

Response to the comments of Anonymous Referee #3

[Atmospheric Chemistry and Physics, MS ID: acp-2018-53]

Title: Characteristics and mixing state of amine-containing particles at a rural site in the Pearl River Delta, China.

General comments:

This paper uses single-particle mass spectrometry to characterize particle-phase amines observed in a rural part of the Pearl River Delta in China. The analysis in this paper builds upon previous observations of amines to examine the types of amines observed and the role of acidity on the partitioning of particle phase amines using single particle mass spectrometry. Before the paper can be considered for publication, more information is needed about which amine markers were observed on the different particle types as I have reservations about the interpretation of the spectra that must be adequately addressed.

Response: Thank you for your comments. We have revised the whole manuscript according to your comments. The classification criteria for BB and nitrate-rich types of particles in the manuscript were inappropriate due to the misinterpretation of several key markers. Thus, we have removed all the description and discussions related with three types of amine-containing particles. Three major amine markers were selected, and the characteristics of these specific amine marker containing particles were investigated. The seasonal different mixing state of amines and ammonium may be influenced by the seasonal variation of source strength of ammonium. Thus, we have added the discussion of ammonium-containing particles in the manuscript. The detailed responses to the comments are itemized below. We appreciate these valuable and helpful comments for improving our paper, as well as the important guiding significance to our researches.

Anything about our paper, please feel free to contact me at limei2007@163.com

Best regards!
Sincerely yours
Mei Li
May 22, 2018

Specific comments and point by point responses:

Major Comments:

I have several major concerns about this work that need to be addressed:

1. For the nitrate-rich particles observed in summer, m/z +46 is claimed to be an amine peak. However, several single-particle studies note the presence of m/z +46 in sea salt spectra due to the presence of $^{46}\text{Na}_2^+$ (e.g., Guazzotti et al., 2001; Gard et al., 1998; Gaston et al., 2011). Was m/z +46 the only “amine” ion peak noted in this particle type? If so, then this ion peak is likely a marker for sodium and not an amine. The text would need to be adjusted and conclusions about marine biogenic amines would need to be removed.

Response: We have reconsidered the classification criteria for the nitrate-rich particles which contained many sea-salt markers. Ion of m/z +46 could be $^{46}\text{Na}_2^+$ except as amine marker of $^{46}(\text{CH}_3)_2\text{NH}_2^+$, because no other amine markers were found and nitrate-rich particles were enriched with sodium salts like $^{62}\text{Na}_2\text{O}^+$, $^{81}\text{Na}_2\text{Cl}^+$ and $^{147}\text{Na}(\text{NO}_3)_2^-$, so we removed nitrate-rich particles from amine-containing particles, and all the related discussions were removed too.

“In this work the m/z +46-containing particles had no other amine markers as listed above, besides, these particles were enriched with sodium salts like $^{62}\text{Na}_2\text{O}^+$, $^{81}\text{Na}_2\text{Cl}^+$ and $^{147}\text{Na}(\text{NO}_3)_2^-$. Thus, m/z +46-containing particles were not classified as amine-containing particles.” have been added in the lines 216-220.

“The nitrate-rich amine-containing particles exhibited spectral features different from those observed in the ECOC and BB spectra. Only a few carbonaceous fragments were observed. In summer, the nitrate-rich amine-containing particles contained abundant sea-salt markers such as m/z s 23 $[\text{Na}]^+$, 62 $[\text{Na}_2\text{O}]^+$, and 63 $[\text{Na}_2\text{OH}]^+$ in the positive mass spectrum and m/z s -93 $[\text{NaCl}_2]^-$ and -147 $[\text{Na}(\text{NO}_3)_2]^-$ in the negative mass spectrum. Chloride signal was not detected due to the depletion of chloride and enrichment of nitrate in the sea-salt particle aging process. In summer, 48-h backward trajectories showed that 60 % of air masses arose from marine areas (Figure S3) and were partly associated with marine aerosols. A small peak of m/z 46 $[(\text{CH}_3)_2\text{NH}_2]^+$ was found in the nitrate-rich amine-containing particle spectra in summer, which likely arose from DMA produced by marine phytoplankton. The backward trajectories and mass spectra of the nitrate-rich particles indicate that marine sources may contribute to the amine distribution in the PRD region during summer, although the amine-containing particles appeared to have been aged during transportation. In winter, air masses were transported largely from urban areas like Guangzhou and Foshan (Figure S3) and brought more anthropogenic pollutants to the sampling site. Hence, the sea-salt markers at m/z s -93 $[\text{NaCl}_2]^-$ and -147 $[\text{Na}(\text{NO}_3)_2]^-$ were not observed in the winter negative mass spectrum. Instead, the m/z 56 $[\text{Fe}]^+$ ion was identified, and, because no dust source marker ion signals (such as Ca^+ , CaO^+ , and SiO_3^-) were found, we speculate that iron arose mainly from industrial emissions. The nitrate-rich amine-containing particles may have resulted from direct industrial emissions or reactions between gaseous amines and particles from industrial emissions. Lastly, the observed nitric acid signal (m/z -125

[HNO₃NO₃]⁻) indicated strong particle acidity in the nitrate-rich amine-containing particles in winter.” have been removed from the manuscript.

“The nitrate-rich amine-containing particles were mixed with abundant sea-salt markers in summer, indicating a possible association between the amine emission source and marine phytoplankton.” have been removed from the abstract.

“In summer, the nitrate-rich amine-containing particles were mixed with abundant sea-salt markers, indicating an association between amines and marine phytoplankton emissions.” have been removed from the conclusion.

2. I have a similar concern for m/z +74 observed in biomass burning particles. This ion peak is also associated with KCl (e.g., 74KCl⁺) and may not be indicative of an amine. I suggest that the authors review Zauscher et al., 2013, which does show evidence of biomass burning particles containing amine markers.

Response: According to the studies of Zauscher et al. (2013), biomass burning particles were detected with strong signals of potassium chloride (¹¹³K₂Cl⁺), potassium nitrate (¹⁴⁰K₂NO₃⁺) and potassium sulfate (²¹³K₃SO₄⁺), so we believe the definition of BB type particles used in this work was inappropriate. Thus, we have removed BB type particles from amine-containing particles, and all the related discussions were removed too. The marker ion of m/z +74 could be ⁷⁴KCl⁺ except as ⁷⁴(C₂H₅)₂NH₂⁺, however, no other significant biomass burning markers like ¹¹³K₂Cl⁺, ¹⁴⁰K₂NO₃⁺ and ²¹³K₃SO₄⁺ were found in the amine-containing particles, so the presence of m/z +74 in amine-containing particles has a very low possibility to be ⁷⁴KCl⁺.

“Amine-containing particles were subsequently clustered using the adaptive resonance theory (ART-2a) neural network algorithm with a vigilance factor of 0.75, a learning rate of 0.05, and a maximum of 20 iterations. The amine-containing particles were classified into three types: elemental and organic carbon (ECOC), biomass burning (BB), and nitrate-rich. The ion markers and selective criterion for these three particle types are as follows (Table S1): (1) ECOC-type particles contain abundant carbon clusters of m/zs ± 12 [C]^{+/-}, ± 24 [C₂]^{+/-}, ± 36 [C₃]^{+/-}, and hydrocarbon clusters at m/zs 37 [C₃H]⁺ and 43 [C₃H₇]⁺/[C₂H₃O]⁺ with relative peak areas higher than 0.5 %; (2) BB-type particles consist of any remaining particles containing abundant signal at m/z 39 [K]⁺ (relative peak area > 30 %) and m/zs -59 [C₂H₃O₂]⁻ and -73 [C₃H₅O₂]⁻ (relative area of both peaks > 0.5 %); (3) any remaining particles containing abundant signal at m/zs -46 [NO₂]⁻ and -62 [NO₃]⁻ with relative peak areas higher than 10% are classified as nitrate-rich. The above classification protocol for amine-containing particles has been used in other studies (Bi et al., 2011; Pratt et al., 2011; Zhang et al., 2013). These three types of amine-containing particles constitute 93.5 % and 94.8 % of the total amine-containing particles in summer and winter, respectively.” have been revised to “Particle size and chemical composition were obtained via SPAMS mass spectral analysis using the Computational Continuation Core (COCO; version 3.0) toolkit in Matlab. According to the field studies of ATOFMS and SPAMS, it is difficult to accurately determine the number concentration of ambient particles using

SPAMS alone due to the size-dependent transmission efficiencies of particles through aerodynamic lens and composition dependent matrix effect (Gross et al., 2000; Pratt and Prather, 2012). Thus, the particle counts and size distributions presented in this work should be interpreted as semi-quantitative and serve as a basis of comparison analysis (Healy et al., 2012). Based on previous studies using ATOFMS and SPAMS instruments (Angelino et al., 2001; Huang et al., 2012; Zhang et al., 2012; Zauscher et al., 2013; Healy et al., 2015), amine-containing particles were characterized by marker ions, including m/z $^{59}(\text{CH}_3)_3\text{N}^+$, $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$, $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$, $^{101}(\text{C}_2\text{H}_5)_3\text{N}^+$, $^{102}(\text{C}_3\text{H}_7)_2\text{NH}_2^+$, and $^{143}(\text{C}_3\text{H}_7)_3\text{N}^+$ (Table 1). In this work, a particle was identified as amine-containing if it contained any of the marker ions listed above with a relative peak area (defined as the percentage contribution of the target ion peak area to the sum of all ion peak areas) greater than 1%. It should be noted that amine-containing particles are operationally defined and not exclusive, which also contained various chemical species in addition to amines. According to this criterion, 57452 and 68026 amine-containing particles were identified in summer and winter, respectively, which accounted for 11.1 % and 9.4 % of the total detected particles. These number fractions are consistent with previously reported observations in the PRD (Zhang et al., 2012). However, due to the absence of fog events during the campaign, no dramatic increases in amine-containing particles associated with high RH conditions (RH > 90 %) were observed. Marker ions of $^{59}(\text{CH}_3)_3\text{N}^+$, $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$, $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ were detected as the most abundant amines species during the sampling period, so particles containing each marker ion were selected to investigate the possible sources and characteristics of amine-containing particles. $^{30}\text{CH}_3\text{NH}^+$ is also an amine marker which has been reported by other single particle studies (Phares et al., 2003; Glagolenko and Phares, 2004). In this work the peak intensity of $^{30}\text{CH}_3\text{NH}^+$ was much lower compared with other amine markers, and all the particles containing $^{30}\text{CH}_3\text{NH}^+$ had strong signal of $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$, so the $^{30}\text{CH}_3\text{NH}^+$ -containing particles were not specifically discussed. Ion of m/z +46 was detected in the ambient single particles, which could be the amine marker of $^{46}(\text{CH}_3)_2\text{NH}_2^+$ and/or $^{46}\text{Na}_2^+$ according to reported studies (Guazzotti et al., 2001; Gaston et al., 2011; Healy et al., 2015). In this work the m/z +46-containing particles had no other amine markers as listed above, besides, these particles were enriched with sodium salts like $^{62}\text{Na}_2\text{O}^+$, $^{81}\text{Na}_2\text{Cl}^+$ and $^{147}\text{Na}(\text{NO}_3)_2^-$. Thus, m/z +46-containing particles were not classified as amine-containing particles.” in lines 183-220.

