# Mapping gaseous dimethylamine, trimethylamine, ammonia, and their particulate counterparts in marine atmospheres of China's marginal seas: Part 1 - Differentiating marine emission from continental transport

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**Abstract.** To study sea-derived gaseous amines, ammonia, and primary particulate aminium ions in the marine atmosphere of China's marginal seas, an onboard URG-9000D Ambient Ion Monitor-Ion chromatography (AIM-IC, Thermo Fisher) was set up on the front deck of the R/V Dongfanghong 3 to semi-continuously measure the spatiotemporal variations in the concentrations of atmospheric trimethylamine ($TMA_{gas}$), dimethylamine ($DMA_{gas}$), and ammonia ($NH_{3gas}$) along with their particulate matter ($PM_{2.5}$) counterparts. In this study, we differentiated marine emissions of the gas species from continental transport using data obtained from December 9 to 22, 2019 during the cruise over the Yellow and Bohai seas, facilitated by additional short-term measurements collected at a coastal site near the Yellow Sea during summer, fall, and winter of 2019. The data obtained from the cruise and coastal sites demonstrated that the observed $TMA_{gas}$ and protonated trimethylamine ($TMAH^+$) in $PM_{2.5}$ over the Yellow and Bohai seas overwhelmingly originated from marine sources. During the cruise, no significant correlation ($P > 0.05$) was observed between the simultaneously measured $TMAH^+$ and $TMA_{gas}$ concentrations. Additionally, the concentrations of $TMAH^+$ in the marine atmosphere varied around $0.28 \pm 0.18$ μg m$^{-3}$ (average $\pm$ standard deviation), with several episodic hourly average values exceeding 1 μg m$^{-3}$, which were approximately one order of magnitude larger than those of $TMA_{gas}$ (approximately $0.031 \pm 0.009$ μg m$^{-3}$). Moreover, there was a significant negative correlation ($P < 0.01$) between the concentrations of $TMAH^+$ and $NH_4^+$ in $PM_{2.5}$. Therefore, the observed $TMAH^+$ in $PM_{2.5}$ was overwhelmingly derived from primary sea-spray aerosols. Using $TMA_{gas}$ and $TMAH^+$ in $PM_{2.5}$ as tracers for sea-derived basic

gases and sea-spray particulate aminium ions, the values of non-sea-derived $DMA_{gas}$, and $NH_{3gas}$, and non-sea-spray particulate $DMAH^+$ in $PM_{2.5}$ were estimated. The estimated average values of each species contributed to 16%, 34%, and 65% of the observed average concentrations for non-sea-derived $DMA_{gas}$, $NH_{3gas}$ and non-sea-spray particulate $DMAH^+$ in $PM_{2.5}$, respectively. Uncertainties remained in the estimations, as $TMAH^+$ may decompose into smaller molecules in seawater to varying extents. The non-sea-derived gases and non-sea-spray particulate $DMAH^+$ likely originated from long-range transport from the upwind continents based on the recorded offshore winds and increased concentrations of non-sea-salt $SO_4^{2-}$ (nss-$SO_4^{2-}$) and $NH_4^+$ in $PM_{2.5}$. The lack of a detectable increase in particulate $DMAH^+$, $NH_4^+$, and nss-$SO_4^{2-}$ concentrations in several $SO_2$ plumes did not support the secondary formation of particulate $DMAH^+$ in the marine atmosphere.

