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

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Abstract. Atmospheric low molecular weight amines play important roles in aerosol physiochemical properties and climate. However, the compositions, sources, and secondary formation mechanisms of amines in offshore aerosols remain unclear. Here, an integrated observation of methylamine (MA), ethylamine (EA), dimethylamine (DMA), iso-propanamine (IPA), propanamine (PA), "trimethylamine + diethylamine" (TMDEA), and over 100 other chemical components was conducted in total suspended particles samples collected during a spring 2018 research cruise across the Yellow Sea and Bohai Sea, China. Concentrations of total amines exhibited a north-to-south gradient from the Bohai Sea to the South Yellow Sea, corresponding to the decreasing influence of terrestrial air masses. Source analyses of amines were performed using specific organic molecular tracers representing primary biogenic sources, higher plant waxes, marine/microbial sources, biogenic secondary organic aerosols, biomass burning, and fossil fuel combustion, and two major secondary formation pathways were inferred. MA, EA, and DMA were largely influenced by terrestrial biogenic and anthropogenic sources, with the majority (74.0%, 52.6%, and 65.7%) formed via nitrate-associated secondary formation pathways. PA was mainly derived from combustion-related sources along with terrestrial and marine biogenic contributions. In contrast, the predominant TMDEA was mostly generated via sulfate-associated secondary formation pathways (61.8%) and contributed by marine emissions, resulting in spatial pattern distinct from other major amines and the north-to-south increasing relative contributions of amines in aerosols. These results 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.

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1 Introduction

Amines, derivatives of ammonia (NH_3) with one or more hydrogen atoms replaced by alkyl or aryl groups, represent an important class of nitrogen-containing organic compounds (Shen et al., 2023; Zhu et al., 2022; Liu et al., 2023). Low molecular weight amines, such as methylamine (MA), dimethylamine (DMA), trimethylamine (TMA), ethylamine (EA), diethylamine (DEA), and propanamine (PA), are the most common and abundant atmospheric amines. They are ubiquitous in both the gas and particle phases due to high water solubility and strong alkalinity (Ge et al., 2011b, a). These amines are primarily emitted in the gas phase and mainly exist in aerosols as aminium salts formed via chemically reactive gas-to-particle conversion, commonly referred to as secondary formation of amines.

Gaseous amines can be oxidized by atmospheric oxidants (including OH, O_3, and NO_x) (Tang et al., 2013; Nielsen et al., 2012), and undergo gas-to-particle conversion through direct dissolution (Liu et al., 2018), acid-base reactions (Liu et al., 2023; Barsanti and Pankow, 2006; Chen et al., 2022), and heterogeneous reactions (Pankow, 2015; Chan and Chan, 2013; Qiu and Zhang, 2013), leading to the formation of secondary organic aerosols (SOA) that aggravate air quality and visibility. Gaseous amines and their oxidization products, such as nitrosamines, pose significant risks to human health (Li et al., 2019a; Lee and Wexler, 2013). The multiphase chemistry of atmospheric amines participates in and accelerates new particle formation (Liu et al., 2022; Huang et al., 2022; Yao et al., 2018; Shen et al., 2019), enhances aerosol hygroscopicity (Chu et al., 2015; Gomez-Hernandez et al., 2016), and promotes the

activation of cloud condensation nuclei (Tang et al., 2014; Corral et al., 2022; Gomez-Hernandez et al., 2016). Additionally, amines can promote the formation of brown carbon (Marrero-Ortiz et al., 2018; Lin et al., 2015), thereby affecting atmospheric radiation and climate. However, challenges in detecting minute levels of amines, the scarcity of ambient measurements, and a limited process-based understanding of aerosol formation have led to the underrepresented of amines in global climate models (Kanawade and Jokinen, 2025).

Atmospheric amines originate from diverse natural (e.g. ocean, soil, and vegetation) and anthropogenic sources (e.g. animal husbandry, biomass burning, coal combustion, vehicle emissions, composting, waste incineration, industrial activities, and sewage) (Shen et al., 2017; Hemmilä et al., 2018; Feng et al., 2022). Ocean is an important natural source of low molecular weight amines, with emissions mainly driven by biological processes (Calderón et al., 2007; Wang and Lee, 1994). Global modeling (Myriokefalitakis et al., 2010) suggested that amines contribute approximately 20% to marine SOA, ranking second to dimethylsulfide (DMS). However, this contribution may be substantially overestimated, given that the actual proportions of amines relative to NH_3 are up to three orders of magnitude lower than the values assumed in the model. Measured concentrations of amines vary across different oceans in both seawater and the atmosphere (Violaki and Mihalopoulos, 2010; Gibb et al., 1999; Van Neste et al., 1987). Elevated concentrations of DMA and TMA are associated with marine biological activities (Carpenter et al., 2012; Welsh, 2000) and algal blooms (Müller et al., 2009; Facchini et al., 2008b). Marine organisms act as both sources and

sinks of amines, and the source/sink capability of the ocean varies with ambient conditions (Pinxteren et al., 2019). For instance, TMA can be released from living tissues or during biodegradation and decay, and can also be utilized by microorganisms for energy metabolism (Sun et al., 2019; Köllner et al., 2017; Lidbury et al., 2015). TMA can be biologically oxidized to trimethylamine oxide (TMAO), an osmotic regulatory compound in marine organisms and a precursor of DMA and MA (Chen et al., 2011; Lidbury et al., 2017). The calculated sea-to-air fluxes of DMA at Cape Verde were both positive and negative, whereas those of MA were mostly positive (Pinxteren et al., 2019). Amines in marine aerosols are originated from sea spray (Bates et al., 2012; Gorzelska and Galloway, 1990), bubble bursting (Milne and Zika, 1993), and gas-to-particle conversion, i.e. secondary formation (Rinaldi et al., 2010; Facchini et al., 2008b; Facchini et al., 2008a). Most low molecular weight amines in marine aerosols are considered to be secondarily formed (Gaston et al., 2013; Dall´osto et al., 2019). For instance, 11−25% of MA, DMA and TMA in the Antarctic sympagic environment originated from primary marine aerosols, whereas 75−89% were incorporated into aerosols after air-sea exchange (Dall´osto et al., 2019). Amines in marine aerosols may also be influenced by inland sources and long-range atmospheric transportation (Nielsen et al., 2012). TMA detected in aerosols off the coast of California was associated with inland animal husbandry activities rather than local marine biogenic emissions (Gaston et al., 2013).

Atmospheric low molecular weight amines have been widely reported in urban (Cheng et al., 2020; Chen et al., 2019; Liu et al., 2017), rural (Cheng et al., 2018; Lin

et al., 2017), and coastal areas (Liu et al., 2022; Hu et al., 2015; Zhou et al., 2019; Du et al., 2021), but relatively few studies have focused on marine regions of China (Zhou et al., 2019; Yu et al., 2016; Hu et al., 2015). The Yellow Sea (YS) and Bohai Sea (BS) are two marginal seas in eastern China that serve as transition zones for atmospheric pollutants and particles transported from East Asia to the Northwest Pacific Ocean (NWPO). The YS is divided into South Yellow Sea (SYS) and North Yellow Sea (NYS), both semi-open sea areas of the NWPO. The BS is the northernmost marginal sea of China, surrounded by land on three sides and bordered to the east by the NYS. Aerosols over the YS−BS are significantly influenced by the transportation of terrestrial emissions from northern and eastern China during the prevailing spring East Asia monsoon (Fang et al., 2016). Previous studies on aerosol amines over the marginal seas of China have mainly focused on DMA and TMDEA, the sum of TMA and DEA (Zhou et al., 2019; Xie et al., 2018; Yu et al., 2016; Hu et al., 2015). Although MA has been observed as the dominant amine in urban aerosols in northern China and the Yangtze River Delta region (Yang et al., 2023; Liu et al., 2023; Huang et al., 2018), its contribution in marine aerosols of China remains unclear. The primary sources and secondary formation pathways of aerosol amines over the YS−BS are poorly constrained due to the combined influence of complex terrestrial and marine emissions, as well as the lack of specific source indicators. To address these, an integrated analysis of six major amines together with more than 100 other chemical components in aerosols was conducted using filter samples collected over the YS−BS during a research cruise in spring 2018. Spatial variations, potential

sources, and secondary formation pathways of aerosol amines were investigated. By elucidating the relationships between individual amines and specific organic molecular tracers representing six source categories, this study provides new observational constraints on the sources and atmospheric processes of amines in marine aerosols. The results suggest that individual amines were associated with different primary sources and likely underwent two distinct major secondary formation pathways. These findings provide a basis for improving the quantitative source apportionment of aerosol amines and for further clarify their origins and gas-to-particle conversion under varying ambient conditions.

