

1 **Diverse mixing states of amine-containing single particles in Nanjing,**
2 **China**

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31 **Abstract:** The mixing states of particulate amines with different chemical
32 components are of great significance in studying the formation and evolution
33 processes of amine-containing particles. In this work, the mixing states of single
34 particles containing trimethylamine (TMA) and diethylamine (DEA) are investigated
35 using a high-performance single-particle aerosol mass spectrometer located in
36 Nanjing, China, in September 2019. TMA- and DEA-containing particles accounted
37 for 22.8% and 5.5% of the total detected single particles, respectively. The particle
38 count and abundance of the TMA-containing particles in total particles notably
39 increased with enhancement of ambient relative humidity (RH), while the
40 DEA-containing particles showed no increase under a high RH. This result suggested
41 the important role of RH in the formation of particulate TMA. Significant
42 enrichments of secondary organic species, including $^{43}\text{C}_2\text{H}_3\text{O}^+$, $^{26}\text{CN}^-$, $^{42}\text{CNO}^-$,
43 $^{73}\text{C}_3\text{H}_5\text{O}_2^-$, and $^{89}\text{HC}_2\text{O}_4^-$, were found in DEA-containing particles, indicating that
44 DEA-containing particles were closely associated with the aging of secondary
45 organics. The differential mass spectra of the DEA-containing particles showed much
46 higher abundance of nitrate and organic nitrogen species during the nighttime than
47 during the daytime, which suggested that the nighttime production of particulate DEA
48 might be associated with reactions of gaseous DEA with HNO_3 and/or particulate
49 nitrate. In the daytime the decrease of DEA-containing particles was observed with
50 the enrichment of oxalate and glyoxylate, which suggested a substantial impact of
51 photochemistry on the aging process of DEA-containing particles. Furthermore,
52 greater than 80% of TMA- and DEA-containing particles internally mixed with nitrate,
53 while the abundance of sulfate was higher in the DEA-containing particles (79.3%)
54 than in the TMA-containing particles (55.3%). This suggested that particulate DEA
55 existed both as nitrate and sulfate aminium salts, while the particulate TMA primarily
56 presented as nitrate aminium salt. The different mixing states of the TMA- and
57 DEA-containing particles suggested their different formation processes and various
58 influencing factors, which are difficult to be investigated using bulk analysis. These
59 results provide insights into the discriminated fates of organics during the evolution

60 process in aerosols, which helps to illustrate the behavior of secondary organic
61 aerosols.

62 **Keywords:** Amines; Single particle; Mixing state; Nighttime chemistry; Aminium
63 salts.

64

65 **1 Introduction**

66 Amines are ubiquitous organic components in aerosols and have a wide range of
67 sources, including animal husbandry, industrial emissions, vehicle exhaust, biomass
68 burning, vegetation emissions, and ocean emissions (Ge et al., 2011b; Facchini et al.,
69 2008; Youn et al., 2015). Due to being highly water-soluble and having strong
70 alkaline properties, amines play an important role in new particle formation and
71 substantially contribute to the secondary organic aerosol (SOA) mass (Zhao et al.,
72 2011; Tao et al., 2016). The formation processes of particulate amines are commonly
73 associated with the gas-to-particle partitioning of gaseous amines and acid-base
74 reactions in the particles (Ge et al., 2011a; Pratt et al., 2009). Therefore, ambient
75 relative humidity (RH) (Rehbein et al., 2011; Zhang et al., 2012), [temperature](#) (Huang
76 et al., 2012), particle acidity (Pratt et al., 2009; Rehbein et al., 2011),
77 amine-ammonium exchange (Chan and Chan, 2013; Chu and Chan, 2017; Qiu et al.,
78 2011), and oxidants (Tang et al., 2013; Price et al., 2016) all influence the formation
79 of particulate amines.

80 Many field observations have been used to investigate the influence of RH on the
81 formation of amines. A high RH is beneficial for the formation of amines in most
82 cases. Zhang et al. (2012) observed a sharp increase in trimethylamine (TMA) during
83 fog events with high RH. Zhou et al. (2019) found that the concentrations of low
84 molecular weight (LMW) amines increased significantly under high RH conditions (>
85 90%). According to the seasonal distributions of amines during the summer and
86 winter, low [temperature](#) was found to be favorable for the partitioning of gaseous
87 amines into particles. Huang et al. (2012) found that the number fraction (N_f) of

88 amine-containing particles during winter was four times higher than that during
89 summer.

90 Gaseous amines can react with sulfuric acid, nitric acid, and organic acids to
91 form aminium salts, which underscores the important roles of sulfate and nitrate
92 information of particulate amines (Berndt et al., 2010; Murphy et al., 2007). Berndt et
93 al. (2010) and Wang et al. (2010) found that the formation of aminium salts via a
94 neutralization reaction can affect the growth of particles and the generation of SOAs.
95 Although the concentrations of amines are generally lower than ammonia, the
96 amine-ammonium exchange still contributes to particulate amine formation due to the
97 stronger alkalinity of amines compared to ammonium (Ge et al., 2011b; Sorooshian et
98 al., 2008). Chan et al. (2013) found that the exchange reactions between ammonia and
99 amines showed different reaction rates and product ratios with changes in the aerosol
100 phase state. Qiu et al. (2011) also found that amines can exchange with ammonium to
101 release ammonia. The particulate amines produced from the above pathways and
102 reactions constitute a substantial proportion of the SOAs that impact the physical and
103 chemical properties of fine particles. In addition to the direct contribution of the SOA
104 mass, the oxidation of amines by OH radicals, NO₃ radicals, and O₃ is also a
105 substantial source of SOA production (Price et al., 2016; Tong et al., 2020). Different
106 amines exhibit inconsistent behaviors under the same oxidation environments (NO₃
107 radicals, OH radicals, or ozone) (Price et al., 2014; Silva et al., 2008; Murphy et al.,
108 2007). In chamber studies, the oxidation of TMA and diethylamine (DEA) by OH vs.
109 NO₃ radicals resulted in different SOA yields, with differences greater than one order
110 of magnitude (Tang et al., 2013). Furthermore, even the same amine showed
111 completely different SOA yields due to OH and NO₃ radical oxidation. Also, the same
112 amine showed distinct trends under the different temperature changing trends. The
113 formation and oxidation processes of particulate amines are not well understood, and
114 these processes require additional comprehensive field observational studies in order
115 to be elucidated.

116 Most of the field observations did not distinguish between the different behaviors
117 of each type of amine molecule under the same ambient influencing factors. Actually,

118 due to the different mixing states of amines with other chemical components, the
119 amine molecules typically exhibited different behaviors in terms of being oxidized by
120 OH radicals, forming aminium salts, and altering the hygroscopicity of the particles
121 (Healy et al., 2015; Cheng et al., 2018; Chu et al., 2015; Price et al., 2016). Therefore,
122 the formation processes of the different amines are important to reveal the evolution
123 process of organic aerosols (OAs), and these processes are of great significance to
124 comprehensively understand the influencing factors of OA production.

125 The mixing states of organics in single particles are commonly investigated by
126 electron microscope and mass spectrometry (Yu et al., 2019; Li et al., 2016a; Cheng
127 et al., 2018). The technique of electron microscope coupled with energy dispersive
128 X-ray spectrometry (EDX) can provide the morphological, physical and some
129 chemical information of organics in single particles (Li et al., 2016b; Li et al., 2021).
130 However, electron microscope coupled with EDX cannot distinguish and identify the
131 specific organic molecules (Li et al., 2016b), which is incapable of analyzing amines
132 in single particles. The technique of single particle mass spectrometry can identify the
133 real-time presence and relative abundance of specific organic ions, which provides
134 substantial data to understand the sources, formation and evolution processes of
135 selective organic markers, providing a feasible approach to investigate the formation
136 processes of different particulate amines (Cheng et al., 2018; Chen et al., 2019;
137 Angelino et al., 2001). Chen et al. (2019) found that high RH was favorable for the
138 uptake of DEA, leading to a DEA-rich substance in the particle phase both during
139 winter and summer. However, Cheng et al. (2018) and Lian et al. (2020) found that
140 RH was not strongly correlated with the formation of amine-containing particles
141 during winter and summer. Pratt et al. (2009) reported that more acidic particles
142 during summer were favorable for the formation of aminium salts compared with the
143 particles present during autumn, indicating that the particle acidity affected the gas to
144 particle partitioning of amines. Rehbein et al. (2011) found more TMA entered the
145 particles as the amount of acidic particles increased. Based on these studies, although
146 the influences of ambient RH and particle acidity on the specific type amines formed

147 have been reported, yet comparative studies between different amines under the same
148 atmospheric environment using field observation are lacking.

