

1 **Secondary formation dominated low molecular weight amines origins**  
2 **in aerosols over the marginal seas of China**

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15

16 **Abstract.** Atmospheric low molecular weight amines play important roles in aerosol  
17 physiochemical properties and climate. However, the compositions, sources, and  
18 secondary formation mechanisms of amines in offshore aerosols remain unclear. Here,  
19 an integrated observation of methylamine (MA), ethylamine (EA), dimethylamine  
20 (DMA), iso-propanamine (IPA), propanamine (PA), “trimethylamine + diethylamine”  
21 (TMDEA), and over 100 other chemical components was conducted in total  
22 suspended particles samples collected during a spring 2018 research cruise across the  
23 Yellow Sea and Bohai Sea, China. Concentrations of total amines exhibited a  
24 north-to-south decrease from the Bohai Sea to the South Yellow Sea, corresponding to  
25 the decreasing influence of terrestrial air masses. Source analyses of amines were  
26 performed using specific organic molecular tracers representing primary biogenic  
27 sources, higher plant waxes, marine/microbial sources, biogenic secondary organic  
28 aerosols, biomass burning, and fossil fuel combustion, and two major secondary  
29 formation pathways were inferred. MA, EA, and DMA were largely influenced by  
30 terrestrial biogenic and anthropogenic sources, with the majority (74.0%, 52.6%, and  
31 65.7%) formed via nitrate-associated secondary formation pathways. PA was mainly  
32 derived from combustion-related sources along with terrestrial and marine biogenic  
33 contributions. In contrast, the predominant TMDEA was mostly generated via  
34 sulfate-associated secondary formation pathways (61.8%) and contributed by marine  
35 emissions, resulting in spatial pattern distinct from other major amines and the  
36 north-to-south increasing relative contributions of amines in aerosols. These results  
37 highlight the impact of terrestrial emissions on offshore aerosol chemistry and the  
38 importance of origins and multiphase chemistry of amines under varying ambient  
39 conditions.

40

## 41 **1 Introduction**

42 Amines, derivatives of ammonia (NH<sub>3</sub>) with one or more hydrogen atoms replaced by  
43 alkyl or aryl groups, represent an important class of nitrogen-containing organic  
44 compounds (Shen et al., 2023; Zhu et al., 2022; Liu et al., 2023). Low molecular  
45 weight amines, such as methylamine (MA), dimethylamine (DMA), trimethylamine  
46 (TMA), ethylamine (EA), diethylamine (DEA), and propanamine (PA), are the most  
47 common and abundant atmospheric amines. They are ubiquitous in both the gas and  
48 particle phases due to high water solubility and strong alkalinity (Ge et al., 2011b, a).  
49 These amines are primarily emitted in the gas phase and mainly occur in aerosols as  
50 aminium salts formed via chemically reactive gas-to-particle conversion, commonly  
51 referred to as secondary formation of amines.

52 Gaseous amines can be oxidized by atmospheric oxidants (including OH, O<sub>3</sub>, and NO<sub>x</sub>)  
53 (Tang et al., 2013; Nielsen et al., 2012), and undergo gas-to-particle conversion  
54 through direct dissolution (Liu et al., 2018), acid-base reactions (Liu et al., 2023;  
55 Barsanti and Pankow, 2006; Chen et al., 2022), and heterogeneous reactions (Pankow,  
56 2015; Chan and Chan, 2013; Qiu and Zhang, 2013), leading to the formation of  
57 secondary organic aerosols (SOA) that aggravate air quality and visibility. Gaseous  
58 amines and their oxidization products, such as nitrosamines, pose significant risks to  
59 human health (Li et al., 2019a; Lee and Wexler, 2013). The multiphase chemistry of  
60 atmospheric amines participates in and accelerates new particle formation (Liu et al.,  
61 2022; Huang et al., 2022; Yao et al., 2018; Shen et al., 2019), enhances aerosol  
62 hygroscopicity (Chu et al., 2015; Gomez-Hernandez et al., 2016), and promotes the  
63 activation of cloud condensation nuclei (Tang et al., 2014; Corral et al., 2022;  
64 Gomez-Hernandez et al., 2016). Additionally, amines can promote the formation of  
65 brown carbon (Marrero-Ortiz et al., 2018; Lin et al., 2015), thereby affecting

66 atmospheric radiation and climate. However, challenges in detecting minute levels of  
67 amines, the scarcity of ambient measurements, and a limited process-based  
68 understanding of aerosol formation have led to the underrepresented of amines in  
69 global climate models (Kanawade and Jokinen, 2025).

70 Atmospheric amines originate from diverse natural sources (e.g. ocean, soil, and  
71 vegetation) and anthropogenic sources (e.g. animal husbandry, biomass burning, coal  
72 combustion, vehicle emissions, composting, waste incineration, industrial activities,  
73 and sewage) (Shen et al., 2017; Hemmilä et al., 2018; Feng et al., 2022). The ocean is  
74 an important natural source of low molecular weight amines, with emissions mainly  
75 driven by biological processes (Calderón et al., 2007; Wang and Lee, 1994). Global  
76 modeling (Myriokefalitakis et al., 2010) suggested that amines contribute ~20% of  
77 marine SOA, ranking second to dimethylsulfide (DMS). However, this contribution  
78 may be substantially overestimated, given that the actual proportions of amines  
79 relative to  $\text{NH}_3$  are up to three orders of magnitude lower than the values assumed in  
80 the model. Measured concentrations of amines varying across different oceans in both  
81 seawater and the atmosphere (Violaki and Mihalopoulos, 2010; Gibb et al., 1999; Van  
82 Neste et al., 1987). Elevated concentrations of DMA and TMA are associated with  
83 marine biological activities (Carpenter et al., 2012; Welsh, 2000) and algal blooms  
84 (Müller et al., 2009; Facchini et al., 2008b). Marine organisms act as both sources and  
85 sinks of amines, and the source/sink capability of the ocean varies with ambient  
86 conditions (Pinxteren et al., 2019). For instance, TMA can be released from living  
87 tissues or during biodegradation and decay, and can also be utilized by  
88 microorganisms for energy metabolism (Sun et al., 2019; Köllner et al., 2017; Lidbury  
89 et al., 2015). TMA can be biologically oxidized to trimethylamine oxide (TMAO), an  
90 osmotic regulatory compound in marine organisms and a precursor of DMA and MA

91 (Chen et al., 2011; Lidbury et al., 2017). The calculated sea-to-air fluxes of DMA at  
92 Cape Verde were both positive and negative, whereas those of MA were mostly  
93 positive (Pinxteren et al., 2019). Amines in marine aerosols can originate from sea  
94 spray (Bates et al., 2012; Gorzelska and Galloway, 1990), bubble bursting (Milne and  
95 Zika, 1993), and gas-to-particle conversion, i.e. secondary formation (Rinaldi et al.,  
96 2010; Facchini et al., 2008b; Facchini et al., 2008a). Most low molecular weight  
97 amines in marine aerosols were considered to be secondarily formed (Gaston et al.,  
98 2013; Dall’osto et al., 2019). For instance, 11–25% of MA, DMA and TMA in the  
99 Antarctic sympagic environment originated from primary marine aerosols, whereas  
100 75–89% were incorporated into aerosols after air-sea exchange (Dall’osto et al., 2019).  
101 Amines in marine aerosols may also be influenced by inland sources and long-range  
102 atmospheric transportation (Nielsen et al., 2012). TMA detected in aerosols off the  
103 coast of California was associated with inland animal husbandry activities rather than  
104 local marine biogenic emissions (Gaston et al., 2013).

105 Atmospheric low molecular weight amines have been widely reported in urban  
106 (Cheng et al., 2020; Chen et al., 2019; Liu et al., 2017), rural (Cheng et al., 2018; Lin  
107 et al., 2017), and coastal areas (Liu et al., 2022; Hu et al., 2015; Zhou et al., 2019; Du  
108 et al., 2021), but relatively few studies have focused on marine regions of China  
109 (Zhou et al., 2019; Yu et al., 2016; Hu et al., 2015). The Yellow Sea (YS) and Bohai  
110 Sea (BS) are two marginal seas in eastern China that serve as transition zones for  
111 atmospheric pollutants and particles transported from East Asia to the Northwest  
112 Pacific Ocean (NWPO). The YS is divided into South Yellow Sea (SYS) and North  
113 Yellow Sea (NYS), both semi-open sea areas of the NWPO. The BS is the  
114 northernmost marginal sea of China, surrounded by land on three sides and bordered  
115 to the east by the NYS. Aerosols over the YS–BS are significantly influenced by the

116 transportation of terrestrial emissions from northern and eastern China during the  
117 prevailing spring East Asia monsoon (Fang et al., 2016). Previous studies on aerosol  
118 amines over the marginal seas of China have mainly focused on DMA and TMDEA,  
119 the sum of TMA and DEA (Zhou et al., 2019; Xie et al., 2018; Yu et al., 2016; Hu et  
120 al., 2015). Although MA has been observed as the dominant amine in urban aerosols  
121 in northern China and the Yangtze River Delta region (Yang et al., 2023; Liu et al.,  
122 2023; Huang et al., 2018), its contribution in marine aerosols of China remains  
123 unclear. The primary sources and secondary formation pathways of aerosol amines  
124 over the YS–BS are poorly constrained due to the combined influence of complex  
125 terrestrial and marine emissions, as well as the lack of specific source indicators. To  
126 address these, an integrated analysis of six major amines together with more than 100  
127 other chemical components in aerosols was conducted using filter samples collected  
128 over the YS–BS during a research cruise in spring 2018. Spatial variations, potential  
129 sources, and secondary formation pathways of aerosol amines were investigated. By  
130 elucidating the relationships between individual amines and specific organic  
131 molecular tracers representing six source categories, this study provides new  
132 observational constraints on the sources and atmospheric processing of amines in  
133 marine aerosols. The results suggest that individual amines were associated with  
134 different primary sources and likely underwent two distinct major secondary  
135 formation pathways. These findings provide a basis for improving the quantitative  
136 source apportionment of aerosol amines and for further clarify their origins and  
137 gas-to-particle conversion under varying ambient conditions.