2 Methods

2.1 Aerosol sampling

During a Chinese oceanographic cruise over the YS−BS (28 March−16 April 2018), total suspended particles (TSP) samples were collected on prebaked (450 °C for 6 h) quartz fiber filters using a high-volume air sampler (ASM-1000, Guangzhou; flow rate: 1 m^3 min^{-1}) aboard the *Dong Fang Hong 2* (Figure S1 and Table S1). The sampler was installed windward on the upper deck at the ship bow (~10 m above the sea surface). To avoid contamination from the ship exhaust, sampling was performed only while the vessel was underway. During the sampling period, a total of 15 samples were collected, and 3 field blank filters were prepared by collecting without airflow. The samples were categorized into SYS, NYS, and BS by sampling positions.

Real-time navigation and meteorological data, including position (longitude and latitude), ambient temperature (T), relative humidity (RH), and wind speed, were recorded by the onboard monitoring system.

2.2 Chemical analysis

Low molecular weight amines can be directly separated and quantified using ion chromatography methods (Feng et al., 2020; Place et al., 2017; VandenBoer et al., 2012). Six major protonated amine species extracted from TSP filter samples, including methylamine ($CH_3NH_3^+$, MA), ethylamine ($CH_3CH_2NH_3^+$, EA), dimethylamine [$(CH_3)_2NH_2^+$, DMA], iso-propanamine [$(CH_3)_2CHNH_3^+$, IPA], propanamine ($CH_3CH_2CH_2NH_3^+$, PA), and the combined species "trimethylamine [$(CH_3)_3NH^+$, TMA] + diethylamine [$(CH_3CH_2)_2NH_2^+$, DEA]" (TMDEA), were measured by a ion chromatography (Thermo Fisher Scientific Dionex ICS-5000+), as described in detail elsewhere (Yang et al., 2023). Before analysis, a 0.8 cm^2 portion of each sampled or blank filter was ultrasonically extracted 3 times with 10−30 mL of ultrapure water for 15 min in an ice-water bath, followed by filtration through a 0.22 μm Teflon filter. The analytical precision was better than 10%, and recoveries for all amines ranged from 90% to 110%. The method detection limits (MDLs) for MA, EA, DMA, IPA, PA, and TMDEA were 0.4 ng m^{-3}, 0.4 ng m^{-3}, 0.5 ng m^{-3}, 0.7 ng m^{-3}, 1.1 ng m^{-3}, and 2.9 ng m^{-3}, respectively.

To provide a comprehensive characterization of aerosols, other key chemical

components in TSP samples were also analyzed, including water-soluble inorganic ions (WSIIs; Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}, etc.), low molecular weight organic acids (CHO_2^-, $C_2H_3O_2^-$, $C_4H_4O_4^{2-}$, $C_5H_6O_4^{2-}$, $CH_3O_3S^-$/MSA^-, etc.), carbonaceous components [Organic carbon (OC) and Elemental carbon (EC)], and organic compositions (polar and nonpolar). Detailed methodologies for analyzing these species had been described elsewhere (Fan et al., 2019; Cao et al., 2024), and the measurement results were summarized in Table S2.

2.3 Auxiliary data

Average chlorophyll *a* (Chl *a*) concentrations in seawater during the sampling period were retrieved from combined Aqua-MODIS and Terra-MODIS datasets (https://oceancolor.gsfc.nasa.gov/) using ArcGIS software (Figure S2). Fire spot information was obtained from the Fire Information for Resource Management System (FIRMS, https://firms.modaps.eosdis.nasa.gov/). Based on the archived Global Data Assimilation System (ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1/) meteorological data, 48 h backward air-mass trajectories at 200 m above ground level were calculated using the Hybrid Single-particle Lagrangian Integrated Trajectory (HYSPLIT) model, and subsequently processed with MeteoInfo software (Figure S3). The trajectories were calculated from the position and time point at the beginning of each sampling, with hourly intervals thereafter.

3 Results and discussion

3.1 Overview of amines in marine aerosols

During the cruise over the YS−BS from 28 March to 16 April 2018, the concentrations of total amines (∑amines; the summation of MA, EA, DMA, IPA, PA, and TMDEA) in TSP ranged from 16.2 ng m^{-3} to 89.1 ng m^{-3} (Figure 1). Lower ∑amines concentrations were observed over the SYS and NYS, averaging 40.4 ± 16.4 ng m^{-3} and 43.5 ± 17.5 ng m^{-3}, respectively, and higher concentrations occurred over the BS, averaging at 63.6 ± 18.3 ng m^{-3}. Concentrations of other chemical components, including total WSIIs, TC, and total measured organic compositions, exhibited a similar spatial pattern (SYS < NYS < BS; Table S2).

TMDEA was the predominant amine species in TSP over the YS−BS, with concentrations ranging from 6.1 ng m^{-3} to 36.3 ng m^{-3} (Figure S4) and averages of 20.7 ± 9.1 ng m^{-3}, 17.8 ± 7.3 ng m^{-3}, and 23.8 ± 3.7 ng m^{-3} over the SYS, NYS, and BS, respectively. The fraction of TMDEA in ∑amines decreased from the SYS (51.2%) to the NYS (40.8%) and BS (37.4%). The concentrations of amines measured in TSP were comparable to those in $PM_{2.5}$ and PM_{10} (Table S3), as amines are predominantly (> 70%) distributed in aerosols with diameters < 1.8 μm (Zhou et al., 2019; Xie et al., 2018; Yu et al., 2016). Compared with other marine and coastal regions, the aerosol TMDEA concentrations in spring over the YS−BS were higher than those reported for the East China Sea (ECS), Huaniao Island (in the ECS), South China Sea (SCS), and Northwest Pacific Ocean (NWPO) (Chen et al., 2022; Zhou et al., 2019; Xie et al., 2018; Yu et al., 2016). Over the YS−BS, aerosol TMDEA

concentrations were higher in summer than in spring and autumn (Xie et al., 2018; Yu et al., 2016).

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

DMA concentrations ranged from 1.3 ng m^{-3} to 10.4 ng m^{-3}, with averages of 3.5 ± 2.1 ng m^{-3}, 3.8 ± 2.6 ng m^{-3}, and 7.9 ± 2.1 ng m^{-3} in TSP over the SYS, NYS, and BS, respectively. Higher DMA contributions to ∑amines were found over the BS (12.4%) than the NYS (8.7%) and SYS (8.6%). The average aerosol DMA concentration over the YS−BS in spring (4.4 ng m^{-3}) was much lower than those reported for coastal Qingdao in winter and for the YS−BS in different seasons in previous years (Table

S3). EA (0.6−4.8 ng m^{-3}), IPA (0.5−3.9 ng m^{-3}), and PA (1.3−5.1 ng m^{-3}) constituted a relatively small fraction of ∑amines (7.3−28.2%), with average concentrations of 2.0 ± 1.2 ng m^{-3}, 1.8 ± 1.0 ng m^{-3}, and 2.9 ± 1.0 ng m^{-3} in TSP over the YS−BS, respectively. The average aerosol EA concentration over the BS (3.0 ng m^{-3}) was comparable to those observed at coastal Qingdao (Liu et al., 2022) and Jeju Island, South Korea (Yang et al., 2004). Comparable data for EA, IPA, and PA concentrations in marine aerosols were currently limited.