149 In the present study, the mixing states of TMA- and DEA-containing single
150 particles are investigated during autumn using a high performance single particle
151 aerosol mass spectrometer (HP-SPAMS) located in Nanjing, China. Nanjing is a
152 typical megacity in the Yangtze River Delta (YRD), which is downwind of other
153 megacities including Shanghai, Changzhou, Suzhou, and Wuxi (Figure S1). In
154 addition, Nanjing suffers from heavy loadings of anthropogenic pollutants as well as
155 the complex impacts of biogenic and ship emissions (Xu et al., 2021; Zhao et al.,
156 2020; Ding et al., 2013a). The investigation of mixing states of amines in Nanjing
157 helps to explore the formation and evolution processes of OAs. Two types of
158 amine-containing particles exhibited different mixing states with secondarily
159 produced OA species. The influences of ambient RH, T, and particle acidity on the
160 mixing states of the two amine-containing particles are evaluated. In addition, the
161 potential heterogeneous formation of DEA during the nighttime is also discussed. The
162 results revealed the distinct chemical behaviors of TMA- and DEA-containing
163 particles and implied the potential role of DEA as an indicator of the aging process of
164 OA.

165 **2 Experimental methods**

166 **2.1 Sampling site**

167 Ambient single particles were sampled using the HP-SPAMS from September 2–
168 16, 2019, in Nanjing, China. The campaign was conducted at the Station for
169 Observing Regional Processes of the Earth System (SORPES) station in Nanjing
170 University Xianlin Campus (Ding et al., 2016; Ding et al., 2013a; Ding et al., 2013b;
171 Liu et al., 2021). The instrument was set up on top of a small hill (40 m above the
172 ground) on the Nanjing University campus. The ambient single particles were
173 introduced into the HP-SPAMS through a copper tube.

174 **2.2 Instrumentation of the HP-SPAMS**

175 In this work HP-SPAMS (Hexin Analytical Instrument Co., Ltd., China) was
176 used to detect single particles. The design and principles of SPAMS had previously
177 been described in detail (Li et al., 2011). In short, particles are introduced into the
178 aerodynamic lens through a critical orifice at a flow rate of 75 mL/min (Gong et al.,
179 2021; Li et al., 2011). Individual particles are focused and accelerated to specific
180 velocities, which are detected by two continuous diode Nd:YAG laser beams (532 nm)
181 and then ionized using a pulsed Nd:YAG laser (266 nm). Finally, the z-shaped bipolar
182 time of the flight mass spectrometer is used to detect the generated ions. The
183 improvements and modifications from the SPAMS to the HP-SPAMS are
184 comparatively presented below. The improvement in the SPAMS primarily includes
185 three parts: the application of a concentration device, a delay extraction technology,
186 and a multichannel acquisition technology (Chen et al., 2020; Li et al., 2018). First,
187 the addition of the concentrator increases the injection flow rate by six times, which
188 allows for improved separation of gas and particles. Second, the generated ions from
189 the laser ionization of single particles firstly enter the zone without electric field. Then,
190 the pulsed electric field will be added to accelerate the same kind of ions flying to the
191 detector. This pulsed electric field instead of the constant electric field will prevent
192 the initial deflection of same kind of ions, and the pulsed electric field also provides
193 sufficient energy in the appropriate time to improve the resolutions of positive and
194 negative ions. The mass resolutions of the positive (> 1000 at maximum half width)
195 and negative (> 2000 at maximum half width) ion spectra are then significantly
196 improved. Third, the multichannel acquisition technology is used to divide the signal
197 into two channels, detecting the high and low intensity signals simultaneously without
198 signal loss. This new acquisition technology enables a detectable dynamic signal from
199 5–20000 mV, which is approximately 40 times higher than that of SPAMS. Generally,
200 the particle size measured by HP-SPAMS ranges from 0.2 to 2.0 μm and was
201 calibrated by polystyrene latex particles before and after the sampling campaign (Li et
202 al., 2011; Li et al., 2018). The field observation result from scanning mobility particle
203 sizer (SMPS) is necessary to scale the measurements of HP-SPAMS to demonstrate
204 the authentic size distributions of specific type particles. Because the SMPS was not

205 available in this sampling campaign, thus, the size distributions of amine-containing
206 particles were not discussed here.

207 2.3 Data analysis

208 The size and chemical compositions of single particles obtained using the
209 HP-SPAMS were analyzed using the Computational Continuation Core (COCO)
210 toolkit in MATLAB software. According to previous studies that have utilized aerosol
211 time-of-flight mass spectrometer (ATOFMS) and SPAMS, the amine-containing
212 particles were identified by querying $^{59}(\text{CH}_3)_3\text{N}^+$, $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$, $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$,
213 $^{101}(\text{C}_2\text{H}_5)_3\text{N}^+$, $^{102}(\text{C}_3\text{H}_7)_2\text{NH}_2^+$, and $^{143}(\text{C}_3\text{H}_7)_3\text{N}^+$ (Healy et al., 2015; Angelino et al.,
214 2001; Cheng et al., 2018; Zhang et al., 2012). In this work, the marker ions of
215 $^{59}(\text{CH}_3)_3\text{N}^+$, $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$, and $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ were detected as the abundant
216 species, and their particle counts and ratios in the total detected single particles are
217 shown in Table 1. Single particles containing $^{86}(\text{C}_2\text{H}_5)_2\text{NCH}_2^+$ only accounted for 3.7%
218 of total particles, which was primarily due to occasional increases on September 5
219 (Figure S2), possibly due to the outburst of special emissions, such as combustion and
220 industry. Thus, in this work, particles containing $^{59}(\text{CH}_3)_3\text{N}^+$ and $^{74}(\text{C}_2\text{H}_5)_2\text{NH}_2^+$ were
221 selected to discuss the mixing states and formation processes of the particulate amines.
222 The marker ions of $^{62}\text{NO}_3^-$, $^{97}\text{HSO}_4^-$, and $^{18}\text{NH}_4^+$ were used to identify the nitrate,
223 sulfate, and ammonium in the amine-containing particles (Zhang et al., 2012). Based
224 on field and chamber studies using SPAMS and ATOFMS, the $^{43}\text{C}_2\text{H}_3\text{O}^+$ ion was
225 identified as the representative oxygen-containing organic (Healy et al., 2015; Pratt et
226 al., 2009). The particles containing $^{26}\text{CN}^-$ and $^{42}\text{CNO}^-$ were considered to be
227 representative of the organic nitrogen-containing particles (Pratt et al., 2011). In
228 addition, the $^{73}\text{C}_3\text{H}_5\text{O}_2^-$ and $^{89}\text{HC}_2\text{O}_4^-$ ions were designated as glyoxylate and oxalate
229 markers, respectively (Cheng et al., 2017; Zhang et al., 2020). It should be noted that
230 HP-SPAMS measurements cannot provide the quantitative mass concentrations of
231 amines and related chemical species due to the size-dependent transmission
232 efficiencies of particles through aerodynamic lens and composition dependent matrix
233 effect (Cheng et al., 2018; Cheng et al., 2021; Gong et al., 2021). Currently, the

234 observational results were used to illustrate the distinct impacts of same influencing
235 factors on the behaviors of amine-containing particles.

236 **3 Results and discussion**

237 **3.1 Characteristics of amine-containing particles**

238 In this work, the amine-containing particles accounted for 32.1% of total
239 detected single particles, which was higher than in previously reported results for the
240 Pearl River Delta (PRD) region (9.4%–11.1%) and Chongqing (8.3%–12.7%), China.
241 The TMA-containing particles showed a much higher abundance in the total particles
242 (22.8%) than the DEA-containing particles (5.5%) (Table 1), which could have been
243 due to their differential emissions and atmospheric processing (Cheng et al., 2018;
244 Chen et al., 2019; Liu et al., 2020; Ge et al., 2011b). Temporal variations in
245 meteorological parameters, PM_{2.5} concentration, and the count of amine-containing
246 particles are shown in Figure 1. Although the TMA- and DEA-containing particles
247 exhibited similar temporal trends at a lower particle count, their increasing peaks
248 appeared at different periods, suggesting that the reasons for their increase in the
249 particle count were different. Generally, peaks in the DEA-containing particles
250 frequently appeared during the nighttime, which was possibly due to their enhanced
251 source emissions and/or favorable nighttime production (Tang et al., 2013). The
252 ambient RH was relatively high during the entire sampling period ($74 \pm 14\%$),
253 especially from September 5–7, when the count of TMA-containing particles sharply
254 increased. However, no obvious enhancement in DEA-containing particles count was
255 found, which suggested other influencing factors on their formation process in
256 addition to the ambient RH.

