Large contributions of anthropogenic sources to amines in fine particles at a coastal area in northern China in winter

Zhiyi Liu [a], Min Li [a], Xinfeng Wang [a,*], Yiheng Liang [a,c,d], Yueru Jiang [a], Jing Chen [a], Jiangshan Mu [a], Yujiao Zhu [a], He Meng [e], Lingxiao Yang [a], Keyong Hou [a], Yifeng Wang [b], Likun Xue [a]

[a] Environment Research Institute, Shandong University, Qingdao 266237, China
[b] School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China
[c] Department of Environmental Systems Science, Swiss Federal Institute of Technology Zurich, Zurich 8092, Switzerland
[d] Department of Water Resources and Drinking Water, Swiss Federal Institute of Aquatic Science and Technology, Duebendorf 8600, Switzerland
[e] Qingdao Eco-Environment Monitoring Center of Shandong Province, Qingdao 266003, China

HIGHLIGHTS

- Fifteen amines in ambient fine particles were identified and quantified by UHPLC-MS.
- DMA and TMA were the most abundant amines in $PM_{2.5}$ in winter in coastal Qingdao.
- Elevated concentrations of amines were associated with coal combustion activities.
- Particulate amines were apt to increase in the condition of high humidity.
- Anthropogenic sources were the major sources of most particulate amines.

GRAPHICAL ABSTRACT
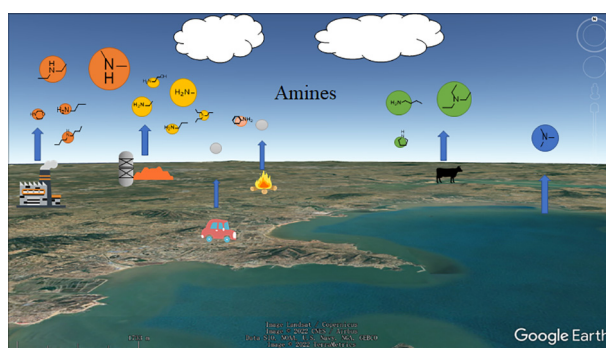
ARTICLE INFO

Editor: Pingqing Fu

ABSTRACT

Amines in fine particles constitute a significant fraction of secondary organic aerosols and have adverse effects on air quality and human health. To understand the chemical composition, variation characteristics, and potential sources of fine particulate amines in the coastal area in northern China, field sampling and chemical analysis were conducted in coastal Qingdao in the winter of 2018 and 2019. A total of 15 major amines were identified and quantified by using an ultra-high-performance liquid chromatography coupled with mass spectrometry. The average concentration of total amines in $PM_{2.5}$ samples was approximately 130 ng m^{-3}. Dimethylamine was the most abundant species with average fractions of 44.8% and 65.0% in the quantified amines during the two field campaigns, followed by triethylamine (22.9% and 8.7%) and methylamine (8.3% and 4.4%). The amines in $PM_{2.5}$ usually exhibited elevated concentrations in the presence of high levels of SO_2 and NO_x or in the condition of high relative humidity. A receptor model of positive matrix factorization was employed and seven major sources were identified, including coal combustion, industrial production, vehicle exhaust, biomass burning, agricultural activities, secondary formation, and marine emission. Surprisingly, most of 15 amines in fine particles primarily originated from the primary emissions of anthropogenic activities particularly related to coal combustion and industrial productions, which should be given close concern to address the amine pollution.

* Corresponding author.
  E-mail address: xinfengwang@sdu.edu.cn (X. Wang).

1. Introduction

Amines, ammonia derivatives with at least one hydrogen atom substituted by alkyl or aryl groups, are an important kind of nitrogen-containing organic compounds in the tropospheric atmosphere. They can be oxidized by oxidants (OH radical, ozone and NO$_x$) and react with inorganic or organic acids *via* acid-base reactions to form secondary organic aerosols (SOAs), aggravating and the air quality atmospheric visibility (Murphy et al., 2007; Pratt et al., 2009; Qiu and Zhang, 2013; Tong et al., 2020). In addition, amines, in particular dimethylamine (DMA), anticipate the H$_2$SO$_4$-H$_2$O multi-component nucleation, promoting the new particle formation (Almeida et al., 2013; Choi et al., 2020; Ma et al., 2020; Quéléver et al., 2022; Yao et al., 2018) and enhancing the particle hygroscopicity (Chu et al., 2015), and further affecting the cloud condensation nuclei (Cai et al., 2021; Tang et al., 2016). The reactions between amines with carbonyl compounds also produce light-absorbing products such as imidazole (De Haan et al., 2009; Lin et al., 2015; Marrero-Ortiz et al., 2019; Rodriguez et al., 2017), and thus influence atmospheric radiation and regional climate. Furthermore, amines or their oxidization products, *e.g.*, carcinogenic nitrosamines generated by amines and nitrites, will increase the human health risk (Lee and Wexler, 2013). Owing to the substantial impacts on air quality, regional climate, and human health, increasing attentions have been paid to amines in the ambient atmosphere.

There are a number of amines in the troposphere and they come from various emission sources or atmosphere processes. Up to now, more than 150 amines have been detected in the atmosphere, among which low-molecular-weight amines are the most abundant (Ge et al., 2011a). As semi-volatile reactive compounds, amines are released to the atmosphere in both gas and particle phases. They are not only emitted from natural sources, such as ocean (Hu et al., 2015; Müller et al., 2019) and vegetation (Chen et al., 2019; Sintermann and Neftel, 2015), but also are produced from many anthropogenic sources including industry (Fuselli et al., 1982; Rappert and Müller, 2005), vehicle exhaust (De Abrantes et al., 2009; Perrone et al., 2016), biomass burning (Simoneit et al., 2003; Toribio et al., 2000), animal husbandry (Cape et al., 2011; Ge et al., 2011a), and so on. Among these emission sources, animal husbandry, ocean, and biomass burning were considered as the important sources of atmospheric amines, with annual global fluxes of methylamines up to 146.28, 80, and 60 Gg N, respectively (Ge et al., 2011a). Recently, however, accompanied by the rapid urbanization, anthropogenic sources especially nonagricultural emissions contribute more in urban areas (Chang et al., 2022; Shen et al., 2017). Once released into the atmosphere, because of the high solubility, the gas-phase amines can transfer into particle phase *via* dissolution in liquid water on aerosol surfaces or small droplets especially in high humidity (Sellegri et al., 2005). Low air temperature and acidic aerosols are in favor of the partitioning of gaseous amines to particles, due to the volatility and alkalinity, respectively (Chen et al., 2019; Ge et al., 2011b; Liu et al., 2018; Zhou et al., 2019). So far, accurate determination of all major components of amines in ambient particulate matters is still a challenge owing to the very low abundances, and extensive filed observations are required to obtain comprehensive understanding on their atmospheric behaviors.

The atmospheric abundances and chemical composition of amines in fine particles vary significantly with locations, seasons, and atmospheric conditions. Generally, the amines in aerosols present elevated concentrations in marine atmosphere due to the strong emissions from biogenic activity, with the average values up to 600 ng m^{-3} (Hu et al., 2015). The concentrations of particulate amine in urban areas are also relatiuvely high, in the level of 45–140 ng m^{-3}, due to the intensive human activities (Akyüz, 2007; Akyüz, 2008; Ho et al., 2016; Ho et al., 2015; Liu et al., 2017). In elevated troposphere, they are substantially low, *e.g.*, 12.4–20.7 ng m^{-3} at a mountain site in Guangdong (Liu et al., 2018). In addition, amines in fine particles exhibit distinct seasonal variations in the abundance. In the coastal region, amine containing particles are usually more abundant in summer than in winter due to the acidity of particles (Lian et al., 2020; Pratt et al., 2009). However, their concentrations can be higher in winter than in summer in continental areas because of the pollutant accumulation within relatively low boundary layer, the enhanced gas-particle partitioning under low temperature, and the enlarged anthropogenic emissions for heating (Akyüz, 2007; Akyüz, 2008; Chen et al., 2019; Cheng et al., 2018; Ho et al., 2015; Müller et al., 2019; Wang et al., 2021b; Xu et al., 2021). Among the major amine components in particles, trimethylamine (TMA), dimethylamine (DMA), methylamine (MA), diethylamine (DEA), and triethylamine (TEA) usually account for large proportions (Chen et al., 2019; Cheng et al., 2018; Du et al., 2021; Ho et al., 2016; Lian et al., 2020). Particularly, extremely high concentrations of DMA and TMA were observed in marine particles (Müller et al., 2019) and relatively high concentrations of particulate TEA was found in the atmosphere predominated by industrial sources (Zhou et al., 2019). As for the coastal region, due to the influences from both marine natural and terrestrial anthropogenic sources (Ditto et al., 2022), amines in atmospheric particulate matters turn to be rather complex. Previous studies have demonstrated the important contributions of marine and anthropogenic sources to aerosol amines in coastal areas near the East Sea (Xu et al., 2021; Zhou et al., 2019); nevertheless, the variation characteristics and major sources remain unclear in polluted coastal atmosphere, especially in the coastal region in northern China.