## 138 2 Methods

### 139 2.1 Aerosol sampling

140 During a Chinese oceanographic cruise over the YS–BS (28 March–16 April 2018),  
141 total suspended particles (TSP) samples were collected on prebaked (450 °C for 6 h)  
142 quartz fiber filters using a high-volume air sampler (ASM-1000, Guangzhou; flow  
143 rate: 1 m<sup>3</sup> min<sup>-1</sup>) aboard the *Dong Fang Hong 2* (Figure S1 and Table S1). The  
144 sampler was installed windward on the upper deck at the ship bow (~10 m above the  
145 sea surface). To avoid contamination from the ship exhaust, sampling was performed  
146 only while the vessel was underway. During the sampling period, a total of 15  
147 samples were collected, and 3 field blank filters were prepared by collecting without  
148 airflow. The samples were categorized into SYS, NYS, and BS by sampling positions.  
149 Real-time navigation and meteorological data, including position (longitude and  
150 latitude), ambient temperature (T), relative humidity (RH), and wind speed, were  
151 recorded by the onboard monitoring system.

152

### 153 2.2 Chemical analysis

154 Low molecular weight amines can be directly separated and quantified using ion  
155 chromatography methods (Feng et al., 2020; Place et al., 2017; VandenBoer et al.,  
156 2012). Six major protonated amine species extracted from TSP filter samples,  
157 including methylamine (CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>, MA), ethylamine (CH<sub>3</sub>CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>, EA),  
158 dimethylamine [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub><sup>+</sup>, DMA], iso-propanamine [(CH<sub>3</sub>)<sub>2</sub>CHNH<sub>3</sub><sup>+</sup>, IPA],  
159 propanamine (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>, PA), and the combined species “trimethylamine  
160 [(CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup>, TMA] + diethylamine [(CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub><sup>+</sup>, DEA]” (TMDEA), were  
161 measured by a Thermo Fisher Scientific Dionex ICS-5000+ system, as described in

162 detail elsewhere (Yang et al., 2023). Before analysis, a 0.8 cm<sup>2</sup> portion of each sample  
163 or blank filter was ultrasonically extracted 3 times with 10–30 mL of ultrapure water  
164 for 15 min in an ice-water bath, followed by filtration through a 0.22 μm Teflon filter.  
165 The analytical precision was better than 10%, and recoveries for all amines ranged  
166 from 90% to 110%. The method detection limits (MDLs) for MA, EA, DMA, IPA, PA,  
167 and TMDEA were 0.4 ng m<sup>-3</sup>, 0.4 ng m<sup>-3</sup>, 0.5 ng m<sup>-3</sup>, 0.7 ng m<sup>-3</sup>, 1.1 ng m<sup>-3</sup>, and 2.9  
168 ng m<sup>-3</sup>, respectively.

169 To provide a comprehensive characterization, other key chemical components in TSP  
170 samples were also analyzed, including water-soluble inorganic ions (WSIIs; Na<sup>+</sup>,  
171 NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, etc.), low molecular weight organic acids  
172 (CHO<sub>2</sub><sup>-</sup>, C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>, C<sub>4</sub>H<sub>4</sub>O<sub>4</sub><sup>2-</sup>, C<sub>5</sub>H<sub>6</sub>O<sub>4</sub><sup>2-</sup>, CH<sub>3</sub>O<sub>3</sub>S<sup>-</sup>/MSA<sup>-</sup>, etc.), carbonaceous  
173 components (TC, OC, and EC), and organic compositions (polar and nonpolar).  
174 Detailed methodologies had been described elsewhere (Fan et al., 2019; Cao et al.,  
175 2024), and the measurement results were summarized in Table S2.

176

### 177 **2.3 Auxiliary data**

178 Average chlorophyll *a* (Chl *a*) concentrations in seawater during the sampling period  
179 were retrieved from combined Aqua-MODIS and Terra-MODIS datasets  
180 (<https://oceancolor.gsfc.nasa.gov/>) using ArcGIS software (Figure S2). Fire spot  
181 information was obtained from the Fire Information for Resource Management  
182 System (FIRMS, <https://firms.modaps.eosdis.nasa.gov/>). Based on the archived  
183 Global Data Assimilation System (<ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1/>)  
184 meteorological data, 48 h backward air-mass trajectories at 200 m above ground level  
185 were calculated using the Hybrid Single-particle Lagrangian Integrated Trajectory

186 (HYSPLIT) model, and subsequently processed with MeteoInfo software (Figure S3).

187 The trajectories were calculated from the position and time point at the beginning of

188 each sampling, with hourly intervals thereafter.

189

## 190 3 Results and discussion

### 191 3.1 Overview of amines in marine aerosols

192 During the research cruise over the YS–BS from 28 March to 16 April 2018, total

193 concentrations of MA, EA, DMA, IPA, PA, and TMDEA ( $\Sigma$ amines) in TSP ranged

194 from 16.2 ng m<sup>-3</sup> to 89.1 ng m<sup>-3</sup> (Figure 1). Lower  $\Sigma$ amines concentrations were

195 observed over the SYS and NYS, averaging 40.4 ± 16.4 ng m<sup>-3</sup> and 43.5 ± 17.5 ng

196 m<sup>-3</sup>, respectively, and higher concentrations occurred over the BS, averaging 63.6 ±

197 18.3 ng m<sup>-3</sup>. Concentrations of other chemical components, including total WSIs, TC,

198 and total measured organic compositions, exhibited a similar spatial pattern (SYS <

199 NYS < BS; Table S2).

200 TMDEA was the predominant amine species in TSP over the YS–BS, with

201 concentrations ranging from 6.1 ng m<sup>-3</sup> to 36.3 ng m<sup>-3</sup> (Figure S4) and averages of

202 20.7 ± 9.1 ng m<sup>-3</sup>, 17.8 ± 7.3 ng m<sup>-3</sup>, and 23.8 ± 3.7 ng m<sup>-3</sup> over the SYS, NYS, and

203 BS, respectively. The fraction of TMDEA in  $\Sigma$ amines decreased from the SYS

204 (51.2%) to the NYS (40.8%) and BS (37.4%). The concentrations of amines measured

205 in TSP were comparable to PM<sub>2.5</sub> and PM<sub>10</sub> (Table S3), as amines are predominantly (>

206 70%) distributed in aerosols with diameters < 1.8 μm (Zhou et al., 2019; Xie et al.,

207 2018; Yu et al., 2016). Compared with other marine and coastal regions, the aerosol

208 TMDEA concentrations in spring over the YS–BS were higher than those reported for

209 the East China Sea (ECS), Huaniao Island (in the ECS), South China Sea (SCS), and

210 Northwest Pacific Ocean (NWPO) (Chen et al., 2022; Zhou et al., 2019; Xie et al.,  
211 2018; Yu et al., 2016). Over the YS–BS, aerosol TMDEA concentrations were higher  
212 in summer than in spring and autumn (Xie et al., 2018; Yu et al., 2016).

213 MA, the second most abundant amine species (range: 0.9–44.0 ng m<sup>-3</sup>), exhibited  
214 average concentrations of 22.8 ± 15.0 ng m<sup>-3</sup> and 15.7 ± 7.7 ng m<sup>-3</sup> in TSP over the  
215 BS and NYS, contributing 35.9% to ∑amines. Relatively lower MA concentrations  
216 (10.0 ± 7.0 ng m<sup>-3</sup>) and a smaller proportion of MA to ∑amines (24.9%) were  
217 observed over the SYS compared with the NYS–BS. A markedly high MA  
218 concentration was found in S14, the cruise track of which was close to land and  
219 largely influenced by terrestrial air masses (Figure S3 and Figure S4). The average  
220 aerosol MA concentration over the YS–BS in spring (13.7 ng m<sup>-3</sup>) was comparable to  
221 that at Jeju Island, South Korea (Yang et al., 2004), and was higher than those at  
222 coastal Qingdao (a port city surrounded by the YS and BS) and Huaniao Island in  
223 winter (Liu et al., 2022; Huang et al., 2018). These values were further higher than  
224 those reported for the Arabian Sea (Gibb et al., 1999) and tropical Atlantic (Pinxteren  
225 et al., 2019), where measurements focused on ultrafine particles may underestimate  
226 aerosol amines concentrations to some extent.

