Response to the comments of Anonymous Referee #2

[Atmospheric Chemistry and Physics, MS ID: acp-2021-593]
Title: Diverse mixing states of amine-containing single particles in Nanjing, China

General comments

This article describes mixing state information for amine-containing particles derived exclusively using a single particle mass spectrometer at a sampling site in Nanjing. TMA and DEA were found to exhibit differing chemical mixing states, particularly with respect to oxidized organic and sulfate content. DEA-containing particles are proposed to be more acidic than TMA-containing particles based on the SPAMS peak area data for ammonium/aminium ions and sulfate/nitrate. The dependence of enhanced particulate TMA formation upon ambient RH has been demonstrated by others previously as cited in the article. Although not particularly novel, the article provides some new information on amine mixing state for this location. The text would benefit from a discussion of the drawbacks of single particle mass spectrometry when attempting quantitative or semiquantitative analyses (such as the acidity calculations). A discussion of the likely sources of gas phase TMA and DEA in the region would also be helpful.

Response: We are grateful to your comments on this paper. These valuable comments are of great help to the revision and improvement. We have addressed the comments and made substantial revisions based on studying these comments carefully. The responses and discussions about the drawbacks of single particle mass spectrometry and the possible sources of two amines are listed below. Our responses to the comments and revisions made in the manuscript are highlighted in blue color.

Anything about our paper, please feel free to contact me at chengcl@jnu.edu.cn

Best regards!
Sincerely yours

Chunlei Cheng
October 11, 2021

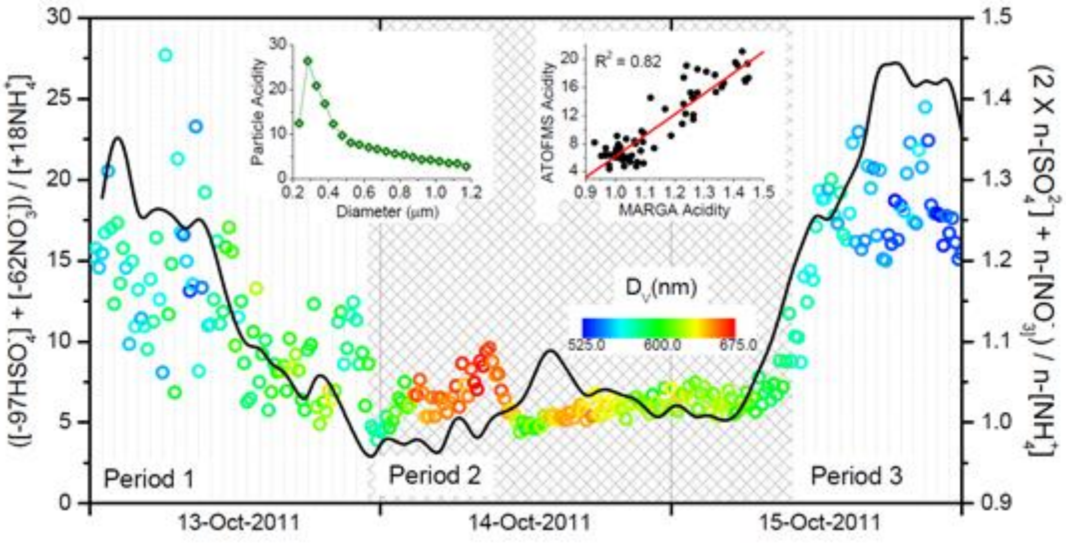
Specific comments and point by point responses:

Major Comments:

1. The text would benefit from a discussion of the drawbacks of single particle mass spectrometry when attempting quantitative or semiquantitative analyses (such as the acidity calculations).

Response: Indeed, it is difficult to accurately quantify the mass concentration of amines in the particles by HP-SPAMS due to the size-dependent transmission efficiencies of particles through aerodynamic lens and composition dependent matrix effect; thus, the quantitative relationship between two amines with sulfate, nitrate and ammonium (SNA) was not considered in this work. Currently, the results were used to illustrate the different effects of same influencing factors on the behaviors of amine-containing particles based on their mixing states.

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 roughly estimated from the peak areas of SNA, which is intend to compare the relative particle acidity of different amine-containing particles. This parameter is only referred in the studies from single particle mass spectrometry. 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) (Huang et al., 2013). The comparison result is as follows:



This graph is from the field study of Huang et al. (2013). The robust linear regression between ATOFMS particle acidity and MARGA particle acidity was obtained, which indicates a feasible estimation of particle acidity through the peak areas of sulfate, nitrate and ammonium obtained from single particle mass spectrometry.