257 Additionally, the periods of high concentration of the amine-containing particles
258 were not consistent with the increase in PM_{2.5} concentration, which could have been
259 due to the integrated effects of the emission sources and the secondary formation
260 processes. The gaseous TMA and DEA are mainly from agriculture, industry, vehicle
261 exhaust, biomass combustion, biological, and marine sources (Zhou et al., 2019;
262 Hemmilä et al., 2018; Sintermann et al., 2014; Ge et al., 2011b; Zhang et al., 2017).

263 Their concentrations vary greatly depending on the influence of source strength near
264 the sampling site. For example, the gaseous concentration of DEA was 14 and 2-5
265 times higher than TMA in polluted urban areas in China (Yao et al., 2016) and US
266 (You et al., 2014), respectively, while higher concentration of TMA than DEA was
267 observed in the forest site (You et al., 2014). Both the online and offline
268 measurements are difficult to quantitatively resolve their emission sources (You et al.,
269 2014; Yao et al., 2016; Kieloaho et al., 2013; Hellén et al., 2014). Here the backward
270 trajectories of the air masses from sampling site were discussed to explore their
271 possible different sources. The backward trajectories of the air masses (48 h, 500 m)
272 associated with the spatial distributions of the two amine-containing particles during
273 the entire sampling period (Figure 2). More than 70% of the air masses (Clusters 1
274 and 4) were from east of the sampling site, which were both connected with
275 anthropogenic emissions in the YRD and marine sources in the East China Sea.
276 TMA-containing particles were primarily from the air masses of Cluster 1 and Cluster
277 4, while the DEA-containing particles were associated with the air masses of Cluster 3
278 and Cluster 4, which underwent long-range transport. These results suggested
279 potential different emission sources and atmospheric formation processes of TMA-
280 and DEA-containing particles, which was further investigated by examining their
281 mixing states.

282 Diurnal variations of TMA- and DEA-containing particles are shown in Figure 3.
283 The particle count of TMA-containing particles and their abundance in the total
284 particles exhibited identical variation patterns. According to molecular
285 characterization of particles from vehicle exhaust, TMA was detected as one of the
286 directly emitted organics from vehicle exhaust (Zhang et al., 2017; Li et al., 2020),
287 which was in accordance with the field studies conducted during traffic hours (Cheng
288 et al., 2018; Chen et al., 2019). Thus, the significant increase of TMA-containing
289 particles in the morning was possibly associated with direct emissions from vehicle
290 exhaust. The DEA-containing particles showed a completely different diurnal pattern
291 compared with the TMA-containing particles. DEA-containing particles increased
292 during nighttime, but sharply decreased during the afternoon, when the

293 photochemistry was the most active. The nighttime increase **could have been** due to
294 the high ambient RH and/or enhanced heterogeneous reactions (Zhou et al., 2019;
295 Huang et al., 2012; Zhang et al., 2019). However, since the increase in the
296 DEA-containing particles was not prominent under high RH (Figure 1), enhanced
297 heterogeneous production of particulate DEA could be a more reasonable explanation.
298 The decrease in the DEA-containing particles during the afternoon could have been
299 associated with the photodegradation of DEA and/or repartitioning of particulate DEA
300 under high temperatures during the day (Ge et al., 2011a; Pitts et al., 1978; Murphy et
301 al., 2007). In order to investigate the impact of RH on the formation process of
302 amine-containing particles, **the particle counts of amine particles and the relative peak**
303 **areas (RPAs) of amines in the particles with an increase in the RH are presented in**
304 **Figure 4.** The particle count of TMA-containing particles and the RPA of the TMA
305 showed remarkable increasing trends with an enhancement in RH during the entire
306 sampling period. This result suggested a significant role of RH in the formation of
307 particulate TMA. This was consistent with a field study conducted in Guangzhou,
308 China, which also found an instant increase in TMA-containing particles after the
309 occurrence of fog events (Zhang et al., 2012). In contrast, the particle count of
310 DEA-containing particles only exhibited increased RH range between 70–80% and
311 decreased with the continuous increase in the RH. Additionally, the RPA of the DEA
312 showed little change with an increase in the RH, which suggested the minor influence
313 of a change in RH on the formation of particulate DEA. The different responses of
314 TMA and DEA with RH changes signified their different formation processes in the
315 particles.

316 **3.2 Different mixing states of amine-containing particles**

317 It is important to understand the chemical compositions of amine-containing
318 particles in order to understand their mixing states and track their formation processes.
319 Hence, the positive and negative mass spectra of the amine-containing particles are
320 shown in Figure 5. **Generally, TMA- and DEA-containing particles both contained**
321 **organic fragments** such as $^{27}\text{C}_2\text{H}_3^+$, $^{37}\text{C}_3\text{H}^+$, $^{43}\text{C}_2\text{H}_3\text{O}^+$, $^{51}\text{C}_4\text{H}_3^+$, and $^{61}\text{C}_5\text{H}^+$ in the
322 positive mass spectra. In addition, their negative mass spectra were both characterized

323 by nitrate, sulfate, and nitric acid ($^{125}\text{H}(\text{NO}_3)_2^-$). However, DEA-containing particles
324 contained many more organic fragments and a higher abundance of hydrocarbon
325 clusters than the TMA-containing particles. In the positive mass spectra, the
326 abundance of the hydrocarbon fragments with an m/z below 60 was 2–3 times higher
327 in DEA-containing particles than that in TMA-containing particles. In addition,
328 hydrocarbon fragments with an m/z above 60 were barely detectable in
329 TMA-containing particles, while abundant hydrocarbon fragments with an m/z
330 ranging from 60–150 were observed in DEA-containing particles. Furthermore, the
331 DEA-containing particles also contained abundant secondary organic marker ions,
332 including organic nitrogen ($^{26}\text{CN}^-$ and $^{42}\text{CNO}^-$), acetate ($^{59}\text{C}_2\text{H}_3\text{O}_2^-$), glyoxylate
333 ($^{73}\text{C}_3\text{H}_5\text{O}_2^-$), and oxalate ($^{89}\text{HC}_2\text{O}_4^-$) in the negative mass spectra, and these were not
334 found in the TMA-containing particles. This was in accordance with the linear
335 regressions between these secondary organic ions containing particles with two
336 amine-containing particles (Table 2), which showed no correlations in the
337 TMA-containing particles ($r^2 < 0.1$), but good correlations in the DEA-containing
338 particles ($r^2 > 0.57$). The differential mass spectral features in the distributions of
339 organics in the two amine-containing particles (Figure 6) suggested that more
340 secondary organics accumulated in DEA-containing particles than in TMA-containing
341 particles. This result also implied that multiple factors influenced the mixing state of
342 DEA-containing particles in addition to ambient RH.

343 In order to further characterize the mixing states of DEA-containing particles
344 with secondary organic ions, temporal variations and diurnal patterns of secondary
345 organic ions in the DEA-containing particles are presented in Figure 7. As the
346 oxidation products of various organics, the abundances of glyoxylate and oxalate
347 commonly increased between 12:00 and 18:00 (Figure 7), when the photochemistry
348 was most active during the daytime. This result suggested the deep photochemical
349 aging state of DEA-containing particles. This might explain the decrease in the
350 particle counts of DEA-containing particles (Figure 3), which was partially associated
351 with the photo-degradation of particulate DEA. Pitts et al. (1978) reported that under
352 sunlight particulate DEA decomposed to acetamide, while DEA in the gas phase was

353 oxidized to acetaldehyde, PAN, amide, and imine. Gaseous DEA can be oxidized into
354 carbonyl compounds and other amines by ozone and OH radicals that primarily
355 include acetaldehyde and N-ethylethanamine (Tuazon et al., 2011; Tong et al., 2020).
356 The organic nitrogen markers of $^{26}\text{CN}^-$ and $^{42}\text{CNO}^-$ showed different temporal trends
357 with glyoxylate and oxalate. Although the abundances of organic nitrogen markers
358 also increased after 12:00 like oxalate, the markers still maintained high abundances
359 during the nighttime, when glyoxylate and oxalate sharply decreased. This result
360 suggested that the aging process of organics during the nighttime was slower than that
361 during the afternoon in the DEA-containing particles. Thus, the increase of
362 DEA-containing particles (Figure 3) could have been due to the enhanced production
363 of particulate DEA during the nighttime. In addition, the differential mass spectra of
364 DEA-containing particles (Figure 8) between the nighttime (22:00–02:00) and
365 daytime (14:00–18:00) showed a significant enrichment of nitrate during the
366 nighttime. This result suggested that nighttime production of particulate DEA was
367 associated with gaseous HNO_3 and/or particulate nitrate (Price et al., 2016).