According to air-mass analyses (Figure S3), S3 and S12−19 (include all samples from the NYS−BS) were strongly influenced by continental outflow, while S5, S6, and S8 (from the SYS) were dominated by marine air masses. The remaining samples were affected by mixed terrestrial and marine air masses. Higher concentrations of MA (16.0 ± 11.5 ng m^{-3}), EA (2.3 ± 1.4 ng m^{-3}), DMA (5.3 ± 2.9 ng m^{-3}), and PA (3.2 ± 1.0 ng m^{-3}) were observed in samples influenced by continental outflow compared to those dominated by marine air masses (MA: 10.0 ± 6.6 ng m^{-3}; EA: 1.3 ± 0.2 ng m^{-3}; DMA: 2.0 ± 0.1 ng m^{-3}; and PA: 2.3 ± 1.0 ng m^{-3}). In contrast, TMDEA concentrations were higher in samples dominated by marine air masses (27.6 ± 9.1 ng m^{-3}) than those influenced by continental outflow (19.8 ± 7.4 ng m^{-3}). Strong positive correlations were observed among MA, EA, and DMA ($R = 0.73–0.77$, $P < 0.01$), whereas no statistically significant correlation ($P > 0.05$) exhibited between IPA, PA, or TMDEA and other amine species. These results suggested that MA, EA, and DMA might share similar sources and secondary formation pathways, whereas IPA, PA, and TMDEA were likely influenced by different sources or atmospheric processes.

3.2 Relative contributions of amines in TSP over the YS−BS

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

Positive correlations were found between NH_4^+ and amines, including MA ($R = 0.78$, $P < 0.01$), DMA ($R = 0.74$, $P < 0.01$), EA ($R = 0.57$, $P < 0.05$), PA ($R = 0.58$, $P < 0.05$), and TMDEA ($R = 0.52$, $P < 0.05$). Aerosol NH_4^+ is formed via the heterogeneous uptake of NH_3, the most abundant alkaline gas in the atmosphere, by acidic aerosols, and exists as ammonium sulfate [$(NH_4)_2SO_4$], ammonium bisulfate (NH_4HSO_4), ammonium nitrate (NH_4NO_3), and ammonium chloride (NH_4Cl) (Behera et al., 2013). Atmosphere NH_3 shares overlapping source profiles with gaseous amines, including animal husbandry, biomass burning, vehicle emissions, industrial activities, soil, and the ocean. This was inferred as the reason for considerable correlations between NH_4^+ and amines in aerosols.

Gaseous low molecular weight amines are more alkaline than NH_3, and may compete with NH_3 in atmospheric acid-base reactions (Sorooshian et al., 2008; Chen et al.,

2022). The molar ratios of aerosol amines to NH_4^+ were calculated to assess their relative contributions to the neutralization of acidic species in aerosols (Hu et al., 2015). The ∑amines/NH_4^+ molar ratios (4.8–17.0‰) were 9.7 ± 3.4‰, 7.6 ± 0.8‰, and 6.8 ± 1.8‰ over the SYS, NYS, and BS, respectively. The spatial pattern of ∑amines/NH_4^+ molar ratios (SYS > NYS > BS) was consistent with that of the ∑amines-C/OC ratios, both indicating a north-to-south increase in the relative contributions of amines to aerosol composition over the YS−BS.

The ∑amines/NH_4^+ molar ratios obtained in this study were of the same order of magnitude as those reported previously (Xie et al., 2018; Yu et al., 2016). Overall, amines contribute negligibly to the neutralization of acidic species in TSP compared with NH_4^+, which is reasonable given the much higher atmospheric abundance of NH_3 relative to gaseous amines (Zheng et al., 2015; You et al., 2014; Ge et al., 2011a, b). However, amines potentially play a more important role in neutralizing acidic species in submicron particles, particularly in the presence of organic compounds (Xie et al., 2018). The composition of NH_4^+, NO_3^-, and SO_4^{2-} may influence aerosol amines, as they can act as competitors for neutralization and as major reactants in aerosol formation. The $NH_4^+/(Cl^- + NO_3^- + 2\times SO_4^{2-})$ molar ratios is commonly used to assess whether NH_4^+ fully neutralizes acidic species (Cl^-, NO_3^-, and SO_4^{2-}) in aerosols. In this study, the ratios in TSP over the YS−BS were mostly < 1 (0.8 ± 0.2; Figure 2 and Figure S5), indicating NH_4^+ deficiency. This deficiency was more markedly over the BS (0.6 ± 0.0) than the YS (0.8 ± 0.2). The NO_3^-/SO_4^{2-} molar ratios in TSP over the SYS (0.8 ± 0.8) were significantly lower than those over the

NYS (2.3 ± 0.4) and NYS (2.3 ± 0.4) and BS (2.5 ± 0.8), indicating that SO_4^{2-} was the dominate acidic species in SYS aerosols, whereas NO_3^- dominated in NYS and BS aerosols. The composition of NH_4^+, NO_3^-, and SO_4^{2-} in NYS aerosols was intermediate between that over the BS and SYS, consistent with the regional variations in amines concentrations and composition. Molar concentrations of ∑amines increased with increasing NH_4^+ deficiency [indicated by $NH_4^+/(Cl^- + NO_3^- + 2\times SO_4^{2-})$ molar ratios; $R = -0.57$, $P < 0.05$] and with NO_3^-/SO_4^{2-} ratios ($R = 0.56$, $P < 0.05$), particularly in BS aerosols. Nevertheless, individual amines responded differently to variations in NH_4^+ deficiency and NO_3^-/SO_4^{2-} molar ratios, likely reflecting differences in their primary sources (terrestrial vs. marine) and formation pathways (nitrate vs. sulfate associated).

3.3 Source analysis of amines in TSP over the YS−BS

3.3.1 Biogenic sources

On a global scale, ocean is a major source of gaseous methylamines (fluxes: TMA > MA >> DMA) (Van Neste et al., 1987; Schade and Crutzen, 1995). Intensive ocean farming is widespread in the coastal areas of the YS−BS (Hu et al., 2015), where marine biogenic sources, including fish emission (Namieśnik et al., 2003), biodegradation of nitrogen-containing materials, and decay process (Calderón et al., 2007) may release gaseous amines into the atmosphere. The concentration of Chl *a* in surface seawater is an indicator of phytoplankton biomass and thus reflects the

intensity of marine biogenic emissions to some extent. Significantly higher Chl *a* concentrations were observed in the BS than in the YS, with relatively elevated values in near shore areas (Figure S2). The spatial distribution of ∑amines in TSP over the YS−BS was broadly consistent with, though not identical to, Chl *a* concentrations in surface seawater. This discrepancy likely reflected secondary formation of amines in aerosols, as well as the influence of long-range transportation of terrestrial emissions driven by the prevailing East Asia monsoon during spring, particularly to S3 and S12−19 (Figure S3).