227 DMA concentrations ranged from 1.3 ng m<sup>-3</sup> to 10.4 ng m<sup>-3</sup>, with averages of 3.5 ±  
228 2.1 ng m<sup>-3</sup>, 3.8 ± 2.6 ng m<sup>-3</sup>, and 7.9 ± 2.1 ng m<sup>-3</sup> in TSP over the SYS, NYS, and BS,  
229 respectively. Higher DMA contributions to ∑amines were found over the BS (12.4%)  
230 than the NYS (8.7%) and SYS (8.6%). The average aerosol DMA concentration over  
231 the YS–BS in spring (4.4 ng m<sup>-3</sup>) was much lower than those reported for coastal  
232 Qingdao in winter and for the YS–BS in different seasons in previous years (Table  
233 S3). EA (0.6–4.8 ng m<sup>-3</sup>), IPA (0.5–3.9 ng m<sup>-3</sup>), and PA (1.3–5.1 ng m<sup>-3</sup>) constituted  
234 a relatively small fraction of ∑amines (7.3–28.2%), with average concentrations of

235  $2.0 \pm 1.2 \text{ ng m}^{-3}$ ,  $1.8 \pm 1.0 \text{ ng m}^{-3}$ , and  $2.9 \pm 1.0 \text{ ng m}^{-3}$  in TSP over the YS–BS,  
236 respectively. The average aerosol EA concentration over the BS ( $3.0 \text{ ng m}^{-3}$ ) was  
237 comparable to those observed at coastal Qingdao (Liu et al., 2022) and Jeju Island,  
238 South Korea (Yang et al., 2004). Comparable data for EA, IPA, and PA concentrations  
239 in marine aerosols were currently limited. Strong positive correlations were observed  
240 among MA, EA, and DMA ( $R = 0.73\text{--}0.77$ ,  $P < 0.01$ ), whereas no statistically  
241 significant correlation ( $P > 0.05$ ) exhibited between IPA, PA, or TMDEA and other  
242 amine species. In contrast to MA, EA, DMA, and PA, which exhibited a clear  
243 north-to-south decrease (SYS < NYS–BS), TMDEA and IPA showed no obvious  
244 spatial variation in concentrations. These results suggested that MA, EA, and DMA  
245 might share similar sources and secondary formation pathways, whereas IPA, PA, and  
246 TMDEA were likely influenced by different sources or atmospheric formation  
247 processes.

248

### 249 3.2 Relative contributions of amines in TSP over the YS–BS

250 Amines, as a subset of water-soluble organic carbon, generally constitute only a minor  
251 fraction of OC. Both OC and EC concentrations in TSP increased from the SYS to the  
252 NYS and BS (Figure 2), consistent with the strengthened influence of atmospheric  
253 pollutants transported from mainland East Asia (Figure S3). However, the  
254  $\sum\text{amines-C/OC}$  ratios (2.1–8.8‰) were relatively higher in aerosols over the SYS ( $5.4$   
255  $\pm 2.2\%$ ) than the NYS ( $4.4 \pm 1.7\%$ ) and BS ( $4.0 \pm 1.4\%$ ; Figure S5), contrary to the  
256 spatial variation of  $\sum\text{amines}$  concentrations.

257 Positive correlations were found between  $\text{NH}_4^+$  and amines, including MA ( $R = 0.78$ ,  
258  $P < 0.01$ ), DMA ( $R = 0.74$ ,  $P < 0.01$ ), EA ( $R = 0.57$ ,  $P < 0.05$ ), PA ( $R = 0.58$ ,  $P < 0.05$ ),

259 and TMDEA ( $R = 0.52$ ,  $P < 0.05$ ). Aerosol  $\text{NH}_4^+$  is formed via the heterogeneous  
260 uptake of  $\text{NH}_3$ , the most abundant alkaline gas in the atmosphere, by acidic aerosols,  
261 and exists as ammonium sulfate  $[(\text{NH}_4)_2\text{SO}_4]$ , ammonium bisulfate ( $\text{NH}_4\text{HSO}_4$ ),  
262 ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), and ammonium chloride ( $\text{NH}_4\text{Cl}$ ) (Behera et al., 2013).  
263 Atmosphere  $\text{NH}_3$  shares overlapping source profiles with gaseous amines, including  
264 animal husbandry, biomass burning, vehicle emissions, industrial activities, soil, and  
265 the ocean. This was inferred as the reason for observed correlations between  $\text{NH}_4^+$   
266 and amines in aerosols.

267 Gaseous low molecular weight amines are more alkaline than  $\text{NH}_3$ , and may compete  
268 with  $\text{NH}_3$  in atmospheric acid-base reactions (Sorooshian et al., 2008; Chen et al.,  
269 2022). The molar ratios of aerosol amines to  $\text{NH}_4^+$  were calculated to assess their  
270 relative contributions to the neutralization of acidic species in aerosols (Hu et al.,  
271 2015). The  $\sum\text{amines}/\text{NH}_4^+$  molar ratios (4.8–17.0‰) were  $9.7 \pm 3.4\%$ ,  $7.6 \pm 0.8\%$ ,  
272 and  $6.8 \pm 1.8\%$  over the SYS, NYS, and BS, respectively. The spatial pattern of  
273  $\sum\text{amines}/\text{NH}_4^+$  molar ratios (SYS > NYS > BS) was consistent with that of the  
274  $\sum\text{amines-C}/\text{OC}$  ratios, both indicating a north-to-south increase in the relative  
275 contributions of amines to aerosol composition over the YS–BS.

276 The  $\sum\text{amines}/\text{NH}_4^+$  molar ratios obtained in this study were of the same order of  
277 magnitude as those reported previously (Xie et al., 2018; Yu et al., 2016). Overall,  
278 amines contribute negligibly to the neutralization of acidic species in TSP compared  
279 with  $\text{NH}_4^+$ , which is reasonable given the much higher atmospheric abundance of  $\text{NH}_3$   
280 relative to gaseous amines (Zheng et al., 2015; You et al., 2014; Ge et al., 2011b, a).  
281 However, amines potentially play a more important role in neutralizing acidic species  
282 in submicron particles, particularly in the presence of organic compounds (Xie et al.,  
283 2018). The composition of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  may influence aerosol amines, as

284 they can act as competitors for neutralization and as major reactants in aerosol  
285 formation. The  $\text{NH}_4^+ / (\text{Cl}^- + \text{NO}_3^- + 2 \times \text{SO}_4^{2-})$  molar ratios is commonly used to  
286 assess whether  $\text{NH}_4^+$  fully neutralizes acidic species ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ ) in  
287 aerosols. In this study, the ratios in TSP over the YS–BS were mostly  $< 1$  ( $0.8 \pm 0.2$ ;  
288 Figure 2 and Figure S5), indicating  $\text{NH}_4^+$  deficiency. This deficiency was more  
289 markedly over the BS ( $0.6 \pm 0.0$ ) than the YS ( $0.8 \pm 0.2$ ). The  $\text{NO}_3^- / \text{SO}_4^{2-}$  molar  
290 ratios in TSP over the SYS ( $0.8 \pm 0.8$ ) were significantly lower than those over the  
291 NYS ( $2.3 \pm 0.4$ ) and BS ( $2.5 \pm 0.8$ ), indicating that  $\text{SO}_4^{2-}$  was the dominate acidic  
292 species in SYS aerosols, whereas  $\text{NO}_3^-$  dominated in NYS and BS aerosols. The  
293 composition of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  in NYS aerosols was intermediate between  
294 that over the BS and SYS, consistent with the regional variations in amines  
295 concentrations and composition. Molar concentrations of  $\sum$ amines increased with  
296 increasing  $\text{NH}_4^+$  deficiency [indicated by  $\text{NH}_4^+ / (\text{Cl}^- + \text{NO}_3^- + 2 \times \text{SO}_4^{2-})$  molar ratios;  
297  $R = -0.57$ ,  $P < 0.05$ ] and with  $\text{NO}_3^- / \text{SO}_4^{2-}$  ratios ( $R = 0.56$ ,  $P < 0.05$ ), particularly in  
298 BS aerosols. Nevertheless, individual amines responded differently to variations in  
299  $\text{NH}_4^+$  deficiency and  $\text{NO}_3^- / \text{SO}_4^{2-}$  molar ratios, likely reflecting differences in their  
300 primary sources (terrestrial vs. marine) and formation pathways (nitrate vs. sulfate  
301 associated).

