Response to the comments of Anonymous Referee #2

[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 reports on field measurements of small amines in atmospheric aerosols by single particle mass spectrometry. The collected information is used to infer the amine and particle sources and also to shed some light on the particle chemistry. The study is timely. Overall, the paper is clearly written, but several important issues need to be resolved before it can be published. I suggest a major revision.

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 corrections. 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. An in-depth discussion of the three particle categories is in order. It must be told to the reader that these categories are defined operationally, based on the analysis technique. The categories do not necessarily correspond to the particle types utilized by the atmospheric aerosol community. The categories are not exclusive - a nitrate particle may contain a strong ECOC signature, and so on. All this must be kept in mind when interpreting the particle compositions based on these three operationally defined categories.

Response: Indeed, the classification criterions are subjectively defined and should be described clearly in the manuscript. "It should be noted that amine-containing particles are operationally defined and not exclusive, which also contained various chemical species in addition to amines." have been added in lines 198-200. Several marker ions of BB and nitrate-rich type particles were misinterpreted during the classification, so we have removed the classification and description of nitrate-rich particles, and combined the ECOC and BB type particles together to investigate the mass spectra and mixing state of amine-containing particles. We characterized the total amine-containing particles and particles containing three major amine markers of $^{59}(CH_3)_3N^+$, $^{74}(C_2H_5)_2NH_2^+$ and $^{86}(C_2H_5)_2NCH_2^+$.

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* $^{59}(CH_3)_3N^+$, $^{74}(C_2H_5)_2NH_2^+$, $^{86}(C_2H_5)_2NCH_2^+$, $^{101}(C_2H_5)_3N^+$, $^{102}(C_3H_7)_2NH_2^+$, and $^{143}(C_3H_7)_3N^+$ (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 $^{59}(CH_3)_3N^+$, $^{74}(C_2H_5)_2NH_2^+$, $^{86}(C_2H_5)_2NCH_2^+$ 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. $^{30}CH_3NH^+$ 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 $^{30}CH_3NH^+$ was much lower compared with other amine markers, and all the particles containing $^{30}CH_3NH^+$ had strong signal of $^{74}(C_2H_5)_2NH_2^+$, so the $^{30}CH_3NH^+$-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 $^{46}(CH_3)_2NH_2^+$ and/or $^{46}Na_2^+$ 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 $^{62}Na_2O^+$, $^{81}Na_2Cl^+$ and $^{147}Na(NO_3)_2^-$. Thus, m/z +46-containing particles were not classified as amine-containing particles." in lines 183-220.

2. (1) The statement of the low ammonium ion abundance in lines 261 and 269 is in contradiction with the information given later in line 321 and also in Figure 6.

Response: We have revised the related discussions about ammonium in the manuscript. The original expressions in line 261, 269 and 321 have been rephrased. "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." and "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 "Interestingly, in this work, the signals of $^{18}NH_4^+$ were weak and only observed in less than 10% of amine-containing particles in summer, but moderate signal of $^{18}NH_4^+$ was detected in half of amine-containing particles in winter. The low $^{18}NH_4^+$ 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 279-284. "Only 6.7 % of the total amine-containing particles contained ammonium in summer, while percentage increased dramatically to 55 % in winter, indicating an ammonium-poor state in summer and an ammonium-rich state in winter." has been revised to "Interestingly, only 8% of amine-containing particles mixed with ammonium (NH_4^+) in summer, while the percentage increased dramatically to 54 % in winter, indicating a relatively NH_4^+-poor state in summer and an NH_4^+-rich state in winter." in lines 305-308.

(2) This also calls for several other questions: - What is the relationship between the peak area and actual abundance of a chemical species? Is it indeed one-to-one? If not, did you perform any calibrations? Did you perform tests and calibrations for single-component particles or for mixtures? - Does the detection of ammonium depend on the particle composition/acidity? For instance, is peak area same for the

particles containing same amounts of ammonium, but in the forms of ammonium nitrate, ammonium bisulfate, and ammonium sulfate?