“Amine-containing particles were categorized as ECOC, BB, and nitrate-rich both in summer and winter. ECOC amine-containing particles were dominant, accounting for 67.2 % and 74.8 % of particle count in summer and winter, respectively (Table 1). ECOC particles exhibited variations similar to those in total amine-containing particles in both summer and winter. Nitrate-rich particles were the second most abundant in summer, during which time they accounted for 13.4 % of total amine-containing particles, while BB particles were the second most abundant in winter, accounting for 16.3 % of total amine-containing particles. Nitrate-rich particles were three times more abundant in summer than in winter, suggesting the existence of aminium nitrate salts in summer. The average mass spectra of ECOC, BB,

and nitrate-rich amine-containing particles in summer and winter are shown in Figure 4. The ECOC amine-containing particles in both summer and winter were characterized by high fractions of 39 [K]⁺; carbonaceous marker ions, including *m/z*s 27 [C₂H₃]⁺, 29 [C₂H₅]⁺, 36 [C₃]⁺, 37 [C₃H]⁺, 43 [C₂H₃O]⁺, 48 [C₄]⁺, 51 [C₄H₃]⁺, 53 [C₄H₅]⁺, 60 [C₅]⁺, 63 [C₅H₃]⁺, 65 [C₅H₅]⁺, and 77 [C₆H₅]⁺; and amine fragment ions at *m/z*s 46 [(CH₃)₂NH₂]⁺, 59[(CH₃)₃N]⁺, 74 [(C₂H₅)₂NH₂]⁺, and 86 [(C₂H₅)₂NCH₂]⁺/[C₃H₇NHC₂H₄]⁺ in the positive mass spectrum. The ECOC particle negative mass spectrum was characterized by strong carbon-nitrogen fragment signals at *m/z*s -26 [CN]⁻ and -42 [CNO]⁻, as well as abundant secondary ions at *m/z*s -46 [NO₂]⁻, -62 [NO₃]⁻, -80 [SO₃]⁻, and -97 [HSO₄]⁻ in both summer and winter. In many field studies, aged carbonaceous particles always contain abundant secondary sulfate, nitrate, and ammonium ions. Interestingly, in this work, the ammonium signal (*m/z* 18 [NH₄]⁺) was not found in ECOC amine-containing particles in summer, and only a very small ammonium peak was detected in winter. The low ammonium signal in ECOC amine-containing particles may have been due to the exchange of particulate ammonium for gas-phase amines (Lloyd et al., 2009; Qiu et al., 2011; Chan and Chan, 2012; Chan and Chan, 2013; Chu and Chan, 2016, 2017; Sauerwein and Chan, 2017). In both summer and winter, the mass spectra of BB amine-containing particles showed carbonaceous markers and secondary ions similar to those found in ECOC amine-containing particles, with additional distinct ion peaks at *m/z* 23 [Na]⁺ and BB markers at *m/z*s -59 [C₂H₃O₂]⁻, -71 [C₃H₃O₂]⁻, and -73 [C₃H₅O₂]⁻. No ammonium was found in BB amine-containing particles in either summer or winter, likely because of exchange reactions similar to those inferred in the ECOC amine-containing particles (see Section 3.3).” have been revised to “Among the three markers we considered, the most abundant amine marker was ⁷⁴(C₂H₅)₂NH₂⁺, which was detected in 90% and 86% of amine-containing particles in summer and winter (Table 2), followed by ⁵⁹(CH₃)₃N⁺ and ⁸⁶(C₂H₅)₂NCH₂⁺ which were detected in less than 10% of amine-containing particles during sampling period. The amine particles containing ⁷⁴(C₂H₅)₂NH₂⁺ and ⁸⁶(C₂H₅)₂NCH₂⁺ both exhibited similar variation pattern with total amine-containing particles suggesting a similar emission source of ⁷⁴(C₂H₅)₂NH₂⁺ and ⁸⁶(C₂H₅)₂NCH₂⁺ (Figure 2). The temporal trend of ⁵⁹(CH₃)₃N⁺-containing particles were different from those of ⁷⁴(C₂H₅)₂NH₂⁺ and ⁸⁶(C₂H₅)₂NCH₂⁺; and the two sudden episodes of ⁵⁹(CH₃)₃N⁺ occurred from 27 to 29 July in summer were possibly due to the special emission sources of trimethylamine (TMA).” in lines 245-256 and “The average mass spectra of amine-containing particles in summer and winter are shown in Figure 4. The amine-containing particles were characterized by high fractions of carbonaceous marker ions, including ²⁷C₂H₃⁺, ²⁹C₂H₅⁺, ³⁶C₃⁺, ³⁷C₃H⁺, ⁴³C₂H₃O⁺, ⁴⁸C₄⁺, ⁵¹C₄H₃⁺, ⁵³C₄H₅⁺, ⁶⁰C₅⁺, ⁶³C₅H₃⁺, ⁶⁵C₅H₅⁺, and ⁷⁷C₆H₅⁺; and amine marker ions of ³⁰CH₃NH⁺, ⁵⁹(CH₃)₃N⁺, ⁷⁴(C₂H₅)₂NH₂⁺ and ⁸⁶(C₂H₅)₂NCH₂⁺ in the positive mass spectrum in both summer and winter. The negative mass spectrum was characterized by strong carbon-nitrogen fragments like ²⁶CN⁻ and ⁴²CNO⁻, as well as abundant secondary ions of ⁴⁶NO₂⁻, ⁶²NO₃⁻, ⁸⁰SO₃⁻, and ⁹⁷HSO₄⁻ in both summer and winter. In many field studies, aged carbonaceous particles always contain abundant secondary ions of sulfate, nitrate, and ammonium. Interestingly, in this work, the signals of

$^{18}\text{NH}_4^+$ were weak and only observed in less than 10% of amine-containing particles in summer, but moderate signal of $^{18}\text{NH}_4^+$ was detected in half of amine-containing particles in winter. The low $^{18}\text{NH}_4^+$ signal in amine-containing particles may have been due to the emission sources of ammonia and particle acidity, which will be discussed in Section 3.3.” in lines 270-284.

“Amine-containing particles were classified into three types: elemental and organic carbon (ECOC), biomass burning (BB), and nitrate-rich. ECOC amine-containing particles were the most abundant, constituting 67.2 % and 74.8 % of amine particles in summer and winter, respectively. Both ECOC and BB type amine-containing particles contained abundant carbonaceous and carbon-nitrogen species, as well as sulfate and nitrate, in summer and winter.” have been removed from the abstract.

“The ECOC and BB amine-containing particles showed strong carbonaceous ion, carbon-nitrogen ion, sulfate, and nitrate signals in summer and winter.” have been removed from the conclusion.

3. The authors need to clarify if one amine is seen on the different particle types or multiple markers. I also suggest adding a figure showing the temporal trends for each amine marker.

Response: Revision made. We reanalyzed the campaign data as you suggested, and the temporal trends of each amine marker-containing particles are shown in Figure 2.

“Marker ions of $^{59}(\text{CH}_3)_3\text{N}^+$, $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$, $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ were detected as the most abundant amines species during the sampling period, so particles containing each marker ion were selected to investigate the possible sources and characteristics of amine-containing particles.” have been added in the lines 206-209.

“Among the three markers we considered, the most abundant amine marker was $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$, which was detected in 90% and 86% of amine-containing particles in summer and winter (Table 2), followed by $^{59}(\text{CH}_3)_3\text{N}^+$ and $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ which were detected in less than 10% of amine-containing particles during sampling period. The amine particles containing $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$ and $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ both exhibited similar variation pattern with total amine-containing particles suggesting a similar emission source of $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$ and $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ (Figure 2). The temporal trend of $^{59}(\text{CH}_3)_3\text{N}^+$ -containing particles were different from those of $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$ and $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$; and the two sudden episodes of $^{59}(\text{CH}_3)_3\text{N}^+$ occurred from 27 to 29 July in summer were possibly due to the special emission sources of trimethylamine (TMA).” have been added in the lines 245-256.

“Among the three markers we considered, the most abundant amine marker was $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$, which was detected in 90% and 86% of amine-containing particles in summer and winter, followed by amine marker ions of $^{59}(\text{CH}_3)_3\text{N}^+$, and $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ which were detected in less than 10% of amine-containing particles during sampling period.” have been added in the abstract in lines 51-55.

“Both seasons were dominated by amine marker of $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$ in 90% and

86% of amine-containing particles in summer and winter, respectively. Amine markers of $^{59}(\text{CH}_3)_3\text{N}^+$ and $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ were detected in 4.5% and 5.5% of amine-containing particles in summer, while their percentages both increased two times in winter. The amine particles contained $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$ and $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ both exhibited similar variation pattern with total amine-containing particles suggesting a similar emission source of $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$ and $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$, while the $^{59}(\text{CH}_3)_3\text{N}^+$ -containing particles showed different temporal trends, and two sudden increase episodes of $^{59}(\text{CH}_3)_3\text{N}^+$ in summer was possibly due to the special sources of trimethylamine.” have been added in the conclusion in lines 403-412.