"It should be noted that HP-SPAMS measurements cannot provide the quantitative mass concentrations of amines and related chemical species due to the size-dependent transmission efficiencies of particles through aerodynamic lens and composition dependent matrix effect (Cheng et al., 2018; Cheng et al., 2021; Gong et al., 2021). Currently, the observational results were used to illustrate the distinct impacts of same influencing factors on the behaviors of amine-containing particles." has been added in the lines 229-235.

"Although the feasibility of Ra has been supported by the robust linear correlation with authentic particle acidity calculated from mass concentrations of inorganic ions (Huang et al., 2013), this semi-quantitative approach should be carefully treated when it comes to the discussion about the actual acidity of atmospheric particles." has been added in the lines 444-448.

2. A discussion of the likely sources of gas phase TMA and DEA in the region would also be helpful.

Response: According to reported studies the gaseous TMA and DEA are mainly from agriculture, industry, vehicle exhaust, biomass combustion, biological, and marine sources (Zhou et al., 2019; Hemmilä et al., 2018; Sintermann et al., 2014; Ge et al., 2011; Zhang et al., 2017). Their concentrations vary greatly depending on the influence of source strength near the sampling site. Since HP-SPAMS measurements cannot provide the quantitative mass concentrations of amines, thus, it is difficult to resolve the proportions of gaseous TMA and DEA from their major sources. We have added some discussions about the gaseous sources of TMA and DEA, which will help to indicate their potential sources in this work.

"The gaseous TMA and DEA are mainly from agriculture, industry, vehicle exhaust, biomass combustion, biological, and marine sources (Zhou et al., 2019; Hemmilä et al., 2018; Sintermann et al., 2014; Ge et al., 2011; Zhang et al., 2017). Their concentrations vary greatly depending on the influence of source strength near the sampling site. For example, the gaseous concentration of DEA was 14 and 2-5 times higher than TMA in polluted urban areas in China (Yao et al., 2016) and US (You et al., 2014), respectively, while higher concentration of TMA than DEA was observed in the forest site (You et al., 2014). Both the online and offline measurements are difficult to quantitatively resolve their emission sources (You et al., 2014; Yao et al., 2016; Kieloaho et al., 2013; Hellén et al., 2014). Here the backward trajectories of the air masses from sampling site were discussed to explorer their possible different sources. " has been added in the lines 260-271.

3. Do the back trajectories help to inform the dominant sources of TMA vs DEA?

Response: As we have discussed in the original manuscript based on the Figure 2, TMA-containing particles were primarily from the air masses of Cluster 1 and Cluster 4, while the DEA-containing particles were associated with the air masses of Cluster 3 and Cluster 4, which underwent long-range transport. The Cluster 1, 3 and 4 were all associated with the strong anthropogenic sources in the YRD (eastern of the sampling site) and marine sources in the East China Sea. Unfortunately, the rough spatial resolution of backward trajectories of the air masses was incapable in matching the real-time changes of amine-containing particles detected by HP-SPAMS. Thus we cannot locate the exact anthropogenic source for TMA and DEA via the results of backward trajectories. Therefore, we kept this part unchanged and no further discussions were added in the revision stage.