**Keywords:** Marine atmospheric $NH_3$, trimethylamine, dimethylamine, particulate aminium, sea-spray aerosol

## 1. Introduction

Gaseous amines and their particulate counterparts are vital for reduced nitrogen compounds in the marine atmosphere (Facchini et al., 2008; Müller et al., 2009; Hu et al., 2015; Hu et al., 2018; van Pinxteren et al., 2015; van Pinxteren et al., 2019; Yu et al., 2016; Xie et al., 2018; Zhou et al., 2019) and are primarily derived from seawater, where glycine betaine (GBT), trimethylamine N-oxide (TMAO), and choline are the three major precursors (Burg and Ferraris, 2008; Lidbury et al., 2015a; Lidbury et al., 2015b; Jameson et al., 2016; Taubert et al., 2017). GBT, TMAO, and choline are critical for maintaining the osmotic pressure in marine organisms. When released into the environment, they can be degraded by bacteria to trimethylamine (TMA), dimethylamine (DMA), or methylamines (MA) (Lidbury et al., 2015a; Lidbury et al., 2015b). Gaseous DMA, TMA, and MA may be vital in the formation of secondary particles in the atmosphere by nucleation (Almeida et al., 2013; Chen et al., 2016; Yao et al., 2018; Zhu et al., 2019). In addition to biogenic amines, anthropogenic emissions are known as important sources of amines in the continental atmosphere, but not in the marine atmosphere (Ge et al., 2011). Modeling studies have shown that the continental amine species in gas and/or particle phases can be transported regionally, including downwind marine atmospheres (Yu and Luo, 2014; Mao et al., 2018). Simultaneous real-time measurement of gaseous amines and their particulate counterparts in the marine atmosphere over the ocean remains challenging because of artifact signals related to self-

vessel emissions and amine-contained dew evaporation; however, this is not the case in the continental atmosphere (VandenBoer et al., 2011). The lack of direct measurements restricts the determination of their sources and the relationship between the reduced nitrogen compounds and acid-base neutralization reactions in the marine atmosphere.

Reduced nitrogen compounds in the ocean can finally decompose into ammonium ions ($NH_4^+$) and other smaller molecules. $NH_4^+$ in surface seawater releases to the marine atmosphere as atmospheric ammonia ($NH_{3gas}$) under favorable conditions (Johnson et al., 2008; Carpenter et al., 2012; Paulot et al., 2015). The ocean is an important source of $NH_{3gas}$, contributing to approximately 40% of the natural $NH_3$ emissions on Earth (Carpenter et al., 2012; Paulot et al., 2015). In the literature, large uncertainties remain in estimating $NH_3$ emissions from the ocean; for example, the annual emission flux ranges from 2 to 23 Tg N a$^{-1}$ (Clarke and Porter, 1993; Dentener and Crutzen, 1994; Sutton et al., 2013; Paulot et al., 2015). These uncertainties are primarily derived from two factors: 1) the major marine sources of $NH_{3gas}$ are still disputed, such as seawater, sea birds, or the photolysis of marine organic nitrogen at the ocean surface or in the atmosphere; and 2) direct $NH_{3gas}$ observations in marine atmospheres are restricted as onboard ambient $NH_{3gas}$ measurement techniques sometimes suffer from large artifacts from $NH_{3gas}$ contamination associated with onboard human activities, dew evaporation, and water vapor interference (Quinn et al., 1990; Clarke and Porter, 1993; Johnson et al., 2008; Keene et al., 2009; Wentworth et al., 2016; Teng et al., 2017). Additionally, the long-range transport of atmospheric $NH_{3gas}$ from the continent may also complicate the source analysis of $NH_{3gas}$ in marine atmospheres (McNaughton et al., 2004; Uematsu et al., 2004; Zhao et al., 2015; Lutsch et al., 2016).

To identify and characterize sea-derived gaseous amines, ammonia, and sea-spray particulate aminium ions, as well as secondary particulate aminium ions from continental transport in the atmospheres of China's marginal seas, we conducted two cruise campaigns: one over the Yellow and Bohai seas in China from December 9 to 22, 2019 (Campaign A), and another over the Eastern China and Yellow seas from December 27, 2019 to January 16, 2020 (Campaign B). Winter cruise campaigns provide great opportunities for observational studies due to the following: 1) higher concentrations of nutrients in the seas at lower sea surface water temperatures, which may favor higher primary production (Guo et al., 2020) and subsequently increase marine emissions of gaseous amines and/or aminum-contained sea-spray aerosols; 2) periodically enhanced air-sea exchanges driven by the strong winter Asian monsoon every 4–10 days (Zhu et al., 2018); and 3) periodically enhanced long-range transport of anthropogenic pollutants from continents to the seas, which may enhance the formation of secondary ammonium

and aminium aerosols (Guo et al., 2016; Yu et al., 2016; Xie et al., 2018; Wang et al., 2019).