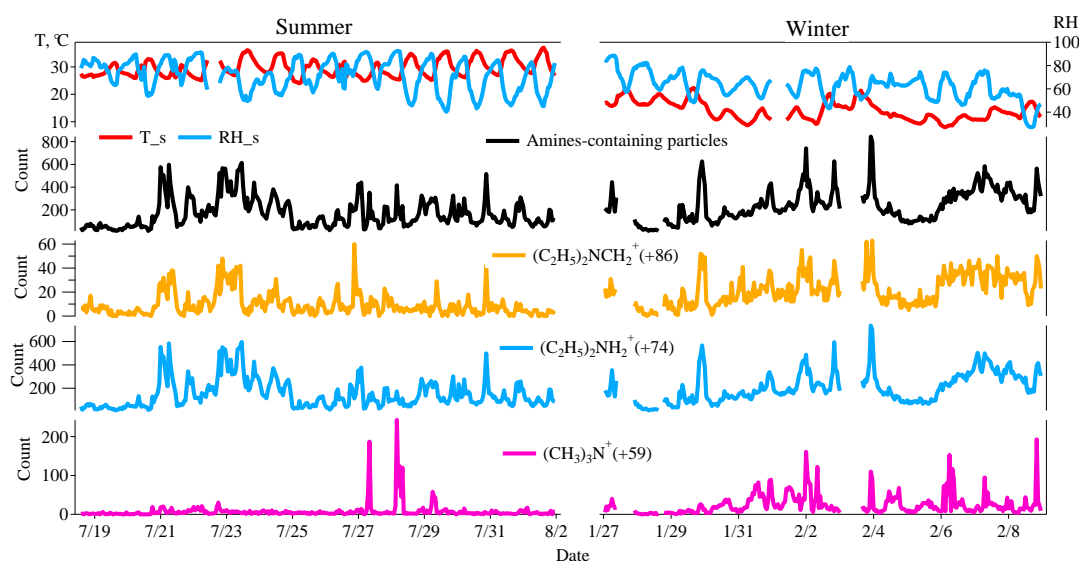


Figure 2. Temporal variations of relative humidity (RH), temperature (T), total amine-containing particles, and three major marker ions-containing amine particles ($^{59}(\text{CH}_3)_3\text{N}^+$, $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$, $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$) in Heshan, China during sampling periods.

4. The spectra in Figure 4 need to clearly show all of the amine markers observed on the different particle types.

Response: The amine markers of $^{30}\text{CH}_3\text{NH}^+$, $^{59}(\text{CH}_3)_3\text{N}^+$, $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$, $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ have been labeled in the mass spectra of amine-containing particles in Figure 4. The other amine markers of $^{101}(\text{C}_2\text{H}_5)_3\text{N}^+$, $^{102}(\text{C}_3\text{H}_7)_2\text{NH}_2^+$, and $^{143}(\text{C}_3\text{H}_7)_3\text{N}^+$ were found with a much lower peak intensity, and the number count of amine particles contained these markers were less than 1%. So $^{101}(\text{C}_2\text{H}_5)_3\text{N}^+$, $^{102}(\text{C}_3\text{H}_7)_2\text{NH}_2^+$, and $^{143}(\text{C}_3\text{H}_7)_3\text{N}^+$ were not labeled in the mass spectra.

The old Figure 4:

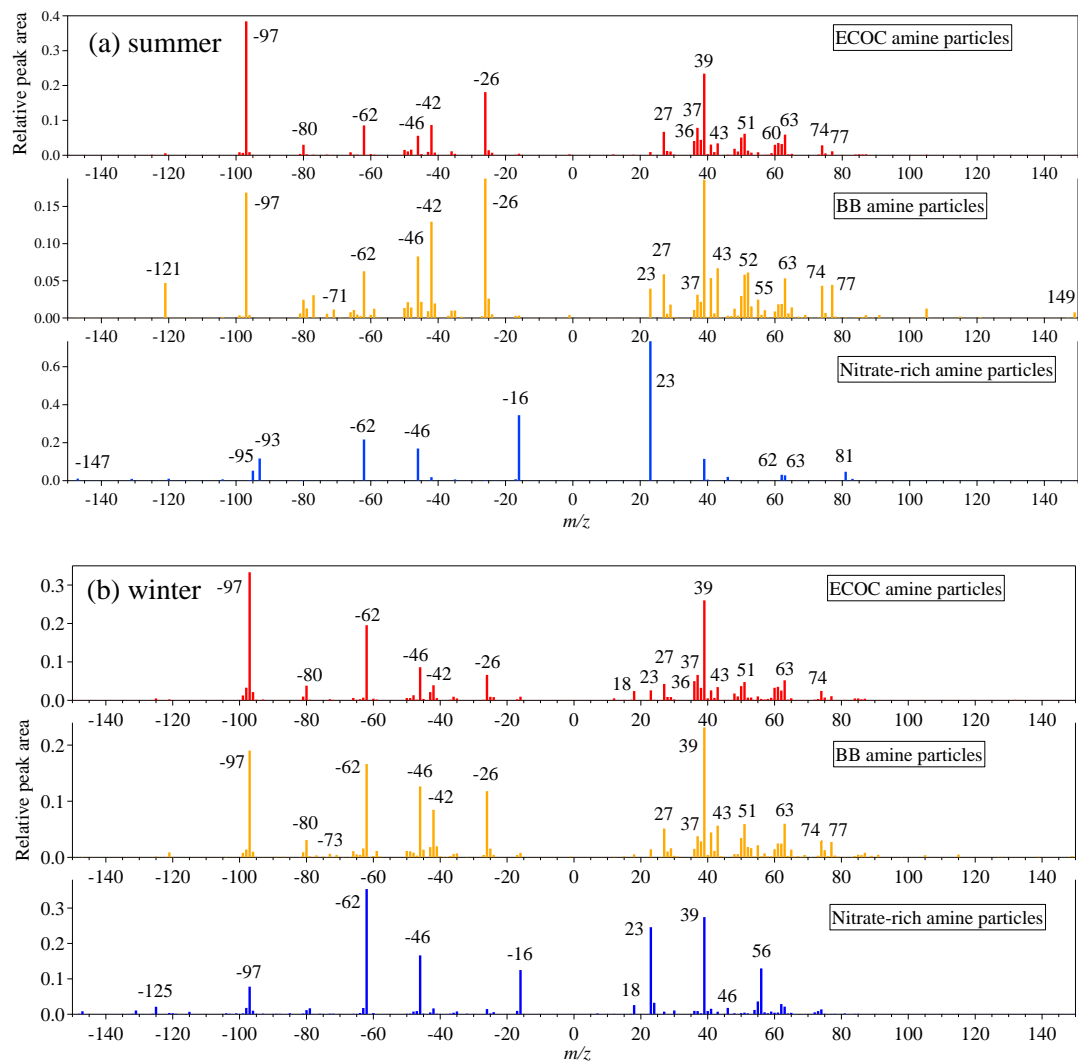


Figure 4. Average ion mass spectra of ECOC, BB, and nitrate-rich amine-containing particles in (a) summer and (b) winter.

The new Figure 4:

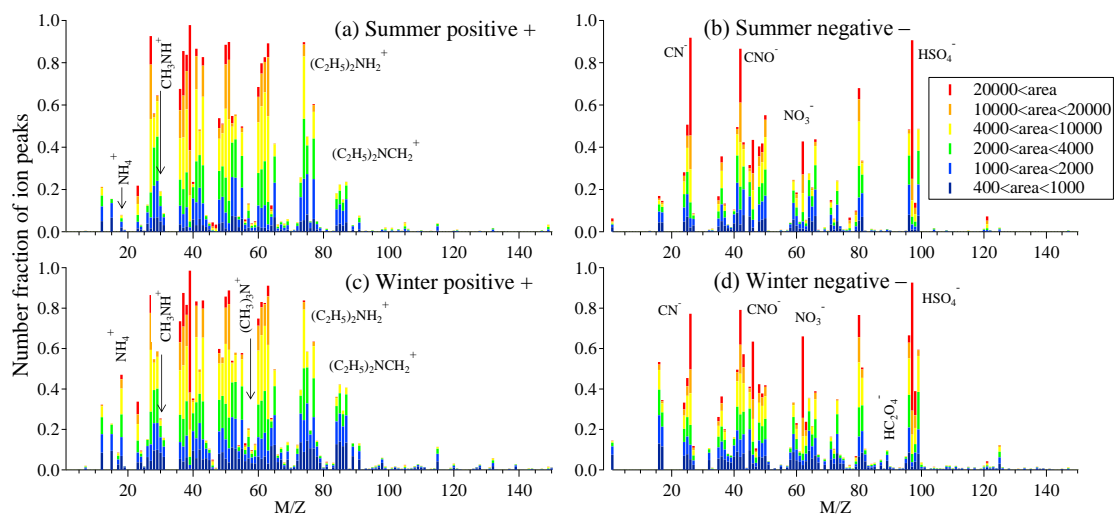


Figure 4. Average ion mass spectra of amine-containing particles in summer and winter.

Specific Comments:

Abstract:

1. It would be useful if the authors specified the percentage of amine containing particles that also contained sulfate and/or nitrate.

Response: As you suggested, we have added “More than 90% of amine-containing particles were found to be internally mixed with sulfate throughout the sampling period, while the percentage of amine particles containing nitrate increased from 43% in summer to 69% in winter. Robust correlations between the peak intensities of amines and the sum of nitrate and sulfate were observed, suggesting the possible formation of aminium sulfate and nitrate salts.” in the abstract in lines 57-62.

2. Lines 54-56: This sentence should be removed. If $m/z +46$ is the only marker on these aged sea salt particles, then it is likely due to $46\text{Na}2+$

Response: Revision made. “The nitrate-rich amine-containing particles were mixed with abundant sea-salt markers in summer, indicating a possible association between the amine emission source and marine phytoplankton.” have been removed from the abstract.

3. Lines 60-61: Is a 9% difference in RH enough to strongly affect the uptake of amines? Could it be that the strength of the ammonium source has a seasonal variation?

Response: As you and other reviewers suggested, we have investigated the seasonal distributions of total ammonium-containing particles and the abundance of ammonium in amine-containing particles. The results suggest that the low abundance of ammonium in amine-containing particles in summer is mainly due to the low emission source of ammonia. In addition, according to the study of Sauerwein and Chan, the co-uptake of dimethylamine (DMA) and ammonia (NH_3) by sulfuric acid particles at 50% RH led to particle-phase dimethylaminium (DMAH^+)/ammonium (NH_4^+) molar ratio up to four times that of gas-phase DMA/ammonia molar ratio (0.1 and 0.5), suggesting the displacement of NH_4^+ by DMA during the uptake process (Sauerwein and Chan, 2017). Thus, it is feasible for the displacement of NH_4^+ by DMA when the concentration of amines is one order of magnitude lower than NH_3 in gas phase. The ammonium–amine exchange reactions occurred in summer had little connection with the 9% seasonal difference of RH. We have revised the discussions about the possible role of ammonium–amine exchange reactions in amine-containing particles in the manuscript. Besides, the influence of ambient RH and particle acidity on the gas to particle partitioning of ammonia has been discussed in the manuscript. In the abstract “The ammonium-poor state of amine-containing particles in summer may have been caused by the displacement of particle-phase ammonium by amine uptake, which was more efficient in summer at higher ambient RH ($72 \pm 13\%$) than in winter ($63 \pm 11\%$).” have been revised to “The total ammonium-containing particles were investigated and showed a much lower abundance in ambient particles in summer (3.6%) than that in winter (32.6%), which suggests the ammonium-poor

state of amine-containing particles in summer may be related to the lower abundance of ammonia/ammonium in gas and particle phase. In addition, higher abundance of amines in ammonium-containing particles than that of ammonium in amine-containing particles suggests a possible contribution of ammonium–amine exchange reactions to the low abundance of ammonium in amine-containing particles at high ambient RH ($72 \pm 13 \%$) in summer.” in lines 65-73.