368 Temporal variations in NO_x and the N_f of the DEA-containing particles in the
369 total detected particles are presented in Figure 9. They showed similar increasing
370 patterns during the nighttime, and a high abundance of nitrate in the DEA-containing
371 particles was also observed. This result suggested the important role of nitrate in the
372 formation of particulate DEA. The particulate DEA during the nighttime could have
373 been produced from the reaction of gaseous DEA with HNO_3 during the gas phase
374 (R1) followed by the gas to particle partitioning (R2) and/or the direct heterogeneous
375 formation pathway (R3) (Price et al., 2016; Nielsen et al., 2012). The high ambient
376 concentration of NO_x is favorable for the production of NO_3 radicals and the
377 heterogeneous production of nitrate, which might explain the distinct enhancement of
378 the DEA-containing particles. However, the same formation pathways were also
379 applied to TMA, yet there was no significant increase in the N_f of the
380 TMA-containing particles in the total particles (Figure 3). This could have been due to
381 the different particle/gas dissociation constant (K_p) for DEA HNO_3 and TMA HNO_3 ,
382 which was several orders of magnitude lower than that for DEA HNO_3 ($7.01\text{E-}09$)

383 compared with TMA HNO₃ (1.65E-06) at 25 °C (Price et al., 2016; Ge et al., 2011a).
 384 During the entire sampling period, the ambient temperature during the nighttime was
 385 approximately 24 °C. Thus, the produced DEA HNO₃ tended to stay in the particles,
 386 while a portion of the TMA HNO₃ repartitioned back into the gas phase. This resulted
 387 in an insignificant increase in the TMA-containing particles. Further studies should
 388 consider the influence of the different volatilities of DEA HNO₃ and TMA HNO₃ on
 389 the formation of particulate amines in chamber experiments due to the lack of
 390 quantitative results in this study.



394 **3.3 Formation of aminium salts**

395 To study the acid-base reactions of TMA and DEA with sulfate and nitrate, the
 396 N_fs of nitrate-, sulfate-, and ammonium-containing particles in total detected particles
 397 and amine-containing particles are shown in Table 3. More than 80% of TMA- and
 398 DEA-containing particles internally mixed with nitrate, which was higher than the N_f
 399 of nitrate in the total particles (72%). Interestingly, the N_f of sulfate in
 400 DEA-containing particles (79.3%) was much higher than that in TMA-containing
 401 particles (55.3%) and in the total particles (60.1%). This was similar to a study
 402 performed by Lian et al. (2020) that found a stronger correlation between
 403 ⁸⁶(C₂H₅)₂NCH₂⁺ with sulfate than that between TMA and sulfate. In addition, in this
 404 work, robust linear correlations (r² > 0.9) between nitrate-containing particles and
 405 amine particles were both observed in TMA- and DEA-containing particles (Table 2).
 406 However, a weak linear correlation (r² = 0.32) was found between the
 407 sulfate-containing particles and the TMA-containing particles, while a better linear
 408 correlation (r² = 0.86) was observed in the DEA-containing particles. According to
 409 reported studies, the vapor pressure of diethylaminium sulfate (DEAS) (0.2*10⁻¹²–
 410 12.8*10⁻¹² Pa) was three orders of magnitude lower than that of trimethylaminium
 411 sulfate (TMAS) (0.6*10⁻⁹–1.8*10⁻⁹ Pa) at 298 k. In addition, the enthalpy of
 412 evaporation was higher than that of TMAS (DEAS: 168 ± 5 kJ mol⁻¹; TMAS: 114 ± 2

413 kJ mol^{-1}) (Lavi et al., 2013). Therefore, the thermo-stability of DEAS was stronger
414 than TMA (Qiu and Zhang, 2012), which led to the higher N_f of sulfate in the
415 DEA-containing particles than in the TMA-containing particles.

416 The N_f of ammonium in DEA-containing particles (13.2%) was lower than in
417 TMA-containing particles (35%) and total particles (19.4%). The low abundance of
418 NH_4^+ in DMA-containing particles had been observed in our previous studies in the
419 PRD region (Cheng et al., 2018), which was partially attributed to the
420 ammonium-amine exchange reactions in the particles. The related laboratory
421 experiments primarily involved the preferential uptake of LMW amines in the H_2SO_4
422 particles (Sauerwein and Chan, 2017; Chan and Chan, 2013; Chu and Chan, 2017). In
423 this work, the distinct low N_f of NH_4^+ in the DEA particles suggested the possible
424 displacement of NH_4^+ by DEA. Moreover, the higher abundance of sulfate in DEA
425 particles than in TMA particles was more favorable for the occurrence of
426 ammonium-amine exchange reactions in DEA particles. This disparity could imply
427 differential roles of DEA and TMA in the new particle formation process (Wang et al.,
428 2010; Yin et al., 2011; Zhao et al., 2011).

429 The temporal trends of the N_f s of nitrate-, sulfate-, and ammonium-containing
430 particles in TMA and DEA particles are shown in Figure 10. The N_f of
431 nitrate-containing amine particles exhibited similar variation patterns with each type
432 of amine particle, while the N_f of sulfate-containing amine particles only showed a
433 similar variation pattern with DEA-containing particles. Although ammonium nitrate
434 and sulfate salts were both produced in TMA- and DEA-containing particles, the
435 different temporal trends of sulfate and nitrate in the two amine particles suggested
436 that both sulfate and nitrate DEA salts existed in the DEA-containing particles, while
437 nitrate TMA salt dominated in TMA-containing particles (Cheng et al., 2018; Pratt et
438 al., 2009). This difference in the form of ammonium salts could signify the potential
439 different influences in the hygroscopic property of secondarily processed particles
440 internally mixing with different amines (Rovelli et al., 2017; Clegg et al., 2013; Lavi
441 et al., 2013). The relative acidity ratio (Ra), defined as the ratio of the sum of the
442 sulfate and nitrate peak areas to the ammonium peak area, has been proposed in field

443 studies that use single particle mass spectrometry to roughly estimate particle acidity
444 (Huang et al., 2013; Cheng et al., 2018). Although the feasibility of Ra has been
445 supported by the robust linear correlation with authentic particle acidity calculated
446 from mass concentrations of inorganic ions (Huang et al., 2013), this
447 semi-quantitative approach should be carefully treated when it comes to the
448 discussion about the actual acidity of atmospheric particles. In this work, temporal
449 variations in Ra in TMA-containing particles (Ra_1) and DEA-containing particles (Ra_2)
450 are shown in Figure 11. The average Ra_1 was 6.3 ± 1.8 in TMA-containing particles,
451 and Ra_2 was 36.1 ± 21.8 in DEA-containing particles. This result could suggest a
452 more acidic nature of DEA particles than TMA particles. However, after including the
453 peak area of amines (TMA/DEA) in the calculation of Ra, the new Ra' reduced to 2.1
454 ± 0.5 in the TMA-containing particles and 6.5 ± 1.2 in the DEA-containing particles.
455 The gap of Ra between the two amine particles significantly decreased after including
456 amines in the calculation. The larger reduction ratio of Ra' in DEA-containing
457 particles than in TMA-containing particles suggested the effective buffering effect of
458 amines under the absence of ammonium in the particles.

459 **3.4 Implications of the diverse mixing states of amines particles**

460 The mixing states and formation processes of the two amine-containing particles
461 were investigated under the same atmospheric environment, and their different
462 atmospheric behaviors against the same influencing factors suggested their
463 differential contributions to SOA mass. The prominent impact of ambient RH on the
464 formation of particulate TMA suggested a significant role for gas-particle partitioning
465 process to the high water-soluble species in the SOA. However, the slight influence of
466 RH on the formation of the particulate DEA implied the inconsistent role of high RH
467 on the same group of water-soluble organic molecules. In addition, the distinct
468 distribution patterns of secondary organic species in two amine-containing particles
469 also signified that the mixing states of the OA are important to explore their formation
470 processes. Furthermore, the heterogeneous processing of the DEA-containing
471 particles during the nighttime and the photochemical degradation of the DEA during
472 the daytime both generated more fractions of nitrogen- and oxygen-containing species

473 in the particles than in the TMA-containing particles. This result suggested different
474 roles of particulate TMA and DEA in the evolution of hygroscopicity and aging state
475 of the SOA. In summary, understanding mixing states and formation processes of
476 different amines in single particles is of great significance to reveal the unique
477 response of each type of amine to the same atmospheric environment. Single-particle
478 analysis provided insights into the mixing states of specific organic species to further
479 understand the formation process of the SOA.

