

Response to the comments of Anonymous Referee #1

[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 manuscript reports the mixing states of particulate amine in ambient environment using a single particle mass spectrometer. The most interesting observation made in this work is the large quantity of amine-rich particles but poor in ammonium which suggests the importance of the displacement of ammonia by amine. This observation also suggests that amines and ammoniums should be considered when calculating the particle acidity. I believe this is a very important observation. The manuscript could be accepted by ACP if the authors could provide more detailed discussions to support this major conclusion.

Response: Thank you for your comments. These comments are valuable and very helpful for revising and improving our paper, as well as the important guiding significance to our researches. We have studied these comments carefully and have made revisions. Our responses to the comments are itemized below.

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:

1. Line 192-205 and Part 3.2: The mass spectral patterns of ECOC and BB particles were almost identical. The size distribution and the temporal variation were also similar. In Part 3.2, no further discussion on the differences of these two particles types. What's the reason or necessity of this kind of classification?

Response: Revision made. We have combined the ECOC and BB types of particles together to investigate the mass spectra and mixing state of amine-containing particles. In addition, we have removed the nitrate-rich particles from the manuscript due to the misinterpretation of amine marker of $^{46}(\text{CH}_3)_2\text{NH}_2^+$. Therefore, we did not rename the new group of combined ECOC and BB type particles. Actually, the amine-containing particles discussed in the revised manuscript were composed of ECOC and BB type 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.

The paragraphs of particle categorization have been replaced by "Particle size and chemical composition were obtained via SPAMS mass spectral analysis using the Computational Continuation Core (COCO; version 3.0) toolkit in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.

The discussions about the abundance and mass spectra of amine-containing particles have been replaced by “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).” 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 $^{27}\text{C}_2\text{H}_3^+$, $^{29}\text{C}_2\text{H}_5^+$, $^{36}\text{C}_3^+$, $^{37}\text{C}_3\text{H}^+$, $^{43}\text{C}_2\text{H}_3\text{O}^+$, $^{48}\text{C}_4^+$, $^{51}\text{C}_4\text{H}_3^+$, $^{53}\text{C}_4\text{H}_5^+$, $^{60}\text{C}_5^+$, $^{63}\text{C}_5\text{H}_3^+$, $^{65}\text{C}_5\text{H}_5^+$, 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.

The old Table 1:

Table 1. Seasonal distributions of major types of amine-containing particles in summer and winter in the PRD, China.

Particle type	Summer (18/7-1/8, 2014)		Winter (27/1-8/2, 2015)	
	Count	Percentage (%)	Count	Percentage (%)

ECOC	44576	67.2	52864	74.8
BB	8546	12.9	11499	16.3
Nitrate-rich	8879	13.4	2597	3.7
Unclassified	4330	6.5	3688	5.2

Abbreviations of major particle types: elemental and organic carbon (ECOC), biomass burning (BB), nitrate-rich.

The new Table 2:

Table 2. Seasonal distributions of amine-containing particles and three major amine markers in summer and winter in the PRD, China.

Particle type	Summer (18/7-1/8, 2014)		Winter (27/1-8/2, 2015)	
	Count	Percentage (%) ^a	Count	Percentage (%) ^a
Total Amines	57452		68026	
⁵⁹ (CH ₃) ₃ N ⁺	2581	4.5	6894	10
⁷⁴ (C ₂ H ₅) ₂ NH ₂ ⁺	51442	90	58272	86
⁸⁶ (C ₂ H ₅) ₂ NCH ₂ ⁺	3185	5.5	6119	9

^aThe percentage of each amine marker ion in total detected amine-containing particles.