302

### 303 3.3 Source analysis of amines in TSP over the YS–BS

#### 304 3.3.1 Biogenic sources

305 On a global scale, the ocean is a major source of gaseous methylamines (fluxes: TMA >  
306 MA >> DMA) (Van Neste et al., 1987; Schade and Crutzen, 1995). Intensive ocean  
307 farming is widespread in the coastal areas of the YS–BS (Hu et al., 2015), where

308 marine biogenic sources, including fish emission (Namieśnik et al., 2003),  
309 biodegradation of nitrogen-containing materials, and decay process (Calderón et al.,  
310 2007) may release gaseous amines into the atmosphere. The concentration of Chl *a* in  
311 surface seawater is an indicator of phytoplankton biomass and thus reflects the  
312 intensity of marine biogenic emissions to some extent. Significantly higher Chl *a*  
313 concentrations were observed in the BS than in the YS, with relatively elevated values  
314 in near shore areas (Figure S2). The spatial distribution of  $\Sigma$ amines in TSP over the  
315 YS–BS was broadly consistent with, though not identical to, Chl *a* concentrations in  
316 surface seawater. This discrepancy likely reflected secondary formation of amines in  
317 aerosols, as well as the influence of long-range transportation of terrestrial emissions  
318 driven by the prevailing East Asia monsoon during spring, particularly to S3 and  
319 S12–19 (Figure S3).

320 Aerosol MA, EA, and DMA exhibited positive linear relationships with total primary  
321 sugars and sugar alcohols (Figure 3 a–c and Table S4), which mainly originate from  
322 primary biogenic sources such as bacteria, pollen, and plant or animal debris (Li et al.,  
323 2019b). These sources can be either marine or terrestrial. Fungal spore OC and plant  
324 debris OC were estimated from mannitol and arabitol (Bauer et al., 2008), and glucose  
325 (Zheng et al., 2018), respectively. Significant positive correlations were observed  
326 between MA, EA, and DMA and fungal spore OC, plant debris OC, and several  
327 individual primary sugars and sugar alcohols (e.g., trehalose,  $\alpha$ -fructose, and sucrose;  
328  $R > 0.50$ ,  $P < 0.05$ ). DMA exhibited the strongest correlation with trehalose ( $R = 0.71$ ,  
329  $P < 0.01$ ), a compound abundant in microorganisms, algae, plants, and invertebrates,  
330 and also acts as an indicator of re-suspended dust (Medeiros et al., 2006; Simoneit et  
331 al., 2004). In addition, MA, DMA, and PA were positively correlated with high  
332 molecular weight *n*-alkanes ( $ALK_{HMW}$ ;  $C_{27}$ ,  $C_{29}$ ,  $C_{31}$  and  $C_{33}$ ) and fatty alcohols

333 (ALC<sub>HMW</sub>; > C<sub>19alc</sub>; Figure 3 d–e), while PA also correlated with low molecular  
334 weight fatty acids (FA<sub>LMW</sub>; ≤ C<sub>19:0</sub>; Figure 3 f). ALK<sub>HMW</sub> (Rogge et al., 1993),  
335 ALC<sub>HMW</sub> (Simoneit et al., 1991), and high molecular weight fatty acids (FA<sub>HMW</sub>; >  
336 C<sub>19:0</sub>) are tracers of higher plant waxes from terrestrial vegetation, whereas FA<sub>LMW</sub> are  
337 associated with marine/microbial sources (Haque et al., 2019). Overall, these results  
338 indicated that amines (MA, EA, DMA, and PA) in TSP over the YS–BS were  
339 contributed by biogenic sources. MA and DMA were largely influenced by terrestrial  
340 biogenic emissions, whereas PA was affected by both terrestrial and marine biogenic  
341 sources.

342 Atmospheric biogenic secondary organic aerosols (BSOA) are formed via the  
343 photochemical oxidation of biogenic volatile organic compounds (BVOCs) by O<sub>3</sub>,  
344 OH and NO<sub>x</sub> (Ng et al., 2011). In this study, **six isoprene SOA** (SOA<sub>I</sub>) tracers, three  
345 monoterpene SOA (SOA<sub>M</sub>) tracers, and one  $\beta$ -caryophyllene SOA (SOA<sub>C</sub>) tracer were  
346 measured in TSP over the YS–BS. Biogenic SOC derived from isoprene,  
347 monoterpene, and  $\beta$ -caryophyllene was estimated using the tracer-based method  
348 (Kang et al., 2018; Kleindienst et al., 2007). Significant positive linearity were  
349 observed between MA and both isoprene and monoterpene SOC (Figure 3 g–h).  
350 Among the SOA<sub>I</sub> tracers, MA exhibited stronger correlations with 2-methyltetrols  
351 (2-MTLs; R = 0.74, P < 0.01) and C<sub>5</sub>-alkene triols (R = 0.66, P < 0.01) than with  
352 2-methylglyceric acid (2-MGA; R = 0.64, P < 0.05). DMA was also positively  
353 correlated with isoprene SOC (R = 0.55, P < 0.05), only driven by its association with  
354 2-MTLs (R = 0.59, P < 0.05). Among the SOA<sub>M</sub> tracers, pinonic acid correlated with  
355 MA (R = 0.73, P < 0.01), EA (R = 0.52, P < 0.05), and DMA (R = 0.58, P < 0.05),  
356 while pinic acid only correlated with MA (R = 0.59, P < 0.05). In addition, PA showed  
357 a positive linearity with  $\beta$ -caryophyllene SOC (R = 0.67, P < 0.01; Figure 3 i). These

358 findings supported that MA, EA, DMA, and PA shared common sources with BVOCs  
359 and/or interacted with BSOA formation processes. High concentrations of amines and  
360 biomarkers were simultaneously observed in aerosols over the BS and NYS, whereas  
361 amines in the SYS aerosols remained at moderate levels despite low tracers  
362 concentrations (Figure 3). These indicated that terrestrial biogenic emissions  
363 contributed more substantially to aerosol amines over the BS and NYS than the SYS.

364

### 365 **3.3.2 Anthropogenic sources**

366 Anthropogenic sources are another important contributor to atmospheric amines and  
367 can be broadly categorized into combustion-related sources (e.g., biomass burning,  
368 coal combustion, vehicle emissions, and waste incineration) and non-combustion  
369 sources (e.g., animal husbandry, composting, industrial activities, sewage, and septic  
370 system). EA ( $R = 0.61$ ,  $P < 0.05$ ) and DMA ( $R = 0.72$ ,  $P < 0.01$ ) concentrations in TSP  
371 over the YS–BS increased with EC, indicating the influence of combustion emissions.  
372 Levoglucosan (Lev) is a well-established tracer for biomass burning (Li et al., 2019b).  
373 Concentrations of Lev derived from biomass burning ( $Lev_{bb}$ ) were estimated using  
374 Lev and non-sea-salt  $K^+$  ( $nss-K^+ = K^+ - 0.037 \times Na^+$ ), considering its atmospheric  
375 degradation and ~25% non-biomass burning sources [ $Lev_{bb} = 0.75 \times Lev \times$   
376  $nss-K^+ / (0.18 \times Lev + 0.08 \times nss-K^+)$ ]. Biomass burning was not a major source of  
377 MA, EA, and DMA in aerosols over the YS–BS (Figure 3 j), but contributed  
378 substantially to PA, as indicated by the positive linear relationships between PA and  
379 both  $Lev_{bb}$  and lignin products (Figure 3 k–l). The most notable contributor to PA  
380 from biomass burning was conifer burning (the second-largest portion of total  
381 biomass burning) according to the correlations between PA and individual lignin

382 products, including 4-hydroxybenzoic acid (4-HBA; a herbaceous burning marker and  
383 the predominate lignin product in this study;  $R = 0.52$ ,  $P < 0.05$ ), vanillic acid (VA; a  
384 softwood and hardwood burning marker;  $R = 0.67$ ,  $P < 0.01$ ), syringic acid (SA; also  
385 indicative of softwood and hardwood burning;  $R = 0.60$ ,  $P < 0.05$ ), and  
386 dehydroabietic acid (DA; a conifer burning marker;  $R = 0.71$ ,  $P < 0.01$ ). In addition,  
387 MA ( $R = 0.57$ ,  $P < 0.05$ ) and DMA ( $R = 0.54$ ,  $P < 0.05$ ) were positively correlated  
388 with polycyclic aromatic hydrocarbons (PAHs), indicating potential contributions  
389 from fossil fuel combustion (Table S4). Among all amines, PA showed the strongest  
390 association with combustion-related sources, as evidenced by its correlations with  
391 multiple fossil fuel combustion tracers (Figure 3 m–o), including low molecular  
392 weight n-alkanes ( $ALK_{LMW}$ ;  $C_{20}$ – $C_{26}$ ;  $R = 0.67$ ,  $P < 0.01$ ), PAHs ( $R = 0.63$ ,  $P < 0.05$ ),  
393 hopanes ( $R = 0.55$ ,  $P < 0.05$ ), and steranes ( $R = 0.57$ ,  $P < 0.05$ ).