480 **4 Summary and conclusions**

481 TMA- and DEA-containing single particles were collected and analyzed on
482 September 2019 using HP-SPAMS in Nanjing, China, and accounted for 22.8% and
483 5.5% of total detected particles, respectively. The mixing states and formation
484 processes of TMA- and DEA-containing particles were studied. With increased RH,
485 the counts of particulate TMA and the RPA of the TMA displayed an obvious upward
486 trend, while the particle count of the particulate DEA slightly increased when the RH
487 was 70–80%. In addition, the RPA of the DEA showed no difference in reaction to
488 RH change during the entire sampling period. This suggested a differential role for
489 ambient RH during the formation processes of particulate TMA and DEA. The
490 possible formation processes were further evaluated by analyzing the mixing states of
491 the amine-containing particles. The mass spectra of the amine-containing particles
492 showed that the secondary organic species were enriched in the DEA-containing
493 particles. The differential distributions of the secondary ions effectively explained the
494 sharp increase in DEA-containing particles during the nighttime, which could have
495 been due to the heterogeneous reactions of gaseous DEA with HNO₃ and/or nitrate
496 particles. The prominent decrease in the DEA-containing particles during the
497 afternoon was attributed to photo-degradation of particulate DEA. Due to the
498 differences in the thermodynamic properties, the N_f of sulfate in the particulate DEA
499 was higher than that in the particulate TMA. The amine-ammonium exchange
500 reaction resulted in particulate DEA containing less NH₄⁺. In addition, the particulate
501 DEA was abundant in sulfate, which was more favorable for the exchange of amine

502 and ammonium. The higher relative acidity ratio in DEA-containing particles relative
503 to TMA-containing particles could suggest that DEA particles are more acidic. After
504 including the peak area of amines (TMA/DEA) in the calculation, the larger reduction
505 ratio of the Ra' in DEA-containing particles than in TMA-containing particles
506 suggested the effective buffering effect of amines under the absence of ammonium in
507 the particles. These results revealed the distinct mixing states and chemical behaviors
508 of TMA- and DEA-containing single particles and could imply a potential role for
509 DEA as an indicator of the OA aging process.

510

511 **Data availability**

512 The observational data, including HP-SPAMS and the meteorological parameters,
513 obtained in this study are available from the corresponding authors upon request
514 (chengcl@jnu.edu.cn).

515

516 **Author contribution**

517 **Qi En Zhong, Chunlei Cheng, Zaihua Wang:** methodology, writing original
518 draft. **Dafeng Ge, Lei Wang, Yuanyuan Li, Wei Nie, Xuguang Chi, Aijun Ding:**
519 methodology, sampling. **Lei Li, Mei Li, Suxia Yang, Duohong Chen, Zhen Zhou:**
520 providing discussions and helping to revise original draft.

521

522 **Competing interests**

523 I declare that I or my co-authors have competing interests as follows: Aijun Ding
524 is editor of ACP.

525

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535

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809 **Tables and figures**

810

811 **Table list:**

812 **Table 1.** Summary of the major species of detected amine-containing particles and
813 fragments in September in Nanjing, China.

814 **Table 2.** The linear correlations (r^2) between secondary ion-containing amine
815 particles within TMA- and DEA-containing particles.

816 **Table 3.** Number fractions sulfate, nitrate, and ammonium in TMA-containing
817 particles, DEA-containing particles, and total particles.

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819 **Figure caption:**

820 **Figure 1.** Temporal variations in relative humidity (RH), temperature (T), O₃
821 concentration, PM_{2.5} concentration, wind speed, wind direction, and TMA- and
822 DEA-containing particles during the entire sampling period.

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

826 **Figure 3.** The diurnal variations in particle counts and number fractions of the two
827 amine-containing particles in total particles during the entire sampling period.

828 **Figure 4.** Particle counts of amine-containing particles and relative peak area (RPA)
829 of the two amines in single particles, with an increase in ambient RH. (a, c)
830 TMA-containing particles; (b, d) DEA-containing particles.

831 **Figure 5.** Mass spectra of TMA- and DEA-containing particles during the entire
832 sampling period.

833 **Figure 6.** Differential mass spectra between DEA- and TMA-containing particles.

834 **Figure 7. (a)** Temporal trends of the relative peak areas (RPAs) of $^{73}\text{C}_3\text{H}_5\text{O}_2^-$,
835 $^{89}\text{HC}_2\text{O}_4^-$, $^{26}\text{CN}^-$, and $^{42}\text{CNO}^-$ in DEA-containing particles. **(b)** Diurnal variations in
836 the relative RPAs of $^{73}\text{C}_3\text{H}_5\text{O}_2^-$, $^{89}\text{HC}_2\text{O}_4^-$, $^{26}\text{CN}^-$, and $^{42}\text{CNO}^-$ in DEA-containing
837 particles.

838 **Figure 8.** Differential mass spectra of DEA-containing particles between 22:00–02:00
839 and 14:00–18:00.

840 **Figure 9.** Temporal trends of RPA nitrate in DEA-containing particles, number
841 fraction of DEA-containing particles in total particles, and NO_x concentration.

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

845 **Figure 11.** Temporal trends of the relative acidity ratios (R_a , R_a') in TMA- and
846 DEA-containing particles.

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877 **Tables**

878 **Table 1.** Summary of the major species of detected amine-containing particles and
 879 fragments in September in Nanjing, China.

| Alkylamine assignment | Count | Percentage (%) |
|--|-----------|----------------|
| All detected particles | 4 693 931 | |
| ⁵⁹ (CH ₃) ₃ N ⁺ (TMA)-containing particles | 1072143 | 22.8 |
| ⁷⁴ (C ₂ H ₅) ₂ NH ₂ ⁺ (DEA) -containing particles | 259913 | 5.5 |
| ⁸⁶ (C ₂ H ₅) ₂ NCH ₂ ⁺ (TEA)-containing particles | 172621 | 3.7 |

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883 **Table 2.** The linear correlations (r^2) between secondary ion-containing amine
 884 particles within TMA- and DEA-containing particles.

| | TMA particles | DEA particles |
|---|---------------|---------------|
| ²⁶ CN ⁻ | 0.13 | 0.70 |
| ⁴² CNO ⁻ | 0.09 | 0.70 |
| ⁷³ C ₃ H ₅ O ₂ ⁻ | 0.01 | 0.66 |
| ⁸⁹ HC ₂ O ₄ ⁻ | 0.09 | 0.57 |
| ⁴³ C ₂ H ₃ O ⁺ | 0.05 | 0.90 |
| ⁶² NO ₃ ⁻ | 0.93 | 0.90 |
| ⁹⁷ HSO ₄ ⁻ | 0.32 | 0.86 |
| ¹⁸ NH ₄ ⁺ | 0.50 | 0.28 |

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889 **Table 3.** Number fractions sulfate, nitrate, and ammonium in TMA-containing
 890 particles, DEA-containing particles, and total particles.

| | TMA particles | DEA particles | Total particles |
|----------|---------------|---------------|-----------------|
| Sulfate | 55.3 | 79.3 | 60.1 |
| Nitrate | 81.6 | 81.8 | 72.0 |
| Ammonium | 35.0 | 13.2 | 19.4 |