The new Figure 4:

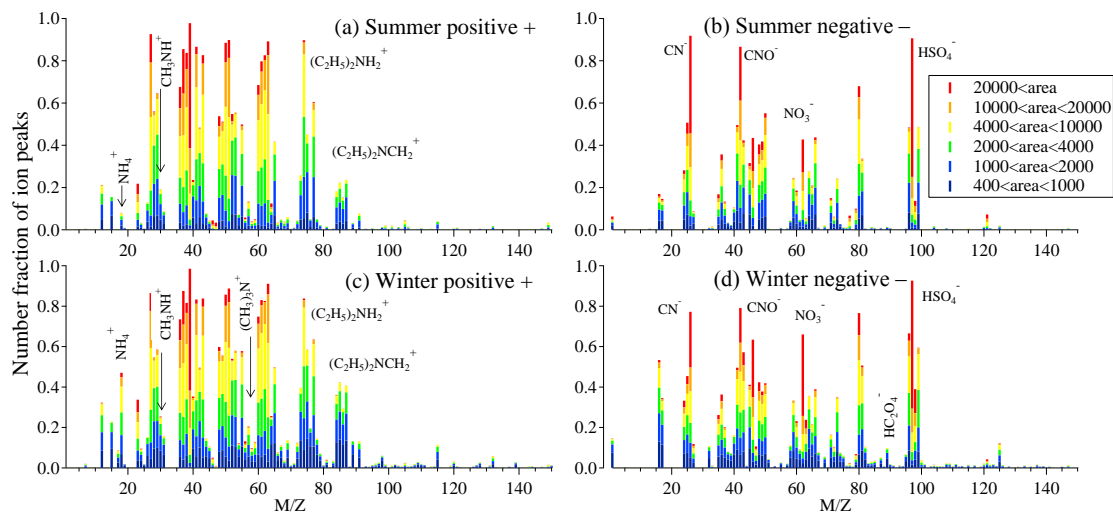


Figure 4. Average ion mass spectra of amine-containing particles in summer and winter. The color bars represent each peak area corresponding to a specific fraction in individual particles.

The new Figure 5:

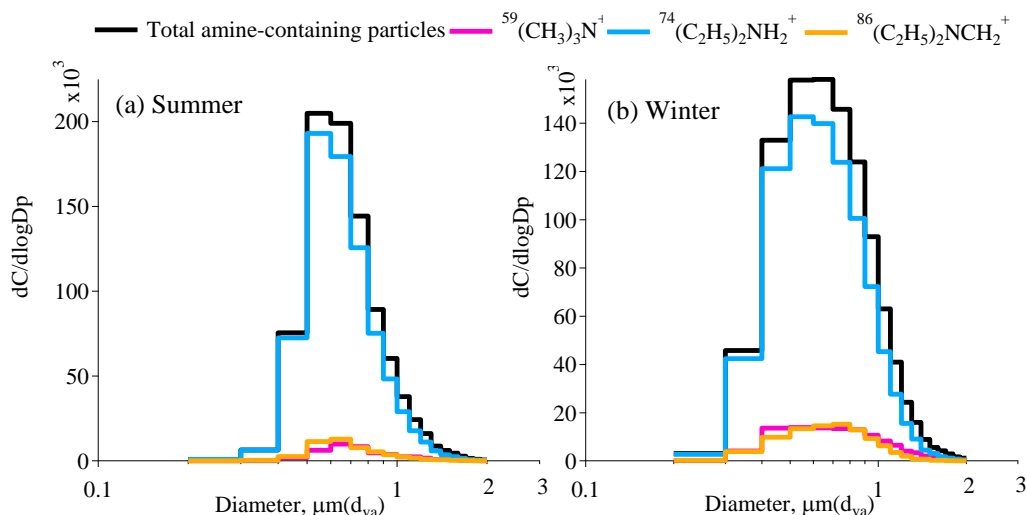


Figure 5. Unscaled size-resolved number distributions of total amine-containing particles and amine particles containing three marker ions of $^{59}(\text{CH}_3)_3\text{N}^+$, $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$, and $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ in summer and winter in Heshan.

2. Line 220-222: What are the different trends? High concentration amine showing on different days are not trends.

Response: We have changed the expression to “The increase of amine-containing particles was mostly associated with high relative humidity (RH) at night in summer, while no direct connection between particle counts and RH was found in winter (Figure S2 a and b). High counts of amine-containing particles that extended in a few days were found from 22 to 24 July (in summer) and from 5 to 8 February (in winter).” in lines 241-245.