Aerosol MA, EA, and DMA exhibited positive linear relationships with total primary sugars and sugar alcohols (Figure 3 a−c and Table S4), which mainly originate from primary biogenic sources such as bacteria, pollen, and plant or animal debris (Li et al., 2019b). These sources can be either marine or terrestrial. Fungal spore OC and plant debris OC were estimated from mannitol and arabitol (Bauer et al., 2008), and glucose (Zheng et al., 2018), respectively. Significant positive correlations were observed between MA, EA, and DMA and fungal spore OC, plant debris OC, and several individual primary sugars and sugar alcohols (e.g., trehalose, α-fructose, and sucrose; $R > 0.50$, $P < 0.05$). DMA exhibited the strongest correlation with trehalose ($R = 0.71$, $P < 0.01$), a compound abundant in microorganisms, algae, plants, and invertebrates, and also acts as an indicator of re-suspended dust (Medeiros et al., 2006; Simoneit et al., 2004). In addition, MA, DMA, and PA were positively correlated with high molecular weight *n*-alkanes (ALK_{HMW}; C_{27}, C_{29}, C_{31} and C_{33}) and fatty alcohols (ALC_{HMW}; > C_{19alc}; Figure 3 d−e), while PA also correlated with low molecular

weight fatty acids (FA_{LMW}; ≤ $C_{19:0}$; Figure 3 f). ALK_{HMW} (Rogge et al., 1993), ALC_{HMW} (Simoneit et al., 1991), and high molecular weight fatty acids (FA_{HMW}; > $C_{19:0}$) are tracers of higher plant waxes from terrestrial vegetation, whereas FA_{LMW} are associated with marine/microbial sources (Haque et al., 2019). Overall, these findings indicated that amines (MA, EA, DMA, and PA) in TSP over the YS−BS were contributed by biogenic sources. MA and DMA were largely influenced by terrestrial biogenic emissions, whereas PA was affected by both terrestrial and marine biogenic sources.

Atmospheric biogenic secondary organic aerosols (BSOA) are formed via the photochemical oxidation of biogenic volatile organic compounds (BVOCs) by O_3, OH and NO_x (Ng et al., 2011). In this study, six isoprene SOA (SOA_I) tracers, three monoterpene SOA (SOA_M) tracers, and one *β*-caryophyllene SOA (SOA_C) tracer were measured in TSP over the YS−BS. Biogenic SOC derived from isoprene, monoterpene, and *β*-caryophyllene was estimated using the tracer-based method (Kang et al., 2018; Kleindienst et al., 2007). Significant positive linearity were observed between MA and both isoprene and monoterpene SOC (Figure 3 g−h). Among the SOA_I tracers, MA exhibited stronger correlations with 2-methyltetrols (2-MTLs; $R = 0.74$, $P < 0.01$) and C_5-alkene triols ($R = 0.66$, $P < 0.01$) than with 2-methylglyceric acid (2-MGA; $R = 0.64$, $P < 0.05$). DMA was also positively correlated with isoprene SOC ($R = 0.55$, $P < 0.05$), only driven by its association with 2-MTLs ($R = 0.59$, $P < 0.05$). Among the SOA_M tracers, pinonic acid correlated with MA ($R = 0.73$, $P < 0.01$), EA ($R = 0.52$, $P < 0.05$), and DMA ($R = 0.58$, $P < 0.05$),

366 while pinic acid only correlated with MA ($R = 0.59$, $P < 0.05$). In addition, PA showed
367 a positive linearity with β-caryophyllene SOC ($R = 0.67$, $P < 0.01$; Figure 3 i). These
368 findings supported that MA, EA, DMA, and PA shared common sources with BVOCs
369 and/or interacted with BSOA formation processes. High concentrations of amines and
370 biomarkers were simultaneously observed in aerosols over the BS and NYS, whereas
371 amines in the SYS aerosols remained at moderate levels despite low tracers
372 concentrations (Figure 3). These indicated that terrestrial biogenic emissions
373 contributed more substantially to aerosol amines over the BS and NYS than the SYS.

374

375 **3.3.2 Anthropogenic sources**

376 Anthropogenic sources are another important contributor to atmospheric amines and
377 can be broadly categorized into combustion-related sources (e.g., biomass burning,
378 coal combustion, vehicle emissions, and waste incineration) and non-combustion
379 sources (e.g., animal husbandry, composting, industrial activities, sewage, and septic
380 system). EA ($R = 0.61$, $P < 0.05$) and DMA ($R = 0.72$, $P < 0.01$) concentrations in TSP
381 over the YS−BS increased with EC, indicating the influence of combustion emissions.
382 Levogluctosan (Lev) is a well-established tracer for biomass burning (Li et al., 2019b).
383 Concentrations of Lev derived from biomass burning (Lev_{bb}) were estimated using
384 Lev and non-sea-salt K^+ ($nss\text{-}K^+ = K^+ - 0.037 \times Na^+$) with considering its
385 atmospheric degradation and ~25% non-biomass burning sources [$Lev_{bb} = 0.75 \times Lev \times nss\text{-}K^+/(0.18 \times Lev + 0.08 \times nss\text{-}K^+)$]. Biomass burning was not a major source of

MA, EA, and DMA in aerosols over the YS−BS (Figure 3 j), but contributed substantially to PA, as indicated by the positive linear relationships between PA and both Lev_{bb} and lignin products (Figure 3 k−l). The most notable contributor to PA from biomass burning was conifer burning (the second-largest portion of total biomass burning) according to the correlations between PA and individual lignin products, including 4-hydroxybenzoic acid (4-HBA; a herbaceous burning marker and the predominate lignin product in this study; $R = 0.52$, $P < 0.05$), vanillic acid (VA; a softwood and hardwood burning marker; $R = 0.67$, $P < 0.01$), syringic acid (SA; also indicative of softwood and hardwood burning; $R = 0.60$, $P < 0.05$), and dehydroabietic acid (DA; a conifer burning marker; $R = 0.71$, $P < 0.01$). In addition, MA ($R = 0.57$, $P < 0.05$) and DMA ($R = 0.54$, $P < 0.05$) were positively correlated with polycyclic aromatic hydrocarbons (PAHs), indicating potential contributions from fossil fuel combustion (Table S4). Among all amines, PA showed the strongest association with combustion-related sources, as evidenced by its correlations with multiple fossil fuel combustion tracers (Figure 3 m−o), including low molecular weight n-alkanes (ALK_{LMW}; C_{20}−C_{26}; $R = 0.67$, $P < 0.01$), PAHs ($R = 0.63$, $P < 0.05$), hopanes ($R = 0.55$, $P < 0.05$), and steranes ($R = 0.57$, $P < 0.05$).

Emissions of amines (MA, DMA, and TMA) from non-combustion anthropogenic sources, including composting, sewage, and septic systems, are largely linked to biodegradation process. Therefore, the contribution of non-combustion anthropogenic sources to amines was encompassed within the primary biogenic sources category. IPA did not show any correlation with organic molecular tracers in TSP over the

409 YS−BS. Given its widespread industrial use (e.g., in pesticides, pharmaceuticals, dye
410 intermediates, emulsifiers, detergents, surfactants, and textile additives), aerosol IPA
411 may be emitted in particulate form from specific industrial activities (Ge et al.,
412 2011a).