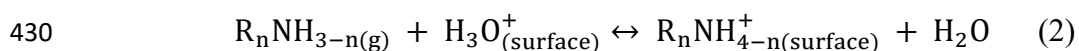
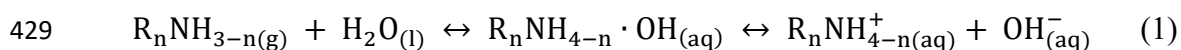
394 Emissions of amines (MA, DMA, and TMA) from non-combustion anthropogenic  
395 sources, including composting, sewage, and septic systems, are largely linked to  
396 biodegradation process. Therefore, the contribution of non-combustion anthropogenic  
397 sources to amines was encompassed within the primary biogenic sources category.  
398 IPA did not show any correlation with organic molecular tracers in TSP over the  
399 YS–BS. Given its widespread industrial use (e.g., in pesticides, pharmaceuticals, dye  
400 intermediates, emulsifiers, detergents, surfactants, and textile additives), aerosol IPA  
401 may be emitted in particulate form from specific industrial activities (Ge et al.,  
402 2011a).

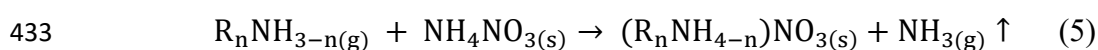
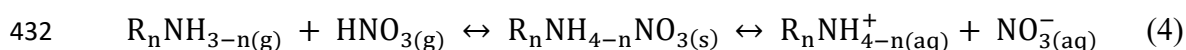
403

### 404 3.3.3 Secondary formation of MA, EA, DMA, and PA

405 Significant correlations were observed between MA, EA, DMA, and PA with  $Cl^-$  and

406  $\text{NO}_3^-$  (Figure 4). The regression intercepts of MA, EA, and DMA against  $\text{Cl}^-$  or  $\text{NO}_3^-$   
 407 were lower than those with primary organic tracers (Figure 3 and Figure S6),  
 408 indicating substantial contributions from secondary formation. The gas-to-particle  
 409 conversion of MA, EA, DMA, and PA was inferred to include direct dissolution  
 410 (Equation 1), uptake onto acidic particle surfaces (Equation 2) (Yin et al., 2011),  
 411 acid-base reactions (Equation 3–4), and displacement reactions with  $\text{NH}_4\text{NO}_3$   
 412 (Equation 5) (Bzdek et al., 2010). For MA, EA, and DMA with high water solubility,  
 413 direct dissolution is considered as a key step in their gas-to-particle conversion.  
 414 Uptake of gaseous amines onto acidic particle surfaces was more important over the  
 415 BS, where aerosol acidic species are significantly in excess relative to  $\text{NH}_4^+$ . MA, EA,  
 416 DMA, and PA in TSP over the YS–BS were formed via acid-base reactions with  
 417 atmospheric HCl and  $\text{HNO}_3$ , while  $\text{CH}_3\text{COOH}$  also contributed to the formation of  
 418 aerosol MA, EA and DMA (Figure 4). In TSP over the YS–BS,  $\text{NO}_3^-$  concentrations  
 419 were significantly higher than those of  $\text{Cl}^-$  and  $\text{C}_2\text{H}_3\text{O}_2^-$  (Table S2), thus, acid-base  
 420 reactions with  $\text{HNO}_3$ , together with displacement reactions involving  $\text{NH}_4\text{NO}_3$ , were  
 421 the major pathways for the secondary formation of aerosol MA, EA, DMA and PA.  
 422 The partitioning of amines into aerosols was further promoted by low T, high aerosol  
 423 acidity, and high RH under dynamic solid/aqueous/gas equilibrium conditions. During  
 424 the cruise, lower average T were observed over the BS (9.0°C) and NYS (6.7°C) than  
 425 the SYS (9.5°C), and RH remained at a high level across the YS–BS (mean: 86.2%;  
 426 median: 87.6%). The relatively abundant acidic species and lower T over the BS and  
 427 NYS favored the partitioning of MA, EA, DMA, and PA into the particle phase  
 428 compared with the conditions over the SYS.





434 Contributions of nitrate-associated secondary formation to aerosol amines were  
 435 estimated from the average amine concentrations weighted by  $NO_3^-$  concentrations  
 436 and regression intercepts (Figure S6). These estimates are semi-quantitative and  
 437 limited by the small sample sizes, rather than representing quantitative source  
 438 apportionment or mechanistic yields. Contributions of nitrate-associated secondary  
 439 formation to  $\sum$ amines were highest in TSP over the BS ( $43.0 \pm 26.9\%$ ), followed by  
 440 the NYS ( $33.8 \pm 19.7\%$ ) and SYS ( $21.8 \pm 18.8\%$ ). Among individual amines,  
 441 nitrate-associated secondary formation contributed most to MA ( $74.0 \pm 61.5\%$ ),  
 442 followed by DMA ( $65.7 \pm 44.3\%$ ), EA ( $52.6 \pm 55.0\%$ ), and PA ( $35.1 \pm 22.4\%$ ). PA  
 443 was less contributed by secondary formation, likely because it can be directly emitted  
 444 in particulate form or condense into aerosols after emission due to its relatively higher  
 445 boiling point ( $47.8^\circ C$ ) compared with MA ( $-6.3^\circ C$ ), EA ( $16.6^\circ C$ ), and DMA ( $7.4^\circ C$ ).

446 The relationships among amines (MA, EA, DMA, and PA), BSOA, and  $NO_3^-$  in TSP  
 447 over the YS–BS suggested potential interactions among their secondary formation  
 448 processes.  $NO_x$ , emitted from soil, biogenic activities, and combustion sources, are  
 449 important precursors for both BSOA and atmospheric  $HNO_3$ , which subsequently  
 450 forms nitrate aerosols. This was supported by significant positive correlations  
 451 between  $NO_3^-$  and  $SOA_I$  ( $R = 0.88$ ,  $P < 0.01$ ),  $SOA_M$  ( $R = 0.86$ ,  $P < 0.01$ ), and  $SOA_C$   
 452 ( $R = 0.64$ ,  $P < 0.05$ ). The formation of MA and DMA in aerosols might occur under  
 453 low  $NO_x$  conditions, as evidenced by their stronger correlations with 2-MTLs or  
 454  $C_5$ -alkene triols (products of isoprene photochemical oxidation under low  $NO_x$   
 455 conditions) (Zheng et al., 2018; Zhang et al., 2011) than with 2-MGA (products of

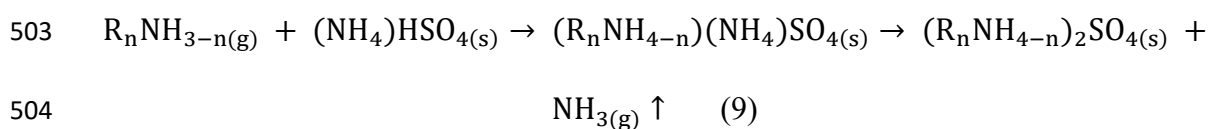
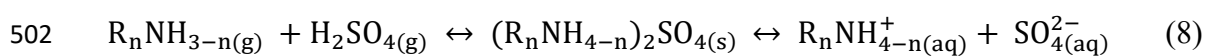
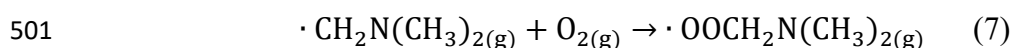
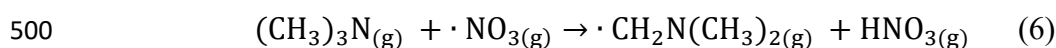
456 isoprene aqueous-phase oxidation under high  $\text{NO}_x$  conditions) (He et al., 2018).  
457 Strong atmospheric photo-oxidation generally accelerates the gas-phase degradation  
458 of amines (Lee and Wexler, 2013), thereby reducing the formation of particle-phase  
459 aminium salts. BVOCs, as precursors of BSOA, can generate  $\text{HNO}_3$  via the “ $\text{NO}_3 +$   
460  $\text{HC}$ ” pathway, further promoting the formation of aminium nitrates. Meanwhile,  
461 BSOA formation consumes atmospheric oxidants, which may reduce the degradation  
462 of gaseous amines. The presence of an organic phase also enhances the  
463 competitiveness of amines relative to  $\text{NH}_4^+$  in aerosols (Xie et al., 2018). In addition,  
464 the gas-to-particle conversion of amines may facilitate BSOA formation by providing  
465 more hygroscopic particulate surfaces.

