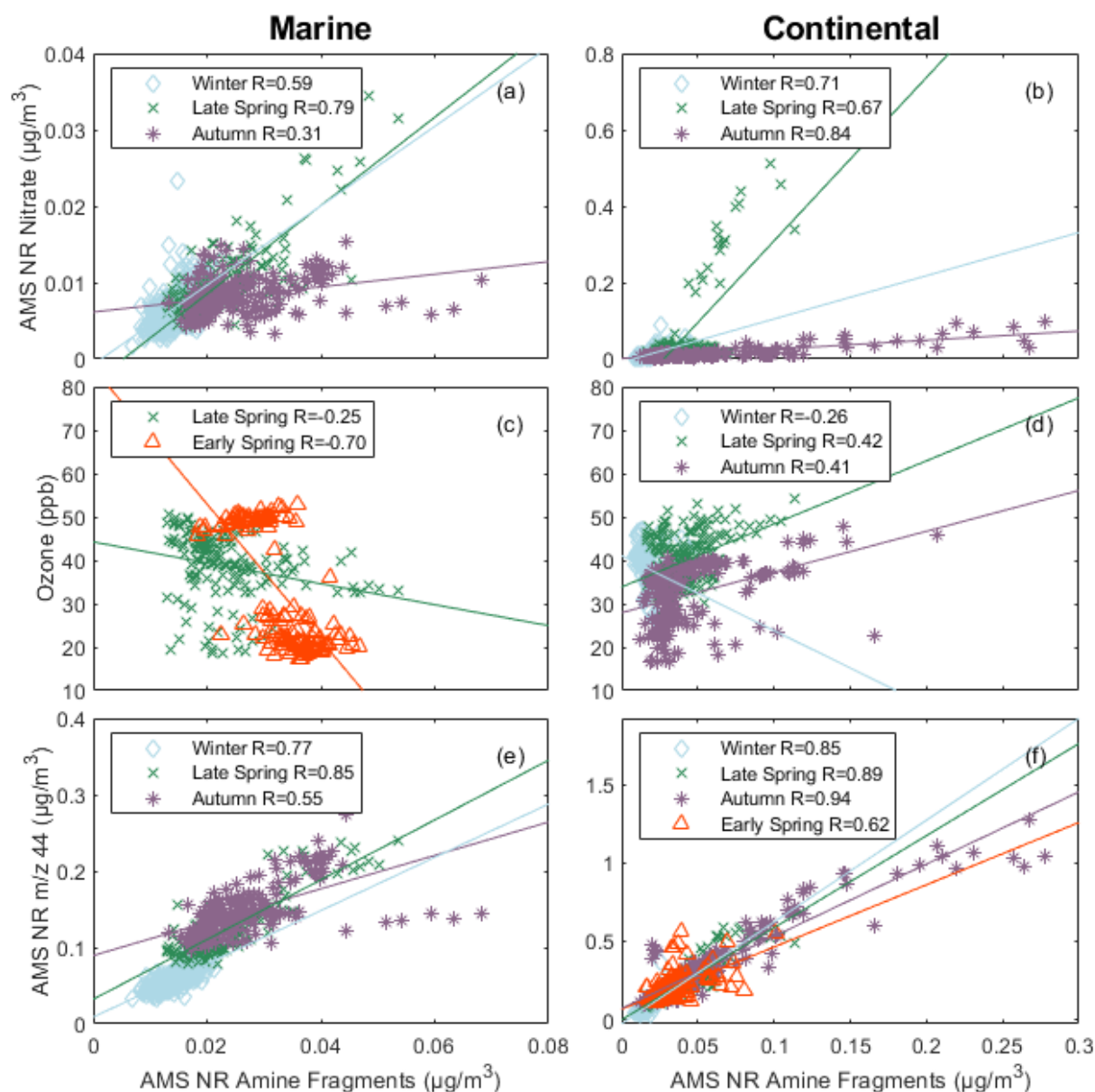
**Figure 5: Scatter plot of secondary tracers versus AMS NR amine fragments for marine periods (a,c,e) and continental periods (b,d,f). The panels include submicron AMS NR nitrate (a,b), ozone (c,d), and AMS NR m/z 44 (e,f). Markers represent each cruise- blue open diamond: Winter, green cross: Late 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.**
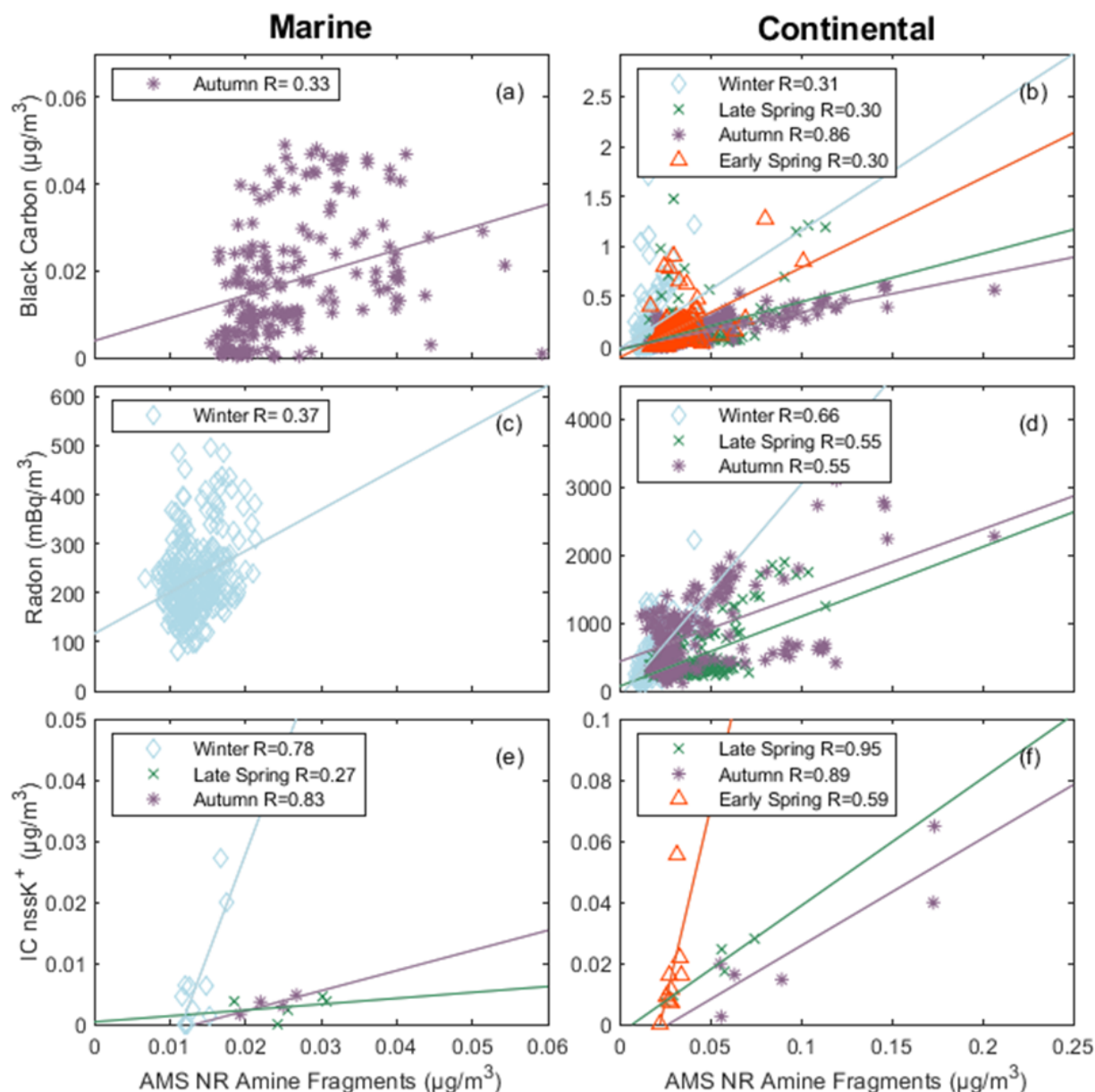