413

414 **3.3.3 Secondary formation of MA, EA, DMA, and PA**

415 Significant correlations were observed between MA, EA, DMA, and PA with Cl^- and
416 NO_3^- (Figure 4). The regression intercepts of MA, EA, and DMA against Cl^- or NO_3^-
417 were lower than those with primary organic tracers (Figure 3 and Figure S6),
418 indicating substantial contributions from secondary formation. Gas-to-particle
419 conversion of MA, EA, DMA, and PA was inferred to include direct dissolution
420 (Equation 1), uptake onto acidic particle surfaces (Equation 2) (Yin et al., 2011),
421 acid-base reactions (Equation 3−4), and displacement reactions with NH_4NO_3
422 (Equation 5) (Bzdek et al., 2010). For MA, EA, and DMA with high water solubility,
423 direct dissolution is considered as a key step in their gas-to-particle conversion.
424 Uptake of gaseous amines onto acidic particle surfaces was more important over the
425 BS, where aerosol acidic species are significantly in excess relative to NH_4^+. MA, EA,
426 DMA, and PA in TSP over the YS−BS were formed via acid-base reactions with
427 atmospheric HCl and HNO_3, while CH_3COOH also contributed to the formation of
428 aerosol MA, EA and DMA (Figure 4). In TSP over the YS−BS, NO_3^- concentrations
429 were significantly higher than those of Cl^- and $C_2H_3O_2^-$ (Table S2), thus, acid-base

reactions with HNO_3, together with displacement reactions involving NH_4NO_3, were the major pathways for the secondary formation of aerosol MA, EA, DMA and PA. The partitioning of amines into aerosols was further promoted by low T, high aerosol acidity, and high RH under dynamic solid/aqueous/gas equilibrium conditions. During the cruise, lower average T were observed over the BS (9.0℃) and NYS (6.7℃) than the SYS (9.5℃), and RH remained at a high level across the YS−BS (mean: 86.2%; median: 87.6%). The relatively abundant acidic species and lower T over the BS and NYS favored the partitioning of MA, EA, DMA, and PA into the particle phase compared with the conditions over the SYS.

$$R_nNH_{3-n(g)} + H_2O_{(l)} \leftrightarrow R_nNH_{4-n} \cdot OH_{(aq)} \leftrightarrow R_nNH^+_{4-n(aq)} + OH^-_{(aq)} \quad (1)$$

$$R_nNH_{3-n(g)} + H_3O^+_{(surface)} \leftrightarrow R_nNH^+_{4-n(surface)} + H_2O \quad (2)$$

$$R_nNH_{3-n(g)} + HCl_{(g)} \leftrightarrow R_nNH_{4-n}Cl_{(s)} \leftrightarrow R_nNH^+_{4-n(aq)} + Cl^-_{(aq)} \quad (3)$$

$$R_nNH_{3-n(g)} + HNO_{3(g)} \leftrightarrow R_nNH_{4-n}NO_{3(s)} \leftrightarrow R_nNH^+_{4-n(aq)} + NO^-_{3(aq)} \quad (4)$$

$$R_nNH_{3-n(g)} + NH_4NO_{3(s)} \rightarrow (R_nNH_{4-n})NO_{3(s)} + NH_{3(g)} \uparrow \quad (5)$$

Contributions of nitrate-associated secondary formation to aerosol amines were estimated from the average amine concentrations weighted by NO_3^- concentrations and regression intercepts (Figure S6). These estimates are semi-quantitative and limited by the small sample sizes, rather than representing quantitative source apportionment or mechanistic yields. Contributions of nitrate-associated secondary formation to ∑amines were highest in TSP over the BS (43.0 ± 26.9%), followed by the NYS (33.8 ± 19.7%) and SYS (21.8 ± 18.8%). Among individual amines, nitrate-associated secondary formation contributed most to MA (74.0 ± 61.5%),

452 followed by DMA (65.7 ± 44.3%), EA (52.6 ± 55.0%), and PA (35.1 ± 22.4%). PA
453 was less contributed by secondary formation, likely because it can be directly emitted
454 in particulate form or condense into aerosols after emission due to its relatively higher
455 boiling point (47.8℃) compared with MA (−6.3℃), EA (16.6℃), and DMA (7.4℃).

456 The relationships among amines (MA, EA, DMA, and PA), BSOA, and NO_3^- in TSP
457 over the YS−BS suggested potential interactions among their secondary formation
458 processes. NO_x, emitted from soil, biogenic activities, and combustion sources, are
459 important precursors for both BSOA and atmospheric HNO_3, which subsequently
460 forms nitrate aerosols. This was supported by significant positive correlations
461 between NO_3^- and SOA_I ($R = 0.88$, $P < 0.01$), SOA_M ($R = 0.86$, $P < 0.01$), and SOA_C
462 ($R = 0.64$, $P < 0.05$). The formation of MA and DMA in aerosols might occur under
463 low NO_x conditions, as evidenced by their stronger correlations with 2-MTLs or
464 C_5-alkene triols (products of isoprene photochemical oxidation under low NO_x
465 conditions) (Zheng et al., 2018; Zhang et al., 2011) than with 2-MGA (products of
466 isoprene aqueous-phase oxidation under high NO_x conditions) (He et al., 2018).
467 Strong atmospheric photo-oxidation generally accelerates the gas-phase degradation
468 of amines (Lee and Wexler, 2013), thereby reducing the formation of particle-phase
469 aminium salts. BVOCs, as precursors of BSOA, can generate HNO_3 via the "NO_3 +
470 HC" pathway, further promoting the formation of aminium nitrates. Meanwhile,
471 BSOA formation consumes atmospheric oxidants, which may reduce the degradation
472 of gaseous amines. The presence of an organic phase also enhances the
473 competitiveness of amines relative to NH_4^+ in aerosols (Xie et al., 2018). In addition,

the gas-to-particle conversion of amines may facilitate BSOA formation by providing more hygroscopic particulate surfaces.

3.3.4 Secondary formation of TMDEA

Compared with other amines, a larger fraction of TMDEA likely originated from marine sources, as evidenced by its relatively high concentrations and proportions in TSP over the SYS, especially in samples dominated by marine air masses. Previous studies also suggested marine emissions as an important potential source of TMDEA (Schade and Crutzen, 1995; Pinxteren et al., 2019). TMDEA in TSP over the YS−BS exhibited no correlation with organic molecular tracers representing primary biogenic sources or BSOA (Table S4), although terrestrial vegetation and non-combustion anthropogenic sources are also potential sources of gaseous TMDEA (Zhu et al., 2022; Ge et al., 2011a). Concentrations of aerosol TMDEA were likely constrained by gas-to-particle conversion efficiency. A hypothesis is that part of gaseous TMA emitted from primary sources is consumed through reactions with NO_3 to form non-aminium-salt SOA (Price et al., 2016; Price et al., 2014) and HNO_3 (Equation 6–7).

$$(CH_3)_3N_{(g)} + \cdot NO_{3(g)} \rightarrow \cdot CH_2N(CH_3)_{2(g)} + HNO_{3(g)} \quad (6)$$

$$\cdot CH_2N(CH_3)_{2(g)} + O_{2(g)} \rightarrow \cdot OOCH_2N(CH_3)_{2(g)} \quad (7)$$

TMDEA in TSP over the YS−BS showed no correlation with Cl^-, or NO_3^-, but exhibited significant positive linear relationships with SO_4^{2-}, $C_4H_4O_4^{2-}$, and $C_5H_6O_4^{2-}$

(Figure 4 and Figure S6). The gas-to-particle conversion of TMDEA was inferred to include uptake onto acidic particle surfaces (Equation 2), acid-base reactions with H_2SO_4 (Equation 8) and dicarboxylic acids ($C_4H_6O_4$ and $C_5H_8O_4$), as well as displacement reactions with $(NH_4)HSO_4$ and $(NH_4)_2SO_4$ (Equation 9−10). Uptake onto acidic particle surfaces is considered as a key step in the gas-to-particle conversion of TMDEA, as TMA exhibits the strongest alkalinity among gaseous amines. TMDEA in TSP over the YS−BS showed limited association with chloride and nitrate, likely due to the much lower competitiveness of TMA in forming these salts (as reflected by dissociation constants) relative to MA, EA, DMA, and NH_3 (Ge et al., 2011b). Instead, acid-base reactions with H_2SO_4, together with displacement reactions involving $(NH_4)HSO_4$ and $(NH_4)_2SO_4$, were the major pathways for the secondary formation of aerosol TMDEA. Contributions of dicarboxylic acids were relatively minor, given the significantly lower concentrations of $C_4H_4O_4^{2-}$ and $C_5H_6O_4^{2-}$ compared with SO_4^{2-} in TSP over the YS−BS (Table S2). These findings were consistent with previous laboratory and theoretical studies showing that TMA preferentially reacts with H_2SO_4 (Johnson and Jen, 2023), and that DEA exhibits the highest uptake coefficient during the irreversible reactive uptake of gaseous ethylamines by H_2SO_4 (Yin et al., 2011).