3. Line 225-234: The authors claimed that no obvious correlation between amine particle counts and RH in this work. However, both summer and winter diurnal variations showed higher counts at night. Did this diurnal pattern correlated with diurnal RH variation?

Response: No good correlations between diurnal amine-containing particles (1-hour average of particle count) and diurnal RH were found. We have added the correlations between diurnal amine-containing particles and diurnal RH.

“In this work, the correlation between amine-containing particle count and ambient RH was not obvious in either summer or winter (Figure S2). Other factors, such as particle acidity, may have contributed to the acid-base reactions that formed the aminium salts (Murphy et al., 2007;Kurten et al., 2008;Silva et al., 2008).” has been revised to “In this work, although the increase of amine-containing particle count mostly occurred at night, no obvious correlations between diurnal amine-containing particles and RH were found in summer ($r^2=0.33$) and winter ($r^2=0.0003$) (Figure S2). The increase of amine-containing particles at night may be

influenced by particle acidity and emission sources of amines (Murphy et al., 2007;Kurten et al., 2008;Silva et al., 2008).” in lines 263-268.

The new Figure S2:

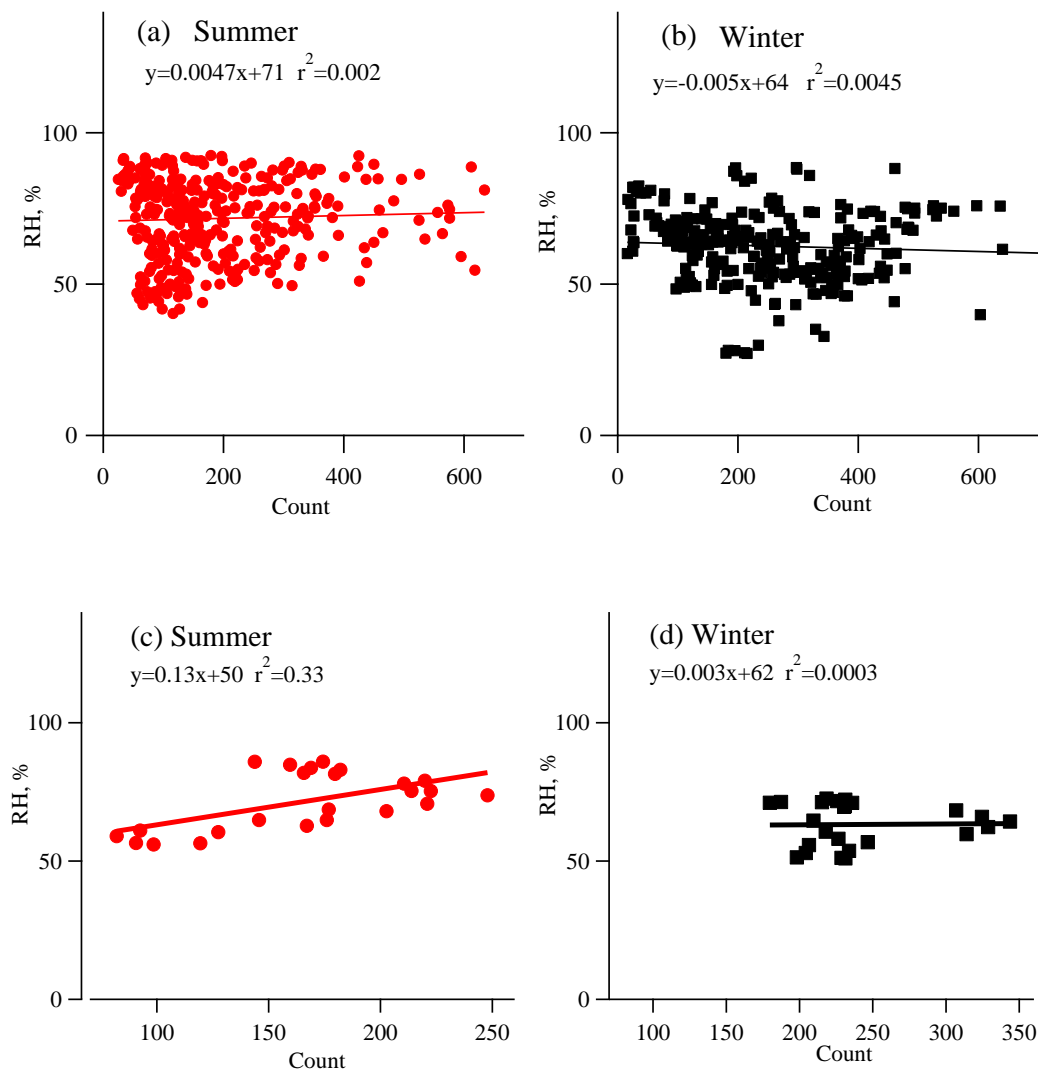