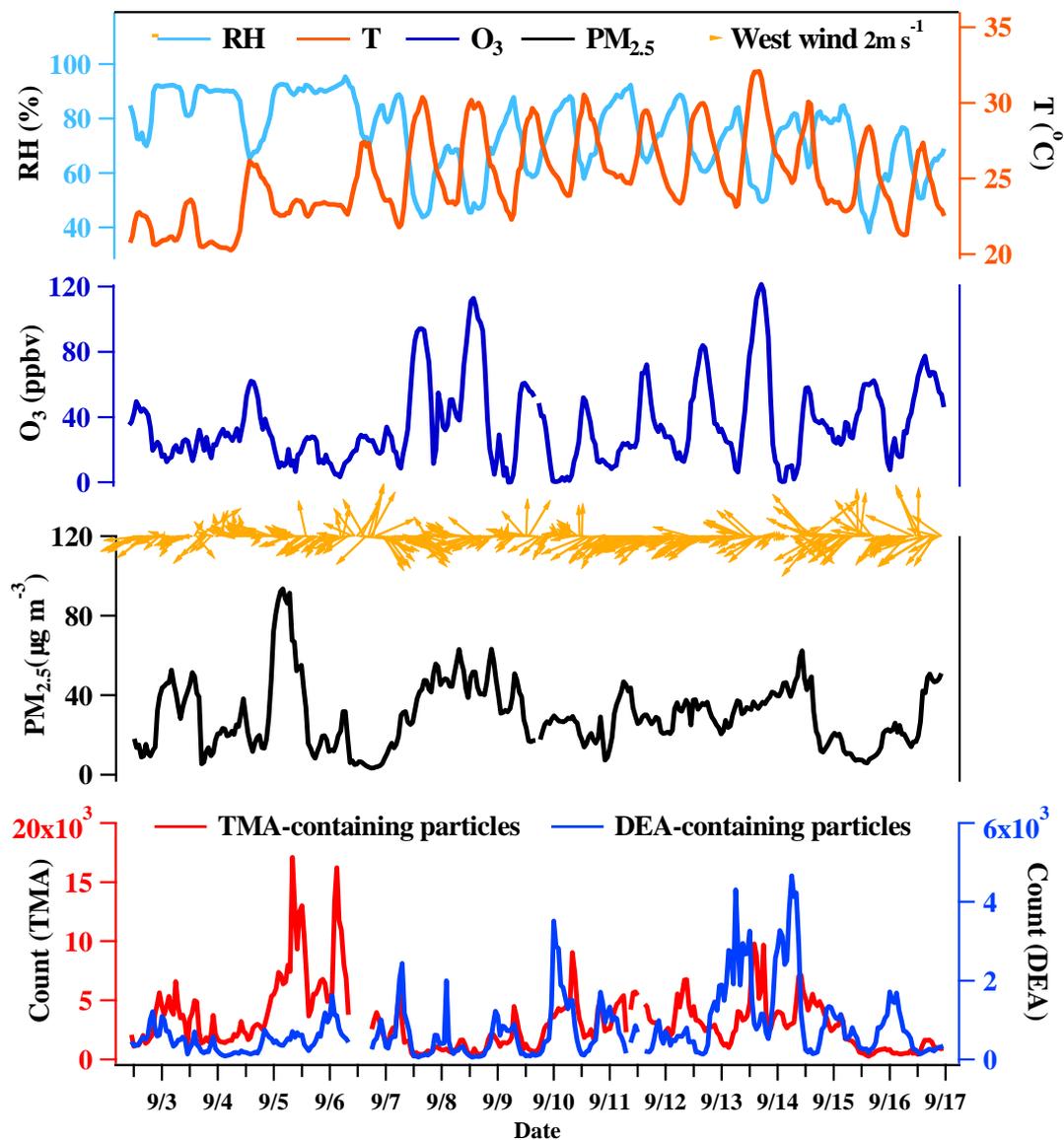
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895 **Figures**



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897 **Figure 1.** Temporal variations in relative humidity (RH), temperature (T), O₃
898 concentration, PM_{2.5} concentration, wind speed, wind direction, and TMA- and
899 DEA-containing particles during the entire sampling period.

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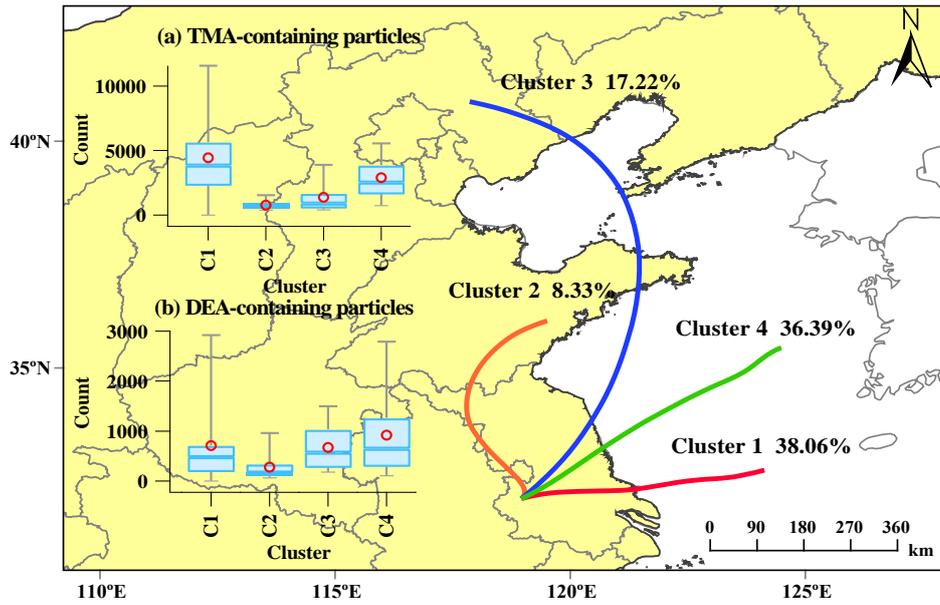
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907 **Figure 2.** Backward trajectories (48 h) of air masses at 500 m above the ground

908 during the sampling period: (a) TMA-containing particles counts; (b) DEA-containing

909 particle counts. C1 to C4 represent cluster 1 to cluster 4.

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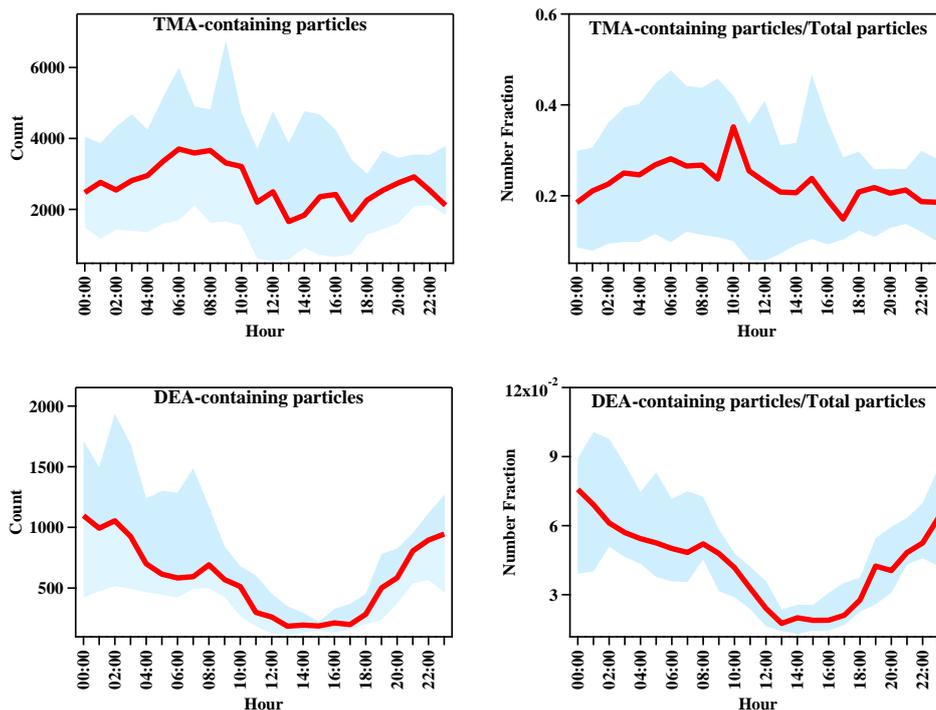
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928 **Figure 3.** The diurnal variations in particle counts and number fractions of the two
929 amine-containing particles in total particles during the entire sampling period. The
930 shaded areas represent the 75th and 25th percentiles.