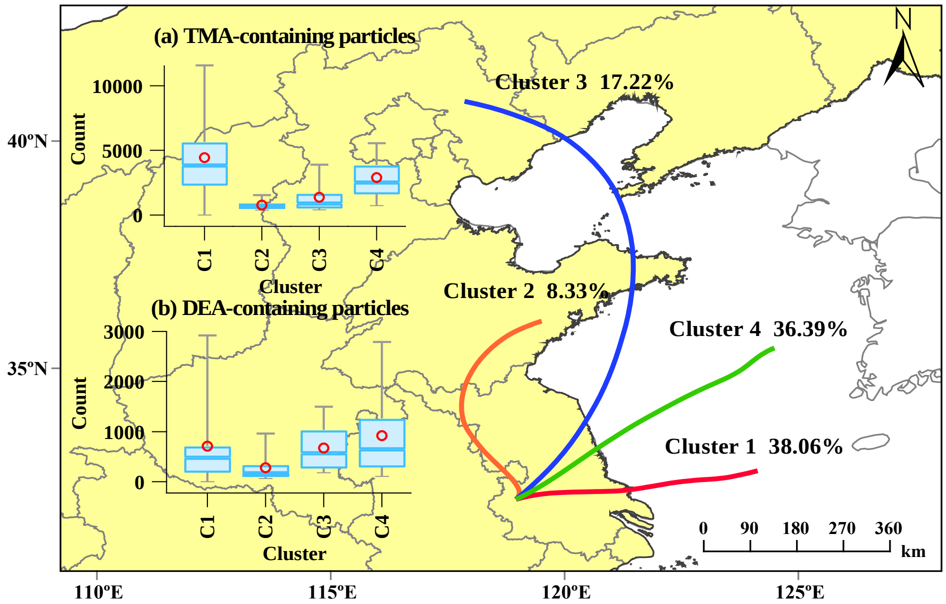


Figure 2. Backward trajectories (48 h) of air masses at 500 m above the ground during the sampling period: (a) TMA-containing particles counts; (b) DEA-containing particle counts. C1 to C4 represent cluster 1 to cluster 4.

4. The abstract should be reduced in length.

Response: "The mixing states of particulate amines with different chemical components are of great significance in studying the formation and evolution processes of amine-containing particles. In this work, the mixing states of single particles containing trimethylamine (TMA) and diethylamine (DEA) are investigated in order to study the formation and aging processes of the single particles using a high-performance single-particle aerosol mass spectrometer located in Nanjing, China, in September 2019. TMA- and DEA-containing particles accounted for 22.8% and 5.5% of the total detected single particles, respectively. The particle count and abundance of the TMA-containing particles in total particles notably increased with enhancement of ambient relative humidity (RH), while the DEA-containing particles showed no increase under a high RH. This result suggested the important role of RH in the formation of particulate TMA. Significant enrichments of secondary organic species, including $^{43}C_2H_3O^+$, $^{26}CN^-$, $^{42}CNO^-$, $^{73}C_3H_5O_2^-$, and $^{89}HC_2O_4^-$, were found in DEA-containing particles, indicating that DEA-containing particles were closely associated with the aging of secondary organics. The particle count and abundance of DEA-containing particles showed a prominent increase during the nighttime, but a sharp decrease during the afternoon. Furthermore, the differential mass spectra of the DEA-containing particles showed a much higher abundance of nitrate during the nighttime than during the daytime. In addition, the number fraction of organic nitrogen species in the DEA-containing particles and ambient NOx both showed consistent increasing trends, similar to the accumulation of DEA-containing particles during the nighttime. This suggested that the nighttime production of particulate DEA might be associated with reactions of gaseous DEA with HNO_3 and/or particulate nitrate. Higher abundances of oxalate and glyoxylate were found in DEA-containing particles during the strong photochemistry period when the abundance of DEA-containing particles decreased to the lowest of the total particles. This result suggested a substantial impact of photochemistry on the aging process of DEA-containing particles. Furthermore, greater than 80% of TMA- and DEA-containing particles internally mixed with nitrate, while the abundance of sulfate was higher in the DEA-containing particles (79.3%) than in the TMA-containing particles (55.3%). In addition, a lesser amount of ammonium was found in the DEA-containing particles (13.2%) compared with the TMA-containing particles (35%). These observations suggested that particulate DEA existed both as nitrate and sulfate aminium salts, while the particulate TMA primarily presented as nitrate aminium salt. Overall, the different mixing states of the TMA- and DEA-containing particles suggested their different formation processes and various influencing factors, which are difficult to investigate using bulk analysis. These results provide insights into the discriminated fates of organics during the evolution process in aerosols, which provides a better illustration of the behavior of secondary organic aerosols.” has been revised to “The mixing states of particulate amines with different chemical components are of great significance in studying the formation and evolution processes of amine-containing particles. In this work, the mixing states of single particles containing trimethylamine (TMA) and diethylamine (DEA) are investigated using a high-performance single-particle aerosol mass spectrometer located in Nanjing, China, in September 2019. TMA- and DEA-containing particles accounted for 22.8% and 5.5% of the total detected single particles, respectively. The particle count and abundance of the TMA-containing particles in total particles notably increased with enhancement of ambient relative humidity (RH), while the DEA-containing particles showed no increase under a high RH. This result suggested the important role of RH in the formation of particulate TMA. Significant enrichments of secondary organic species, including $^{43}C_2H_3O^+$, $^{26}CN^-$, $^{42}CNO^-$, $^{73}C_3H_5O_2^-$, and $^{89}HC_2O_4^-$, were found in DEA-containing particles, indicating that DEA-containing particles were closely associated with the aging of secondary organics. The differential mass spectra of the DEA-containing particles showed much higher abundance of nitrate and organic nitrogen species during the nighttime than during the daytime, which suggested that the nighttime production of particulate DEA might be associated with reactions of gaseous DEA with HNO_3 and/or particulate nitrate. In the daytime the decrease of DEA-containing particles was observed with the enrichment of oxalate and glyoxylate, which suggested a substantial impact of photochemistry on the aging process of DEA-containing particles. Furthermore, greater than 80% of TMA- and DEA-containing particles internally mixed with nitrate, while the abundance of sulfate was higher in the DEA-containing particles (79.3%)