In this study, an onboard URG-9000D Ambient Ion Monitor-Ion chromatography (AIM-IC, Thermo Fisher) instrument was used to simultaneously measure the spatiotemporal variations in the concentrations of gaseous amines and $NH_{3gas}$, along with their counterparts in $PM_{2.5}$. Semi-continuous measurement data were analyzed to identify the study targets. This study was divided into two parts. In this section, we distinguish the marine sources from the continental transport of reduced nitrogen compounds in marine atmospheres and subsequently quantify each contribution to the observed species during the December 9-22, 2019 campaign. In the companion paper (Gao et al., 2021), we analyzed the spatiotemporal heterogeneity and related causes, and subsequently delivered a hypothesis regarding the marine emissions of reduced nitrogen compounds using the data from the two campaigns and an additional cruise campaign previously reported by Hu et al. (2015).

## 2. Experimental

### 2.1 Sampling periods, locations, and instruments

Campaign A was conducted from December 9 to 19, 2019 on the R/V Dongfanghong-3 with a displacement tonnage of 5000. The research vessel was still within its testing period and used state-of-the-art combustion technology with low-sulfur diesel. Campaign B started from December 27, 2019 to January 17, 2020, and was organized by another research team. During December 20-22, the vessel was anchored at the port while the sampling continued. The 44 hours were referred to as the transition period between campaigns A and B. A standard-sized air-conditioned container was set up on the front deck to house a suite of instruments including the AIM-IC, a fast-mobility particle sizer (FMPS, Tsi), a cloud condensation nuclei counter (CCN-100, Droplet MT), and a single particle aerosol mass spectrometer (SPAMS 05, Hexin). No human activities occurred on the front deck during cruising, excluding anchoring at the port. Even during the anchoring period, human activity on the front deck was rare. The use of the container on the front deck effectively minimized the self-vessel contamination by $NH_{3gas}$ and gaseous amines. The front deck was approximately 10 m above sea level, and the container height was 2.8 m.

To ensure that the onboard AIM-IC was operated properly, it was housed in a mobile air-conditioned mini-container, which was further placed in a standard container with a 1 m stainless steel sampling probe connected to the ambient air. The inlet of the sampling probe extended from the top corner of the standard container facing the sea. The AIM-IC consists of two major

parts: an ambient air sampling system and an ion chromatography analysis system. For the sampling system, the AIM-IC was equipped with a PM$_{2.5}$ cyclone and operated at a rate of 3 L/min. The sampled gases and particles in the water solution were stored in two syringes prior to their injection for analysis. The ion chromatography analysis system measured the semi-continuous concentrations of chemically reactive gases. These included NH$_{3gas}$, gaseous amines, and acidic gases such as SO$_2$ and HNO$_3$, along with their particulate counterparts, at a temporal resolution of 1 h. This facilitated the identification of possible interference from onboard dew evaporation, which typically occurs with sunrise (Teng et al., 2017).

An automatic weather system providing real-time meteorological data is available on the R/V Dongfanghong-3. The heading wind was corrected to determine the true wind speed and direction. The surface seawater temperature was not measured during this cruise campaign, and typically had a delay of a few hours compared to the ambient air temperature (Deng et al., 2014).

On August 1-9, September 12 to October 1, and November 16 to December 1, 2019, the AIM-IC was set up at a coastal site in Qingdao (36.34° N, 120.67° E) to conduct routine measurements (Fig. 1). Coastal measurement data were obtained from two weeks to four months before the winter cruise campaign. The sampling site was located in a new high-technology zone near the Yellow Sea, with the shortest distance from the sea being approximately 1 km in the south. The AIM-IC was housed in a research lab on the fifth floor of a building, approximately 16 m above ground level. The sampling probe extended out of the window and was directly connected to the ambient air. Typically, higher biogenic emissions of reduced nitrogen compounds over the continents are expected in the summer than in the winter owing to the temperature effect (Yu et al., 2016; Teng et al., 2017).

## 2.2 Chemical analysis

The AIM-IC includes an ICS-1100 ion chromatograph, wherein an analytical column (Ion Pac CS17A (2×250 mm)) was used to measure cations, including Na$^+$, NH$_4^+$, protonated dimethylamine (DMAH$^+$), and protonated trimethylamine (TMAH$^+$), and an AS11-HC (2×50 mm) was used to measure anions, including SO$_4^{2-}$, NO$_3^-$, Cl$^-$, and organic ions. Methanesulfonic acid solution (5 mM) was used as the eluent for cation analysis, while potassium hydroxide solution (varying from 3 to 40 mM) was used as the gradient eluent for anion analysis. Each analysis took 26-28 mins to obtain a complete ion spectrum. The volume of the injection loop installed on the low-pressure valve was 250 μL, which substantially reduced the limits of detection