In this study, a method in combination of ultra-high- performance liquid chromatography (UHPLC) and mass spectrometer (MS) was deployed to identify and quantify 15 low-molecular-weight amines in fine particles at a coastal area in northern China in cold season. The concentrations and the compositions of measured amines in fine particles during the sampling period are firstly presented. The variation characteristics and the key influencing factors were then analyzed. Finally, the major sources and the contributions were investigated by using a receptor model.

2. Experiments and methods

2.1. Sampling site

In-situ sampling and measurements were conducted at a coastal area in Qingdao in northern China, an important port city surrounded by the Yellow Sea and the Bohai Sea. The sampling site in winter of 2018 is situated at the rooftop of a four-floor education building in the Qingdao Campus of Shandong University (36.36° N, 120.69° E). The site in winter of 2019 is located at the rooftop of a five-floor office building in the Entrepreneurship Center of Blue Silicon Valley (36.35° N, 120.67° E). The two sites are very close to the ocean (within a range of 1.1 km) and are also close to each other (with a linear distance only 2.2 km). They are surrounded by educational buildings, office buildings, residential districts, villages, and farmlands and several low-volume roads and a few small factories are scattered nearby. Overall, the sampling sites represent a typical rural coastal environment influenced by multiple anthropogenic and natural sources. More information on the sampling sites can be seen in our previous studies by Liang et al. (2020), Yang et al. (2021), and Zhang et al. (2022).

2.2. Field sampling and online measurements

In this study, a medium-volume particulate matter sampler (TH-150A, Wuhan Tianhong, China) was used to collect PM$_{2.5}$ samples on quartz fiber filters (Pall, USA) at a flow rate of 100 L min^{-1}. Two filter samples were obtained each day with the daytime sample collected from 8:00 to19:30 (local time) and the nighttime sample from 20:00 to7:30 in the next morning. Prior to sampling, the filters were pre-heated at 560 °C for 3 h in a muffle furnace to remove the adsorbed organics. After sampling, the filters were stored in a refrigerator at −20 °C until subsequent chemical analysis. Before and after sampling, the filters were weighed with an electronic microbalance (ME5-F, Sartorius, Germany) under constant temperature (20 ± 0.5 °C) and humidity (50 ± 2%) to determine the mass concentrations of PM$_{2.5}$. The PM$_{2.5}$ filter samples were collected from January 10 to February 23, 2019 (winter of 2018) and November 11 to December 25, 2019 (winter of 2019). A total of 145 filter samples were collected

during the sampling periods with five extra field blank samples collected without taking in any air.

During the sampling periods, the concentrations of trace gases and the data of meteorological parameters were simultaneously measured or obtained from the published data at the adjacent station. Specifically, in January and February 2019, the concentrations of nitrogen oxides ($NO_x = NO + NO_2$), sulfur dioxide (SO_2), carbon monoxide (CO), and ozone (O_3) were measured with optical methods by using trace level gas analyzers in the measurement site (Thermo Scientific, USA) and the data of relative humidity (RH), temperature (T), wind speed, wind direction were adopted from the Weather Underground (Cloud, 2021; Liang et al., 2020). In November and December 2019, the data of trace gases and meteorological parameters were all obtained from the air quality monitoring station on the same building (Zhang et al., 2022).

2.3. Analytical method of amines

A half of the sample filter was cut and organic matters in the sample were extracted with a shaker by using 15 mL methanol for three times at constant temperature of 18 °C. After settling for more than 12 h, the extract solution was evaporated to near dryness with a rotary evaporator. Then, the residues were re-dissolved in 2 mL methanol and further filtrated through a 0.22 μm polytetrafluoroethylene syringe filter (Millex-FG, Millipore) to remove insoluble impurity. Finally, the extracts were concentrated with a gentle stream of ultra-high purity nitrogen and then were re-dissolved in 300 μL methanol for qualitative and quantitative analysis.

Amines in sample solutions were analyzed by using UHPLC (Ultimate 3000, Thermo Scientific) equipped with a quadrupole mass spectrometer (MS, ISQ EC, Thermo Scientific) detector. The separation of different amine compounds was performed with a Hydrophilic Interaction Liquid Chromatography column (HILIC, 2.1 mm × 150 mm, 3.5 μm particle size, Merck). Sample solution of 3 μL was directly injected into the UHPLC-MS without derivatization. The mobile phase consisted of eluent A (methanol) and eluent B (20 mM ammonium formate in deionized water). The gradient-elution program was started with 80% eluent A in the first 2 min. It gradually decreased to 60% within 2 min and then was then kept at 60% for 24 min. After that, it increased to 80% in 2 min and then kept at 80% for the last 10 min. The electrospray ionization (ESI) source was deployed in this study. The ion source temperature was set at 128 °C and the ion transfer tube temperature was maintained at 300 °C. High-purity nitrogen was used as the auxiliary gas and sweep gas. The mass spectrometer was operated in positive mode and selected ion monitoring (SIM) mode. Eleven m/z ratios including 32,46, 60, 62, 72, 74, 88, 94, 102, 130, and 144 amu were monitored in real time. The following eleven low-molecular-weight aliphatic amines, alcohol amine, two alicyclic amines, and aromatic amine were measured: MA, DMA, TMA, ethylamine (EA), DEA, TEA, propylamine (PA), dipropylamine (DPA), tripropylamine (TPA), butylamine (BA), dibutylamine (DBA), ethanolamine (MEA), morpholine (MOR), pyrrolidine (PYR), and aniline (AN). Detailed information of the identified amine species can be seen in Table 1. Individual standards were used to identify the specific amines based on the retention time in the spectrum and the gradient standard mixtures were used to obtain multi-point standard curves ($R^2 > 0.99$) for the quantification of the 15 amines. The amines standards and the reagent chemicals in this study were ordered from Sigma-Aldrich (USA), AccuStandard (USA), Merck (Germany), TCI (Japan), and ALAF (UK).

To exclude potential interferences to mass spectrometry signals of the targeted amines in $PM_{2.5}$ samples, high-resolution orbitrap mass spectrometer was also deployed to confirm the qualitative results and no apparent interfering substance was found. In addition, field and laboratory blank samples were also analyzed in the same way as the field samples. The concentrations of amines in field blanks were usually below the detection limits and all data were corrected according to the blank signals. To evaluate the recovery of the amines during the treatment processes, 10 μg mL^{-1} standard solutions were spiked onto blank filters with subsequent same treatment procedure and same analytical method. The recovery rates of the 15

Table 1
Detailed information on the identified 15 amines in fine particles in this study.

Full name	Chemical Structure	Molecular formula	Molecular weight	Retention time (min)	Recovery rate (%)
Aliphatic amines					
Methylamine (MA)	H_2N-	CH_5N	31.06	10.7	63
Dimethylamine (DMA)		C_2H_7N	45.08	11.3	64
Trimethylamine (TMA)		C_3H_9N	59.11	13.6	74
Ethylamine (EA)	H_2N-	C_2H_7N	45.08	9.1	64
Diethylamine (DEA)		$C_4H_{11}N$	73.14	8.2	80
Triethylamine (TEA)		$C_6H_{15}N$	101.19	9.4	84
Propylamine (PA)	H_2N-	C_3H_9N	59.11	7.9	59
Dipropylamine (DPA)		$C_6H_{15}N$	101.19	6.3	92
Tripropylamine (TPA)		$C_9H_{21}N$	143.27	5.9	76
Butylamine (BA)	$H_2N\sim\sim$	$C_4H_{11}N$	73.14	7.0	78
Dibutylamine (DBA)		$C_8H_{19}N$	129.24	5.3	84
Alcohol amine					
Ethanolamine (MEA)	H_2N-OH	C_2H_7NO	61.08	10.6	62
Alicyclic amines					
Morpholine (MOR)	HN O	C_4H_9NO	87.12	10.5	81
Pyrrolidine (PYR)		C_4H_9N	71.12	10.8	65
Aromatic amine					
Aniline (AN)	$-NH_2$	C_6H_7N	93.13	2.6	63

amines ranged from 59% to 92% (also shown in Table 1). The reproducibility of the analytical method was substantially good, with the relative standard deviations for all standards less than 10%.

In addition to amines, the contents of nitrated phenols in the PM$_{2.5}$ filter samples were also analyzed with UHPLC-MS (Liang et al., 2020). Organic carbon (OC) concentration were determined with an OCEC analyzer (Sunset, USA) by thermal–optical method under the protocol of NIOSH5040. The organic matter (OM) concentrations were estimated from the OC concentration with a factor of 1.59 based on the previous coefficient for Qingdao in winter (Xing et al., 2013).