than in the TMA-containing particles (55.3%). This suggested that particulate DEA existed both as nitrate and sulfate aminium salts, while the particulate TMA primarily presented as nitrate aminium salt. The different mixing states of the TMA- and DEA-containing particles suggested their different formation processes and various influencing factors, which are difficult to be investigated using bulk analysis. These results provide insights into the discriminated fates of organics during the evolution process in aerosols, which helps to illustrate the behavior of secondary organic aerosols." in the lines 31-61.

Specific comments:

1. Line 94: Use the word temperature

Response: Revisions made. The T was changed to temperature in the lines 75 and 86.

2. Line 102: rewrite

Response: "Berndt et al. (2010) and Wang et al. (2010) found that the formation of aminium salts via a neutralization reaction can affect the growth of particles and the generation of SOAs, which was even stronger than that of NH_3. Although amine concentrations are generally lower than ammonia and ammonium, the amine-ammonium exchange still contributes to particulate amine formation due to the stronger alkalinity of amines compared to ammonium" has been revised to "Berndt et al. (2010) and Wang et al. (2010) found that the formation of aminium salts via a neutralization reaction can affect the growth of particles and the generation of SOAs. Although the concentrations of amines are generally lower than ammonia, the amine-ammonium exchange still contributes to particulate amine formation due to the stronger alkalinity of amines compared to ammonium." in the lines 92-97.

3. Line 113: rewrite, the species in parentheses are not amines

Response: "Different amines (NO_3 radicals, OH radicals, and ozone) exhibit inconsistent behaviors under the same oxidation environments" has been revised to "Different amines exhibit inconsistent behaviors under the same oxidation environments (NO_3 radicals, OH radicals, or ozone) (Price et al., 2014; Silva et al., 2008; Murphy et al., 2007)." in the lines 105-108.

4. Line 170: what flow rate?

Response: The flow rate used here was 75 mL/min. (Li et al., 2011; Gong et al., 2021). "In short, particles are introduced into the aerodynamic lens through a critical orifice at a specific flow rate" has been revised to "In short, particles are introduced into the aerodynamic lens through a critical orifice at a flow rate of 75 mL/min (Gong et al., 2021; Li et al., 2011).” in the lines 177-179.

5. Line 206 “marker”

Response: “maker” has been revised to “marker” in the line 222.

6. Line 252: Explain for readers why vehicle exhaust is expected to drive TMA particle formation

Response: The molecular characterization of PM samples from gasoline cars found TMA as one of the directly emitted organics from vehicle exhaust (Zhang et al., 2017). Besides, it is demonstrated that vehicle emission was one of the important contributions of particulate TMA by positive matrix factorization analysis, which reached 23% (Li et al., 2020). Thus, the high peaks of TMA found in the traffic hours were usually interpreted as substantial contribution from vehicle exhaust according to recent studies (Chen et al., 2019; Cheng et al., 2018).

“These patterns exhibited significant increases in the morning, possibly associated with direct emissions from vehicle exhaust (Chen et al., 2019; Cheng et al., 2018).” has been revised to “According to molecular characterization of particles from vehicle exhaust, TMA was detected as one of the directly emitted organics from vehicle exhaust (Zhang et al., 2017; Li et al., 2020), which was in accordance with the field studies conducted during traffic hours (Cheng et al., 2018; Chen et al., 2019). Thus, the significant increase of TMA-containing particles in the morning was possibly associated with direct emissions from vehicle exhaust.” in the lines 284-290.

7. Figure 10: It is difficult to distinguish the red and orange lines in this figure

Response: Revision made. The colors of lines have been revised.