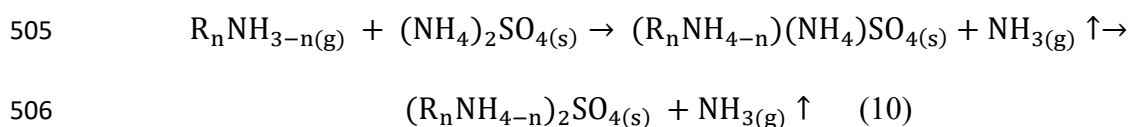
466

#### 467 **3.3.4 Secondary formation of TMDEA**

468 Compared with other amines, a larger fraction of TMDEA likely originated from  
469 marine sources, as indicated by its relatively high concentrations and proportions in  
470 TSP over the SYS. Previous studies also suggested marine emissions as an important  
471 potential source of TMDEA (Schade and Crutzen, 1995; Pinxteren et al., 2019).  
472 TMDEA in TSP over the YS–BS exhibited no correlation with organic molecular  
473 tracers representing primary biogenic sources or BSOA (Table S4), although  
474 terrestrial vegetation and non-combustion anthropogenic sources are also potential  
475 sources of gaseous TMDEA (Zhu et al., 2022; Ge et al., 2011a). Concentrations of  
476 aerosol TMDEA were likely constrained by gas-to-particle conversion efficiency. A  
477 hypothesis is that part of the gaseous TMDEA emitted from primary sources is  
478 consumed through reactions with  $\text{NO}_3$  to form non-aminiium-salt SOA (Price et al.,  
479 2016; Price et al., 2014) and  $\text{HNO}_3$  (Equation 6–7).

480 TMDEA in TSP over the YS–BS showed no correlation with  $\text{Cl}^-$ , or  $\text{NO}_3^-$ , but  
 481 exhibited significant positive linear relationships with  $\text{SO}_4^{2-}$ ,  $\text{C}_4\text{H}_4\text{O}_4^{2-}$ , and  $\text{C}_5\text{H}_6\text{O}_4^{2-}$   
 482 (Figure 4 and Figure S6). The gas-to-particle conversion of TMDEA was inferred to  
 483 include uptake onto acidic particle surfaces (Equation 2), acid-base reactions with  
 484  $\text{H}_2\text{SO}_4$  (Equation 8) and dicarboxylic acids ( $\text{C}_4\text{H}_6\text{O}_4$  and  $\text{C}_5\text{H}_8\text{O}_4$ ), as well as  
 485 displacement reactions with  $(\text{NH}_4)\text{HSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  (Equation 9–10). Uptake  
 486 onto acidic particle surfaces is considered as a key step in the gas-to-particle  
 487 conversion of TMDEA, as TMA exhibits the strongest alkalinity among gaseous  
 488 amines. TMDEA in TSP over the YS–BS showed limited association with chloride  
 489 and nitrate, likely due to the much lower competitiveness of TMA in forming these  
 490 salts (as reflected by dissociation constants) relative to MA, EA, DMA, and  $\text{NH}_3$  (Ge  
 491 et al., 2011b). Instead, acid-base reactions with  $\text{H}_2\text{SO}_4$ , together with displacement  
 492 reactions involving  $(\text{NH}_4)\text{HSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$ , were the major pathways for the  
 493 secondary formation of aerosol TMDEA. Contributions of dicarboxylic acids were  
 494 relatively minor, given the significantly lower concentrations of  $\text{C}_4\text{H}_4\text{O}_4^{2-}$  and  
 495  $\text{C}_5\text{H}_6\text{O}_4^{2-}$  compared with  $\text{SO}_4^{2-}$  in TSP over the YS–BS (Table S2). These findings  
 496 were consistent with previous laboratory and theoretical studies showing that TMA  
 497 preferentially reacts with  $\text{H}_2\text{SO}_4$  (Johnson and Jen, 2023), and that DEA exhibits the  
 498 highest uptake coefficient during the irreversible reactive uptake of gaseous  
 499 ethylamines by  $\text{H}_2\text{SO}_4$  (Yin et al., 2011).





507 Sulfate-associated secondary formation contributed  $61.8 \pm 31.6\%$  to TMDEA in TSP  
 508 over the YS–BS, as estimated from average TMDEA concentrations weighted by  
 509  $\text{SO}_4^{2-}$  concentrations and regression intercept (Figure S6). The contributions were  
 510 highest over the SYS ( $63.4 \pm 36.2\%$ ), followed by the BS ( $61.4 \pm 16.2\%$ ) and NYS  
 511 ( $55.8 \pm 29.3\%$ ). Correspondingly, sulfate-associated secondary formation contributed  
 512  $23.0 \pm 6.0\%$ ,  $22.8 \pm 13.7\%$ , and  $32.5 \pm 22.1\%$  to  $\sum\text{amines}$  over the BS, NYS, and  
 513 SYS, respectively. The spatial pattern of average contributions from sulfate-associated  
 514 secondary formation (SYS > BS > NYS) was consistent with that of average T,  
 515 indicating that T conditions influenced the relative advantages of sulfate and nitrate  
 516 formation.

517 Significant positive correlations were observed between non-sea-salt sulfate  
 518 ( $\text{nss-SO}_4^{2-} = \text{SO}_4^{2-} - 0.2516 \times \text{Na}^+$ ) and the dicarboxylates ( $\text{C}_4\text{H}_4\text{O}_4^{2-}$  and  $\text{C}_5\text{H}_6\text{O}_4^{2-}$ ;  
 519  $R = 0.78$  and  $0.66$ ,  $P < 0.01$ ), indicating that these species shared similar potential  
 520 terrestrial anthropogenic or marine biogenic origins (Miyazaki et al., 2010; Mochida  
 521 et al., 2003). Molar concentrations of biogenic- $\text{SO}_4^{2-}$  were estimated from T and  
 522  $\text{MSA}^-$ , as both  $\text{MSA}^-$  and  $\text{SO}_4^{2-}$  are oxidation products of DMS emitted from marine  
 523 biogenic sources (Nakamura et al., 2005; Bates et al., 1992). Anthropogenic- $\text{SO}_4^{2-}$   
 524 was then calculated by subtracting biogenic- $\text{SO}_4^{2-}$  from  $\text{nss-SO}_4^{2-}$ . Biogenic- $\text{SO}_4^{2-}$   
 525 accounted for 11.1% of total  $\text{SO}_4^{2-}$  in TSP over the SYS, markedly higher than the  
 526 NYS (4.3%) and BS (2.1%), yet still representing a minor fraction relative to  
 527 anthropogenic- $\text{SO}_4^{2-}$ . Consequently, TMDEA in TSP over the YS–BS was  
 528 predominantly taken up by anthropogenic sulfate aerosols.

529 High concentrations of TMDEA,  $\text{SO}_4^{2-}$ ,  $\text{C}_4\text{H}_4\text{O}_4^{2-}$ , and  $\text{C}_5\text{H}_6\text{O}_4^{2-}$  were simultaneously  
530 observed in S5 and S6 over the SYS, along with relatively high marine biogenic  
531 contributions (Biogenic- $\text{SO}_4^{2-}/\text{SO}_4^{2-}$ : 11.2% and 10.3%).  $\text{NH}_4^+$  deficiency [ $\text{NH}_4^+ / (\text{Cl}^-$   
532  $+ \text{NO}_3^- + 2 * \text{SO}_4^{2-})$ ]: 0.8 and 0.6], high T (12.2°C and 12.1°C), high wind speed (6.9 m  
533  $\text{s}^{-1}$  and 7.2  $\text{m s}^{-1}$ ), and saturated humidity (RH = 100%) were also found in S5 and S6  
534 (Table S1). Under high RH, more amines partition into aqueous aerosols via direct  
535 dissolution, promoting aminium salts formation, whereas high T shifts the  
536 solid/aqueous/gas equilibrium of aminium salts toward the gas phase. Compared with  
537 the chlorides and nitrates of MA, EA, DMA, and PA, TMDEA sulfates are more  
538 thermally stable. In addition, strong winds enhance the emission of primary marine  
539 aerosols from sea spray and bubble bursting, providing additional amines to TSP, as  
540 amines are present in both seawater and primary marine aerosols. The source  
541 contributions and major secondary formation pathways of amines were summarized in  
542 Figure 5.

543

#### 544 **4 Conclusions**

545 This study systematically analyzed the spatial variations, potential sources, and  
546 secondary formation mechanisms of six major low molecular weight amines in  
547 aerosols over the marginal seas of China. Concentrations of total amines, water  
548 soluble inorganic ions, carbonaceous components, and more than 100 organic  
549 compositions generally exhibited a north-to-south decreasing pattern from the BS to  
550 the NYS and SYS. This trend was consistent with the decreasing influence of  
551 continental emissions from mainland East Asia, coupled with the increasing  
552 contribution of the marine atmosphere.

553 Offshore aerosols exhibited distinct compositions of amines compared to terrestrial  
554 aerosols, with TMDEA surpassing MA as the predominant amine. The proportions of  
555 TMDEA in  $\Sigma$ amines and the relative contributions of  $\Sigma$ amines in aerosols increased  
556 from north to south (BS < NYS < SYS), highlighting the ocean as a substantial source  
557 of amines, particularly TMDEA, despite the significant influence of terrestrial  
558 emissions. Distinct potential sources and major secondary formation pathways were  
559 identified for different amine species. MA, EA, and DMA were mainly derived from  
560 terrestrial biogenic and non-combustion anthropogenic sources, followed by fossil  
561 fuel combustion, with over 50% formed via nitrate-associated secondary formation  
562 pathways, **interacting with BSOA formation in the NO<sub>x</sub>-involved oxidation of BVOCs.**  
563 In comparison, PA mainly originated from combustion-related sources along with  
564 terrestrial and marine biogenic sources, with only ~35% contributed by  
565 nitrate-associated secondary formation. **In contrast to other amines,** TMDEA was  
566 mostly (~60%) generated via sulfate-associated secondary formation pathways, and  
567 also contributed by primary marine aerosols from sea spray and bubble bursting.