Introduction

1. I suggest adding more references on amines and single-particle observations of amines. Please add Zauscher et al., 2013 in order to comment on biomass burning particles containing amines.

Response: “Zauscher et al. (2013) detected strong signals of amine marker ($^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$) in biomass burning aerosols associated with the increase of ambient relative humidity, indicating the direct emission of amines from biomass burning and the important influence of high RH (>90%) on the partitioning process of amines.” have been added in the introduction in lines 120-124.

Besides, the reference of Angelino et al. (2001) has also been added in the manuscript. “The mixing state and single-particle characteristics of amines have been investigated in laboratory and field environments (Moffet et al., 2008;Silva et al., 2008;Pratt et al., 2009;Huang et al., 2012;Zhang et al., 2012).” have been revised to “The mixing state and single-particle characteristics of amines have been investigated in laboratory and field environments (Angelino et al., 2001;Moffet et al., 2008;Silva et al., 2008;Pratt et al., 2009;Huang et al., 2012;Zhang et al., 2012).” in lines 111-113.

Methods

1. Lines 173-180: Which fragment goes with which amine? Many ATOFMS studies also note the presence of $m/z +30$, was this ion also observed? $m/z +86$ and $m/z +118$ are some of the most prevalent amines observed using ATOFMS, why wasn't $m/z +118$ searched for?

Response: We have added a table to show the marker ions chosen for amines and assignments as follows:

Marker ion	Alkylamine assignment
$^{59}(\text{CH}_3)_3\text{N}^+$	Trimethylamine (TMA)
$^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$	Diethylamine (DEA)
$^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$	DEA, TEA, DPA
$^{101}(\text{C}_2\text{H}_5)_3\text{N}^+$	Triethylamine (TEA)
$^{102}(\text{C}_3\text{H}_7)_2\text{NH}_2^+$	Dipropylamine (DPA)
$^{143}(\text{C}_3\text{H}_7)_3\text{N}^+$	Tripropylamine (TPA)

The marker ion of $^{30}\text{CH}_3\text{NH}^+$ was observed with low peak intensity in 20% of amine-containing particle, and all the particles containing $^{30}\text{CH}_3\text{NH}^+$ had strong signal of $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$, so the $^{30}\text{CH}_3\text{NH}^+$ -containing particles were not specifically

discussed. We have added the related discussion about $^{30}\text{CH}_3\text{NH}^+$ in the manuscript. “In this work the peak intensity of $^{30}\text{CH}_3\text{NH}^+$ was much lower compared with other amine markers, and all the particles containing $^{30}\text{CH}_3\text{NH}^+$ had strong signal of $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$, so the $^{30}\text{CH}_3\text{NH}^+$ -containing particles were not specifically discussed.” have been added in the lines 211-214.

The ion of $m/z +86$ was detected in 5.5% and 9% of amine-containing particles in summer and winter separately. The ion of $m/z +118$ was detected in less than 100 single particles with very low peak intensity, so we didn't put $m/z +118$ in the searching list.

2. Lines 173-180: citations are needed for the ion peaks listed and the amines that they correspond to.

Response: Revision made. “Based on previous studies using ATOFMS and SPAMS instruments (Angelino et al., 2001;Huang et al., 2012;Zhang et al., 2012;Healy et al., 2015), amine-containing particles were characterized by ionic markers, including m/z s 46 $[(\text{CH}_3)_2\text{NH}_2]^+$, 59 $[(\text{CH}_3)_3\text{N}]^+$, 74 $[(\text{C}_2\text{H}_5)_2\text{NH}_2]^+$, 86 $[(\text{C}_2\text{H}_5)_2\text{NCH}_2]^+$ or $[\text{C}_3\text{H}_7\text{NHC}_2\text{H}_4]^+$, 101 $[(\text{C}_2\text{H}_5)_3\text{N}]^+$, 102 $[(\text{C}_3\text{H}_7)_2\text{NH}_2]^+$, 114 $[(\text{C}_3\text{H}_7)_2\text{NCH}_2]^+$, and 143 $[(\text{C}_3\text{H}_7)_3\text{N}]^+$, which correspond to dimethylamine (DMA), trimethylamine (TMA), diethylamine (DEA), triethylamine (TEA), dipropylamine (DPA), and tripropylamine (TPA).” have been revised to “Based on previous studies using ATOFMS and SPAMS instruments (Angelino et al., 2001;Huang et al., 2012;Zhang et al., 2012;Zauscher et al., 2013;Healy et al., 2015), amine-containing particles were characterized by marker ions, including m/z $^{59}(\text{CH}_3)_3\text{N}^+$, $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$, $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$, $^{101}(\text{C}_2\text{H}_5)_3\text{N}^+$, $^{102}(\text{C}_3\text{H}_7)_2\text{NH}_2^+$, and $^{143}(\text{C}_3\text{H}_7)_3\text{N}^+$ (Table 1).” in lines 191-195.

Table 1. Marker ions chosen for the amine-containing particles

Marker ion	Alkylamine assignment
$^{59}(\text{CH}_3)_3\text{N}^+$	Trimethylamine (TMA)
$^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$	Diethylamine (DEA)
$^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$	DEA, TEA, DPA
$^{101}(\text{C}_2\text{H}_5)_3\text{N}^+$	Triethylamine (TEA)
$^{102}(\text{C}_3\text{H}_7)_2\text{NH}_2^+$	Dipropylamine (DPA)
$^{143}(\text{C}_3\text{H}_7)_3\text{N}^+$	Tripropylamine (TPA)

3. A search criterion for biomass burning aerosol was $m/z -59$ and $m/z -73$, please review Zauscher et al., 2013 for better search criteria for biomass burning aerosols.

Response: Thank you for your suggestion. According to the study of Zauscher et al. (2013), biomass burning particles were detected with strong signals of potassium chloride ($^{113}\text{K}_2\text{Cl}^+$), potassium nitrate ($^{140}\text{K}_2\text{NO}_3^+$) and potassium sulfate ($^{213}\text{K}_3\text{SO}_4^+$), so we believe the definition of BB type particles used in this work was inappropriate. Thus, we removed BB type particles from amine-containing particles, and all the related discussions were removed too. The detailed revision has been presented in the

response to Major comment 2.

Results

1. Figure 1 isn't very descriptive. I suggest showing this figure on a map with different sources pointed out so that the reader can see the seasonal impact of different potential sources of amines.

Response: Revision made.

The old Figure 1:

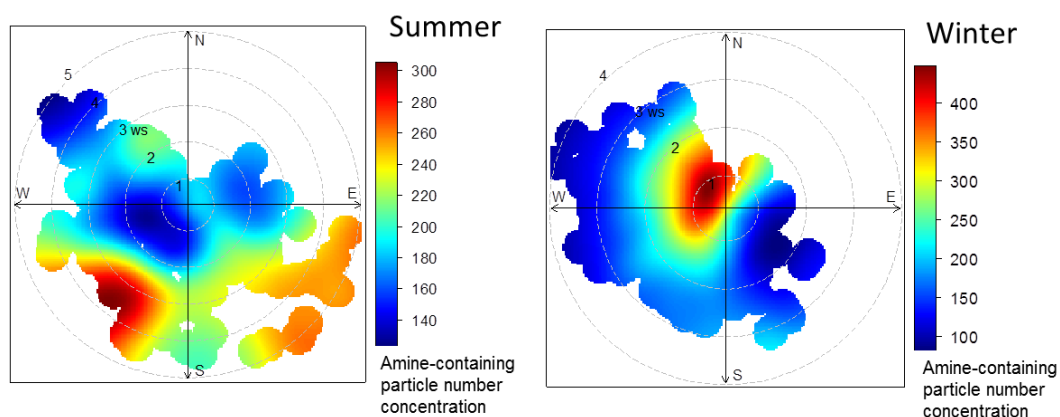
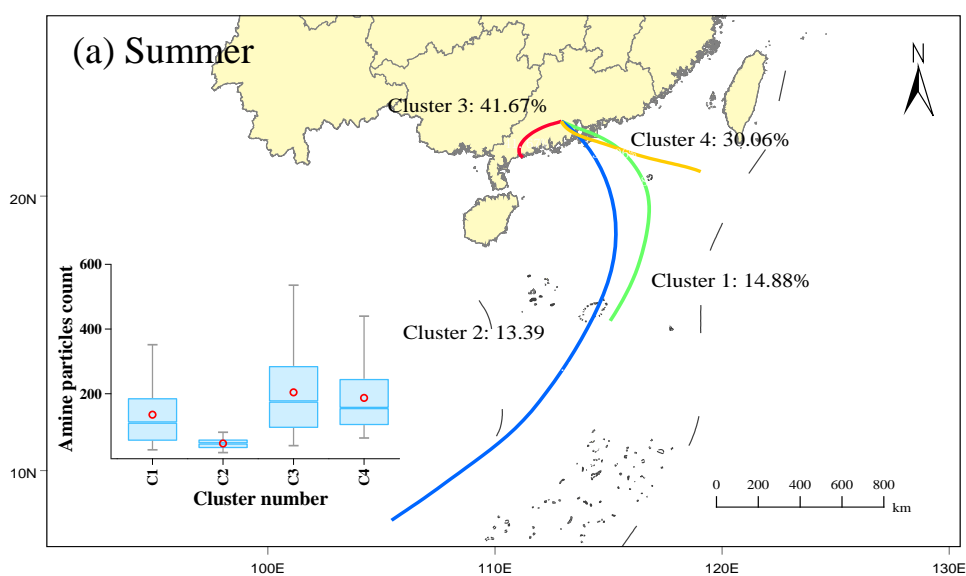


Figure 1. Seasonal distributions of amine-containing particle number concentrations associated with wind direction and wind speed in (left) summer and (right) winter.