The old Figure 10:

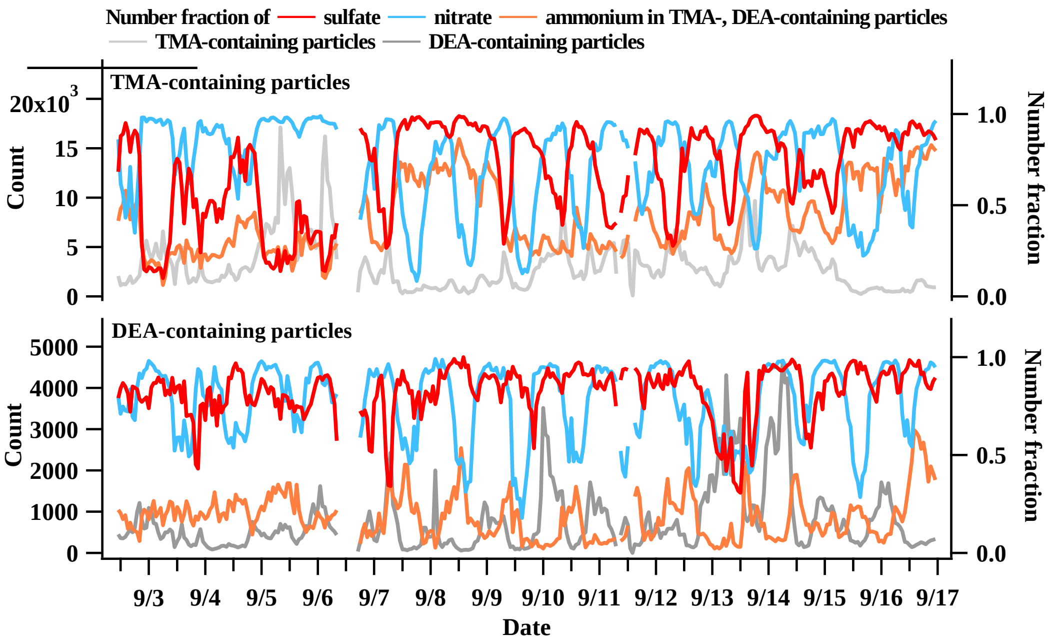


Figure 10. Temporal trends of TMA- and DEA-containing particle counts, and number fractions of nitrate, sulfate, and ammonium in TMA- and DEA-containing particles.

The new Figure 10:

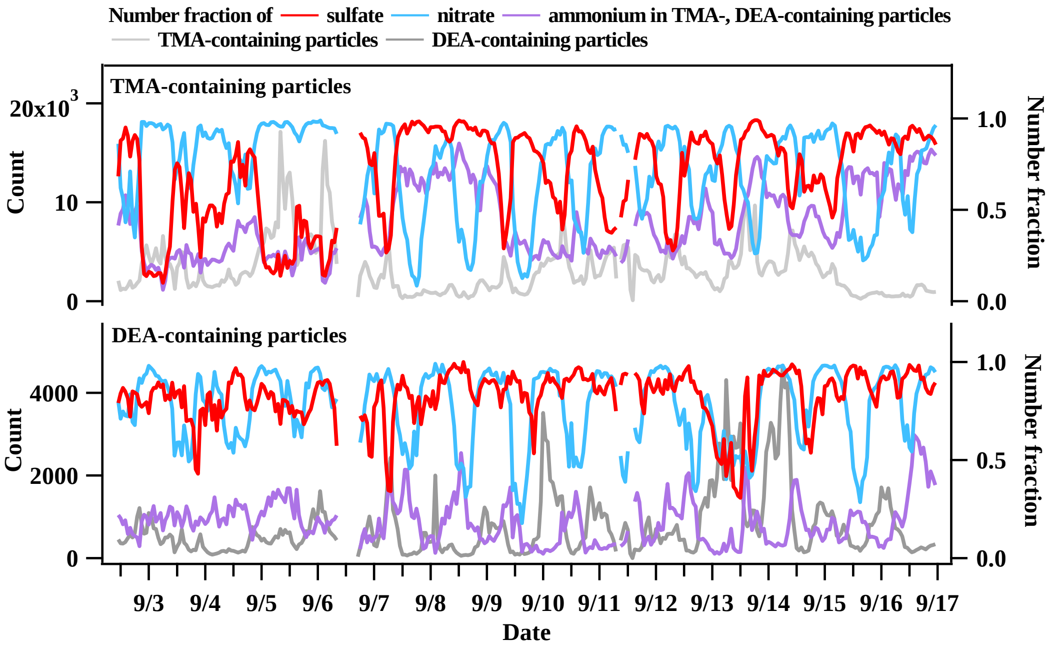


Figure 10. Temporal trends of TMA- and DEA-containing particle counts, and number fractions of nitrate, sulfate, and ammonium in TMA- and DEA-containing particles.

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