**Figure 6: Scatter plot of non-marine tracers versus AMS NR amine fragments for marine periods (a,c,e) and continental periods (b,d,f). The panels include black carbon (a,b), radon (c,d), IC nssK⁺ (e,f). Markers represent each cruise- blue open diamond: Winter, green cross: Late Spring, purple asterisk: 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.**
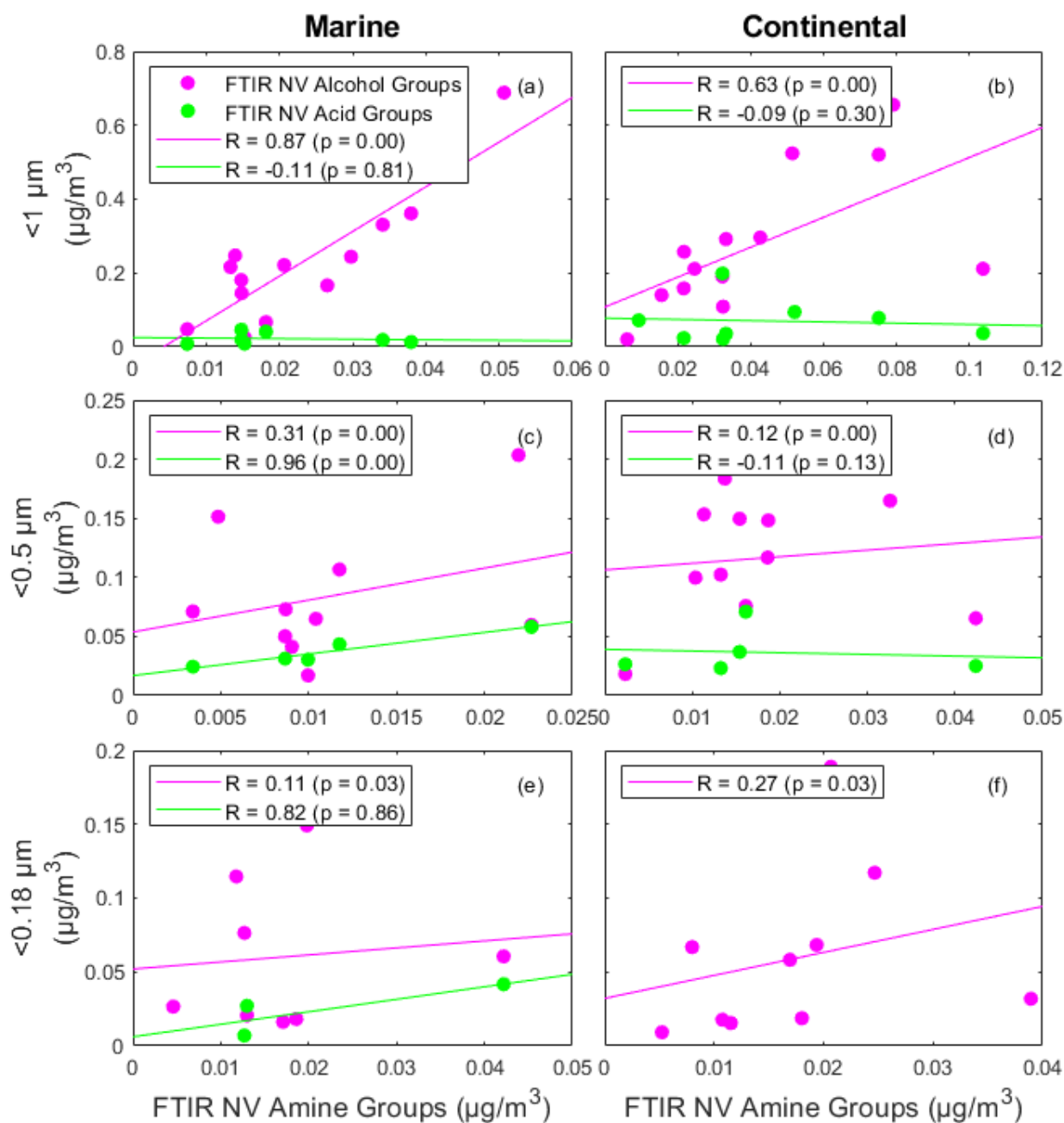
**Figure 7:** Scatter plot of FTIR primary (FTIR NV alcohol group: pink) and secondary (FTIR NV carboxylic acid group: green) tracers versus FTIR NV amine groups for marine filters (a,c,e) and continental filters (b,d,f) with functional group concentrations twice the standard deviation. The panels show 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.