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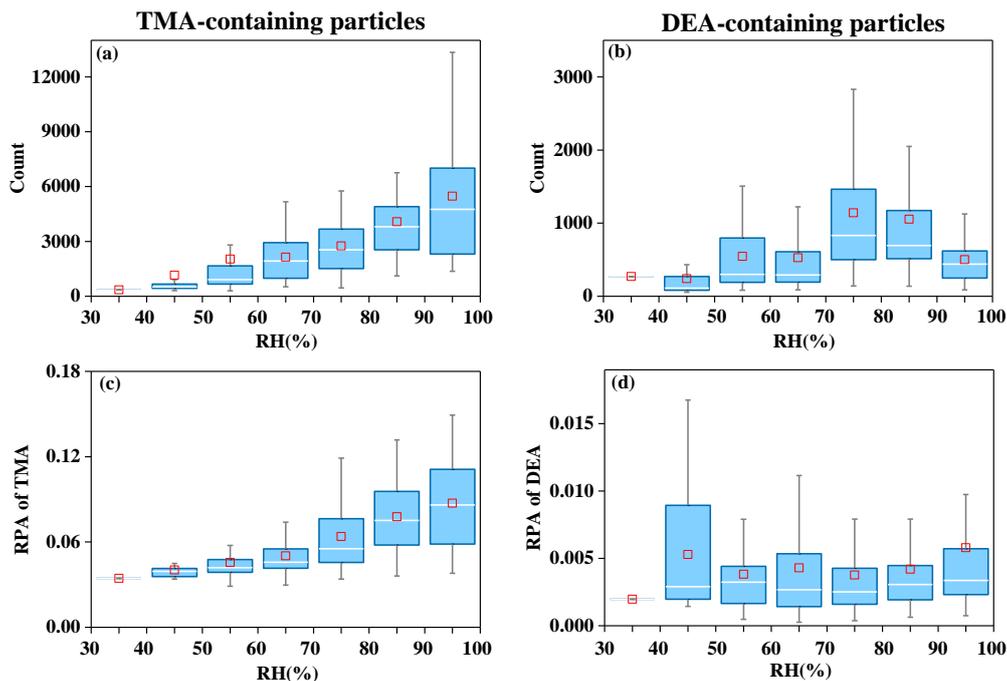
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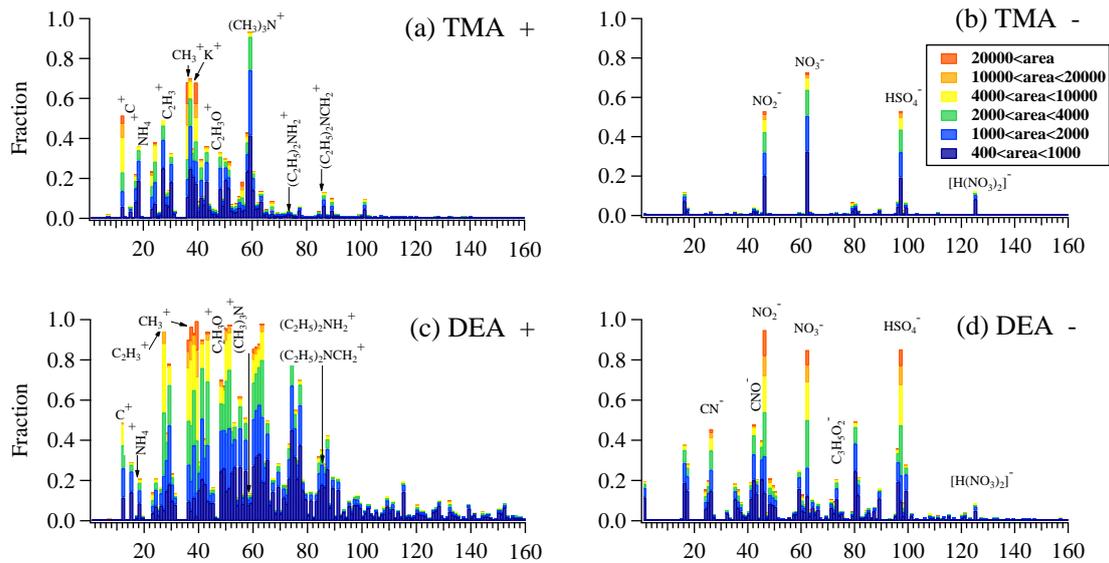
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 947 **Figure 4.** Particle counts of amine-containing particles and relative peak area (RPA)
 948 of the two amines in single particles, with an increase in ambient RH. (a, c)
 949 TMA-containing particles; (b, d) DEA-containing particles. Squares represent the
 950 average values. The line inside the box indicates the median. Upper and lower
 951 boundaries of the box represent the 75th and the 25th percentiles; the whiskers above
 952 and below each box represent the 95th and 5th percentiles.

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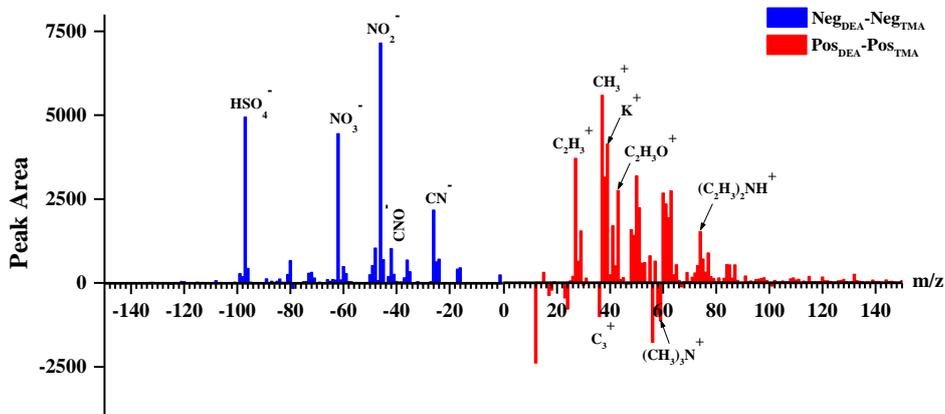
966 **Figure 5.** Mass spectra of TMA- and DEA-containing particles during the entire
 967 sampling period.

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973 **Figure 6.** Differential mass spectra between DEA- and TMA-containing particles.

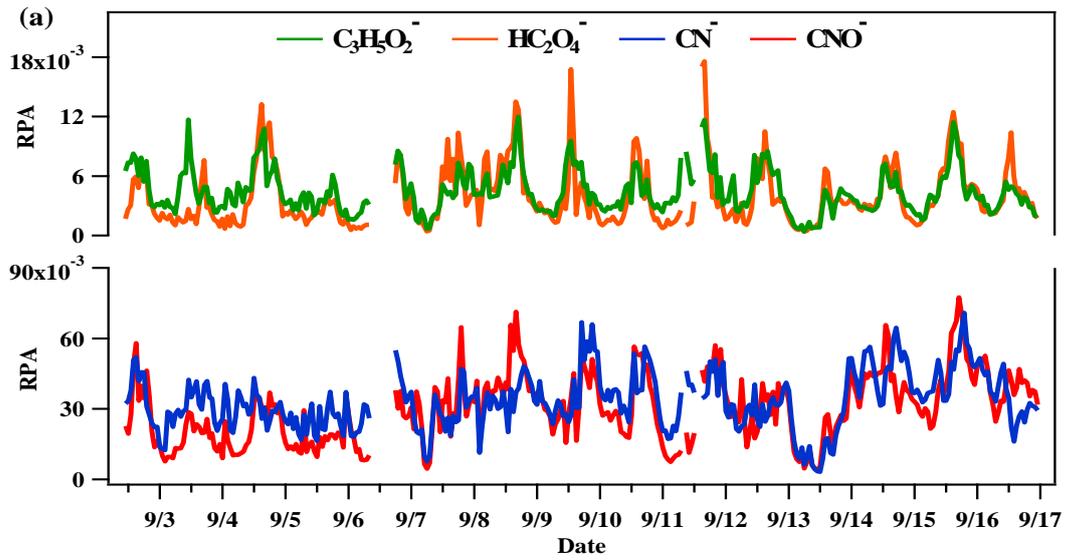
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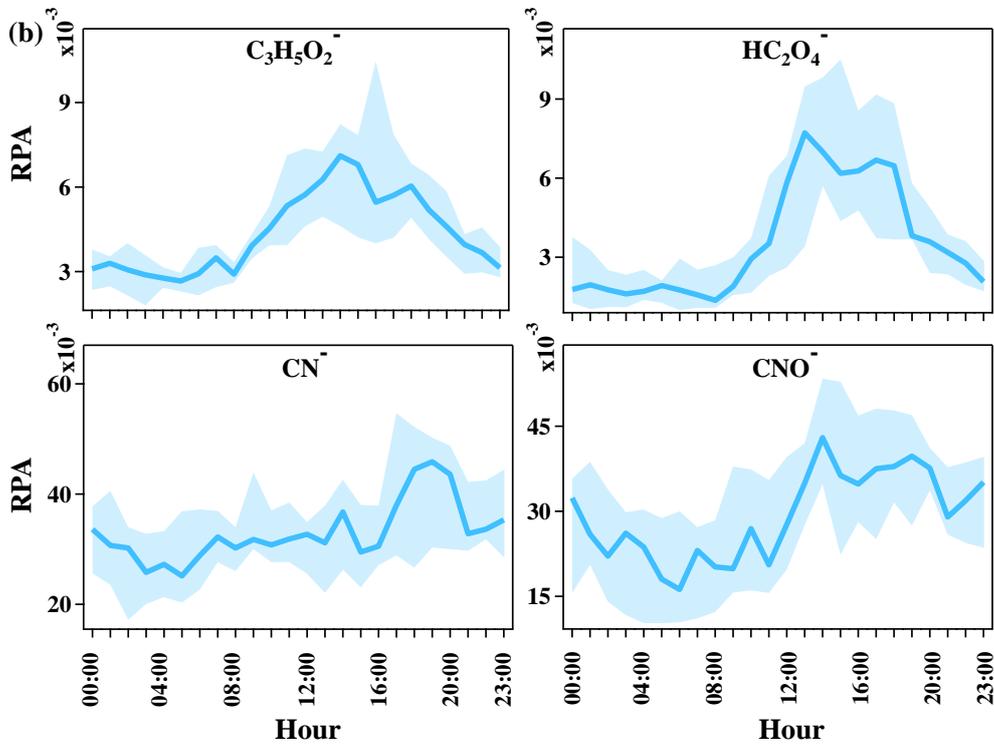
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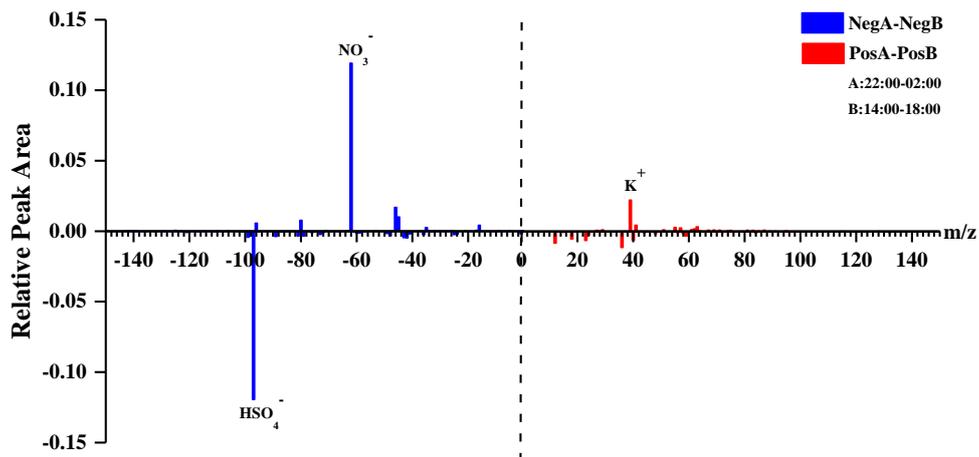
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981 **Figure 7.** (a) Temporal trends of the relative peak areas (RPAs) of $^{73}\text{C}_3\text{H}_5\text{O}_2^-$,
 982 $^{89}\text{HC}_2\text{O}_4^-$, $^{26}\text{CN}^-$, and $^{42}\text{CNO}^-$ in DEA-containing particles. (b) Diurnal variations in
 983 the relative RPAs of $^{73}\text{C}_3\text{H}_5\text{O}_2^-$, $^{89}\text{HC}_2\text{O}_4^-$, $^{26}\text{CN}^-$, and $^{42}\text{CNO}^-$ in DEA-containing
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989 **Figure 8.** Differential mass spectra of DEA-containing particles between 22:00–02:00
 990 and 14:00–18:00.