$$R_nNH_{3-n(g)} + H_2SO_{4(g)} \leftrightarrow (R_nNH_{4-n})_2SO_{4(s)} \leftrightarrow R_nNH^+_{4-n(aq)} + SO^{2-}_{4(aq)} \quad (8)$$

$$R_nNH_{3-n(g)} + (NH_4)HSO_{4(s)} \rightarrow (R_nNH_{4-n})(NH_4)SO_{4(s)} \rightarrow (R_nNH_{4-n})_2SO_{4(s)} + NH_{3(g)} \uparrow \quad (9)$$

$$R_nNH_{3-n(g)} + (NH_4)_2SO_{4(s)} \rightarrow (R_nNH_{4-n})(NH_4)SO_{4(s)} + NH_{3(g)} \uparrow \rightarrow$$

517 $$(R_nNH_{4-n})_2SO_{4(s)} + NH_{3(g)} \uparrow \quad (10)$$

518 Sulfate-associated secondary formation contributed 61.8 ± 31.6% to TMDEA in TSP
519 over the YS−BS, as estimated from average TMDEA concentrations weighted by
520 SO_4^{2-} concentrations and regression intercept (Figure S6). The contributions were
521 highest over the SYS (63.4 ± 36.2%), followed by the BS (61.4 ± 16.2%) and NYS
522 (55.8 ± 29.3%). Correspondingly, sulfate-associated secondary formation contributed
523 23.0 ± 6.0%, 22.8 ± 13.7%, and 32.5 ± 22.1% to ∑amines over the BS, NYS, and
524 SYS, respectively. The spatial pattern of average contributions from sulfate-associated
525 secondary formation (SYS > BS > NYS) was consistent with that of T, indicating that
526 T conditions influenced the relative advantages of sulfate and nitrate formation.

527 Significant positive correlations were observed between dicarboxylates ($C_4H_4O_4^{2-}$ and
528 $C_5H_6O_4^{2-}$; R = 0.78 and 0.66, P < 0.01) and non-sea-salt sulfate (nss-SO_4^{2-} = SO_4^{2-} −
529 0.2516 × Na^+), indicating that these species shared similar potential terrestrial
530 anthropogenic or marine biogenic origins (Miyazaki et al., 2010; Mochida et al.,
531 2003). Molar concentrations of biogenic-SO_4^{2-} were estimated from T and MSA^-, as
532 both MSA^- and SO_4^{2-} are oxidation products of DMS emitted from marine biogenic
533 sources (Nakamura et al., 2005; Bates et al., 1992). Anthropogenic-SO_4^{2-} was then
534 calculated by nss-SO_4^{2-} subtracting biogenic-SO_4^{2-}. The result showed that
535 biogenic-SO_4^{2-} accounted for 11.1% of total SO_4^{2-} in TSP over the SYS, markedly
536 higher than the NYS (4.3%) and BS (2.1%), yet still representing a minor fraction
537 relative to anthropogenic-SO_4^{2-}. Consequently, TMDEA in TSP over the YS−BS was
538 predominantly taken up by anthropogenic sulfate aerosols.

High concentrations of TMDEA, SO_4^{2-}, $C_4H_4O_4^{2-}$, and $C_5H_6O_4^{2-}$ were simultaneously observed in S5 and S6 over the SYS, along with relatively high marine biogenic contributions (Biogenic-SO_4^{2-}/SO_4^{2-}: 11.2% and 10.3%). NH_4^+ deficiency [NH_4^+/(Cl^- + NO_3^- + 2*SO_4^{2-}): 0.8 and 0.6], high T (12.2℃ and 12.1℃), high wind speed (6.9 m s^{-1} and 7.2 m s^{-1}), and saturated humidity (RH = 100%) were also found in S5 and S6 (Table S1). Under high RH, more amines partition into aqueous aerosols via direct dissolution, promoting aminium salts formation, whereas high T shifts the solid/aqueous/gas equilibrium of aminium salts toward the gas phase. Compared with the chlorides and nitrates of MA, EA, DMA, and PA, TMDEA sulfates are more thermally stable. In addition, strong winds enhance the emission of primary marine aerosols from sea spray and bubble bursting, providing additional amines to TSP, as amines are present in both seawater and primary marine aerosols. The source contributions and major secondary formation pathways of amines were summarized in Figure 5.

4 Conclusions

This study systematically analyzed the spatial variations, potential sources, and secondary formation mechanisms of six major low molecular weight amines in aerosols over the marginal seas of China. Concentrations of total amines, water soluble inorganic ions, carbonaceous components, and more than 100 organic compositions generally exhibited a north-to-south decreasing pattern from the BS to

the NYS and SYS. This trend was consistent with the decreasing influence of continental emissions from mainland East Asia, coupled with the increasing contribution of the marine atmosphere.

Offshore aerosols exhibited distinct compositions of amines compared to terrestrial aerosols, with TMDEA surpassing MA as the predominant amine. The proportions of TMDEA in ∑amines and the relative contributions of ∑amines in aerosols increased from north to south (BS < NYS < SYS), highlighting the ocean as a substantial source of amines, particularly TMDEA, despite the significant influence of terrestrial emissions. Distinct potential sources and major secondary formation pathways were identified for different amine species. MA, EA, and DMA were mainly derived from terrestrial biogenic and non-combustion anthropogenic sources, followed by fossil fuel combustion, with over 50% formed via nitrate-associated secondary formation pathways, interacting with BSOA formation in the NO_x-involved oxidation of BVOCs. In comparison, PA was mainly originated from combustion-related sources along with terrestrial and marine biogenic sources, with only ~35% contributed by nitrate-associated secondary formation. In contrast to other amines, TMDEA was mostly (~60%) generated via sulfate-associated secondary formation pathways, and also contributed by primary marine aerosols from sea spray and bubble bursting.

Terrestrial sources not only emit gaseous amines but also contribute acidic aerosols that can further uptake amines from marine sources during the transportation of air masses from the mainland to the ocean. This process affects the physiochemical properties and climate effects of marine aerosols, as well as the carbon and nitrogen

582 cycles. In addition to precursors abundance, ambient conditions also influence the
583 secondary formation of aerosol amines, leading to temporal and spatial variations in
584 their concentrations and compositions. Overall, our findings improve the
585 understanding of amines in marine aerosols, highlight the impact of terrestrial
586 emissions on offshore aerosol chemistry, and underscore the importance of multiphase
587 chemical processes of amines under diverse ambient conditions.

588

589 *Data availability.* Data are available from the corresponding author on request
590 (dryanlinzhang@outlook.com).