2.4. Source appointment by positive matrix factorization (PMF) model

In this study, the positive matrix factorization (PMF, EPA 5.0) receptor model was deployed to identify the major sources of amines in fine particles. Two files of concentration data and the corresponding uncertainty were required to run the PMF model. Their values were determined as follows (Li et al., 2021; Polissar et al., 1998):
if

$$c_{ij} \leq DL_i, x_{ij} = DL_i/2, \sigma_{ij} = 5/6 DL_i \tag{1}$$

if

$$DL_i < c_{ij} \leq 3DL_i, x_{ij} = c_{ij}, \sigma_{ij} = c_{ij}/5 + DL_i/3 \tag{2}$$

if

$$c_{ij} > 3DL_i, x_{ij} = c_{ij}, \sigma_{ij} = 0.1 \times c_{ij}/10 + DL_i/3 \tag{3}$$

where c_{ij} is the measured concentration value of the species i for the sample j, DL_i is the detection limit for the species i, x_{ij} is the input concentration value of the species i for the sample j, and σ_{ij} is the uncertainty vales of the species i for the sample j.

Potential factor profiles and contributions were obtained by minimization the objective function Q (Paatero and Tapper, 1993). Four to eight factors were tested in this study and the resulting Q values, scaled residuals, and solution matrices were used to determine the most reasonable results. The PMF solutions showed decreased Q_{true}/Q_{robust} ratios from 1.48 to 1.27 with the number of factors rising from 4 to 8 factors, indicating that the data were all converging. The solutions with less than six factors did not distinguish the source factor related to coal combustion from that related to vehicle exhaust. The solutions with more than six factors, however, exhibited two source factors featured with high levels of methyl-nitrocatechols. Therefore, a six-factor solution was finally chosen as the optimal choice. The reconstructed concentrations of most compounds agreed well with their observed concentrations with the linear correlation coefficient r between 0.70 and 0.99.

3. Results and discussion

3.1. Concentrations and compositions of amines

As shown in Table 2, the total concentration of the 15 amines (Σamines) in the winter of 2018 was on average 130.7 ng m^{-3}. The total concentration in the winter of 2019 was close to that in the winter of 2018, with an average value of 132.9 ng m^{-3}, respectively. Among the 15 detected amines, DMA was the most abundant species, with average concentrations of 58.7 and 86.3 ng m^{-3} during the two sampling periods. The concentrations of TEA were also relatively high, with average values of 29.9 and 11.8 ng m^{-3}. The concentrations of TMA, DEA, MA, BA, EA, DBA, MOR, and AN were moderate, with average values generally between 1 and 10 ng m^{-3}. Other amine species including PA, MEA, PYR, DPA, and TPA were in low levels, with the average concentrations no more than 1 ng m^{-3}.

When compared with previous observations in other locations in winter by using similar analytical techniques, the total concentrations of amines in fine particles observed in coastal Qingdao in the present study are generally comparable with those measured in coastal and inland cities in northern

Table 2
Average concentrations (average ± standard deviation) of amines in fine particles in coastal Qingdao during the sampling periods in the winter of 2018 and 2019 with unit in ng m^{-3}.

Compounds	Winter of 2018	Winter of 2019
MA	8.5 ± 2.7	6.9 ± 2.0
EA	2.7 ± 1.1	2.4 ± 1.3
DMA	58.7 ± 25.8	86.3 ± 20.2
PA	0.9 ± 0.6	0.9 ± 0.5
TMA	10.9 ± 8.0	5.9 ± 4.8
MEA	0.8 ± 0.3	0.5 ± 0.2
PYR	0.6 ± 0.3	0.3 ± 0.2
BA	4.3 ± 4.4	3.7 ± 2.4
DEA	8.4 ± 4.4	8.7 ± 3.9
MOR	2.1 ± 1.2	2.0 ± 0.9
AN	1.4 ± 1.0	0.3 ± 0.2
DPA	0.3 ± 0.4	0.3 ± 0.4
TEA	29.9 ± 22.6	11.8 ± 14.6
DBA	1.2 ± 1.0	2.8 ± 1.9
TPA	0.1 ± 0.2	0.1 ± 0.1
Σamines	130.7 ± 51.9	132.9 ± 31.3

China, *e.g.*, average concentrations of 69.8 ng m^{-3} in Shanghai (Zhou et al., 2019), 133.2 ng m^{-3} in Beijing (Ho et al., 2016), and 105.3 ng m^{-3} in Xi'an (Ho et al., 2016). However, they are substantially higher than those in coastal cities in southern China, *e.g.*, average values of 45.7 ng m^{-3} in Hong Kong and 53.7 ng m^{-3} in Xiamen (Ho et al., 2016). As to individual amine species, the DMA concentration in coastal Qingdao was obviously higher than those in most other coastal and inland areas (averagely in the range of 3.6–27.3 m^{-3}) (Akyüz, 2008; Cheng et al., 2019; Du et al., 2021; Ho et al., 2016; Zhou et al., 2019). For TEA, the average concentration in coastal Qingdao is similar to the high value observed in Shanghai (35.2 ng m^{-3}) and greater than in Xianghe (0.86 ng m^{-3}) (Wang et al., 2021a; Zhou et al., 2019). For other amine compounds, the concentrations measured in this study were comparable to those observed in China and around the world or among the high values (Akyüz, 2008; Ho et al., 2016; Shen et al., 2017; Zhou et al., 2019). Overall, the concentrations of quantified amines in fine particle observed in coastal Qingdao are generally high, which
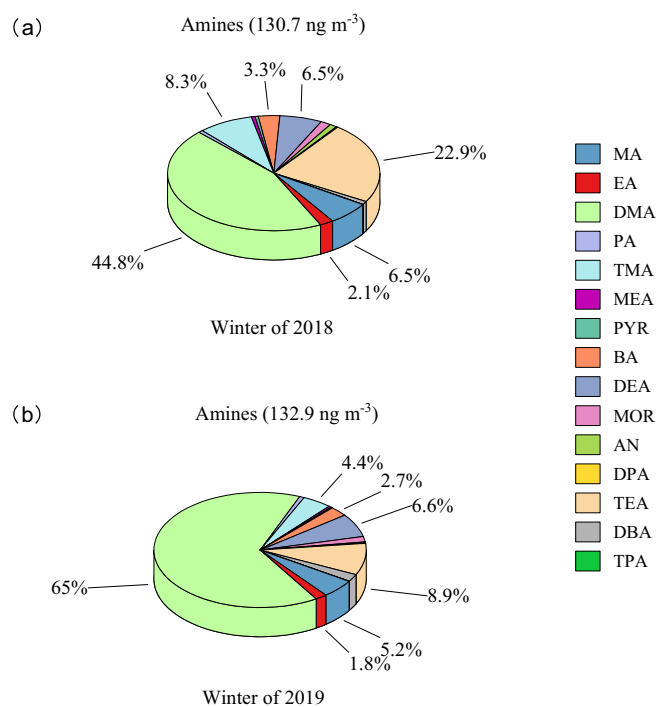

Fig. 1. Average proportions of 15 amines in fine particles in coastal Qingdao site in the winter of 2018 (a) and 2019 (b).

is mainly attributed to intensive emissions from natural and anthropogenic sources near our sampling site and is partly resulted from the comprehensive measurements of major amines with the improvement in separation and detection methods in this study. Particularly, some amines such as TMA, TEA, DBA, which were rarely measured in previous field studies, were quantified in this study and presented relatively high abundances.

As shown in Fig. 1, DMA accounted for approximately half of the total quantified amine concentration, with average proportions of 44.8% and 65.0% in the winter of 2018 and 2019, respectively. TEA also constituted