Figure S2. The linear regressions between total amine-containing particle count and relative humidity (RH) in summer (a) and winter (b), and diurnal amine-containing particle count and diurnal RH in summer (c) and winter (d) in Heshan: the diurnal amine-containing particles were averaged from hourly particle counts during sampling period in summer and winter separately.

4. Line 259-263: Since this is the most important observation in this work, I strongly suggest that the author should also examine the ammonium-containing particles separately and compare with the amine-containing particles to see the differences in number fraction and temporal variation.

Response: As suggested by you, the total ammonium-containing particles were

selected, which contained $^{18}\text{NH}_4^+$ with relative area larger than 1%. With this threshold, 18 336 and 235 312 of ammonium-containing particles were detected in summer and winter separately, accounting for 3.6% and 32.6% of the total detected particles. The temporal variation and mass spectra of ammonium-containing particles were discussed in the manuscript. The lower abundance of NH_4^+ in particulate phase may be due to the low emission sources of ammonia and preferred partitioning in gas phase in summer.

“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 (RH = $72 \pm 13\%$) than in winter (RH = $63 \pm 11\%$).” has been added to the manuscript in lines 309-335.

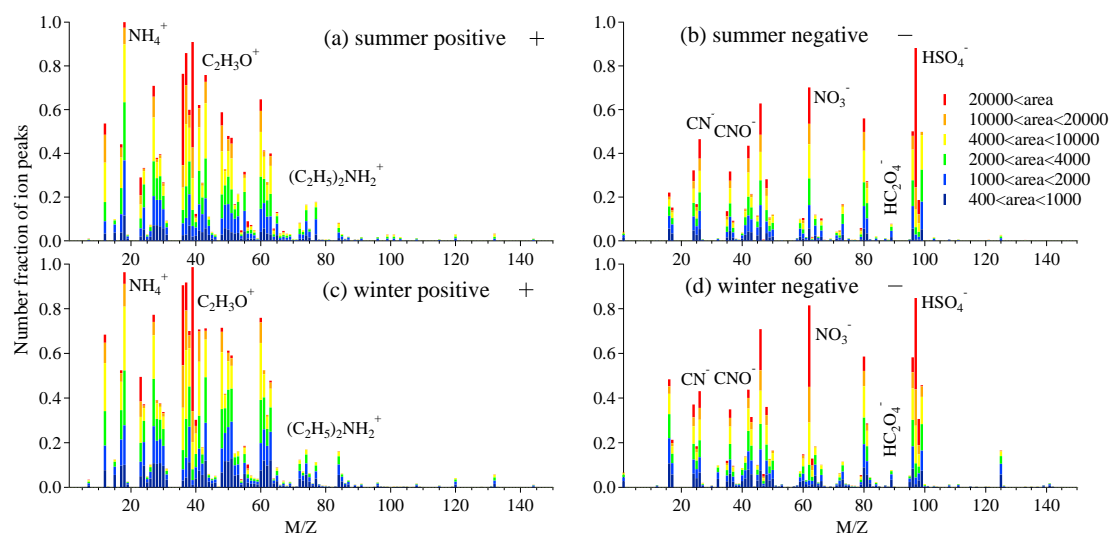


Figure 6. Mass spectra of total ammonium-containing (NH_4^+ -containing) particles in summer and winter. The color bars represent each peak area corresponding to a specific fraction in individual particles.