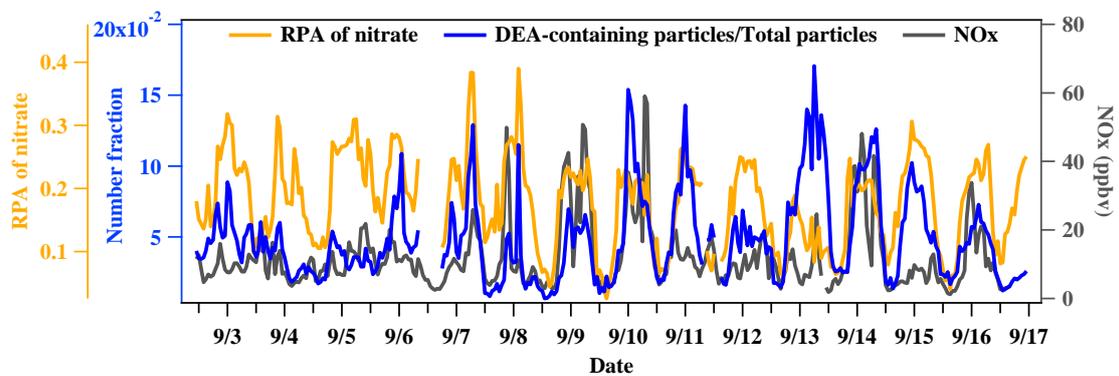
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997 **Figure 9.** Temporal trends of RPA nitrate in DEA-containing particles, number
 998 fraction of DEA-containing particles in total particles, and NOx concentration.

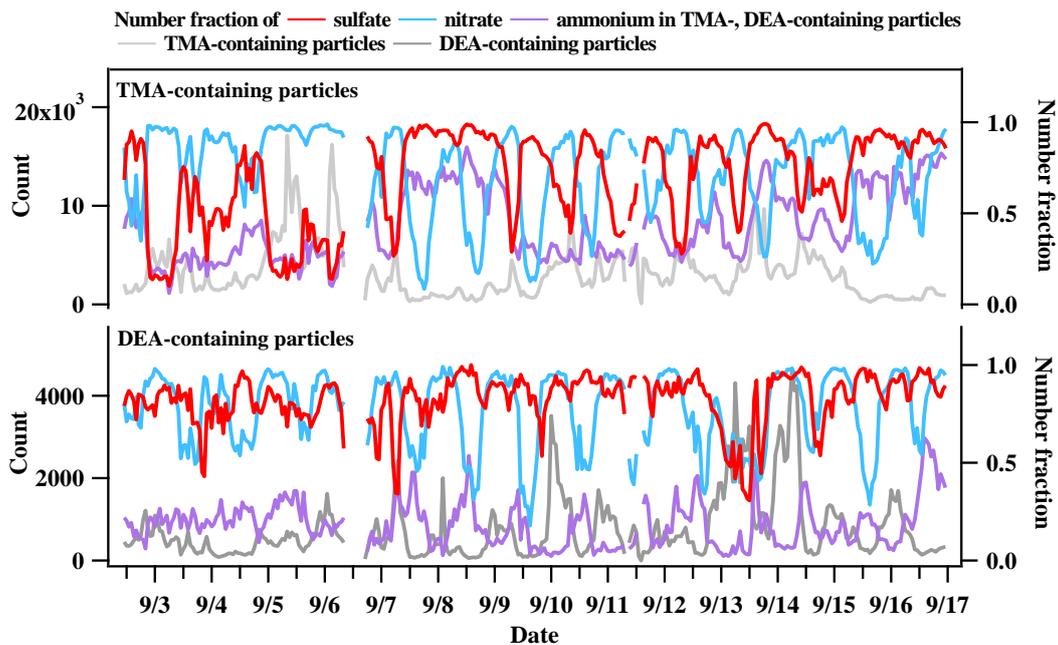
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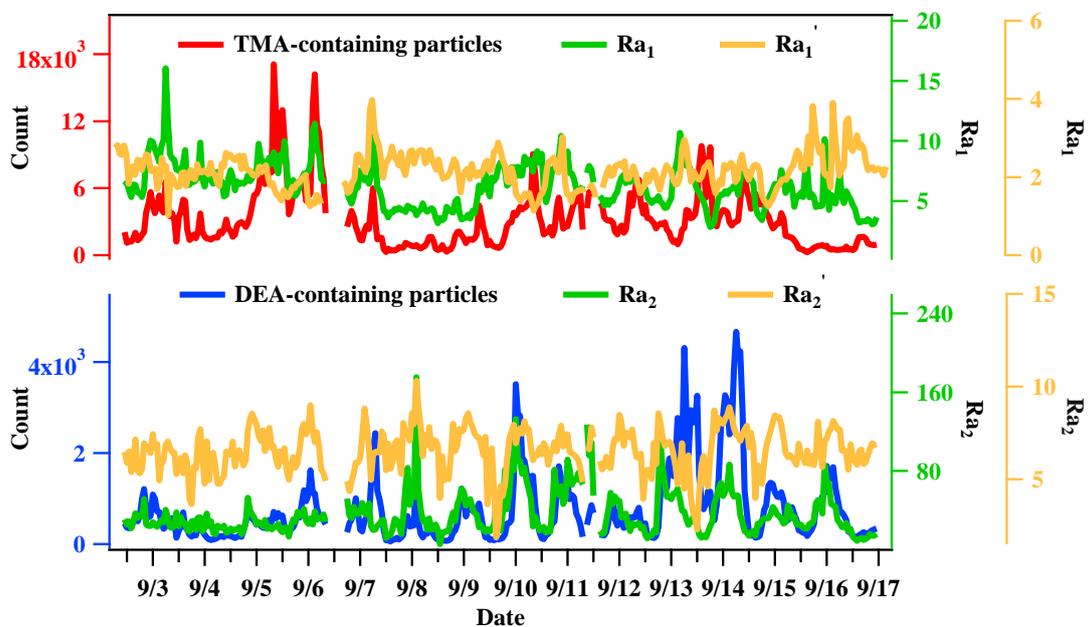


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1005 **Figure 10.** Temporal trends of TMA- and DEA-containing particle counts, and
 1006 number fractions of nitrate, sulfate, and ammonium in TMA- and DEA-containing
 1007 particles.

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1011 **Figure 11.** Temporal trends of the relative acidity ratios (Ra_1 , Ra_2) in TMA- and
 1012 DEA-containing particles.

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