568 Terrestrial sources not only emit gaseous amines but also contribute acidic aerosols  
569 that can further uptake amines from marine sources during the transportation of air  
570 masses from the mainland to the ocean. This process affects the physiochemical  
571 properties and climate effects of marine aerosols, as well as the carbon and nitrogen  
572 cycles. In addition to precursors abundance, ambient conditions also influence the  
573 secondary formation of aerosol amines, leading to temporal and spatial variations in  
574 their concentrations and compositions. Overall, these findings improve the  
575 understanding of amines in marine aerosols, highlight the impact of terrestrial  
576 emissions on offshore aerosol chemistry, and underscore the importance of multiphase  
577 chemical processes of amines under diverse ambient conditions.

578

579 *Data availability.* Data are available from the corresponding author on request  
580 ([dryanlinzhang@outlook.com](mailto:dryanlinzhang@outlook.com)).

581

582 *Supplement.* The supplement related to this article is available online at: .

583

584 *Author contributions.* Xiao-Ying Yang wrote the draft and produced all the figures and  
585 tables. Fang Cao, Yu-Chi Lin, and Yan-Lin Zhang provided useful comments and  
586 revised the paper. Chang-Liu Wu, Yu-Xian Zhang, and Wen-Huai Song provided the  
587 measurement data.

588

589 *Competing interests.* The authors declare that they have no conflict of interest.

590

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596

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599

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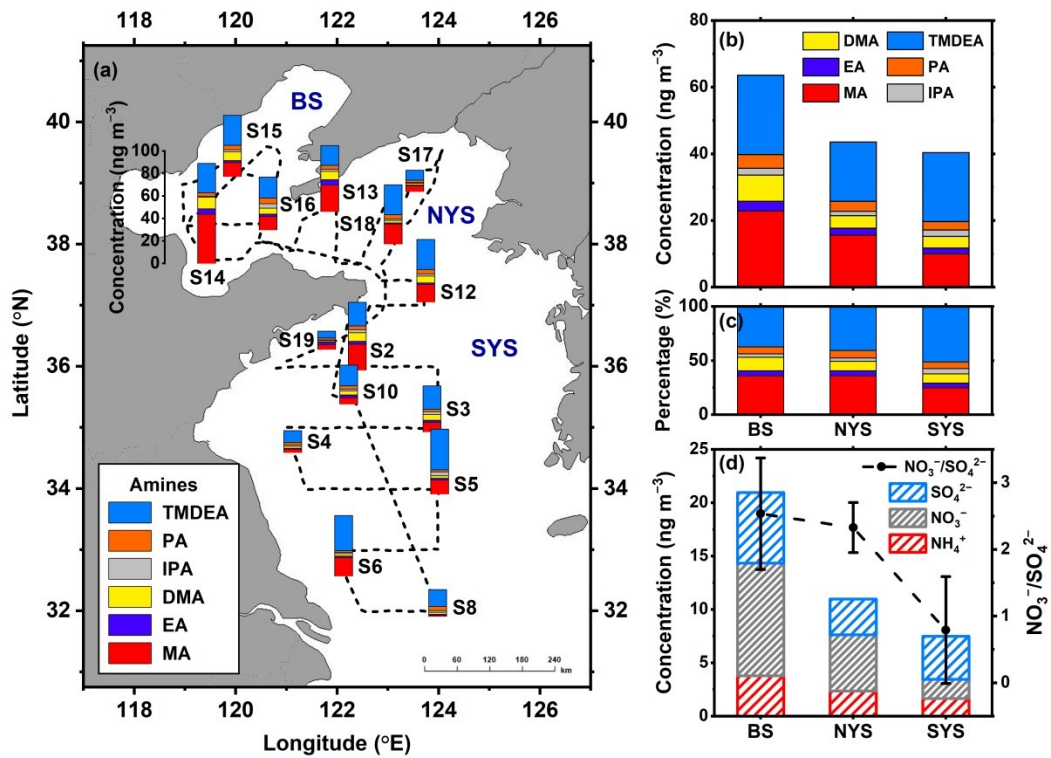
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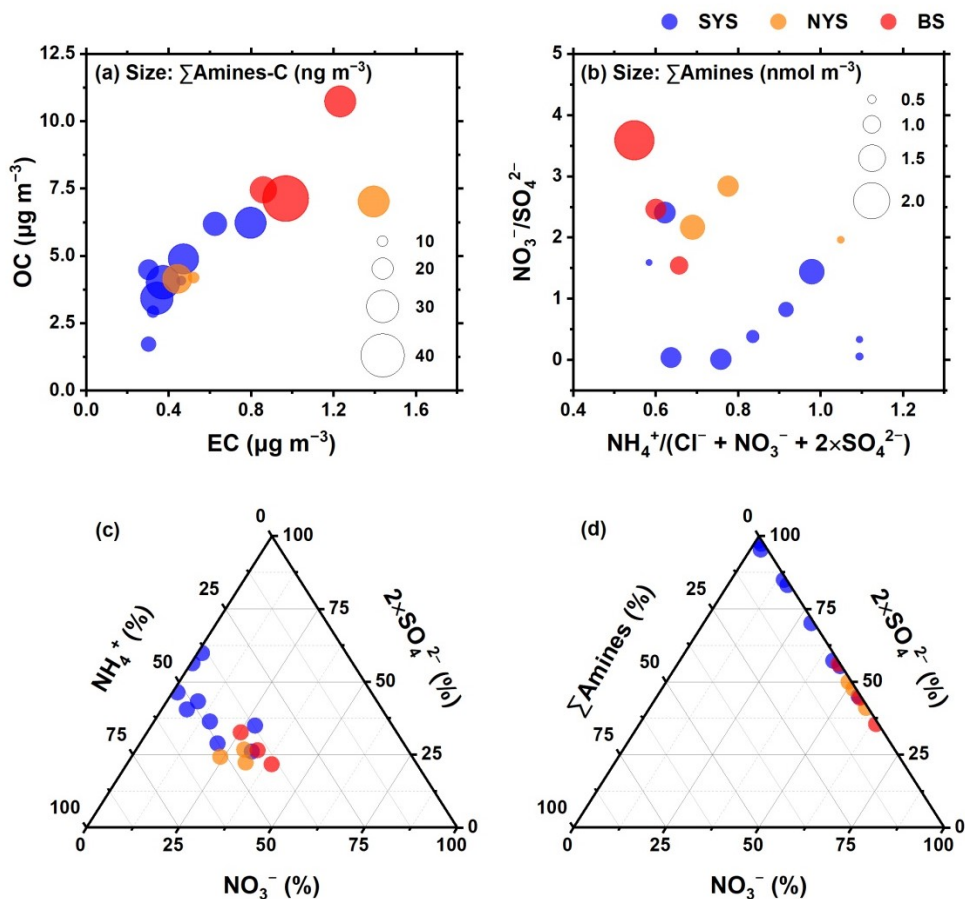
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959 **Figure 1.** Concentrations of amines in 15 TSP samples (a) collected along the cruise  
 960 track (black dotted line); average concentrations (b) and relative contributions (c) of  
 961 amines; and concentrations of NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>, along with NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> molar  
 962 ratios (d), in TSP over the SYS, NYS, and BS.