591

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

593

594 *Author contributions*. Xiao-Ying Yang wrote the draft and produced all the figures and
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596 revised the paper. Chang-Liu Wu, Yu-Xian Zhang, and Wen-Huai Song provided the
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598

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600

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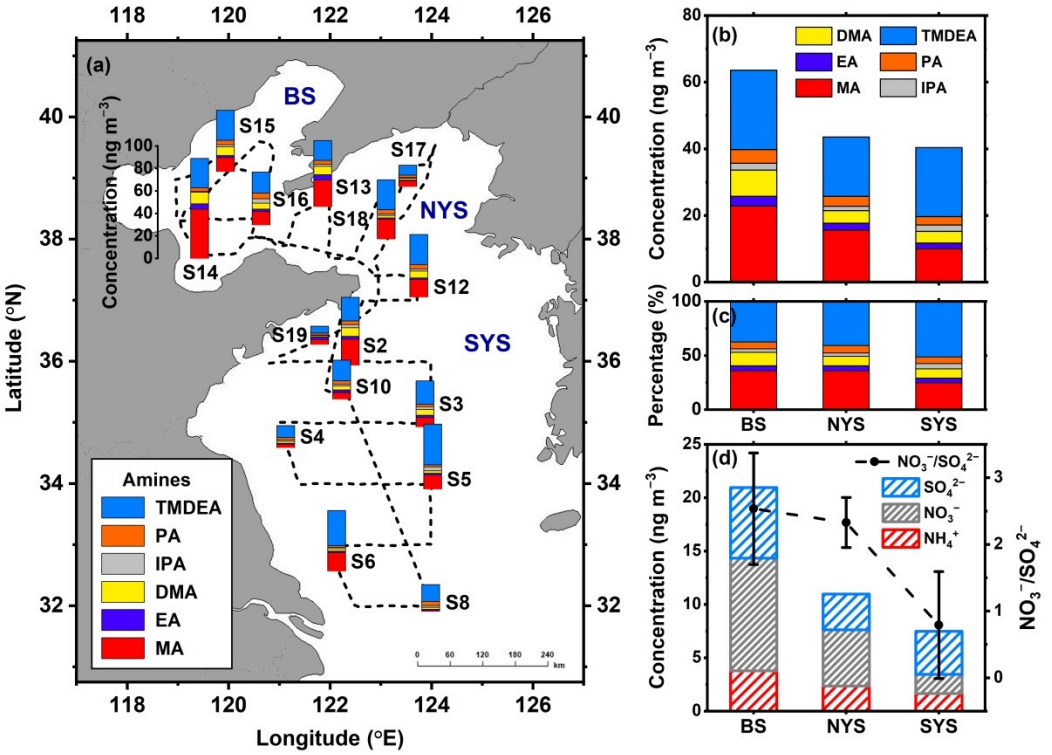

966

967 **Figure 1.** Concentrations of amines in 15 TSP samples (a) collected along the cruise
968 track (black dotted line); average concentrations (b) and relative contributions (c) of
969 amines; and concentrations of NH_4^+, NO_3^-, and SO_4^{2-}, along with NO_3^-/SO_4^{2-} molar
970 ratios (d), in TSP over the SYS, NYS, and BS.

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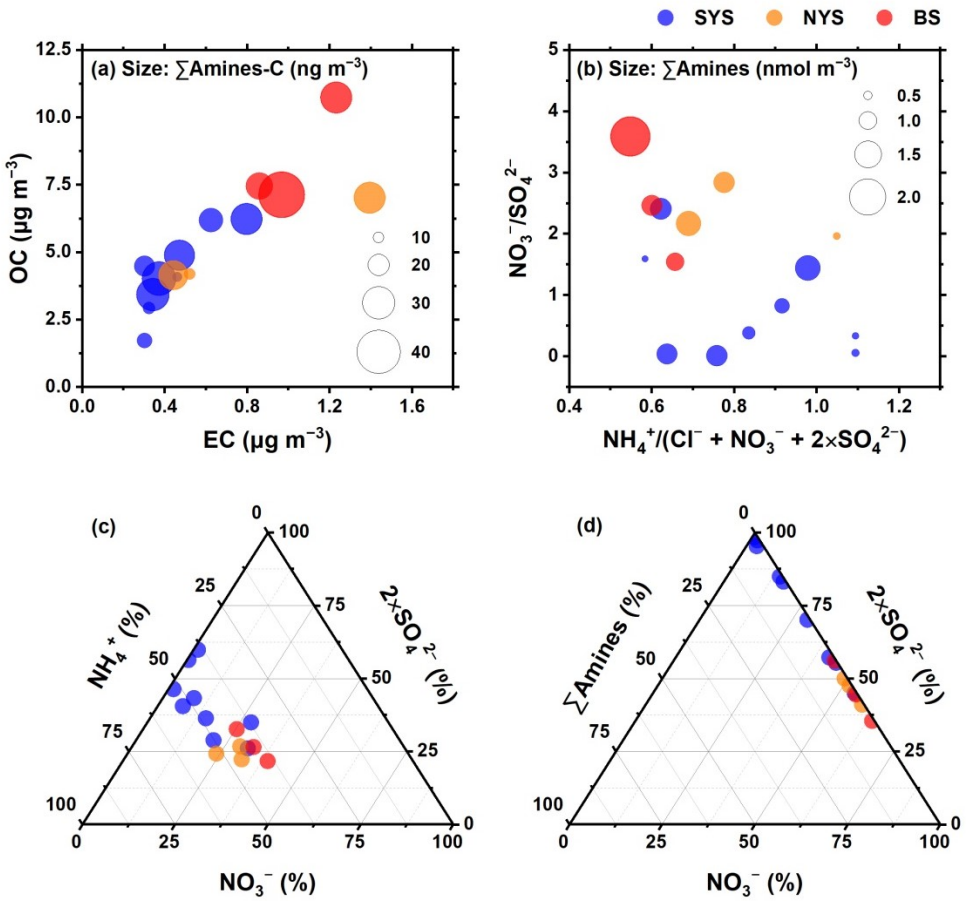
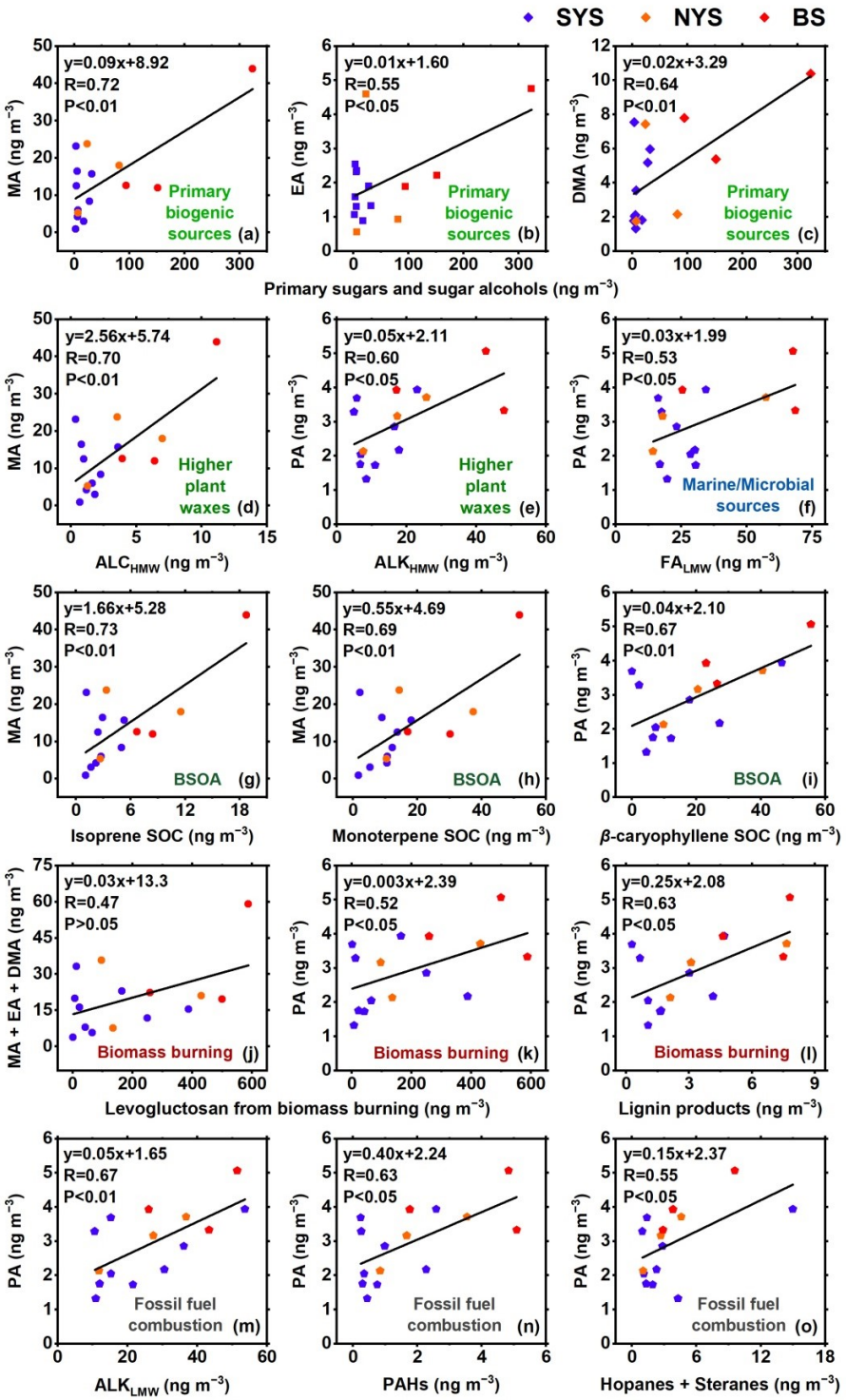