Response: The peak area of a chemical species provides a semi-quantitative result of its actual abundance in single particles, although in some cases comparison between peak area and concentration was poor due to matrix effect and transmission efficiency (Dall'Osto et al., 2006). After scaling/normalizing ATOFMS/SPAMS data based on particle counter such as SMPS (scanning mobility particle sizer) and aerodynamic particle sizer (APS), the quantitative agreement can be obtained between peak area and atmospheric concentration for major constituents of ambient aerosols. There is a great deal of work investigating the relationship between atmospheric concentrations and peak area/relative peak area from single particle mass spectrometer (ATOFMS and SPAMS) (Mansoori et al., 1994;Gross et al., 2000;Bhave et al., 2002;Bein et al., 2006;Dall'Osto and Harrison, 2006;Dall'Osto et al., 2006;Qin et al., 2006;Spencer and Prather, 2006;Snyder et al., 2009;Sullivan et al., 2009;Huang et al., 2013;Zauscher et al., 2013)

Most peak signals are corresponding to specific chemical species, such as elemental carbon, nitrate, sulfate, ammonium, oxalic acid, carbon-nitrogen fragments and most metals. Some metals (such as Al, Cu, Ti, V) and organic ions receive strong isobaric interferences with commonly observed organic fragments. For the controversial peak assignment, the abundances of other marker ions are often used to identify the most possible ions. For example, the ion of m/z +46 can be amine marker of $^{46}(CH_3)_2NH_2^+$ and $^{46}Na_2^+$ 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 and the commonly observed organic fragments are not found, besides, these particles were enriched with sodium salts like $^{62}Na_2O^+$, $^{81}Na_2Cl^+$ and $^{147}Na(NO_3)_2^-$. Thus, m/z +46 was identified as $^{46}Na_2^+$ in this work.

In this work, no particle counter was used during the sampling campaign, so the reported number count of ambient particles were not scaled or calibrated, but the peak intensity and particle counts can still provide a semi-qualitative approach to investigate the seasonal characteristics and mixing state of amine-containing particles (Dall'Osto and Harrison, 2006;Healy et al., 2012).

The peak intensity of ammonium is largely dependent on its abundance in particles (Gross et al., 2000;Kane and Johnston, 2001;Liu et al., 2003;Wenzel et al., 2003;Lake et al., 2004). The particle acidity can impact the partitioning of ammonium from gas to particles, but has no influence on the ionization of ammonium. For the particles containing ammonium nitrate, ammonium bisulfate, and ammonium sulfate, the peak area of ammonium with same abundance will vary in a certain range due to the matrix effect; however, the good relationship between peak intensity of ammonium and actual concentration suggests a semi-quantitative approach through peak intensity to study the mixing state of ammonium with other species such as amines(Kane and Johnston, 2001).

(3) The replacement of ammonia by amines is indeed possible. However, how

realistic is it to expect that most of the ammonium will be replaced, considering that amines are an order of magnitude less atmospherically abundant than ammonia?

Response: Indeed, the concentration of ammonia in gas phase is two orders of magnitude higher than that of amines, so the variation of gas phase concentration of ammonia could have a substantial impact on the gas to particle partitioning into amine-containing particles. The seasonal different mixing state of amines and ammonium may be influenced by the seasonal variation of source strength of ammonium. However, 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.

Thus, we have revised the discussions about ammonium–amine exchange reactions 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 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." in lines 356-373.

(4) Similarly, how likely is it that most of chloride has been evicted from the sea-salt particles by the aging process? Could the lack of detected chloride be traced down to some other reason, such as the detection technique itself? Any calibrations with authentic chloride aerosols? What about the presence of NaCl2- clusters? Is it where all of the chloride go?

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 $^{46}Na_2^+$ except as amine marker of $^{46}(CH_3)_2NH_2^+$, because no other amine markers were found and nitrate-rich particles were enriched with sodium salts like $^{62}Na_2O^+$, $^{81}Na_2Cl^+$ and $^{147}Na(NO_3)_2$-, so we removed nitrate-rich particles from amine-containing particles, and all the related discussions were removed too. The SPAMS has a good sensitivity to the detection of chloride, so the lack of chloride signal in particles was mainly due to the low abundance of chloride in particles. As we have removed the sea-salt particles from amine-containing particles, the depletion process of chloride is no longer discussed in this work.