The new Figure 1:



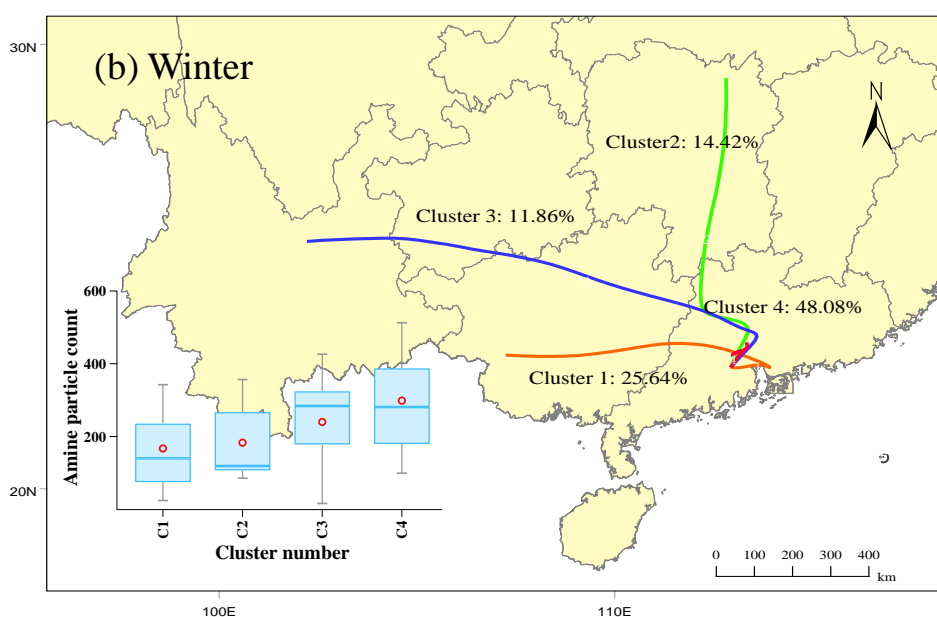


Figure 1. Spatial distributions of amine-containing particle counts associated with backward trajectories (48 hour) of air masses at 500m levels above the ground during the sampling period: (a) summer (from July 18 to August 1, 2014), (b) winter (from January 27 to February 8, 2015).

“Meteorological conditions, namely wind speed and wind direction, are shown during the sampling period in Figure 1. In summer, high amine-containing particle number concentrations were associated with southwesterly and southeasterly winds at speeds of 3–5 m s⁻¹, suggesting that the majority of amine-containing particles came from regional transport. However, in winter, large amounts of amine-containing particles were associated with northwesterly winds at speeds of 0.5–2 m s⁻¹, indicating that amine-containing particles were related primarily with local emissions, such as animal husbandry, biomass burning, and vehicle exhaust.” have been revised to “Spatial distributions of amine-containing particles associated with backward trajectories (48 hour) of air masses at 500m levels above the ground during the sampling period are shown in Figure 1. Cluster trajectories were calculated by MeteoInfo (Wang, 2014), and the box plots were conducted by Igor Pro-based program Histbox (Wu et al., 2018;Wu and Yu, 2018). In summer, high amine-containing particle counts were associated with air masses of Cluster 3 (41.67%) and Cluster 4 (30.06%) (Figure 1a) from continent and South China Sea separately, suggesting that the majority of amine-containing particles came from anthropogenic and marine sources. However, in winter, large amounts of amine-containing particles were associated with air masses of Cluster 4 (48.08%) (Figure 1b), indicating that amine-containing particles were related primarily with local emissions, such as animal husbandry, biomass burning, and vehicle exhaust.

Anthropogenic emissions from Foshan and Guangzhou may also have contributed, as the sampling site is only 40 km and 56 km from these cities, respectively (Figure S1).” in lines 223-236.

2. Figure 2 has too many traces. I suggest removing wind direction and better separating the amines and the RH. I also suggest showing a temporal trace for each amine marker.

Response: We have revised the Figure 2 as you suggested.

The old Figure 2:

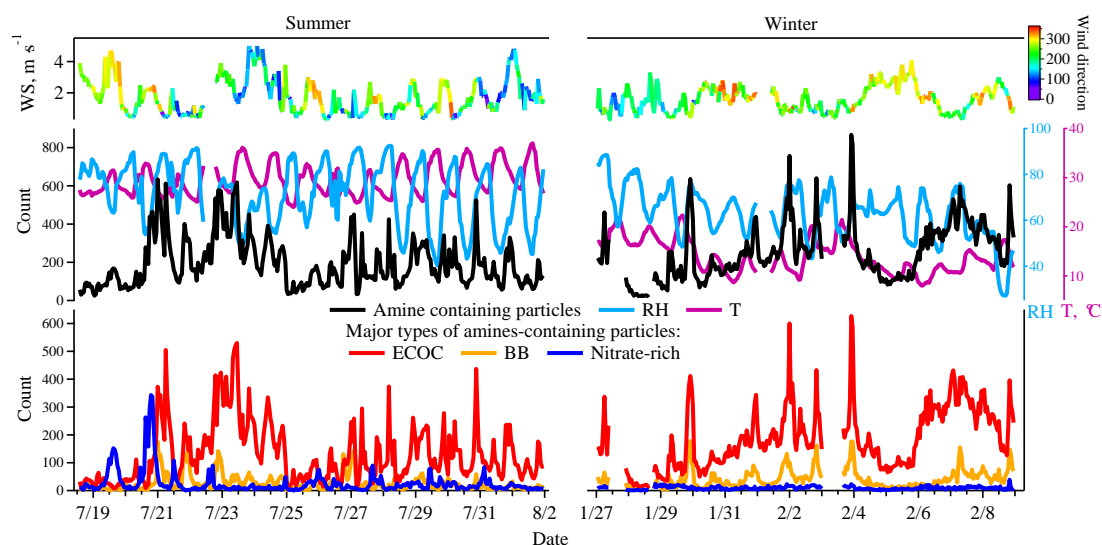


Figure 2. Temporal variations in amine-containing particles, relative humidity (RH), temperature (T), wind speed (WS), wind direction, and three types of amine particles in Heshan, China during the entire sampling periods. Abbreviations of major particle types: elemental and organic carbon (ECOC); biomass burning (BB).

The new Figure 2:

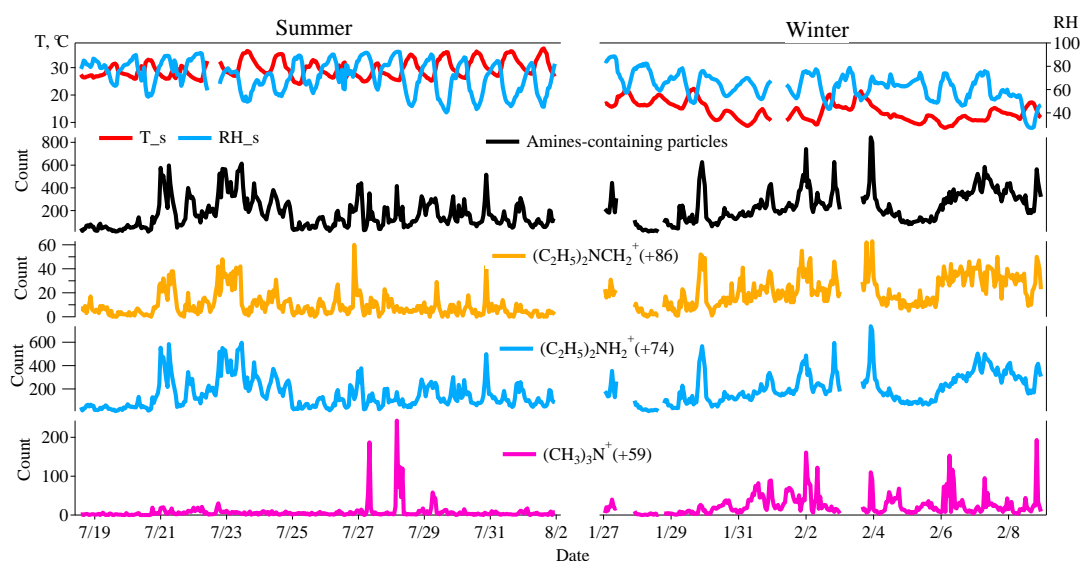


Figure 2. Temporal variations of relative humidity (RH), temperature (T), total

amine-containing particles, and amine particles containing three major marker ions of $^{59}(\text{CH}_3)_3\text{N}^+$, $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$, $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ in Heshan, China during the entire sampling periods.

3. Figure 3 needs standard error bars. Do different amine peaks show different diurnal trends?

Response: We have revised the Figure 3 as you suggested.

The old Figure 3:

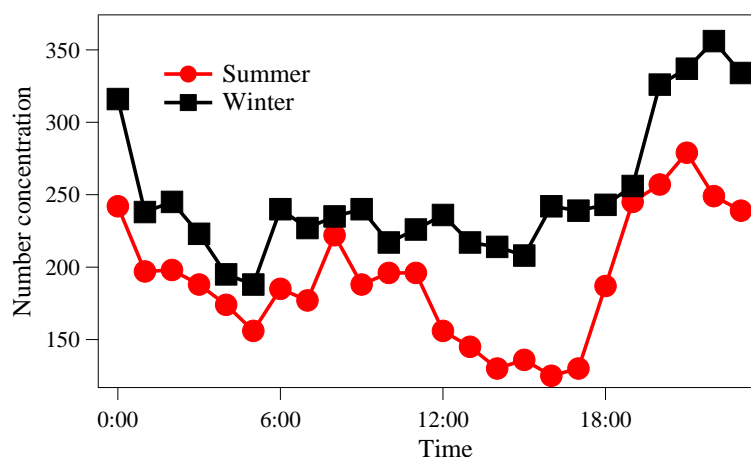


Figure 3. Diurnal variations in amine-containing particle number concentrations in summer and winter in Heshan.

The new Figure 3:

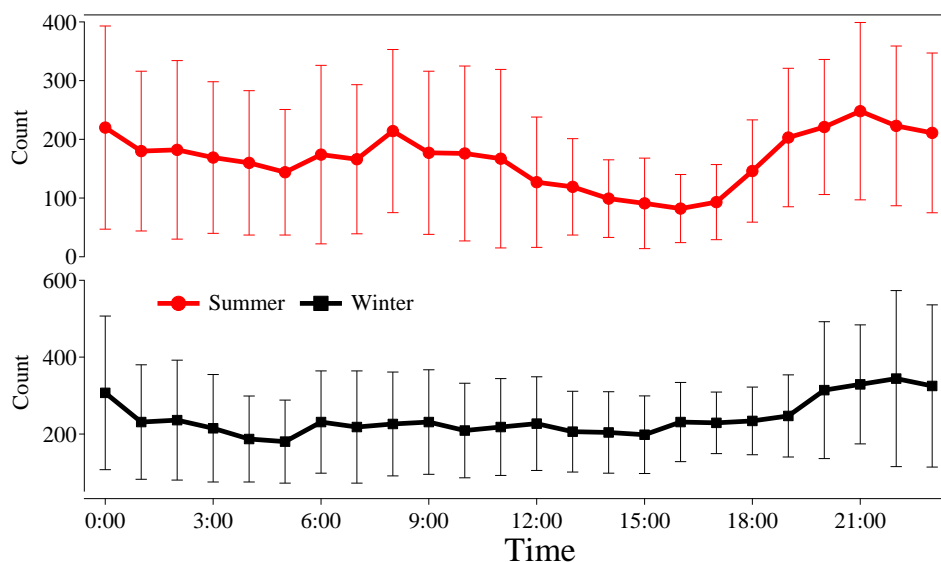


Figure 3. Diurnal variations of amine-containing particle counts in summer and winter in Heshan.