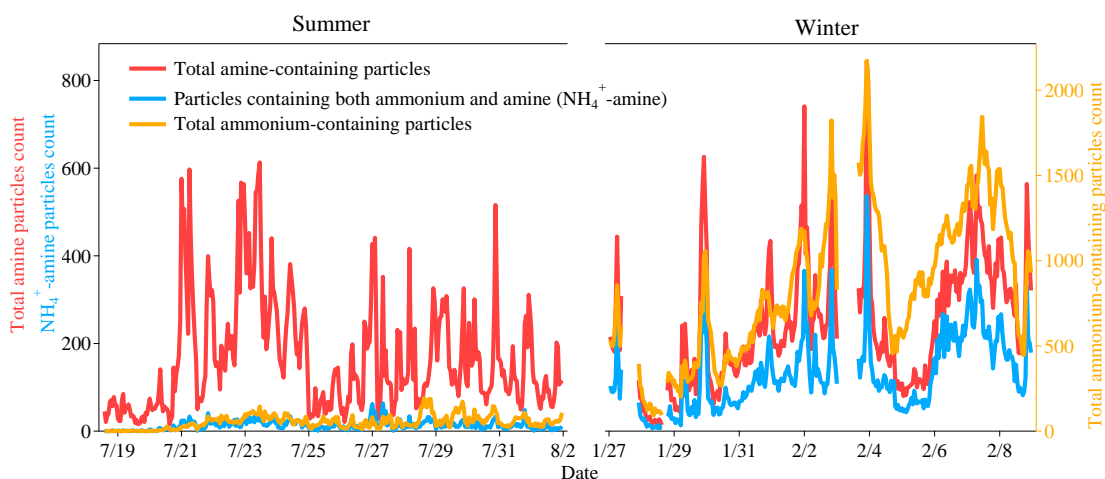


Figure 7. Temporal variations of total amine-containing particles, total ammonium-containing particles and particles containing both ammonium and amine (NH_4^+ -amine) during sampling period in Heshan.

5. Line 283-286: More discussions should be given on the assignment of the marine source. The observed amines could be the results of secondary partitioning since the primary amines could have aged during the long-distance transport. I would suggest some detailed analysis on the other nitrate-rich particles with no sea salt mass patterns to see the differences in amine signals.

Response: Indeed, the amines in the nitrate-rich particles could be formed from the gas to particle partitioning process in addition to direct marine emissions. However, as pointed by the reviewer #3, $m/z +46$ could be $^{46}\text{Na}_2^+$ in addition to 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.” has 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 $[\text{HNO}_3\text{NO}_3]^-$) indicated strong particle acidity in the nitrate-rich amine-containing particles in winter.” has been removed from the manuscript.

6. Line 340-342: How similar? Any correlation coefficient?

Response: Revision made. “The peak areas of amines and the sum of nitrate and sulfate in ECOC particles varied similarly in summer and winter, indicating the formation of aminium salts.” have been revised to “The peak areas of amines and the sum of nitrate and sulfate had similar variation patterns both in summer and winter. The linear regression between them showed robust correlations both in summer ($r^2=0.74$) and winter ($r^2=0.88$) (Figure S3), indicating the formation of aminium salts.” in lines 337-341.