"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 $^{62}Na_2O^+$, $^{81}Na_2Cl^+$ and $^{147}Na(NO_3)_2^-$. 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 $[Na]^+$, 62 $[Na_2O]^+$, and 63$[Na_2OH]^+$ in the positive mass spectrum and *m/z*s -93 $[NaCl_2]^-$ and -147 $[Na(NO_3)_2]^-$ 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 $[(CH_3)_2NH_2]^+$ 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 $[NaCl_2]^-$ and -147 $[Na(NO_3)_2]^-$ were not observed in the winter negative mass spectrum. Instead, the *m/z* 56 $[Fe]^+$ 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 $[HNO_3NO_3]^-$) indicated strong particle acidity in the nitrate-rich amine-containing particles in winter." have been removed from the manuscript.

3. The authors must be very careful when referring to the particle mixing state. It appears that they confuse the abundances of different particles with the abundances of different chemicals in the same particle. For instance, in Line 314, do they imply that

nitrate and sulfate were present in the same particles and were elevated during summer or that sulfate- and nitrate-containing particles had a high occurrence during summer? Similarly, if I am interpreting the text and Figure 6 correctly, the figure caption should not be the 'mixing state', but the fraction of particles containing different components.

Response: The old Figure 6 caption and related expressions were confusing and should be revised as the abundances of ammonium-, nitrate- and sulfate-containing particles instead of "mixing state". In order to demonstrate the abundances of ammonium-, nitrate- and sulfate-containing amine particles in total amine-containing particles, the old Figure 6 has been changed to Table 3, and the related discussions were revised as follows:

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

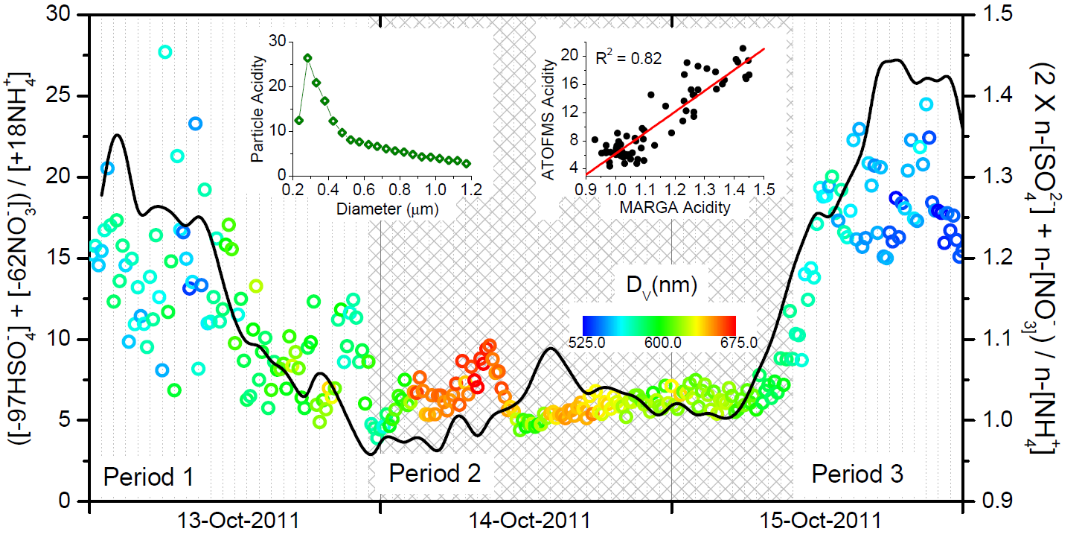
Marker ions	Summer	Winter
$^{18}NH_4^+$	8%	54%
$^{62}NO_3^-$	43%	69%
$^{97}HSO_4^-$	91%	94%

The marker ions of $^{18}NH_4^+$, $^{62}NO_3^-$ and $^{97}HSO_4^-$ were chosen to represent ammonium, nitrate and sulfate.