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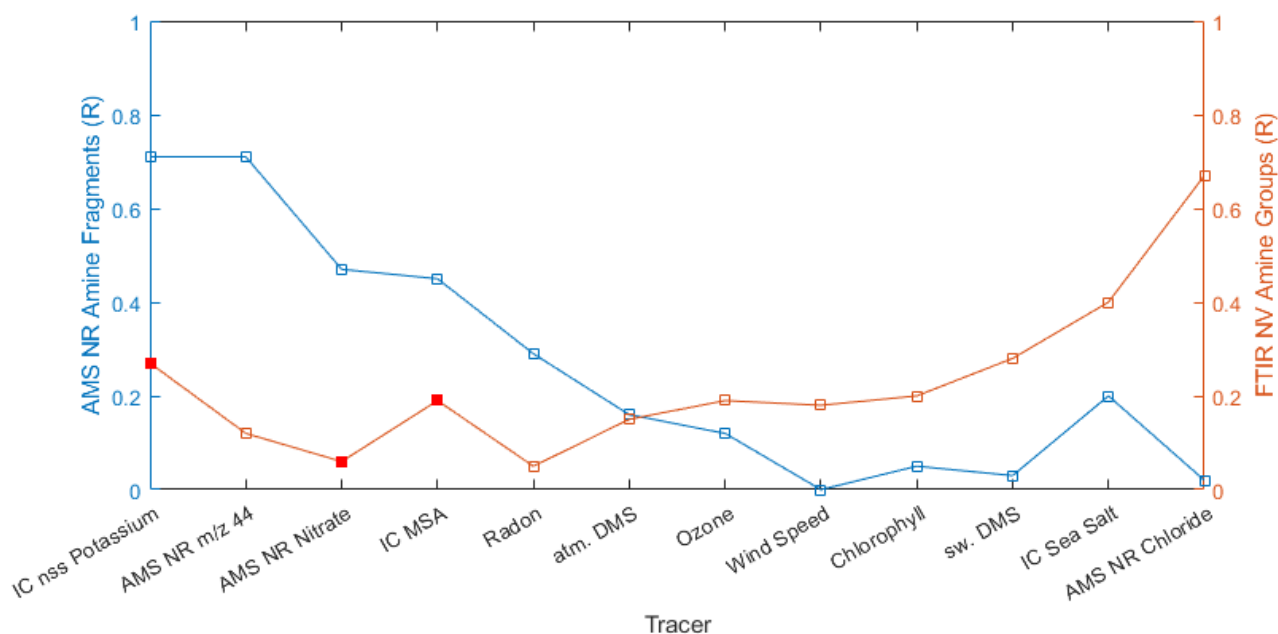
755 **Figure 8: Plot of average Pearson correlation coefficients (R) of AMS NR amine fragments (blue) and FTIR NV amine groups in particles with diameters <1 μm (orange) with selected tracers. Negative correlations were averaged as 0 and only statistically significant (p < 0.05) correlations were included, except for markers shown as solid red (which were not significant).**