Figure 2. Variations of ∑amines-C with OC and EC concentrations (a); variations of ∑amines molar concentrations with the NO_3^-/SO_4^{2-} and $NH_4^+/(Cl^- + NO_3^- + 2\times SO_4^{2-})$ molar ratios (b); ternary diagram of the molar ratio of NH_4^+, NO_3^-, and SO_4^{2-} (c); and ternary diagram of the molar ratio of ∑amines, NO_3^-, and SO_4^{2-} (d) in TSP over the SYS, NYS, and BS.



979

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

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

982 BS.

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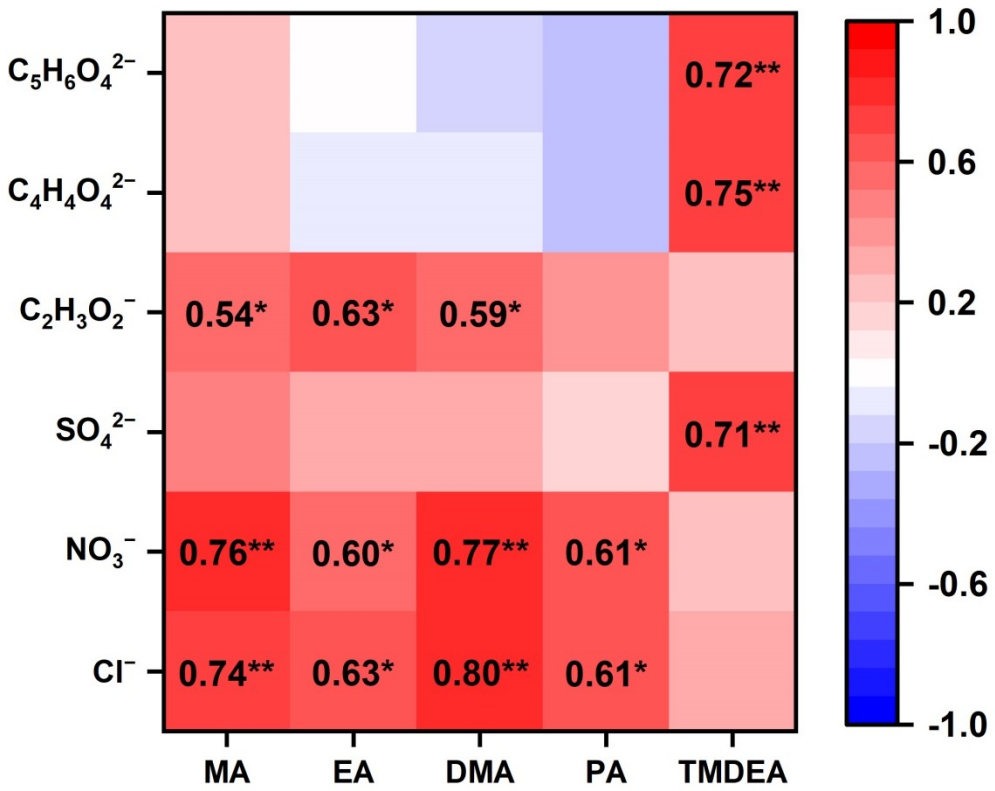

984

985 **Figure 4.** Correlation coefficient matrix between amines and acidic species in TSP

986 over the YS−BS. Numbers indicate correlation coefficients that passed the

987 significance test; ** denotes $P < 0.01$, and * denotes $P < 0.05$.

988

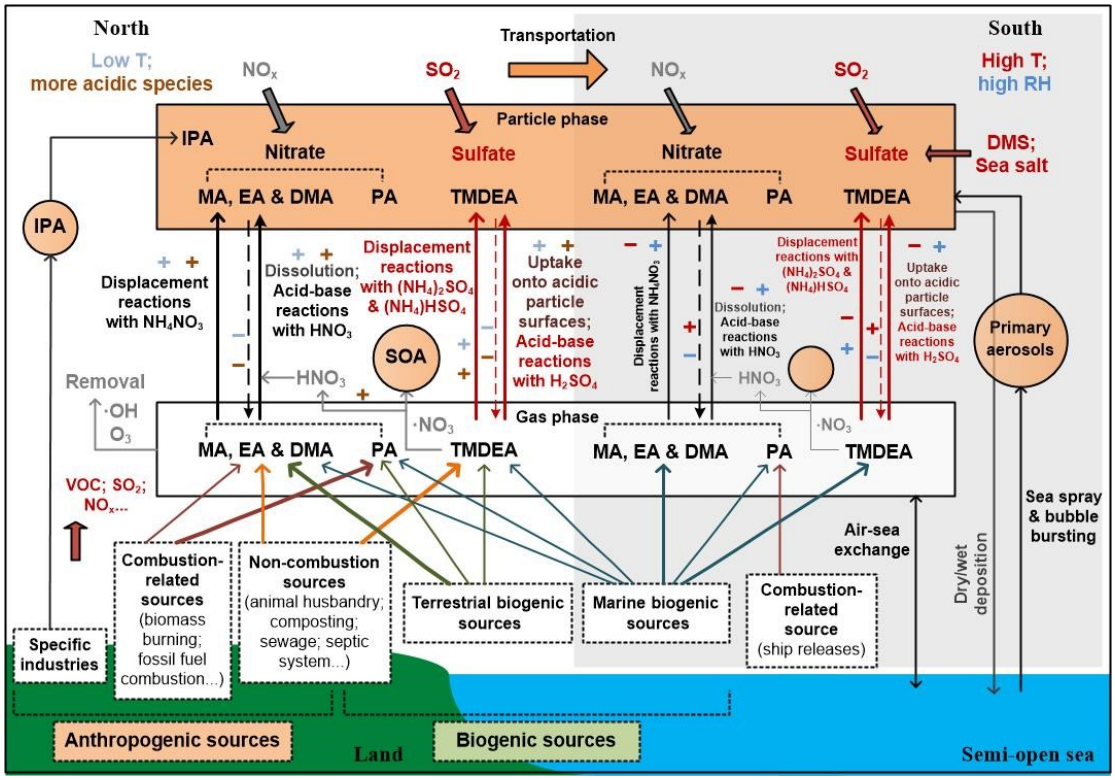

Figure 5. Schematic diagram illustrating the source contributions and major secondary formation mechanisms of amines, along with the influences of environmental conditions over the YS−BS.