"To investigate the seasonal mixing states of amines with sulfate, nitrate, and ammonium (SNA), the relative abundances of SNA-containing amine particles are shown in Figure 6. The color scale represents the percentage contribution of SNA-containing amine particles to total amine particles. ECOC and BB amine-containing particles were both found to be internally mixed with sulfate throughout the sampling period. Only a small percentage of nitrate-rich amine-containing particles were mixed with sulfate during summer, but this percentage increased to 53 % during winter. Amine particles containing nitrate accounted for 39 % and 59 % of the ECOC and BB particles in summer, respectively, and 68 % and 79 % in winter. The internal mixing state of sulfate and nitrate with amines in single particles suggests the possible formation of aminium sulfate and nitrate salts. Only 6.7 % of the total amine-containing particles contained ammonium in summer, while percentage increased dramatically to 55 % in winter, indicating an ammonium-poor state in summer and an ammonium-rich state in winter." have been revised to "To investigate the aging state of amine-containing particles, the abundances of sulfate-, nitrate-, and ammonium-containing amine particles are shown in Table 3. More than 90% of amine-containing particles were found to be internally mixed with sulfate throughout the sampling period. The abundance of nitrate in amine particles increased from 43% in summer to 69% in winter. The high abundances of sulfate and nitrate in amine-containing particles suggest the possible formation of aminium sulfate and nitrate salts. Interestingly, only 8% of amine-containing particles mixed with ammonium (NH_4^+) in summer, while the percentage increased dramatically to 54 % in winter, indicating a relatively NH_4^+-poor state in summer and an NH_4^+-rich state in winter.” in lines 299-308.

4. As written, it appears that the authors do not treat the charge balance (ion equivalency) correctly when calculating the relative acidity. One cannot simply add the peaks of nitrate and sulfate because the former corresponds to monoprotic and the latter to diprotic acid, respectively. Also, are peak intensities proportional to actual abundancies of chemical species?

Response: The relative acidity ratio used in this work is not an equivalent result of the calculation of mass concentrations of anions and cations. It is only used in the studies of single particles mass spectrometer to compare the relative particle acidity of different particles groups. Several related field studies have used this method to discuss the variation of particle acidity (Denkenberger et al., 2007;Pratt et al., 2009;Yao et al., 2011;Huang et al., 2013;Cheng et al., 2017), and Huang et al. (2013) have compared the actual particle acidity calculated from inorganic ions (MARGA data) and relative acidity ratio obtained from single particle mass spectrometer (ATOFMS). The comparison result is as follows:



This graph is from the field study of Huang et al. (2013). The right inset graph shows the linear regression between ATOFMS particle acidity and MARGA particle acidity. The robust correlation between them indicates a feasible estimation of particle acidity through the peak areas of sulfate, nitrate and ammonium obtained from ATOFMS.

We have added the related discussion in the manuscript to state this issue. “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).” have been added in lines 185-191.

“Huang et al. (2013) obtained a robust correlation (r^2=0.82) between the particle acidity calculated from inorganic ions obtained from MARGA and relative acidity ratio obtained from single particle mass spectrometer, allowing us to use R_a for comparison of particle acidity(Huang et al., 2013).” have been added in lines 350-354 .

The peak area of a chemical species provides a semi-quantitative result of its actual abundance in single particles, which has been specifically discussed in the response to “Comment 2(2)” in detail.

5. Figure 5 is problematic. Does ‘size’ refer to the radius or diameter? If the y-axis is the particle count, then the plotted curves cannot be size distributions. A size distribution is expressed as dCount/dSize, but shown are apparently counts for different size bins. Those must be presented are individual points or bars, not a continuous curve. What is the bin size?

Response: We have revised the Figure 5 and related discussions in the manuscript as you suggested. The “size” refers to the diameter of particles, and the y-axis has been changed from “count”to “dC/dlogDp” in Figure 5. The size bin measured by SPAMS is 0.1 μm.