large proportions, 22.9% in the winter of 2018 and 8.7% in the winter of 2019 while TMA accounted for 8.3% and 4.4%, respectively. Overall, the sum of DMA, TEA, and TMA took rather high proportions in the detected amines, larger than three fourths. The proportions of MA, DEA, TMA, BA, and EA were moderate, generally within the range from 2% to 7%. Other amines including MOR, DBA, AN, PA, MEA, PYR, DPA, and TPA only had a minor contribution, with individual proportions less than 2%. The dominance of DMA, TEA, and TMA in coastal Qingdao is similar to that found in Shanghai (Zhou et al., 2019), but different from the situation dominated by
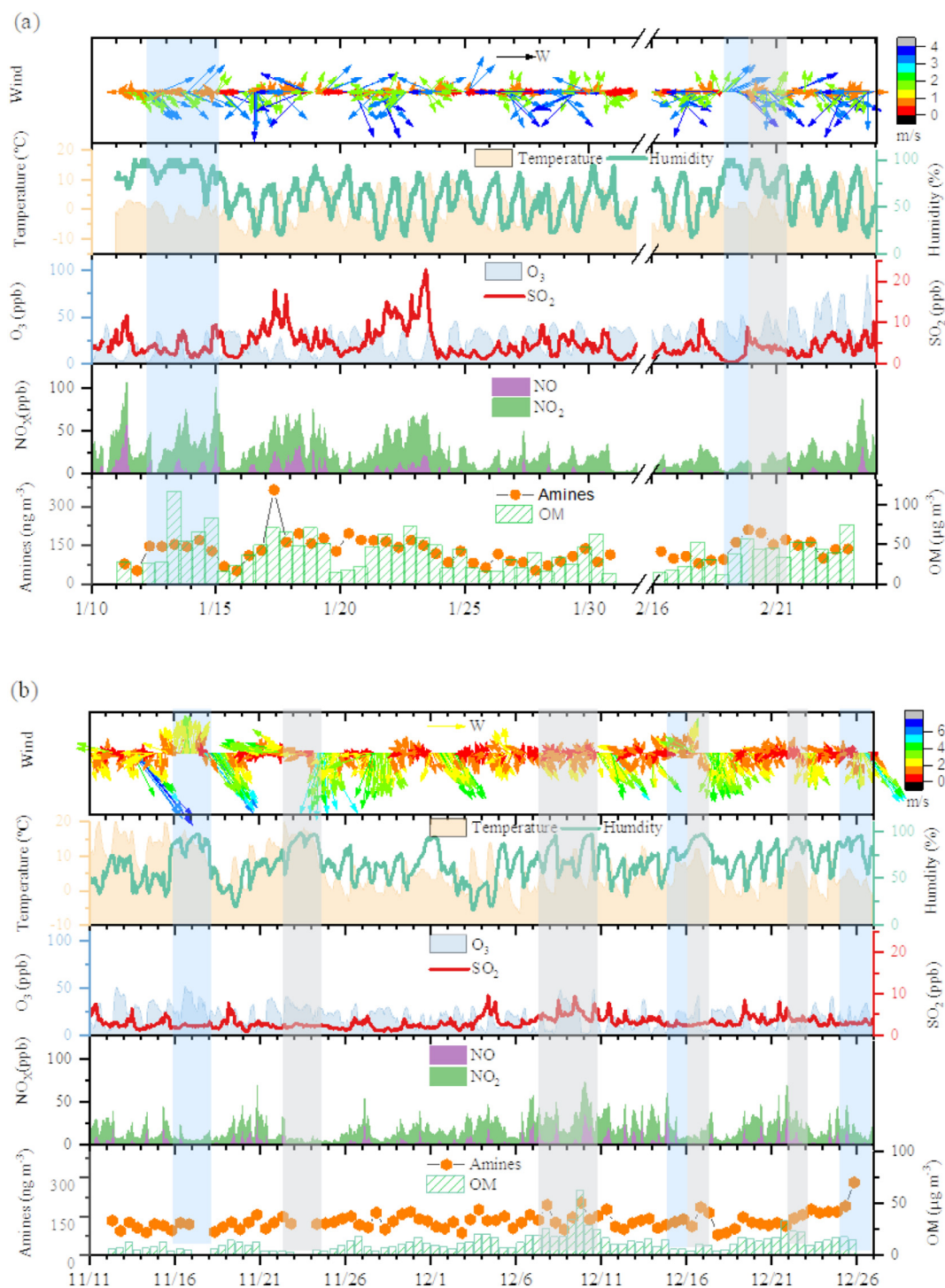

Fig. 2. Time series of concentrations of amines, organic matter, trace gases, and meteorological parameters during the sampling periods in the winter of 2018 (a) and 2019 (b). Foggy and raining weather are marked in gray and blue, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

MA in Xi'an and Guangzhou (Ho et al., 2016; Liu et al., 2017), due to different source contributions.

3.2. Temporal variations and influencing factors

During the sampling periods, the abundance of amines in fine particles exhibited large variations and changed with atmospheric conditions. As shown in Fig. 2, the total concentration of amines varied with the ranges from 51.7 to 364.3 ng m^{-3} and from 79.0 to 281.6 ng m^{-3} in the winter of 2018 and 2019, respectively. In the winter of 2018, the maximum concentrations of 364 ng m^{-3} appeared at the night of January 17, 2019, when high levels of SO$_2$ and NO$_x$ occurred. The concurrent presence of high levels of amines and SO$_2$ and NO$_x$ indicates that this pollution episode was likely associated with coal combustion. In the winter of 2019, the highest concentration appeared at the night of December 24, 2019, accompanied by high humidity (RH > 80%).

With examination of the relationships between amine abundances and the levels of trace gases and meteorological parameters, moderately strong correlations were found between amines of MA, EA, and PYR and trace

gases of SO$_2$ and NO$_x$ with the linear correlation coefficients r ranging from 0.5 to 0.8 (the data with high relative humidity (>70%) were excluded), indicating that coal-combustion related activities could be an important emission source of amines (Zheng et al., 2015). Previously, high levels of MA, DMA, and EA were observed in fine particles in coal burning plumes (Shen et al., 2017). Moreover, PYR was recognized as a typical nitrogenous species in coal (Hayhurst and Lawrence, 1996; Higashio and Shoji, 2004), and thus was possibly emitted from coal combustion activities. It has been also reported that the acidic oxidation products of SO$_2$ and NO$_x$ could promote the partitioning of gaseous amines into acidic particles owing to relatively strong alkalinity (Li et al., 2021; Shen et al., 2017). In addition, elevated concentrations of amines were observed that accompanied by high humidity when it was foggy or raining (*i.e.*, January 12–14, February 19–20, December 7–10, December 16–17, and December 24, shown in Fig. 2a and b). Moreover, an increase tendency in this ratio of amines to PM$_{2.5}$ was found with the rising of relatively humidity. When the RH rose from 30% to 90%, the Σamines/PM$_{2.5}$ ratio increased from 0.16% to 0.42%. On the one hand, the high liquid water content in the conditions of high humidity was favorable for the gas-to-particle partitioning of
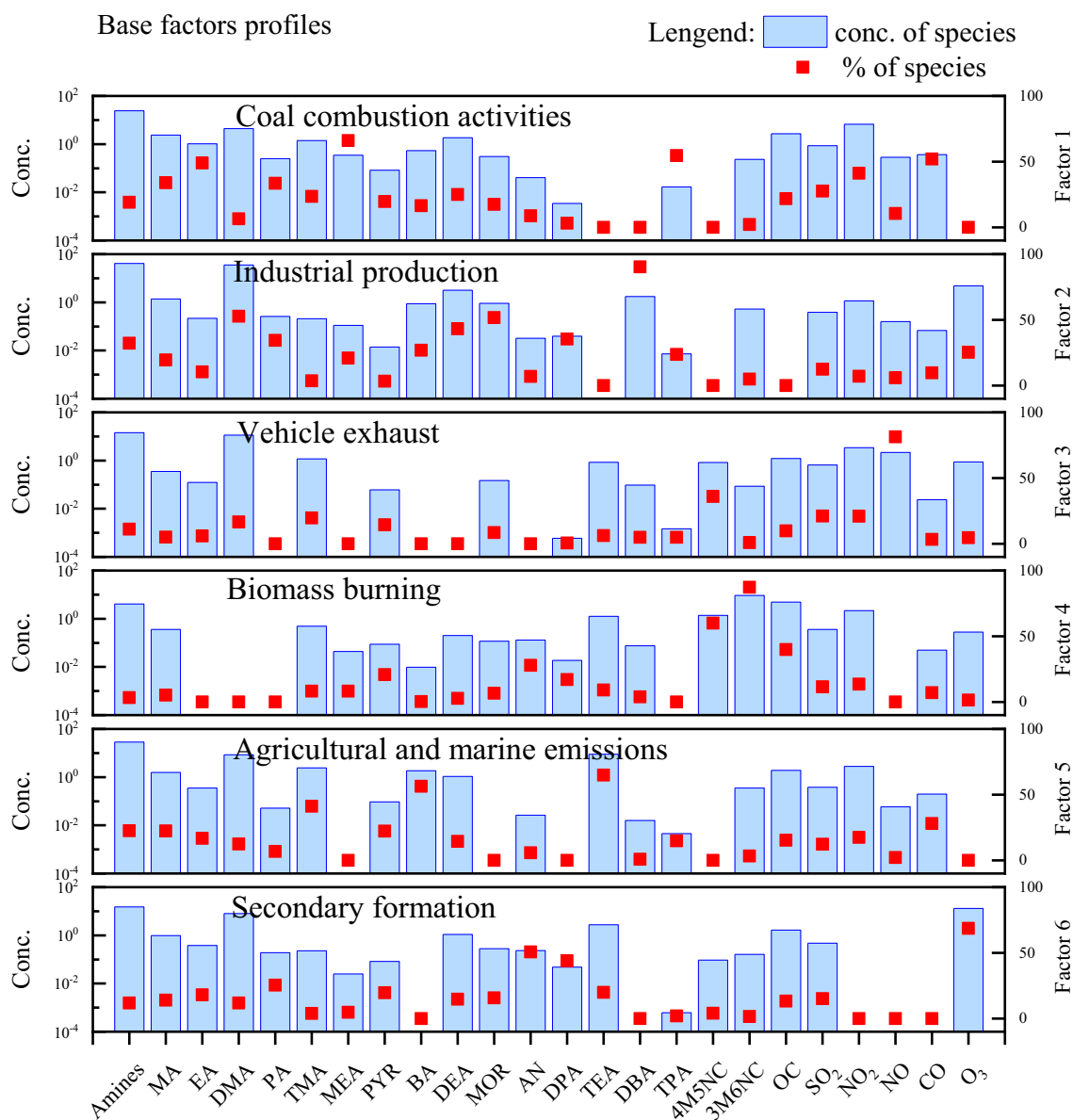

Fig. 3. Source profiles of amines and related air pollutants derived from the PMF receptor model.

amines to wet particles due to the high solubility (Huang et al., 2012; Rehbein et al., 2011; Yu et al., 2016; Zhang et al., 2012). On the other hand, the air masses with high moisture content usually came from or passed over the ocean where TMA and other amines were intensively emitted (Zhou et al., 2019).