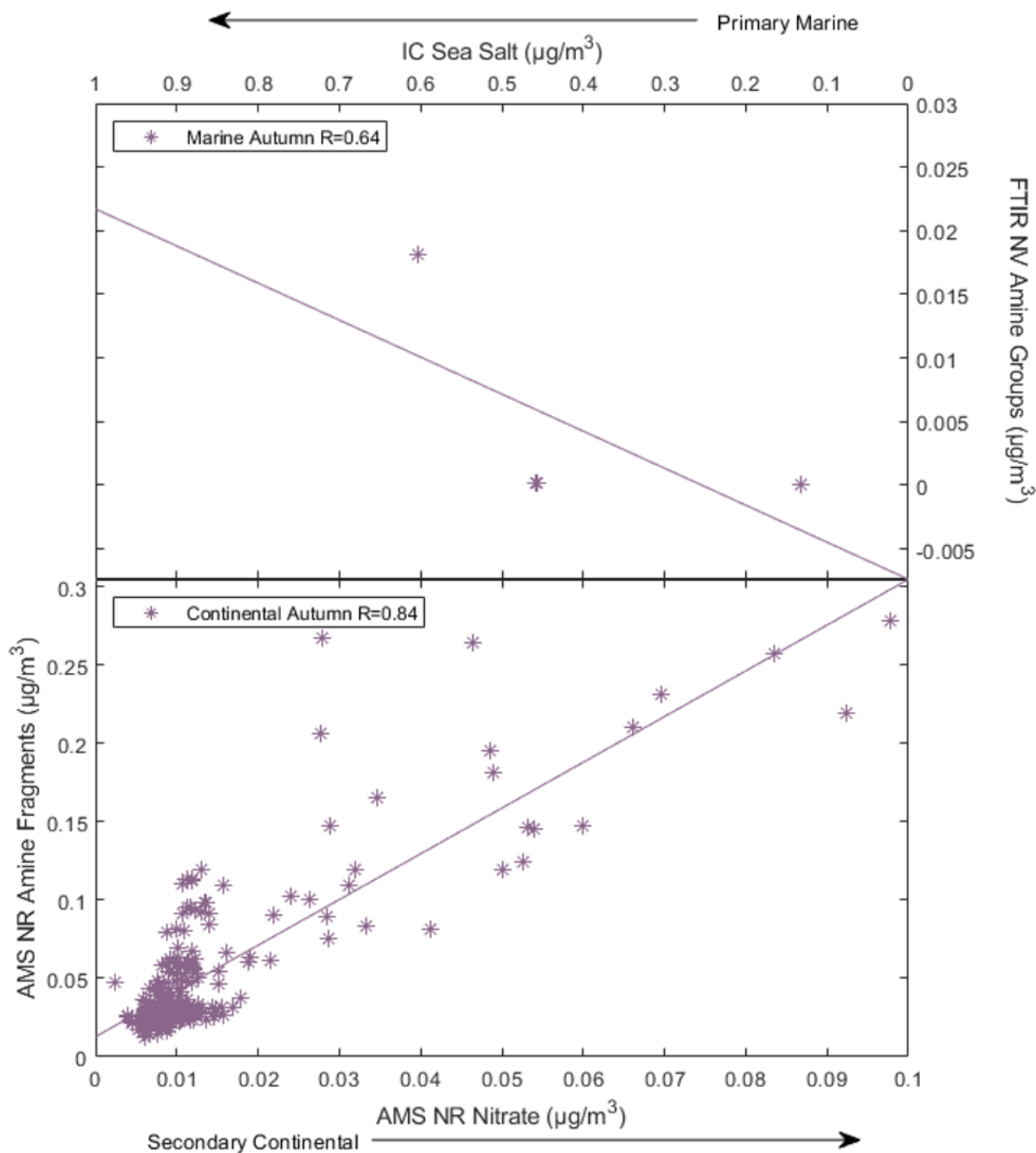
**Figure 9: Scatter plot of (top) FTIR NV amine groups in particles with diameters <1 µm versus a primary marine tracer (IC sea salt) and (bottom) AMS NR amine fragments versus a secondary continental tracer (AMS NR nitrate) during the Autumn season. Both correlations are statistically significant (p < 0.05). 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.**