The old Figure 5:

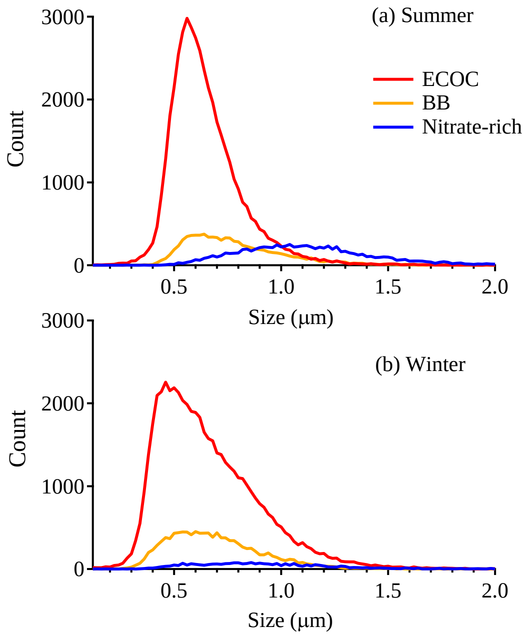


Figure 5. Size distributions of the three types of amine-containing particles in (a) summer and (b) winter.

The new Figure 5:

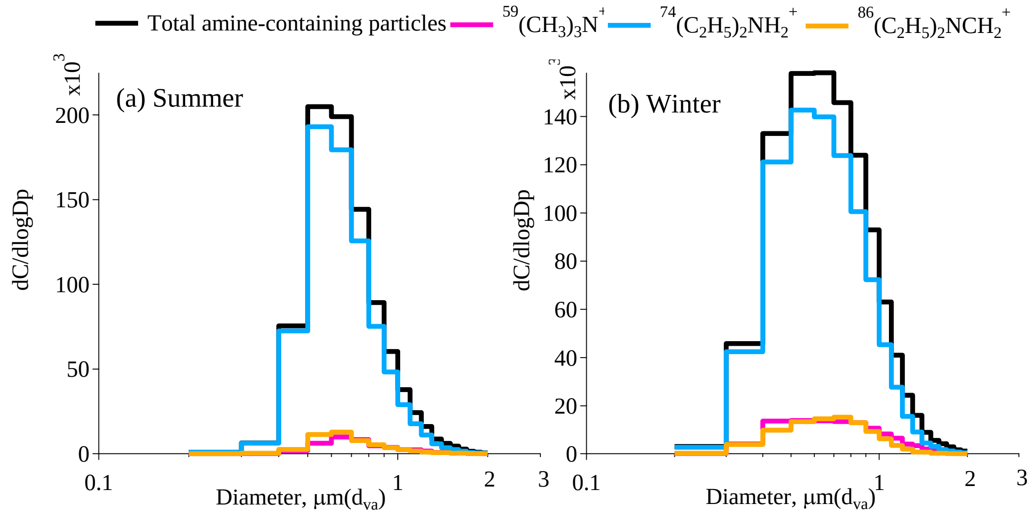


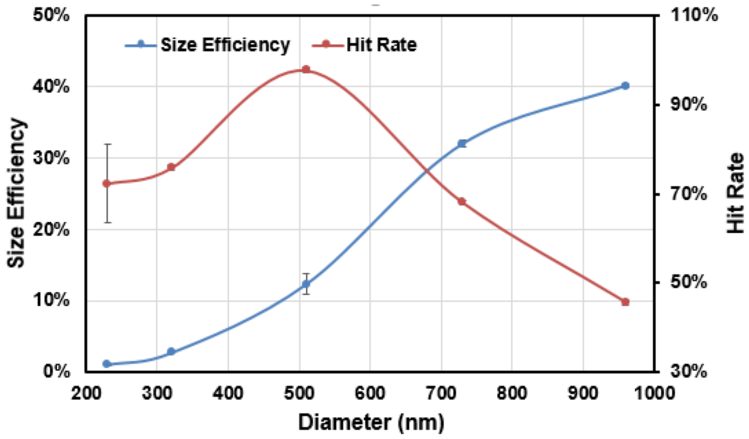
Figure 5. Unscaled size-resolved number distributions of total amine-containing particles and amine particles containing three marker ions of $^{59}(CH_3)_3N^+$, $^{74}(C_2H_5)_2NH_2^+$, and $^{86}(C_2H_5)_2NCH_2^+$ in summer and winter in Heshan.