“The amine particles containing $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$ and $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ both exhibited similar variation pattern with total amine-containing particles suggesting a similar emission source of $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$ and $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ (Figure 2). The

temporal trend of $^{59}(\text{CH}_3)_3\text{N}^+$ -containing particles were different from those of $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$ and $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$; and the two sudden episodes of $^{59}(\text{CH}_3)_3\text{N}^+$ occurred from 27 to 29 July in summer were possibly due to the special emission sources of trimethylamine (TMA).” have been added in the lines 249-256.

4. Figure 4 needs amine markers clearly labeled on each particle type. I am also surprised to not see $m/z +86$ and $m/z +118$ as these are some of the most prevalent amine markers observed by single particle mass spectrometry.

Response: Revision made. The amine markers of $^{30}\text{CH}_3\text{NH}^+$, $^{59}(\text{CH}_3)_3\text{N}^+$, $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$, $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ have been labeled in the mass spectra of amine-containing particles in Figure 4. The other amine markers of $^{101}(\text{C}_2\text{H}_5)_3\text{N}^+$, $^{102}(\text{C}_3\text{H}_7)_2\text{NH}_2^+$, and $^{143}(\text{C}_3\text{H}_7)_3\text{N}^+$ were found with a much lower peak intensity, and the number count of amine particles contained these markers were less than 1%. So $^{101}(\text{C}_2\text{H}_5)_3\text{N}^+$, $^{102}(\text{C}_3\text{H}_7)_2\text{NH}_2^+$, and $^{143}(\text{C}_3\text{H}_7)_3\text{N}^+$ were not labeled in the mass spectra. The ion of $m/z +118$ was detected in less than 100 single particles with very low peak intensity, so $m/z +118$ was not labeled in the Figure 4.

The new Figure 4:

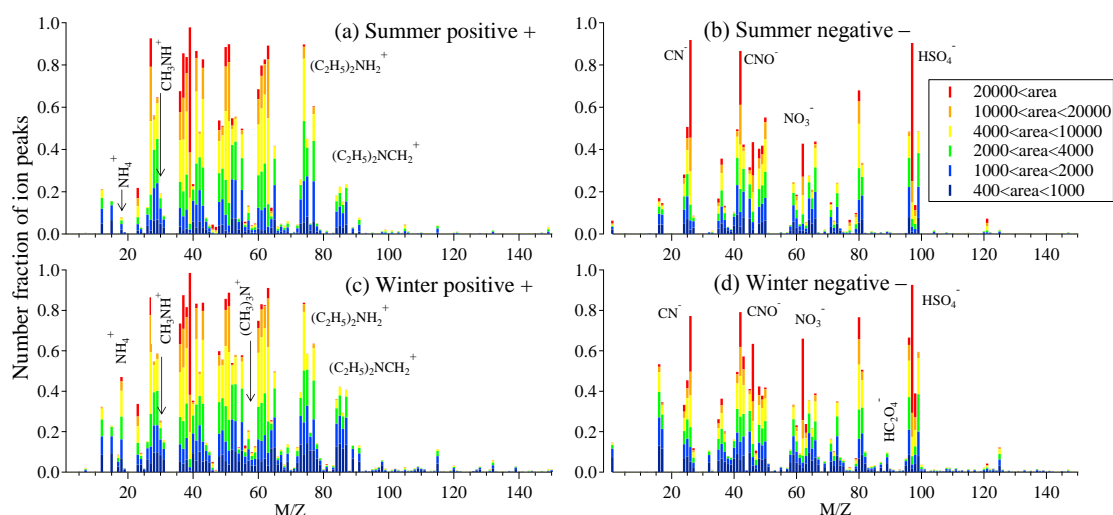


Figure 4. Average ion mass spectra of amine-containing particles in summer and winter. The color bars represent each peak area corresponding to a specific ion in individual particles.

5. From Figure 4, it appears as though $m/z +74$ is the only amine marker observed on biomass burning aerosols. $m/z +74$ is also a marker for KCl (e.g., $^{74}\text{KCl}^+$) as noted in Zauscher et al., 2013 and may be misclassified as an amine in this work. Were any other amine markers observed on this particle type?

Response: According to the study of Zauscher et al. (2013), biomass burning particles were detected with strong signals of potassium chloride ($^{113}\text{K}_2\text{Cl}^+$), potassium nitrate ($^{140}\text{K}_2\text{NO}_3^+$) and potassium sulfate ($^{213}\text{K}_3\text{SO}_4^+$), so we believe if $m/z +74$ was $^{74}\text{KCl}^+$, the significant biomass burning markers listed above should be detected in the particles. Biomass burning markers like $^{113}\text{K}_2\text{Cl}^+$, $^{140}\text{K}_2\text{NO}_3^+$ and

$^{213}\text{K}_3\text{SO}_4^+$ were not found in the amine-containing particles, so the presence of $m/z +74$ in amine-containing particles has a very low possibility to be $^{74}\text{KCl}^+$. In this work the ions of $^{30}\text{CH}_3\text{NH}^+$ and $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ were also detected in the amine particles containing $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$.

6. Figure 5 should clearly state that the x-axis is vacuum aerodynamic diameter.

Response: The label of x-axis has been revised as you suggested:

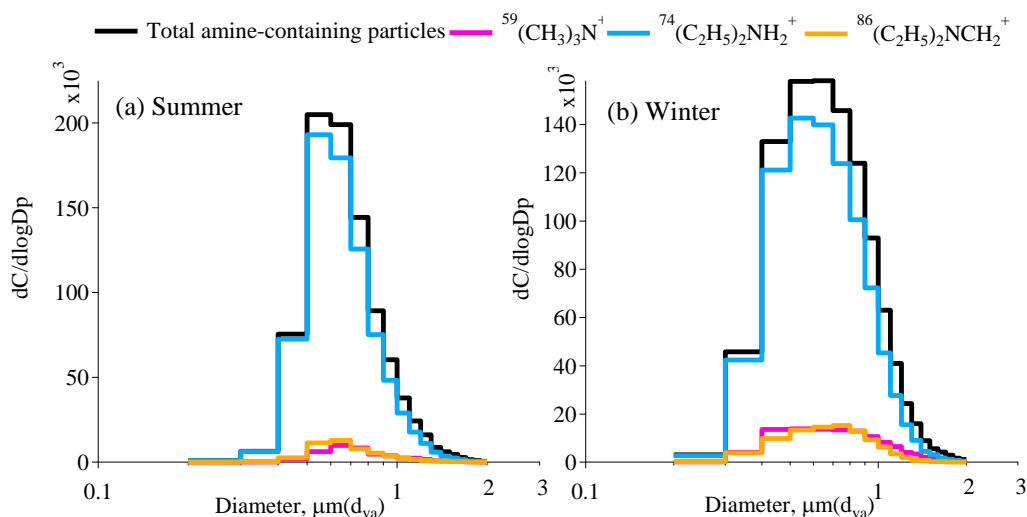


Figure 5. Unscaled size-resolved number distributions of total amine-containing particles and amine particles containing three marker ions of $^{59}(\text{CH}_3)_3\text{N}^+$, $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$, and $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ in summer and winter in Heshan.

7. Figure 6 could be a subtraction plot between the two seasons to better illustrate the seasonal difference in the mixing-state of the amine-containing particles.

Response: Indeed, the seasonal different abundance of sulfate, nitrate and ammonium are not easily identified in Figure 6 through the illustration of color squares. Thus, we have put the percentages of amine particles containing sulfate, nitrate and ammonium in Table 3 instead of Figure 6.

Table 3. The abundances of ammonium-, nitrate- and sulfate-containing amine particles in total amine-containing particles.

Marker ions	Summer	Winter
$^{18}\text{NH}_4^+$	8%	54%
$^{62}\text{NO}_3^-$	43%	69%
$^{97}\text{HSO}_4^-$	91%	94%

The marker ions of $^{18}\text{NH}_4^+$, $^{62}\text{NO}_3^-$ and $^{97}\text{HSO}_4^-$ were chosen to represent ammonium, nitrate and sulfate.

8. The biomass burning spectra and ECOC spectra look the same. I think these should be the same particle type. See Ault et al., 2010 for representative ECOC spectra, which do not contain intense ions at 39K+.

Response: As suggested by you, the classification criteria were inappropriate for the BB and nitrate-rich type particles. Thus, we no longer use the art-2a method to classify the amine-containing particles. We have combined the ECOC and BB types of particles together to investigate the mass spectra and mixing state of amine-containing particles. The mass spectra and size distributions of ECOC and BB type particles were replaced by total amine-containing particles, and all the discussions about ECOC and BB type particles were all replaced by total amine-containing particles.

“Amine-containing particles were categorized as ECOC, BB, and nitrate-rich both in summer and winter. ECOC amine-containing particles were dominant, accounting for 67.2 % and 74.8 % of particle count in summer and winter, respectively (Table 1). ECOC particles exhibited variations similar to those in total amine-containing particles in both summer and winter. Nitrate-rich particles were the second most abundant in summer, during which time they accounted for 13.4 % of total amine-containing particles, while BB particles were the second most abundant in winter, accounting for 16.3 % of total amine-containing particles. Nitrate-rich particles were three times more abundant in summer than in winter, suggesting the existence of ammonium nitrate salts in summer.