3.3. Sources and contributions

3.3.1. Source identification

To understand the major sources of quantified amines in fine particles in winter in coastal Qingdao, the PMF receptor model was performed with the observed data of 15 amines, two nitrated phenols (3-mehtyl-6-nitrocatechol and 4-methyl-5-nitrocatechol; abbr. 3M6NC and 4M5NC, respectively), organic matter, and five tracer gases (SO_2, NO_2, NO, CO, and O_3) in the sampling periods. Based on the results derived from the PMF model, six sources were identified (as shown in Fig. 3).

Factor 1 is featured with high concentrations of SO_2, NO_2, and MEA and contributed approximately half to SO_2 and NO_x. It is thus considered to be coal combustion activities. In the previous study, remarkable amount of MA, EA, and DMA were observed in fine particles from coal burning plumes with the emission factors up to 14.6–30.1 mg kg^{-1} coal (Shen et al., 2017). In addition, MEA was commonly used as an organic absorption solvent for carbon dioxide (CO_2) capture, with the emission factor of gas-phase MEA ranging from 110 to 720 mg kg^{-1} CO_2 for coal-fired power plants (Thitakamol et al., 2007). This source was associated with the direct emissions from the nearby residential coal burning for heating and cooking and industrial coal combustion in the northwest direction as well as the indirect release from coal-fired boiler plumes accompanied by the use of carbon capture agents. In addition, the enhanced gas-to-particle partitioning of amines to acidic particles also contributed to the fine particulate amines in coal combustion plumes.

Factor 2, characterized by high levels of MOR, DMA, DEA, DBA, and PA, is recognized as industrial production. These compounds have been proposed as tracers for liquid corrosion inhibitors for mechanical and auto parts processes. They are also used in medicinal, agrochemical and rubber manufacturing (Ge et al., 2011a). This source primarily came from the emissions of mechanical and auto parts processing factories located in the west of the sampling sites.

Factor 3, showing the highest loading and contribution of NO, is recognized as vehicle exhaust. Previous studies have indicated that amines can be emitted from vehicle exhausts, due to the use of polyether-amines and isobutyl-amines as additives (De Abrantes et al., 2009; Cadle and Mulawa, 1980; Perrone et al., 2016; Pierson and Brachaczek, 1983). This source was attributed to road traffic around the sampling sites.

Factor 4 is characterized by high loadings of methyl-nitrocatechols which are important tracers for biomass burning smoke (Iinuma et al., 2010; Wang et al., 2018; Wang et al., 2017), and thus is considered to be biomass burning. Biomass burning has been indicated as an important source of C_1 to C_5 amines in the previous study (Ge et al., 2011a). This source mainly included biomass burning activities from straw burning in nearby farmlands and wood burning for residential heating and cooking in the villages.

Factor 5, featured with high loadings and high contributions of BA, TEA and TMA, was ascribed to agricultural (*e.g.* poultry and livestock farming) and marine emissions. It has been reported that animal husbandry made large contributions to BA, TEA, and TMA (Hutchinson et al., 1982; Miner and Hazen, 1969; Rabaud et al., 2003; Rappert and Müller, 2005). In addition, ocean emissions have been recognized as a main source for TMA in marine and coastal regions in previous studies (Chen et al., 2021; Hu et al., 2015; Xie et al., 2018; Xu et al., 2021; Yu et al., 2016; Zhou et al., 2019). This source mainly involved the scattered small and large farms nearby and the ocean in the east. Note that the samples with air masses passing through the ocean were possibly influenced by the enhanced gas-to-particle partitioning due to the relatively high moisture content.

Factor 6, characterized by the highest concentration and the largest contributions for atmospheric oxidant ozone, was identified as secondary formation. Recent study in Guangzhou found that tropospheric oxidants could promote the gas-particle partitioning of amines *via* enhancing the formation of sulfuric and nitric acids (Liu et al., 2018). It needs to point out that the derived source factor of secondary formation here did not include all major secondary formation pathways for amines (particularly the enhanced gas-to-particle partitioning to wet or acidic particles) due to the lack of a proper tracer.
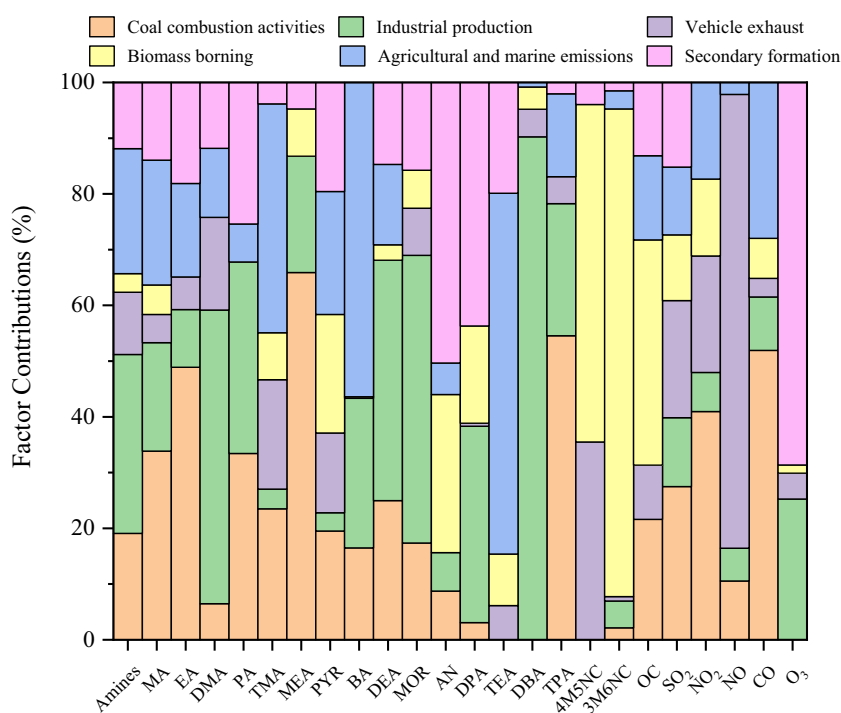

Fig. 4. Average contributions of seven source factors to amines in the winter in coastal Qingdao.

3.3.2. Source contributions

Fig. 4 depicts the contributions of the six source factors to total amines and the 15 individual amine compounds. Surprisingly, anthropogenic sources turn to be the dominant sources for most amines in fine particles even in the coastal rural area of Qingdao. Particularly, coal combustion activities contributed more than 60% for MEA, more than 30% for MA, EA, PA, and TPA, about 20% for TMA, PYR, BA, DEA, and MOR, and close to 10% for DMA and AN. Industrial production contributed to approximately 80% for DBA, more than 50% for MOR and DMA, and more than 30% for PA and DPA. Taken together, these two anthropogenic sources made a contribution of more than 50% for total amines, MA, EA, DMA, PA, MEA, DEA, MOR, DBA, and TPA. The high contributions of coal combustion activities and industrial production highlight the large influences of untreated residential coal combustion and the extensive uses of amine-containing compounds in CO_2 capture and mechanical processing to the abundances of amines in the atmosphere. It demonstrates that anthropogenic activities served as important emission sources not only for methylamines (Du et al., 2021; Liu et al., 2020; Mao et al., 2018; Qi et al., 2021; Wang et al., 2022), but also for other major amines. Urgen needs are required to address the the problem of large emissions of amines from coal combustion activities and industrial processes.

Except for coal combustion activities and industrial production, other emission sources contributed relatively small fractions to total amines and only made remarkable contributions to a few species of the 15 amines. Specifically, agricultural and marine emissions contributed more than 40% to TEA, BA, and TMA, about 20% to MA, EA, and PYR, and around 10% for DMA, DEA, and TPA. Biomass burning contributed more than 15% to PYR, AN, and DPA, and approximately 10% to TMA, MEA, MOR, and TEA. Vehicle exhaust contributed approximately 20% for DMA, TMA, and PYR. When compared with the results observed in Shanghai (Du et al., 2021), the contribution of marine source to measured amines in $PM_{2.5}$ in winter in coastal Qingdao is relatively small (less than 19%), mainly due to the small proportion of air masses originating from or passing through the ocean during the sampling periods.