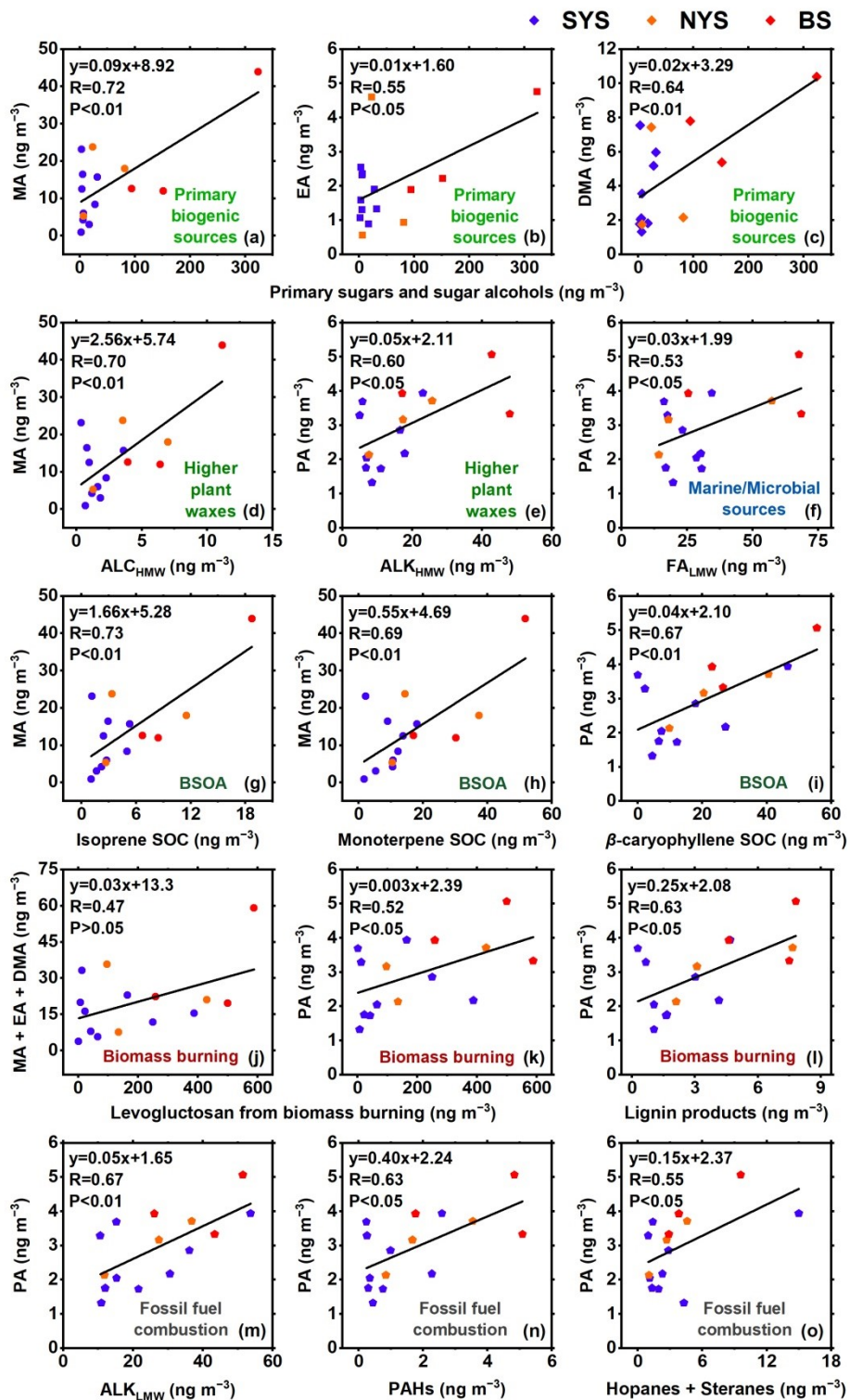
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965 **Figure 2.** Variations of  $\Sigma\text{amines-C}$  with OC and EC concentrations (a); variations of  
 966  $\Sigma\text{amines}$  molar concentrations with the  $\text{NO}_3^-/\text{SO}_4^{2-}$  and  $\text{NH}_4^+ / (\text{Cl}^- + \text{NO}_3^- + 2 \times \text{SO}_4^{2-})$   
 967 molar ratios (b); ternary diagram of the molar ratio of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  (c); and  
 968 ternary diagram of the molar ratio of  $\Sigma\text{amines}$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  (d) in TSP over the  
 969 SYS, NYS, and BS.

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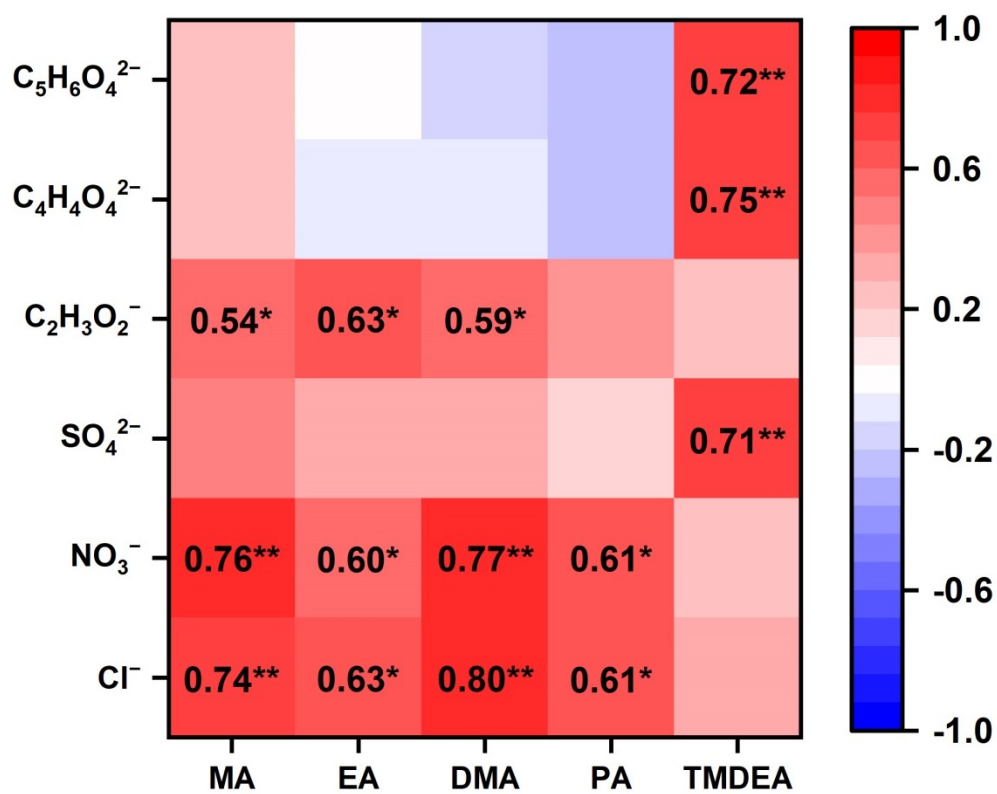
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972 **Figure 3.** Linear regressions between amines and biomarkers (a–i), biomass burning

973 tracers (j–l), and fossil fuel combustion tracers (m–o) in TSP over the SYS, NYS, and

974 BS.

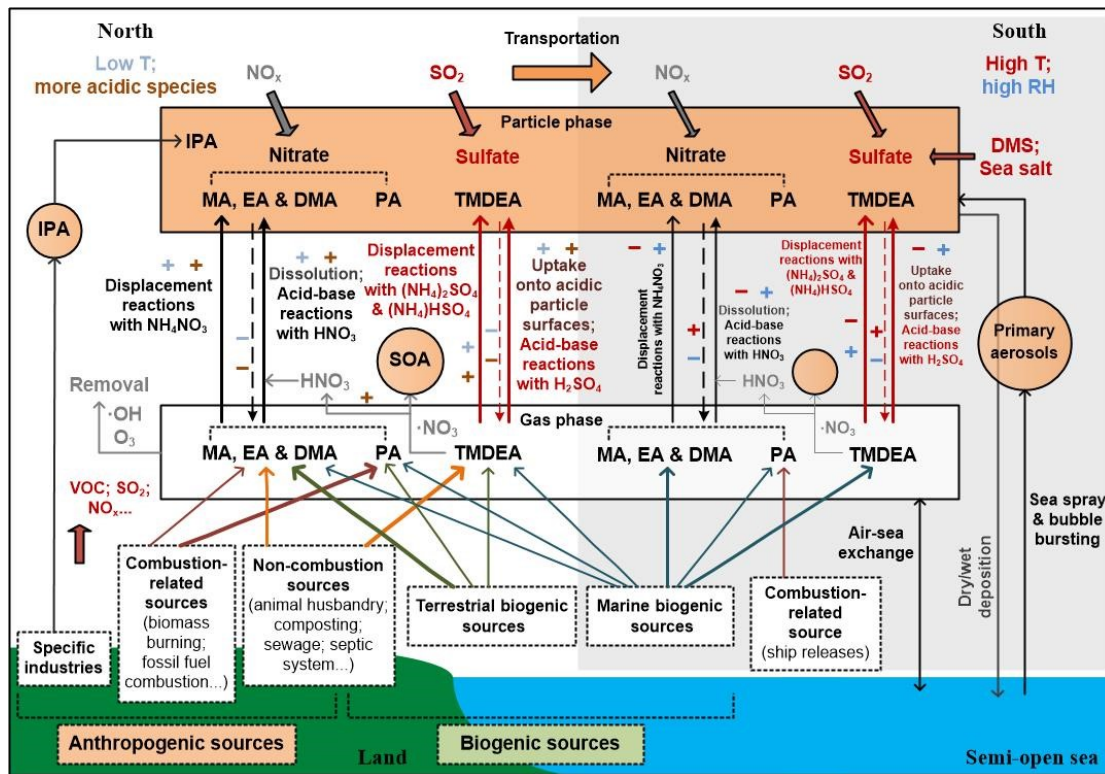
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977 **Figure 4.** Correlation coefficient matrix between amines and acidic species in TSP  
 978 over the YS–BS. Numbers indicate correlation coefficients that passed the  
 979 significance test; \*\* denotes  $P < 0.01$ , and \* denotes  $P < 0.05$ .

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981

982 **Figure 5.** Schematic diagram illustrating the source contributions and major  
 983 secondary formation mechanisms of amines, along with the influences of  
 984 environmental conditions over the YS-BS.

985