The average mass spectra of ECOC, BB, and nitrate-rich amine-containing particles in summer and winter are shown in Figure 4. The ECOC amine-containing particles in both summer and winter were characterized by high fractions of 39 $[K]^+$; carbonaceous marker ions, including m/z s 27 $[C_2H_3]^+$, 29 $[C_2H_5]^+$, 36 $[C_3]^+$, 37 $[C_3H]^+$, 43 $[C_2H_3O]^+$, 48 $[C_4]^+$, 51 $[C_4H_3]^+$, 53 $[C_4H_5]^+$, 60 $[C_5]^+$, 63 $[C_3H_3]^+$, 65 $[C_3H_5]^+$, and 77 $[C_6H_5]^+$; and amine fragment ions at m/z s 46 $[(CH_3)_2NH_2]^+$, 59 $[(CH_3)_3N]^+$, 74 $[(C_2H_5)_2NH_2]^+$, and 86 $[(C_2H_5)_2NCH_2]^+ / [C_3H_7NHC_2H_4]^+$ in the positive mass spectrum. The ECOC particle negative mass spectrum was characterized by strong carbon-nitrogen fragment signals at m/z s -26 $[CN]^-$ and -42 $[CNO]^-$, as well as abundant secondary ions at m/z s -46 $[NO_2]^-$, -62 $[NO_3]^-$, -80 $[SO_3]^-$, and -97 $[HSO_4]^-$ in both summer and winter. In many field studies, aged carbonaceous particles always contain abundant secondary sulfate, nitrate, and ammonium ions. Interestingly, in this work, the ammonium signal (m/z 18 $[NH_4]^+$) was not found in ECOC amine-containing particles in summer, and only a very small ammonium peak was detected in winter. The low ammonium signal in ECOC amine-containing particles may have been due to the exchange of particulate ammonium for gas-phase amines (Lloyd et al., 2009; Qiu et al., 2011; Chan and Chan, 2012; Chan and Chan, 2013; Chu and Chan, 2016, 2017; Sauerwein and Chan, 2017). In both summer and winter, the mass spectra of BB amine-containing particles showed carbonaceous markers and secondary ions similar to those found in ECOC amine-containing particles, with additional distinct ion peaks at m/z 23 $[Na]^+$ and BB markers at m/z s -59 $[C_2H_3O_2]^-$, -71 $[C_3H_3O_2]^-$, and -73 $[C_3H_5O_2]^-$. No ammonium was found in BB amine-containing particles in either summer or winter, likely because of exchange reactions similar to those inferred in the ECOC amine-containing particles (see Section 3.3).

The nitrate-rich amine-containing particles exhibited spectral features different from those observed in the ECOC and BB spectra. Only a few carbonaceous

fragments were observed. In summer, the nitrate-rich amine-containing particles contained abundant sea-salt markers such as m/z s 23 $[\text{Na}]^+$, 62 $[\text{Na}_2\text{O}]^+$, and 63 $[\text{Na}_2\text{OH}]^+$ in the positive mass spectrum and m/z s -93 $[\text{NaCl}_2]^-$ and -147 $[\text{Na}(\text{NO}_3)_2]^-$ in the negative mass spectrum. Chloride signal was not detected due to the depletion of chloride and enrichment of nitrate in the sea-salt particle aging process (Gard et al., 1998). In summer, 48-h backward trajectories showed that 60 % of air masses arose from marine areas (Figure S3) and were partly associated with marine aerosols. A small peak of m/z 46 $[(\text{CH}_3)_2\text{NH}_2]^+$ was found in the nitrate-rich amine-containing particle spectra in summer, which likely arose from DMA produced by marine phytoplankton (Facchini et al., 2008). The backward trajectories and mass spectra of the nitrate-rich particles indicate that marine sources may contribute to the amine distribution in the PRD region during summer, although the amine-containing particles appeared to have been aged during transportation. In winter, air masses were transported largely from urban areas like Guangzhou and Foshan (Figure S3) and brought more anthropogenic pollutants to the sampling site. Hence, the sea-salt markers at m/z s -93 $[\text{NaCl}_2]^-$ and -147 $[\text{Na}(\text{NO}_3)_2]^-$ were not observed in the winter negative mass spectrum. Instead, the m/z 56 $[\text{Fe}]^+$ ion was identified, and, because no dust source marker ion signals (such as Ca^+ , CaO^+ , and SiO_3^-) were found, we speculate that iron arose mainly from industrial emissions. The nitrate-rich amine-containing particles may have resulted from direct industrial emissions or reactions between gaseous amines and particles from industrial emissions. Lastly, the observed nitric acid signal (m/z -125 $[\text{HNO}_3\text{NO}_3]^-$) indicated strong particle acidity in the nitrate-rich amine-containing particles in winter.” have been revised to “The average mass spectra of amine-containing particles in summer and winter are shown in Figure 4. The amine-containing particles were characterized by high fractions of carbonaceous marker ions, including $^{27}\text{C}_2\text{H}_3^+$, $^{29}\text{C}_2\text{H}_5^+$, $^{36}\text{C}_3^+$, $^{37}\text{C}_3\text{H}^+$, $^{43}\text{C}_2\text{H}_3\text{O}^+$, $^{48}\text{C}_4^+$, $^{51}\text{C}_4\text{H}_3^+$, $^{53}\text{C}_4\text{H}_5^+$, $^{60}\text{C}_5^+$, $^{63}\text{C}_5\text{H}_3^+$, $^{65}\text{C}_5\text{H}_5^+$, and $^{77}\text{C}_6\text{H}_5^+$; and amine marker ions of $^{30}\text{CH}_3\text{NH}^+$, $^{59}(\text{CH}_3)_3\text{N}^+$, $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$ and $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ in the positive mass spectrum in both summer and winter. The negative mass spectrum was characterized by strong carbon-nitrogen fragments like $^{26}\text{CN}^-$ and $^{42}\text{CNO}^-$, as well as abundant secondary ions of $^{46}\text{NO}_2^-$, $^{62}\text{NO}_3^-$, $^{80}\text{SO}_3^-$, and $^{97}\text{HSO}_4^-$ in both summer and winter. In many field studies, aged carbonaceous particles always contain abundant secondary ions of sulfate, nitrate, and ammonium. Interestingly, in this work, the signals of $^{18}\text{NH}_4^+$ were weak and only observed in less than 10% of amine-containing particles in summer, but moderate signal of $^{18}\text{NH}_4^+$ was detected in half of amine-containing particles in winter. The low $^{18}\text{NH}_4^+$ signal in amine-containing particles may have been due to the emission sources of ammonia and particle acidity, which will be discussed in Section 3.3.” in lines 270-284.

9. Lines 277-279: chloride is not completely displaced and is detected as 81, 83Na2Cl+ and 93, 95NaCl2-.

Response: Thanks for the correction. The depletion of chloride in nitrate-rich particles is worthy of discussion. However, because the m/z +46 was not identified as

amine marker, all the discussions about nitrate-rich type particles have been removed. Although this issue is no longer investigated in this work, the comment from you is still valuable and helpful to our future research.

10. Lines 281-283: I am not convinced that this is an observation of a marine-derived amine. The spectra clearly show aged sea salt particles, which should contain an ion peak at 46Na^+ . Therefore, the peak at $m/z +46$ is likely not an amine.

Response: Revision made. We have made an incorrect assignment of $m/z +46$, and the discussions about the marine contribution to amines have been removed.

“The nitrate-rich amine-containing particles exhibited spectral features different from those observed in the ECOC and BB spectra. Only a few carbonaceous fragments were observed. In summer, the nitrate-rich amine-containing particles contained abundant sea-salt markers such as m/zs 23 $[\text{Na}]^+$, 62 $[\text{Na}_2\text{O}]^+$, and 63 $[\text{Na}_2\text{OH}]^+$ in the positive mass spectrum and m/zs -93 $[\text{NaCl}_2]^-$ and -147 $[\text{Na}(\text{NO}_3)_2]^-$ in the negative mass spectrum. Chloride signal was not detected due to the depletion of chloride and enrichment of nitrate in the sea-salt particle aging process (Gard et al., 1998). In summer, 48-h backward trajectories showed that 60 % of air masses arose from marine areas (Figure S3) and were partly associated with marine aerosols. A small peak of m/z 46 $[(\text{CH}_3)_2\text{NH}_2]^+$ was found in the nitrate-rich amine-containing particle spectra in summer, which likely arose from DMA produced by marine phytoplankton (Facchini et al., 2008). The backward trajectories and mass spectra of the nitrate-rich particles indicate that marine sources may contribute to the amine distribution in the PRD region during summer, although the amine-containing particles appeared to have been aged during transportation. In winter, air masses were transported largely from urban areas like Guangzhou and Foshan (Figure S3) and brought more anthropogenic pollutants to the sampling site. Hence, the sea-salt markers at m/zs -93 $[\text{NaCl}_2]^-$ and -147 $[\text{Na}(\text{NO}_3)_2]^-$ were not observed in the winter negative mass spectrum. Instead, the m/z 56 $[\text{Fe}]^+$ ion was identified, and, because no dust source marker ion signals (such as Ca^+ , CaO^+ , and SiO_3^-) were found, we speculate that iron arose mainly from industrial emissions. The nitrate-rich amine-containing particles may have resulted from direct industrial emissions or reactions between gaseous amines and particles from industrial emissions. Lastly, the observed nitric acid signal (m/z -125 $[\text{HNO}_3\text{NO}_3]^-$) indicated strong particle acidity in the nitrate-rich amine-containing particles in winter.” have been removed from the manuscript.

11. Lines 333-334: could it be that the source strength of ammonium shows a seasonal cycle? This is a more likely explanation than differences in partitioning caused by a very small change in RH.

Response: As suggested by you, we have studied the total ammonium-containing particles during sampling period to investigate the source strength of ammonium. The results show that the low abundance of ammonium in amine-containing particles in summer could be a possible result of low emission source of ammonia.

“The seasonal differences of the mixing state of amines and NH_4^+ may be influenced by the seasonal variation of source strength of NH_4^+ . To investigate the temporal variation and abundance of NH_4^+ in total detected single particles, the total NH_4^+ -containing particles were identified with relative area of $^{18}\text{NH}_4^+$ larger than 1%. Using this criterion, 18336 and 235312 of NH_4^+ -containing particles were detected in summer and winter separately, accounting for 3.6% and 32.6% of the total detected particles. The averaged positive and negative ion mass spectra of NH_4^+ -containing particles are exhibited in Figure 6. During entire sampling period the NH_4^+ -containing particles were characterized by abundant hydrocarbon fragments and secondary organic species like $^{43}\text{C}_2\text{H}_3\text{O}^+$ and $^{89}\text{HC}_2\text{O}_4^-$, as well as strong signals of $^{26}\text{CN}^-$, $^{42}\text{CNO}^-$, $^{62}\text{NO}_3^-$ and $^{97}\text{HSO}_4^-$, indicating an aging state of NH_4^+ -containing particles. Also, 20% of NH_4^+ -containing particles contained $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$, which indicates a close connection between NH_3 and diethylamine (DEA), possibly due to the similar emission sources. Temporal variations of total amine-containing particles, total ammonium-containing (NH_4^+ -containing) particles and particles containing both ammonium and amine (NH_4^+ -amine) are shown in Figure 7. The total NH_4^+ -containing particles and NH_4^+ -amine particles were both much lower in summer than in winter. This seasonal difference may be due to the low emission sources of ammonia and preferred partitioning in gas phase in summer. Backward trajectories analysis (Figure 1) showed that in summer the air mass was mainly from south of the sampling site and linked to the marine region with low emission of anthropogenic pollutants. By contrast, in winter, the air mass was mainly from northwest of the sampling site and associated with relatively polluted megacities like Guangzhou and Foshan. RH does not seem to exert a major influence on particulate NH_4^+ (Huang et al., 2012), because lower abundance of NH_4^+ was observed in summer ($\text{RH} = 72 \pm 13\%$) than in winter ($\text{RH} = 63 \pm 11\%$).” have been added in the manuscript in lines 309-335.