for all ions. The limits of detection for $NH_4^+$, $DMAH^+$, and $TMAH^+$ were 0.0004, 0.004, and 0.002 µg m$^{-3}$, respectively, in ambient air. The limits of detection for $NO_3^-$ and $SO_4^{2-}$ were 0.05 and 0.015 µg m$^{-3}$, respectively, in ambient air. The ICS-1100 was calibrated onboard prior to obtaining regular measurements, and the second calibration was conducted when the vessel was anchored at the port. The AIM-IC analysis was not affected by ambient water vapor, as the device directly measured the ions. Detailed information regarding the AIM-IC analysis is provided in Teng et al. (2017) and Xie et al. (2018). Notably, strong $K^+$ interference occurred unexpectedly and occasionally, and then disappeared during different campaigns. When the interference occurred, $DMAH^+$ and $TMAH^+$ were undetectable because of the increased baseline at the corresponding residence time in the ion chromatograph (Fig. S1); consequently, some PM$_{2.5}$ $DMAH^+$ and $TMAH^+$ concentration data are unavailable in Fig. 1. However, the concentrations of gaseous amines were still detected correctly, with a low baseline at the residence. $K^+$ interference remains to be investigated. Additionally, a few surface seawater samples were collected from different sea zones. The $NH_4^+$ and aminium ion concentrations in the samples were not measured, as the analytical methods were still hindered by high sea-salt ion contents.

## 3. Results

### 3.1 Temporal variations in the concentrations of basic gases and their PM$_{2.5}$ counterparts in the coastal atmosphere

Before analyzing the basic gases and their counterparts in the marine atmosphere, we initially presented their continental concentrations at the coastal site facing the Yellow Sea as important evidence to facilitate the analysis of the contributors to these species in the marine atmosphere. Figs. 1a & b show that the TMA$_{gas}$ and $TMAH^+$ concentrations in PM$_{2.5}$ were mostly below the detection limit, varying at approximately 0.001±0.001 µg m$^{-3}$ (average ± standard deviation), regardless of the presence of offshore or onshore winds during short-term measurements in the three seasons of 2019. The DMA$_{gas}$ and $DMAH^+$ concentrations varied at 0.018±0.021 and 0.017±0.013 µg m$^{-3}$, respectively, which were approximately one order of magnitude larger than those of TMA$_{gas}$ and $TMAH^+$. TMA$_{gas}$ and $TMAH^+$ concentrations in the upwind continental and coastal atmospheres were substantially lower than those reported in the literature, by up to a few tens of ng m$^{-3}$ (Ge et al., 2011). However, Gibb et al. (1999) reported a low average TMA$_{gas}$ (0.5 ng m$^{-3}$) and particulate $TMAH^+$ (0.5 ng m$^{-3}$) in the marine atmosphere over the Arabian Sea on November 16 to December 19, 1994. Xie et al. (2018) reported that $TMAH^+$

concentrations were comparable to those of DMAH$^+$ in atmospheric particles collected at two other coastal sites located approximately 20 km from the study area, as listed in Table S1. The cause of this change is beyond the scope of this study, but may be due to the large decrease in manure application, based on our recent survey in the Qingdao area.

150    The DMA$_{gas}$ and DMAH$^+$ concentrations in PM$_{2.5}$ with offshore winds from the north were substantially higher than those with onshore winds from the south or southeast (top of Fig. 1a), suggesting that their continental emissions and related secondary sources were stronger. Moreover, the concentrations of DMA$_{gas}$ and DMAH$^+$ were moderately correlated with those of NH$_{3gas}$ and NH$_4^+$; namely, [DMA$_{gas}$] = $5.6\times10^{-3}\times$[NH$_{3gas}$] ($R^2$=0.79, P<0.01), and [DMAH$^+$]$_{PM2.5}$=$5.9\times10^{-3}\times$ [NH$_4^+$]$_{PM2.5}$ ($R^2$=0.84, P<0.01). Generally, the DMA$_{gas}$ and DMAH$^+$ concentrations were approximately 1/200 of those of the corresponding NH$_{3gas}$

155    and NH$_4^+$.