In addition to primary sources, secondary formation processes also acted as a non-negligible source to measured amines in fine particles. Specifically, it contributed 12% to total amines and made a contribution of more than 40% for AN and DPA, and more than 10% for MA, EA, DMA, PA, PYR, DEA, MOR, and TEA. Additionally, the samples with high contributions from secondary formation were mostly associated with moderate and low humidity and only a few were related to high humidity, which is attributed to that the source factor of secondary formation in this study was mainly related to photochemical oxidation processes instead of aqueous processes. The relatively large contribution of secondary formation to amines has also been observed in other locations in China (Chen et al., 2019; Cheng et al., 2019; Gao et al., 2022).

4. Conclusions

Comprehensive measurements of 15 amines including 11 aliphatic amines, one alcohol amine, two alicyclic amines, and one aromatic amine in $PM_{2.5}$ were conducted in the winter of 2018 and 2019 at a coastal rural site in Qingdao in northern China. The average concentration of total quantified amines in fine particles was around 130 ng m^{-3}. DMA and TEA were the predominant amines and accounted for more than two thirds of total amines. Elevated concentrations of quantified amines in $PM_{2.5}$ were found to be associated with high levels of SO_2 and NO_x and foggy or raining weather. Moderately high correlations were recognized between the concentrations of amines and the SO_2 and NO_x levels. With the deployment of positive matrix factorization model, six source factors of measured amines in $PM_{2.5}$ were identified, including coal combustion activities, industrial production, vehicle exhaust, biomass burning, agricultural and marine activities emissions, and secondary formation. Among them, anthropogenic coal combustion activities and industrial production contributed more than half to most quantified amines, particularly for MEA and DBA, respectively. Agricultural and marine emissions were the

largest source for TEA, BA, and TMA, while industrial production served as the main source for DBA, DMA and MOR. In addition, secondary formation also made non-ignorable contributions to many amines. This work highlights the large influence of scattering coal combustion and industrial use of amine-containing compounds on ambient abundances of amines in fine particles, to which close attentions should be paid to address the atmospheric amine pollution. Further laboratory and field studies are required to evaluate the anthropogenic emissions of amines.

CRediT authorship contribution statement

Zhiyi Liu: Validation, Formal analysis, Investigation, Data curation, Writing-Original draft. **Min Li**: Methodology, Writing-Review & editing. **Xinfeng Wang**: Conceptualization, Methodology, Resources, Writing-Review & editing, Supervision, Project administration, Funding acquisition. **Yiheng Liang**: Investigation. **Yueru Jiang**: Investigation. **Jing Chen**: Investigation. **Jiangshan Mu**: Data curation. **Yujiao Zhu**: Investigation. **He Meng**: Data curation. **Lingxiao Yang**: Resources. **Keyong Hou**: Resources. **Yifeng Wang**: Funding acquisition. **Likun Xue**: Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

References

Akyüz, M., 2007. Simultaneous determination of aliphatic and aromatic amines in indoor and outdoor air samples by gas chromatography-mass spectrometry. Talanta 71 (1), 486–492.

Akyüz, M., 2008. Simultaneous determination of aliphatic and aromatic amines in ambient air and airborne particulate matters by gas chromatography-mass spectrometry. Atmos. Environ. 42 (16), 3809–3819.

Almeida, J., Schobesberger, S., Kurten, A., Ortega, I.K., Kupiainen-Maatta, O., Praplan, A.P., Adamov, A., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue, N.M., Downard, A., Dunne, E., Duplissy, J., Ehrhart, S., Flagan, R.C., Franchin, A., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Henschel, H., Jokinen, T., Junninen, H., Kajos, M., Kangasluoma, J., Keskinen, H., Kupc, A., Kurten, T., Kvashin, A.N., Laaksonen, A., Lehtipalo, K., Leiminger, M., Leppa, J., Loukonen, V., Makhmutov, V., Mathot, S., McGrath, M.J., Nieminen, T., Olenius, T., Onnela, A., Petaja, T., Riccobono, F., Riipinen, I., Rissanen, M., Rondo, L., Ruuskanen, T., Santos, F.D., Sarnela, N., Schallhart, S., Schnitzhofer, R., Seinfeld, J.H., Simon, M., Sipila, M., Stozhkov, Y., Stratmann, F., Tome, A., Trostl, J., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P.E., Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K.S., Kulmala, M., Curtius, J., Baltensperger, U., Worsnop, D.R., Vehkamaki, H., Kirkby, J., 2013. Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere. Nature 502 (7471), 359–363.

Cadle, S.H., Mulawa, P.A., 1980. Low molecular weight aliphatic amines in exhaust from catalyst-equipped cars. Environ. Sci. Technol. 14 (6), 718–723.

Cai, R., Yan, C., Yang, D., Yin, R., Lu, Y., Deng, C., Fu, Y., Ruan, J., Li, X., Kontkanen, J., Zhang, Q., Kangasluoma, J., Ma, Y., Hao, J., Worsnop, D.R., Bianchi, F., Paasonen, P., Kerminen, V.-M., Liu, Y., Wang, L., Zheng, J., Kulmala, M., Jiang, J., 2021. Sulfuric acid–amine nucleation in urban Beijing. Atmos. Chem. Phys. 21 (4), 2457–2468.

Cape, J.N., Cornell, S.E., Jickells, T.D., Nemitz, E., 2011. Organic nitrogen in the atmosphere — where does it come from? A review of sources and methods. Atmos. Res. 102 (1–2), 30–48.

Chang, Y., Wang, H., Gao, Y., Jing, S., Lu, Y., Lou, S., Kuang, Y., Cheng, K., Ling, Q., Zhu, L., Tan, W., Huang, R.-J., 2022. Nonagricultural emissions dominate urban atmospheric

amines as revealed by mobile measurements. Geophys. Res. Lett. 49 (10), e2021GL097640.

Chen, Y., Tian, M., Huang, R.-J., Shi, G., Wang, H., Peng, C., Cao, J., Wang, Q., Zhang, S., Guo, D., Zhang, L., Yang, F., 2019. Characterization of urban amine-containing particles in southwestern China: seasonal variation, source, and processing. Atmos. Chem. Phys. 19 (5), 3245–3255.

Chen, D., Shen, Y., Wang, J., Gao, Y., Gao, H., Yao, X., 2021. Mapping gaseous amines, ammonia, and their particulate counterparts in marine atmospheres of China's marginal seas: part 1 - differentiating marine emission from continental transport. Atmos. Chem. Phys. 21, 16413–16425.

Cheng, C., Huang, Z., Chan, C.K., Chu, Y., Li, M., Zhang, T., Ou, Y., Chen, D., Cheng, P., Li, L., Gao, W., Huang, Z., Huang, B., Fu, Z., Zhou, Z., 2018. Characteristics and mixing state of amine-containing particles at a rural site in the Pearl River Delta,China. Atmos. Chem. Phys. 18 (12), 9147–9159.

Cheng, G., Hu, Y., Sun, M., Chen, Y., Chen, Y., Zong, C., Chen, J., Ge, X., 2019. Characteristics and potential source areas of aliphatic amines in PM$_{2.5}$ in Yangzhou, China. Atmos.Pollut. Res. 11 (2), 296–302.

Choi, N.R., Lee, J.Y., Ahn, Y.G., Kim, Y.P., 2020. Determination of atmospheric amines at Seoul, South Korea via gas chromatography/tandem mass spectrometry. Chemosphere 258, 127367.

Chu, Y., Sauerwein, M., Chan, C.K., 2015. Hygroscopic and phase transition properties of alkyl aminium sulfates at low relative humidities. Phys. Chem. Chem. Phys. 17 (30), 19789–19796.

Cloud, 2021. IBM [Online]. Available https://www.wunderground.com. (Accessed 10 January 2021).

De Abrantes, R., Vicente de Assunção, J., Pesquero, C.R., Bruns, R.E., Nóbrega, R.P., 2009. Emission of polycyclic aromatic hydrocarbons from gasohol and ethanol vehicles. Atmos. Environ. 43 (3), 648–654.

De Haan, D.O., Tolbert, M.A., Jimenez, J.L., 2009. Atmospheric condensed-phase reactions of glyoxal with methylamine. Geophys. Res. Lett. 36 (11), L11819.

Ditto, J.C., Machesky, J., Gentner, D.R., 2022. Analysis of reduced and oxidized nitrogen-containing organic compounds at a coastal site in summer and winter. Atmos. Chem. Phys. 22 (5), 3045–3065.

Du, W., Wang, X., Yang, F., Bai, K., Wu, C., Liu, S., Wang, F., Lv, S., Chen, Y., Wang, J., Liu, W., Wang, L., Chen, X., Wang, G., 2021. Particulate amines in the background atmosphere of the Yangtze River Delta, China: concentration, size distribution, and sources. Adv. Atmos. Sci. 38 (7), 1128–1140.