"Size-resolved number distributions are shown in Figure 5 for the three types of amine-containing particles. Both ECOC and BB amine-containing particles exhibited unimodal distributions in the submicron mode and had a broad distribution from 0.4 to 1.0 μm in both summer and winter, which may have resulted from amine condensation on and reaction with fine mode particles from anthropogenic emissions. Interestingly, in summer, 37 % of the nitrate-rich amine-containing particles were submicron in size, while 63 % were supermicron; this is reasonable, as the majority of nitrate-rich amine-containing particles were associated with sea-salt particles from marine sources. Healy et al. (2015) also reported large amounts of supermicron amine-containing particles internally mixed with sea-salt particles on the island of Corsica, France." have been revised to "The unscaled size-resolved number distributions of total amine-containing particles and amine particles containing three marker ions of $^{59}(CH_3)_3N^+$, $^{74}(C_2H_5)_2NH_2^+$, and $^{86}(C_2H_5)_2NCH_2^+$ are shown in Figure 5. The amine-containing particles exhibited unimodal distributions in the submicron mode from 0.4 to 1.5 μm in both summer and winter, which may have resulted from gaseous amine condensation on and/or reaction with fine mode particles from anthropogenic emissions. Although amine-containing particles peaked at the size range of 0.5-0.7 μm in both summer and winter, a broader size range of amine-containing particles was observed in winter, which may be due to more complex anthropogenic emission sources of primary particles in winter. The $^{74}(C_2H_5)_2NH_2^+$-containing particles showed similar variation patterns as total amine-containing particles both in summer and winter. However, $^{59}(CH_3)_3N^+$- and $^{86}(C_2H_5)_2NCH_2^+$-containing particles showed less distinct peaks in winter." in lines 285-297.

6. What is the shape of the particle transmission function of the aerodynamic lens?

Have plots shown in Figure 5 been corrected for the size-dependent particle transmission? Frankly, I do not expect the abundance of amine-containing particles to taper off at the smaller sizes. In fact, an opposite should be true. It takes significantly less time to enrich the smaller particles with amines through the substitution reaction than to enrich the larger particles.

Response: The size efficiency and hit rate for particles at each size during the measurement by SPAMS are as follows:



Because we didn’t have SMPS to measure the ambient particles, size distribution of amine-containing particles was not scaled, thus, we called it “unscaled size distribution”. The available size information of particles from SPAMS was used to compare its seasonal difference.

The amines detected in this work were observed in particles with size ranging from 0.4 to 1 µm, which is due to two reasons. Firstly, the SPAMS data is unscaled and many small particles (<300 nm) were undetected during the sampling. Secondly, according to the studies of Sauerwein and Chan, the uptake of dimethylamine (DMA) by acidic particles was severely influenced by the extent of neutralization and the particle phase state. In fully neutralized droplets at 50 % RH, the limited availability of H_3O^+ ions for acid-base reactions led to a partial displacement of NH_4^+ by the stronger base DMA. At uptake equilibrium, molar ratio of $DMAH/NH_4^+$ in the particles was four times higher than the gas-phase DMA/NH_3 concentration ratio, indicating an enrichment of DMA in acidic particles through the displacement of NH_4^+ by DMA. In this work the high ambient RH (72 ± 13 %) and acidic particles containing abundant sulfate and nitrate in summer were similar to the experimental conditions used in Sauerwein and Chan (2017). So it is possible that larger particles, with higher degree of neutralization, contain more amines.

7. L175 and everywhere: replace ‘m/zs’ with ‘m/z’ L175-180: I suggest placing this information in a table L188-191: provide a reference to the processing method

Response: All the “m/zs” have been revised to “m/z” in the manuscript. The marker ions chosen for alkylamines and assignments have been listed in Table 1 as follows.:

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

Marker ion	Alkylamine assignment
$^{59}(CH_3)_3N^+$	Trimethylamine (TMA)
$^{74}(C_2H_5)_2NH_2^+$	Diethylamine (DEA)
$^{86}(C_2H_5)_2NCH_2^+$	DEA, TEA, DPA
$^{101}(C_2H_5)_3N^+$	Triethylamine (TEA)
$^{102}(C_3H_7)_2NH_2^+$	Dipropylamine (DPA)
$^{143}(C_3H_7)_3N^+$	Tripropylamine (TPA)

Because the classification rules for ECOC, BB and nitrate-rich type particles are inappropriate, so we removed the description of ART-2a method. "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." have been removed from the manuscript.

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