### 3.2 Spatiotemporal variations in the concentrations of basic gases over the seas

Throughout Campaign A, the TMA$_{gas}$ concentrations varied at approximately 0.031±0.009 µg m$^{-3}$ (Figs. 2a-c), with three peaks occurring at 4–5 day intervals (gray shadowing in Fig. 2c). Peaks 1 and 2 were generally associated with offshore winds, while peak 3 was mostly associated with onshore winds (Fig. 2b). The peaks lasted from tens to dozens of hours and were not induced

160    by the onboard dew evaporation at sunrise. For example, the highest value (0.060 µg m$^{-3}$) occurred at 23:00 on December 16. The observed TMA$_{gas}$ concentrations were one order of magnitude higher than those measured in the coastal atmosphere during the summer, fall, and winter. This suggested that the TMA$_{gas}$ observed during Campaign A was largely derived from marine sources rather than from long-range continental transport. The same conclusion can be drawn by analyzing the three peaks of TMA$_{gas}$ and its temporal variations during the anchoring port period. For example, during peak 1 (Fig. 2a), the concentrations

165    of TMA$_{gas}$ increased by approximately 100% from 20:00 on December 9 to 11:00 on December 10, with an approximately 30% decrease in the non-sea-salt SO$_4^{2-}$ (nss-SO$_4^{2-}$) concentration (from 22 to 16 µg m$^{-3}$; Fig. 2b). Moreover, the peaks in the TMA$_{gas}$ concentrations corresponded to troughs in the nss-SO$_4^{2-}$ concentrations during peak 3, as shown in Figs. 2c & d. The self-vessel emissions of nss-SO$_4^{2-}$ in PM$_{2.5}$ were negligible because of the use of low-sulfur diesel, which is discussed later. The increased nss-SO$_4^{2-}$ concentrations in PM$_{2.5}$ may be a good indicator of continental transport, and vice versa.

170    The concentrations of DMA$_{gas}$ varied at approximately 0.006±0.006 µg m$^{-3}$ (Fig. 2d) and were significantly higher than those

of $TMA_{gas}$ (P<0.01). Unlike $TMA_{gas}$, continental transport was likely an important contributor to the $DMA_{gas}$ and $NH_{3gas}$ observed in the marine atmosphere, particularly during peak 1, when higher $nss\text{-}SO_4^{2-}$ concentrations were observed in $PM_{2.5}$ (Figs. 2c-e). The $DMA_{gas}$ and $NH_{3gas}$ concentrations were negatively correlated with those of $TMA_{gas}$ during peak 1; namely, $R^2=0.35$ (P<0.01) between $TMA_{gas}$ and $DMA_{gas}$, and $R^2=0.17$ (P<0.01) between $TMA_{gas}$ and $NH_{3gas}$. This suggested that most of the $DMA_{gas}$ and $NH_{3gas}$ were likely derived from continental transport, rather than marine sources. During peak 2, increased $TMA_{gas}$, $DMA_{gas}$, and $NH_{3gas}$ concentrations were concurrently observed with increasing $nss\text{-}SO_4^{2-}$ concentrations, suggesting that both marine emissions and continental transport simultaneously contributed to the observed $DMA_{gas}$ and $NH_{3gas}$. During the port-anchoring period from December 20-22, the $DMA_{gas}$ and $NH_{3gas}$ concentrations varied slightly, and were moderate and low, respectively. However, the $TMA_{gas}$ concentrations continuously increased by over 100% as the ambient temperature increased (Figs. 2c and f). Additionally, the $nss\text{-}SO_4^{2-}$ concentrations of $PM_{2.5}$ varied greatly and followed a bell-shaped pattern during the port-anchoring period.

Additionally, the $NH_{3gas}$ concentrations varied at approximately $0.53 \pm 0.53$ μg m$^{-3}$ from December 9-22. The variation narrowed to approximately $0.24 \pm 0.07$ μg m$^{-3}$ during the port-anchoring period from December 20-22. When the data during Campaign A were used for the analysis, the $NH_{3gas}$ concentrations were significantly correlated with those of $DMA_{gas}$; namely, $[DMA_{gas}] = 9.2 \times 10^{-3} \times [NH_{3gas}]$ ($R^2=0.71$, P<0.01). However, there was no correlation between $NH_{3gas}$ and $TMA_{gas}$ concentrations.