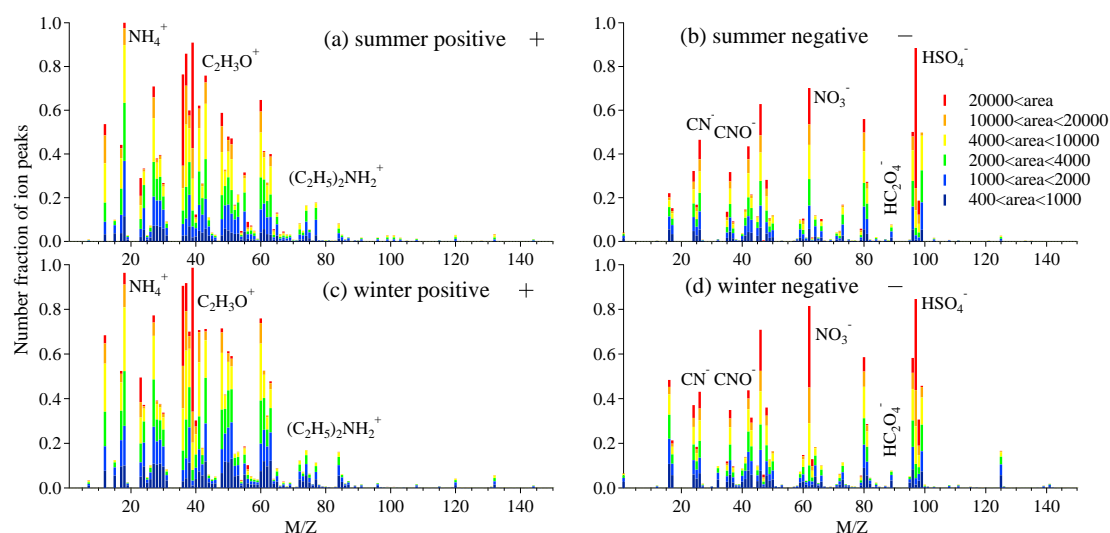


Figure 6. Mass spectra of total ammonium-containing (NH_4^+ -containing) particles in summer and winter. The color bars represent each peak area corresponding to a specific fraction in individual particles.

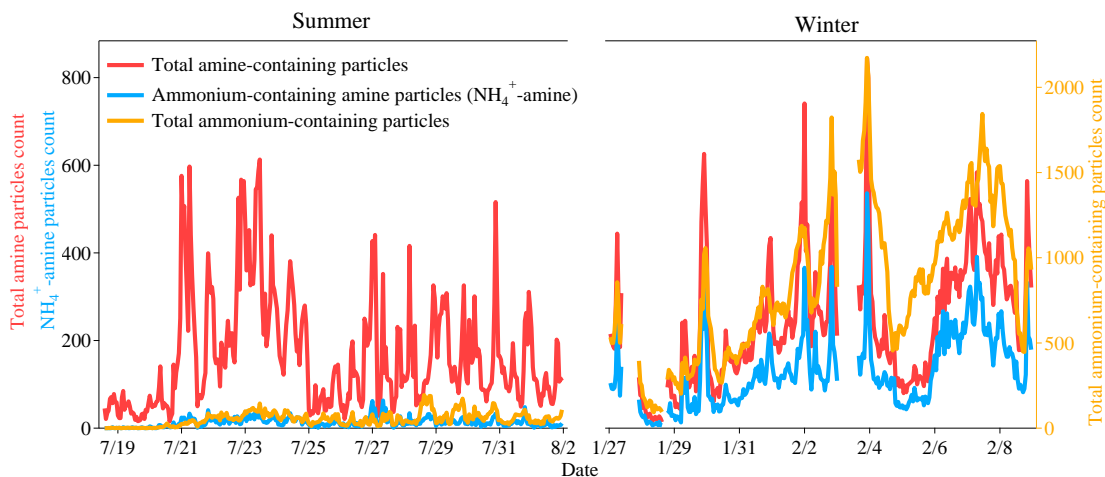


Figure 7. Temporal variations of total amine-containing particles, total ammonium-containing particles and ammonium-containing amine particles (NH_4^+ -amine) during sampling period in Heshan.

12. The authors are quite redundant about the displacement of ammonium by amines. This should be re-read and redundancies should be reduced.

Response: Revision made. As suggested by you, we have investigated the ammonium-containing particles in summer, and the low abundance of ammonium in amine-containing particles in summer is closely associated with the low emission of ammonia. In addition, according to the study of Sauerwein and Chan, the co-uptake of dimethylamine (DMA) and ammonia (NH_3) by sulfuric acid particles at 50% RH led to particle-phase dimethylaminium (DMAH^+)/ammonium (NH_4^+) molar ratio up to four times that of gas-phase DMA/ammonia molar ratio (0.1 and 0.5), suggesting the displacement of NH_4^+ by DMA during the uptake process (Sauerwein and Chan, 2017). In this work, the ambient RH and acidic particles containing abundant sulfate and nitrate were similar to the experimental conditions used in Sauerwein and Chan (2017). In summer 8% of amine-containing particles contained NH_4^+ , while 25% of ammonium-containing particles contained amines (Figure 7). Although the gas-phase concentrations of amines and NH_3 are not quantified, higher abundance of amines in ammonium-containing particles than that of ammonium in amine-containing particles suggests a possible ammonium–amine exchange reactions in acidic particles in summer. Thus, we have extended the related discussion about ammonium–amine exchange reactions.

“Although high acidity is favorable for gaseous ammonia partitioning, extremely low ammonium peak areas were found for the amine-containing particles in summer (Figure 7), which may have been caused by the displacement of ammonium in the particle phase by amines to form aminium sulfate and nitrate salts; this displacement depends on RH and the phase of the ammonium salts (Chan and Chan, 2013; Chu and Chan, 2016). The ambient RH in summer ($72 \pm 13\%$) was higher than that in winter ($63 \pm 11\%$). Thus, it is feasible that particles contained more water and

a larger fraction of aqueous ammonium salts in summer than in winter, which facilitated the displacement of ammonium by amines, decreasing the ammonium concentration in the particle phase. Particle-phase organics other than amines and ammonium salts also affect amine–ammonia exchange (Chu and Chan, 2016, 2017). However, because the SPAMS alone cannot provide quantitative data on particle-phase organics, this issue will be discussed in a subsequent study.” have been revised to “Although high acidity promotes gaseous ammonia partitioning, extremely low ammonium peak areas were found for the amine-containing particles in summer (Figure 8), which may be associated with ammonium–amine exchange reactions in addition to the low emission source of ammonia. The exchange between amine gases and particulate NH₃ and/or ammonium highly depends on the RH and particle acidity (Chan and Chan, 2013; Chu and Chan, 2016). According to the study of Sauerwein and Chan, the co-uptake of dimethylamine (DMA) and ammonia (NH₃) by sulfuric acid particles at 50% RH led to particle-phase dimethylammonium (DMAH⁺) to ammonium (NH₄⁺) molar ratio up to four times that of gas-phase DMA to ammonia molar ratio (0.1 and 0.5), suggesting the displacement of NH₄⁺ by DMA during the uptake process (Sauerwein and Chan, 2017). In this work, the ambient RH and acidic particles containing abundant sulfate and nitrate were similar to the experimental conditions used in Sauerwein and Chan (2017). In summer 8% of amine-containing particles contained NH₄⁺, while 25% of ammonium-containing particles contained amines (Figure 7). Although the gas-phase concentrations of amines and NH₃ are not quantified, higher abundance of amines in ammonium-containing particles than that of ammonium in amine-containing particles suggests a possible ammonium–amine exchange reactions in acidic particles in summer.” in lines 356-373.

In the abstract, “The ammonium-poor state of amine-containing particles in summer may have been caused by the displacement of particle-phase ammonium by amine uptake, which was more efficient in summer at higher ambient RH (72 ± 13 %) than in winter (63 ± 11 %).” have been revised to “In addition, higher abundance of amines in ammonium-containing particles than that of ammonium in amine-containing particles suggests a possible contribution of ammonium–amine exchange reactions to the low abundance of ammonium in amine-containing particles at high ambient RH (72 ± 13 %) in summer.” in lines 69-73.

In the conclusion, “The ammonium-poor state of the amine-containing particles in summer may have been caused by the displacement of ammonium in the particle phase by amines to form ammonium sulfate and nitrate salts.” have been revised to “Besides, 8% of amine-containing particles contained ammonium while 25% of ammonium-containing particles contained amines in summer, suggesting a possible contribution of ammonium–amine exchange reactions to the low abundance of ammonium in amine-containing particles at high ambient RH (72 ± 13 %) in summer.” in lines 424-428.

Conclusions:

1. The authors should comment on which amine markers were most prevalent and on

which particle types. This would be an interesting conclusion that may also tie into different potential amine sources.

Response: Revision made, “Both seasons were dominated by amine marker of $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$ in 90% and 86% of amine-containing particles in summer and winter, respectively. Amine markers of $^{59}(\text{CH}_3)_3\text{N}^+$ and $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ were detected in 4.5% and 5.5% of amine-containing particles in summer, while their percentages both increased two times in winter. The amine particles contained $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$ and $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ both exhibited similar variation pattern with total amine-containing particles suggesting a similar emission source of $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$ and $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$, while the $^{59}(\text{CH}_3)_3\text{N}^+$ -containing particles showed different temporal trends, and two sudden increase episodes of $^{59}(\text{CH}_3)_3\text{N}^+$ in summer was possibly due to the special sources of trimethylamine.” have been added in the conclusion in lines 403-412.

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