Fuselli, S., Benedetti, G., Mastrangeli, R., 1982. Determination of methylamines in air using activated charcoal traps and gas chromatographic analysis with an alkali flame detector (AFD). Atmos. Environ. 16 (12), 2943–2946.

Gao, Y., Chen, D., Shen, Y., Gao, Y., Gao, H., Yao, X., 2022. Mapping gaseous dimethylamine, trimethylamine, ammonia, and their particulate counterparts in marine atmospheres of China's marginal seas – part 2: spatiotemporal heterogeneity, causes, and hypothesis. Atmos. Chem. Phys. 22 (2), 1515–1528.

Ge, X., Wexler, A.S., Clegg, S.L., 2011a. Atmospheric amines – part I.A review. Atmos. Environ. 45 (3), 524–546.

Ge, X., Wexler, A.S., Clegg, S.L., 2011b. Atmospheric amines – part II. Thermodynamic properties and gas/particle partitioning. Atmos. Environ. 45 (3), 561–577.

Hayhurst, A.N., Lawrence, A.D., 1996. The effect of solid CaO on the production of NO$_x$ and N$_2$O in fluidized bed combustors: studies using pyridine as a prototypical nitrogen fuel. Combust. Flame 105 (4), 511–527.

Higashio, Y., Shoji, T., 2004. Heterocyclic compounds such as pyrrole, pyridines, pyrrolidine, piperidine, indole, imidazol and pyrazines. Appl. Catal. A Gen. 260 (2), 251–259.

Ho, K.F., Ho, S.S.H., Huang, R.-J., Liu, S.X., Cao, J.-J., Zhang, T., Chuang, H.-C., Chan, C.S., Hu, D., Tian, L., 2015. Characteristics of water-soluble organic nitrogen in fine particulate matter in the continental area of China. Atmos. Environ. 106, 252–261.

Ho, K.-F., Ho, S.S.H., Huang, R.-J., Chuang, H.-C., Cao, J.-J., Han, Y., Lui, K.-H., Ning, Z., Chuang, K.-J., Cheng, T.-J., Lee, S.-C., Hu, D., Wang, B., Zhang, R., 2016. Chemical composition and bioreactivity of PM$_{2.5}$ during 2013 haze events in China. Atmos. Environ. 126, 162–170.

Hu, Q., Yu, P., Zhu, Y., Li, K., Gao, H., Yao, X., 2015. Concentration, size distribution, and formation of trimethylaminium and dimethylaminium ions in atmospheric particles over marginal seas of China. J. Atmos. Sci. 72 (9), 3487–3498.

Huang, Y., Chen, H., Wang, L., Yang, X., Chen, J., 2012. Single particle analysis of amines in ambient aerosol in Shanghai. Environ. Chem. 9 (3), 202–210.

Hutchinson, G.L., Mosier, A.R., Andre, C.E., 1982. Ammonia and amine emissions from a large cattle feedlot. J. Environ. Qual. 11 (2), 288–293.

Iinuma, Y., Boge, O., Graefe, R., Herrmann, H., 2010. Methyl- nitrocatechols: atmospheric tracer compounds for biomass burning secondary organic aerosols. Environ. Sci. Technol. 44, 8453–8459.

Lee, D., Wexler, A.S., 2013. Atmospheric amines – part III: photochemistry and toxicity. Atmos. Environ. 71, 95–103.

Li, Z., Zhou, R., Wang, Y., Wang, G., Chen, M., Li, Y., Wang, Y., Yi, Y., Hou, Z., Guo, Q., Meng, J., 2021. Characteristics and sources of amine-containing particles in the urban atmosphere of Liaocheng, a seriously polluted city in North China during the COVID-19 outbreak. Environ. Pollut. 289, 117887.

Lian, X., Zhang, G., Lin, Q., Liu, F., Peng, L., Yang, Y., Fu, Y., Jiang, F., Bi, X., Chen, D., Wang, X., Peng, P.A., Sheng, G., 2020. Seasonal variation of amine-containing particles in urban Guangzhou, China. Atmos. Environ. 222, 117102.

Liang, Y., Wang, X., Dong, S., Liu, Z., Mu, J., Lu, C., Zhang, J., Li, M., Xue, L., Wang, W., 2020. Size distributions of nitrated phenols in winter at a coastal site in north China and the impacts from primary sources and secondary formation. Chemosphere 250, 126256.

Lin, P., Laskin, J., Nizkorodov, S.A., Laskin, A., 2015. Revealing brown carbon chromophores produced in reactions of methylglyoxal with ammonium sulfate. Environ. Sci. Technol. 49 (24), 14257–14266.

Liu, F., Bi, X., Zhang, G., Peng, L., Lian, X., Lu, H., Fu, Y., Wang, X., Peng, P.A., Sheng, G., 2017. Concentration, size distribution and dry deposition of amines in atmospheric particles of urban Guangzhou, China. Atmos. Environ. 171, 279–288.

Liu, F., Bi, X., Zhang, G., Lian, X., Fu, Y., Yang, Y., Lin, Q., Jiang, F., Wang, X., Peng, P.A., Sheng, G., 2018. Gas-to-particle partitioning of atmospheric amines observed at a mountain site in southern China. Atmos. Environ. 195, 1–11.

Liu, Z., Chen, H., Li, Q., Sun, J., Wang, L., Yang, X., Xiao, H., Li, M., Chen, J., 2020. Size-resolved mixing states and sources of amine-containing particles in the East China Sea. J. Geophys. Res. Atmos. 125 (18), e2020JD033162.

Ma, X., Zhao, X., Ding, Z., Wang, W., Wei, Y., Xu, F., Zhang, Q., Wang, W., 2020. Determination of the amine-catalyzed SO$_3$ hydrolysis mechanism in the gas phase and at the air-water interface. Chemosphere 252, 126292.

Mao, J., Yu, F., Zhang, Y., An, J., Wang, L., Zheng, J., Yao, L., Luo, G., Ma, W., Yu, Q., Huang, C., Li, L., Chen, L., 2018. High-resolution modeling of gaseous methylamines over a polluted region in China: source-dependent emissions and implications of spatial variations. Atmos. Chem. Phys. 18 (11), 7933–7950.

Marrero-Ortiz, W., Hu, M., Du, Z., Ji, Y., Wang, Y., Guo, S., Lin, Y., Gomez-Hermandez, M., Peng, J., Li, Y., Secrest, J., Zamora, M.L., Wang, Y., An, T., Zhang, R., 2019. Formation and optical properties of brown carbon from small alpha-dicarbonyls and amines. Environ. Sci. Technol. 53 (1), 117–126.

Miner, J.R., Hazen, T.E., 1969. Ammonia and amines components of swine building odor. Trans. ASABE 12 (6), 0772–0774.

Müller, C., Iinuma, Y., Karstensen, J., van Pinxteren, D., Lehmann, S., Gnauk, T., Herrmann, H., 2019. Seasonal variation of aliphatic amines in marine sub-micrometer particles at the Cape Verde islands. Atmos. Chem. Phys. 9, 9587–9597.

Murphy, S.M., Sorooshian, A., Kroll, J.H., Ng, N.L., Chhabra, P., Tong, C., Surratt, J.D., Knipping, E., Flagan, R.C., Seinfeld, J.H., 2007. Secondary aerosol formation from atmospheric reactions of aliphatic amines atmos. Chem. Phys. 7, 2313–2337.

Paatero, P., Tapper, U., 1993. Analysis of different modes of factor analysis as least square fit problems. Chemom. Intell. Lab. Syst. 18 (2), 183–194.

Perrone, M.G., Zhou, J., Malandrino, M., Sangiorgi, G., Rizzi, C., Ferrero, L., Dommen, J., Bolzacchini, E., 2016. PM chemical composition and oxidative potential of the soluble fraction of particles at two sites in the urban area of Milan, Northern Italy. Atmos. Environ. 128, 104–113.

Pierson, W.R., Brachaczek, W.W., 1983. Emissions of ammonia and amines from vehicles on the road. Environ. Sci. Technol. 17, 757–760.

Polissar, A.V., Hopke, P.K., Paatero, P., Malm, W.C., Sisler, J.F., 1998. Atmospheric aerosol over Alaska: 2. Elemental composition and sources. J. Geophys. Res. Atmos. 103 (D15), 19045–19057.

Pratt, K.A., Hatch, L.E., Prather, K.A., 2009. Seasonal volatility dependence of ambient particle phase amines. Environ. Sci. Technol. 43, 5276–5281.

Qi, L., Bozzetti, C., Corbin, J.C., Daellenbach, K.R., El Haddad, I., Zhang, Q., Wang, J., Baltensperger, U., Prevot, A.S.H., Chen, M., Ge, X., Slowik, J.G., 2021. Source identification and characterization of organic nitrogen in atmospheric aerosols at a suburban site in China. Sci. Total Environ. 818, 151800.

Qiu, C., Zhang, R., 2013. Multiphase chemistry of atmospheric amines. Phys. Chem. Chem. Phys. 15 (16), 5738–5752.