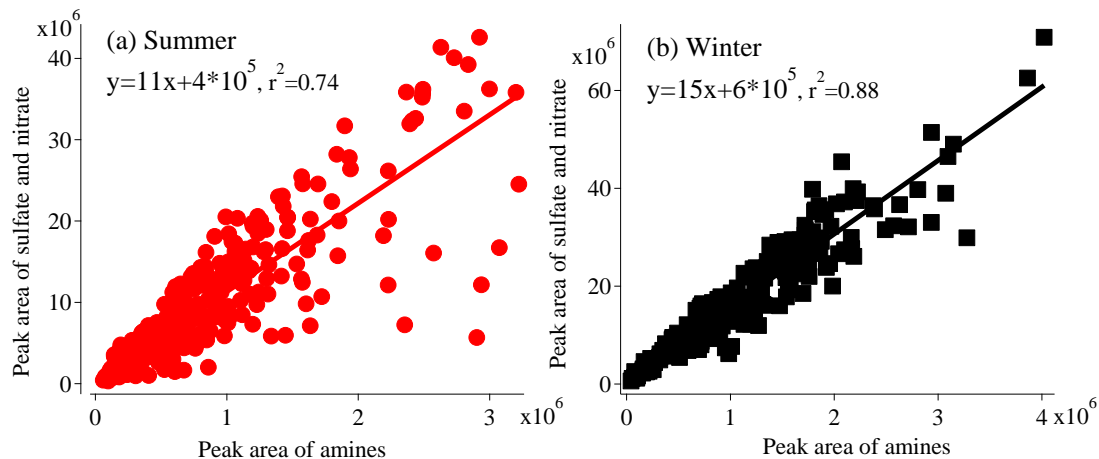


Figure S3. The linear regression between peak area of amines and the peak area of sulfate and nitrate in summer and winter.

7. Line 362-364: High water content or particle acidity could also attract more ammonia to the particle phase considering the much higher concentration of ammonia in ambient environment (one or two magnitudes higher than those of amines). The authors should give more detailed discussions on the formation mechanism of these amine-rich but ammonium-poor particles. Discussion on ammonia and amine sources around sampling site is also necessary to exclude the special sources of amines.

Response: Revision made. The analysis of backward trajectories (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. The low abundance of ammonium in amine-containing particles in summer is likely due to 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). 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. We have extended 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.

“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 and revised in lines 323-335.

“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 NH_3 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 (NH_3) by sulfuric acid particles at 50% RH led to particle-phase dimethylaminium (DMAH^+) to ammonium (NH_4^+) molar ratio up to four times that of gas-phase DMA to 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.” have been revised in lines 356-373.

8. Figure 1: This figure shows the spatial distributions in different seasons, not the seasonal distribution of amines.

Response: In order to clearly show the impact of different sources on the variation of amine-containing particles, we use the results of backward trajectories to show the connection between the abundance of amine-containing particles and the air sources. The “seasonal distributions” has been changed to “spatial distributions”, and all the related revisions are as follows:

“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 $3\text{--}5 \text{ m s}^{-1}$, 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 $0.5\text{--}2 \text{ m s}^{-1}$, 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).” 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.

The old Figure 1:

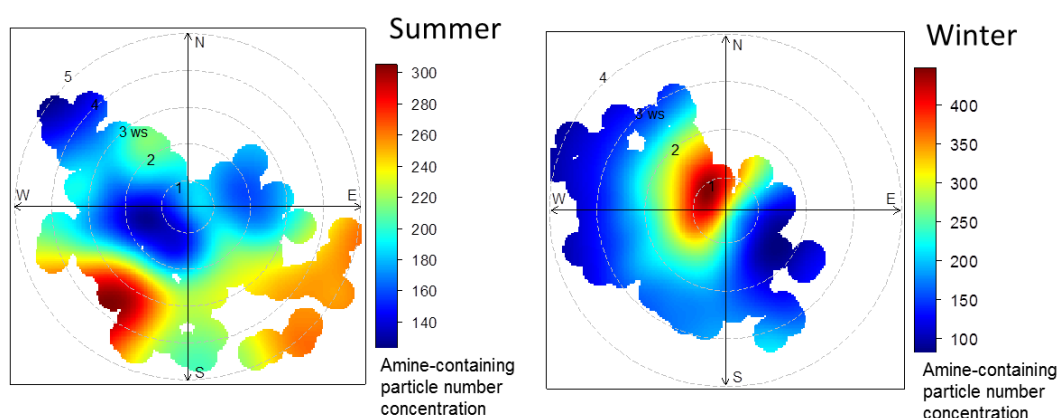


Figure 1. Seasonal distributions of amine-containing particle number concentrations associated with wind direction and wind speed in (left) summer and (right) winter.

The new Figure 1:

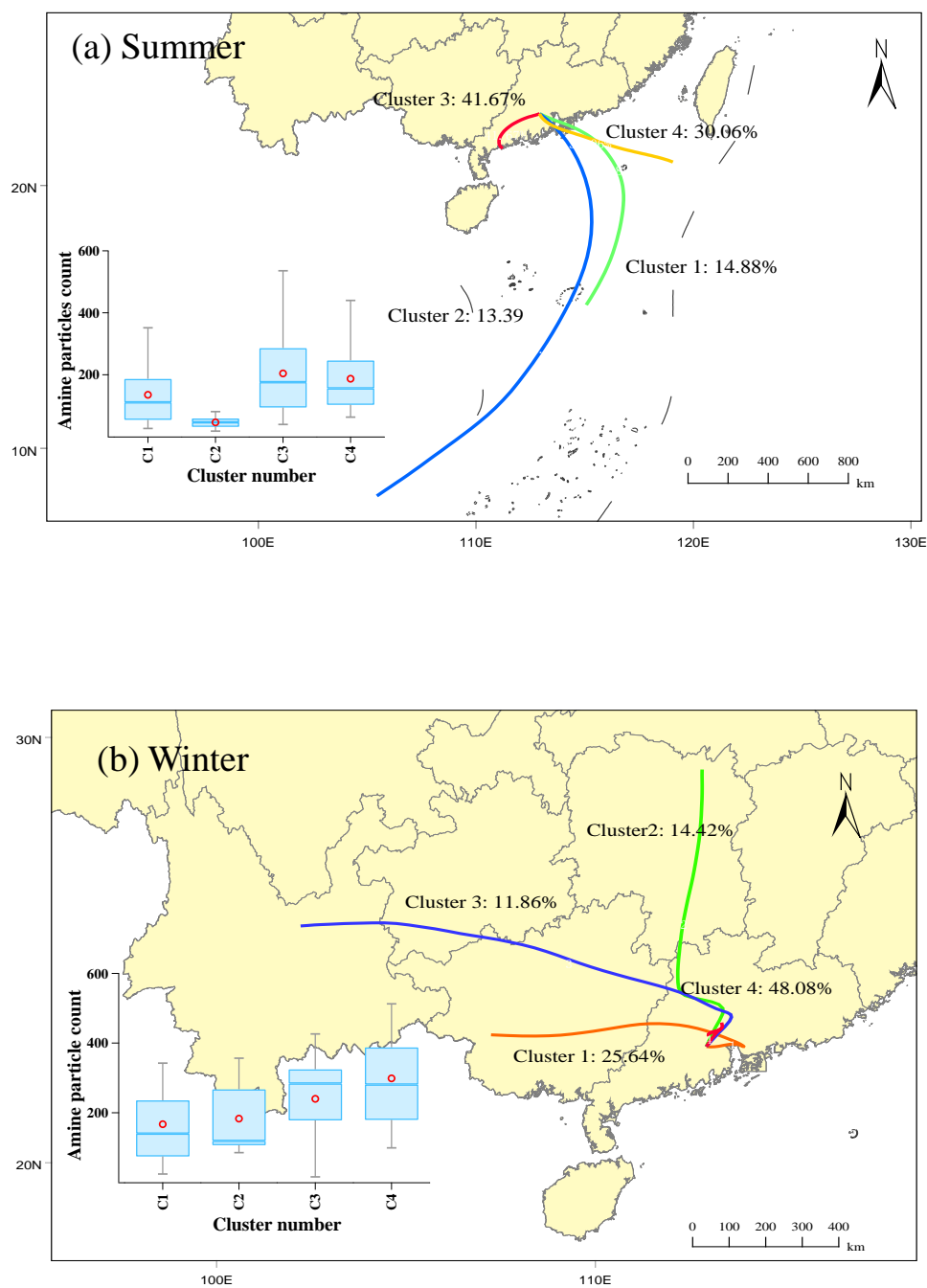


Figure 1. Spatial distributions of amine-containing particle counts associated with backward trajectories (48 hour) of air masses at 500m levels above the ground during the sampling period: (a) summer (from July 18 to August 1, 2014), (b) winter (from January 27 to February 8, 2015).

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