Quéléver, L.L.J., Dada, L., Asmi, E., Lampilahti, J., Chan, T., Ferrara, J.E., Copes, G.E., Pérez-Fogwill, G., Barreira, L., Aurela, M., Worsnop, D.R., Jokinen, T., Sipila, M., 2022. Investigation of new particle formation mechanisms and aerosol processes at the Marambio Station, Antarctic Peninsula. Atmos. Chem. Phys.Discuss. 1–26.

Rabaud, N.E., Ebeler, S.E., Ashbaugh, L.L., Flocchini, R.G., 2003. Characterization and quantification of odorous and non-odorous volatile organic compounds near a commercial dairy in California. Atmos. Environ. 37 (7), 933–940.

Rappert, S., Müller, R., 2005. Odor compounds in waste gas emissions from agricultural operations and food industries. Waste Manag. 25 (9), 887–907.

Rehbein, P.J., Jeong, C.H., McGuire, M.L., Yao, X., Corbin, J.C., Evans, G.J., 2011. Cloud and fog processing enhanced gas-to-particle partitioning of trimethylamine. Environ. Sci. Technol. 45 (10), 4346–4352.

Rodriguez, A.A., de Loera, A., Powelson, M.H., Galloway, M.M., De Haan, D.O., 2017. Formaldehyde and acetaldehyde increase aqueous-phase production of imidazoles in methylglyoxal/amine mixtures: quantifying a secondary organic aerosol formation mechanism. Environ. Sci. Technol. Lett. 4 (6), 234–239.

Sellegri, K., Hanke, M., Umann, B., Arnold, F., Kulmala, M., 2005. Measurements of organic gases during aerosol formation events in the boreal forest atmosphere during QUEST. Atmos. Chem. Phys. 5, 373–384.

Shen, W., Ren, L., Zhao, Y., Zhou, L., Dai, L., Ge, X., Kong, S., Yan, Q., Xu, H., Jiang, Y., He, J., Chen, M., Yu, H., 2017. C1–C2 alkyl aminiums in urban aerosols: insights from ambient and fuel combustion emission measurements in the Yangtze River Delta region of China. Environ. Pollut. 230, 12–21.

Simoneit, B., Rushdi, A., Abas, M.B., Didyk, B., 2003. Alkyl amides and nitriles as novel tracers for biomass burning. Environ. Sci. Technol. 37 (1), 16–21.

Sintermann, J., Neftel, A., 2015. Ideas and perspectives: on the emission of amines from terrestrial vegetation in the context of new atmospheric particle formation. Biogeosciences 12 (11), 3225–3240.

Tang, M., Alexander, J.M., Kwon, D., Estillore, A.D., Laskina, O., Young, M.A., Kleiber, P.D., Grassian, V.H., 2016. Optical and physicochemical properties of brown carbon aerosol: light scattering, FTIR extinction spectroscopy, and hygroscopic growth. J. Phys. Chem. A 120 (24), 4155–4166.

Thitakamol, B., Veawab, A., Aroonwilas, A., 2007. Environmental impacts of absorption-based CO$_2$ capture unit for post-combustion treatment of flue gas from coal-fired power plant. Int. J. Greenhouse Gas Control 1 (3), 318–342.

Tong, D., Chen, J., Qin, D., Ji, Y., Li, G., An, T., 2020. Mechanism of atmospheric organic amines reacted with ozone and implications for the formation of secondary organic aerosols. Sci. Total Environ. 737, 139830.

Toribio, F., Moyano, E., Puignou, L., Galceran, M.T., 2000. Determination of heterocyclic aromatic amines by liquid chromatography-ion-trap atmospheric pressure chemical ionization mass spectrometry. J. Chromatogr. A 869, 307–317.

Wang, X., Gu, R., Wang, L., Xu, W., Zhang, Y., Chen, B., Li, W., Xue, L., Chen, J., Wang, W., 2017. Emissions of fine particulate nitrated phenols from the burning of five common types of biomass. Environ. Pollut. 230, 405–412.

Wang, L., Wang, X., Gu, R., Wang, H., Yao, L., Wen, L., Zhu, F., Wang, W., Xue, L., Yang, L., Lu, K., Chen, J., Wang, T., Zhang, Y., Wang, W., 2018. Observations of fine particulate nitrated phenols in four sites in northern China: concentrations, source apportionment, and secondary formation. Atmos. Chem. Phys. 18 (6), 4349–4359.

Wang, M., Wang, Q., Ho, S.S.H., Li, H., Zhang, R., Ran, W., Qu, L., Lee, S.C., Cao, J., 2021a. Chemical characteristics and sources of nitrogen-containing organic compounds at a regional site in the North China Plain during the transition period of autumn and winter. Sci. Total Environ. 812, 151451.

Wang, W., Zhang, Y., Jiang, B., Chen, Y., Song, Y., Tang, Y., Dong, C., Cai, Z., 2021b. Molecular characterization of organic aerosols in Taiyuan, China: seasonal variation and source identification. Sci. Total Environ. 800, 149419.

Wang, W., Zhang, Y., Cao, G., Song, Y., Zhang, J., Li, R., Zhao, L., Dong, C., Cai, Z., 2022. Influence of COVID-19 lockdown on the variation of organic aerosols: insight into its molecular composition and oxidative potential. Environ. Res. 206, 112597.

Xie, H., Feng, L., Hu, Q., Zhu, Y., Gao, H., Gao, Y., Yao, X., 2018. Concentration and size distribution of water-extracted dimethylaminium and trimethylaminium in atmospheric particles during nine campaigns - implications for sources, phase states and formation pathways. Sci. Total Environ. 631–632, 130–141.

Xing, L., Fu, T.M., Cao, J.J., Lee, S.C., Wang, G.H., Ho, K.F., Cheng, M.C., You, C.F., Wang, T.J., 2013. Seasonal and spatial variability of the OM/OC mass ratios and high regional correlation between oxalic acid and zinc in chinese urban organic aerosols. Atmos. Chem. Phys. 13 (8), 4307–4318.

Xu, Z., Zhou, S., Zhu, Y., Chen, Y., 2021. Different characteristics and source contributions to aerosol aminiums over a coastal city and adjacent marginal seas. Environ. Chem. 18 (6), 274–284.

Yang, J., Shen, H., Guo, M.-Z., Zhao, M., Jiang, Y., Chen, T., Liu, Y., Li, H., Zhu, Y., Meng, H., Wang, W., Xue, L., 2021. Strong marine-derived nitrous acid (HONO) production observed in the coastal atmosphere of northern China. Atmos. Environ. 244, 117948.

Yao, L., Garmash, O., Bianchi, F., Zheng, J., Yan, C., Kontkanen, J., Junninen, H., Mazon Stephany, B., Ehn, M., Paasonen, P., Sipilä, M., Wang, M., Wang, X., Xiao, S., Chen, H., Lu, Y., Zhang, B., Wang, D., Fu, Q., Geng, F., Li, L., Wang, H., Qiao, L., Yang, X., Chen, J., Kerminen, V.-M., Petäjä, T., Worsnop Douglas, R., Kulmala, M., Wang, L., 2018. Atmospheric new particle formation from sulfuric acid and amines in a Chinese megacity. Science 361, 278–281.

Yu, P., Hu, Q., Li, K., Zhu, Y., Liu, X., Gao, H., Yao, X., 2016. Characteristics of dimethylaminium and trimethylaminium in atmospheric particles ranging from supermicron to nanometer sizes over eutrophic marginal seas of China and oligotrophic open oceans. Sci. Total Environ. 572, 813–824.

Zhang, G., Bi, X., Chan, L.Y., Li, L., Wang, X., Feng, J., Sheng, G., Fu, J., Li, M., Zhou, Z., 2012. Enhanced trimethylamine-containing particles during fog events detected by single particle aerosol mass spectrometry in urban Guangzhou,China. Atmos. Environ. 55, 121–126.

Zhang, H., Li, R., Dong, S., Wang, F., Zhu, Y., Meng, H., Huang, C., Ren, Y., Wang, X., Hu, X., Li, T., Peng, C., Zhang, G., Xue, L., Wang, X., Tang, M., 2022. Abundance and fractional solubility of aerosol iron during winter at a coastal city in Northern China: similarities and contrasts between fine and coarse particles. J. Geophys. Res. Atmos. 127 (1), e2021JD036070.

Zheng, J., Ma, Y., Chen, M., Zhang, Q., Wang, L., Khalizov, A.F., Yao, L., Wang, Z., Wang, X., Chen, L., 2015. Measurement of atmospheric amines and ammonia using the high resolution time-of-flight chemical ionization mass spectrometry. Atmos. Environ. 102, 249–259.

Zhou, S., Li, H., Yang, T., Chen, Y., Deng, C., Gao, Y., Chen, C., Xu, J., 2019. Characteristics and sources of aerosol aminiums over the eastern coast of China: insights from the integrated observations in a coastal city, adjacent island and the marginal seas. Atmos. Chem. Phys. 19, 10447–10467.