### 3.3 Spatiotemporal variations in the aminium and $NH_4^+$ ion concentrations of $PM_{2.5}$ over the seas

Figs. 3a-f show the spatiotemporal variations in the $TMAH^+$, $DMAH^+$, and $NH_4^+$ concentrations of $PM_{2.5}$ throughout Campaign A from December 9-22, during which the $TMAH^+$ concentrations varied greatly at approximately $0.28 \pm 0.18$ μg m$^{-3}$. However, they narrowed at approximately $0.21 \pm 0.04$ μg m$^{-3}$ during the port-anchoring period. The $TMAH^+$ concentrations generally increased from $0.13 \pm 0.05$ μg m$^{-3}$ on December 9 to $0.46 \pm 0.05$ μg m$^{-3}$ on December 16 (Fig. 3a), and subsequently decreased to approximately 0.2 μg m$^{-3}$ thereafter, excluding some strong peaks from 0.62–1.24 μg m$^{-3}$ at 03:00–05:59 and 1.02–1.81 μg m$^{-3}$ at 14:00–16:59 on December 18 (grey shadowing representing peak 4 in Figs. 3a-d). The peaks reproduced the episodes observed in the marine atmosphere over the Yellow Sea in May 2012 (Hu et al., 2015) and were repeatedly observed during

Campaign B (Gao et al., 2021). However, they were not observed in several other marine cruise campaigns conducted across the marginal seas of China and the northwestern Pacific Ocean (Hu et al., 2018; Xie et al., 2018).

As the $TMAH^+$ concentrations were approximately two orders of magnitude higher than those observed at the coastal site during the three seasons of 2019, the observed $TMAH^+$ was largely derived from marine sources. The $TMAH^+$ concentrations followed a spatiotemporal pattern that clearly differed from those of $DMAH^+$ and $NH_4^+$, while the latter two ions exhibited a similar spatiotemporal pattern during most periods of Campaign A (Figs. 3a-c). A significant negative correlation ($P<0.01$) was observed between the concentrations of $TMAH^+$ and $NH_4^+$ in $PM_{2.5}$ (not shown). The spatiotemporal pattern of the $TMAH^+$ concentration also significantly differed from those of $nss-SO_4^{2-}$ (Fig. 2d) and $SO_2$ (Fig. 3b), which are regarded as tracers of long-range transported continental pollutants and fresh vessel plumes. For example, extremely strong $TMAH^+$ peaks occurred concurrently with low $nss-SO_4^{2-}$, $NH_4^+$, and $SO_2$ concentrations, accompanied by high $Na^+$ concentrations under high wind speeds, which are common indicators of sea spray aerosols (Feng et al., 2017). Moreover, the $TMAH^+$ concentrations were approximately one order of magnitude larger than those of $TMA_{gas}$, and no significant correlation was observed between them ($P>0.05$). This suggests that the observed $TMAH^+$ may not be derived from the neutralization reactions of $TMA_{gas}$ with acids in the marine atmosphere, and may have been derived from primary sea-spray organic aerosols (Hu et al., 2015, 2018). Primary sea-spray organic aerosols mainly contain primary and degraded biogenic organics (Ault et al., 2013; Prather et al., 2013; Quinn et al., 2015; Dall'Osto et al., 2019).

The $DMAH^+$ concentrations varied at approximately $0.065\pm0.068$ µg m$^{-3}$ from December 9-22; however, they varied at approximately $0.10 \pm0.04$ µg m$^{-3}$ during the port-anchoring period. The 25th percentile value of $DMAH^+$ during Campaign A was $0.021$ µg m$^{-3}$, suggesting a low background concentration in the marine area. The $DMAH^+$ concentrations were significantly correlated with those of $NH_4^+$ ($R^2=0.71$, $P<0.01$; data not shown). When the data obtained at 03:00–05:59 and 14:00–16:59 on December 18 (strong peaks of $TMAH^+$ with a simultaneous increase in $DMAH^+$) were removed for correlation, the $R^2$ value improved to 0.78. Unlike $TMAH^+$, the observed $DMAH^+$ may have been partially derived from acid-basic neutralization reactions in the ambient air, in addition to the primary sea-spray organic aerosols. For example, a large increase in $DMAH^+$ concentrations occurred concurrently with strong peaks in the $TMAH^+$ concentrations (gray shadowed peak 4 in Figs. 3a & b).

220    The $NH_4^+$ concentrations of $PM_{2.5}$ varied greatly at approximately $4.7 \pm 7.2$ µg m$^{-3}$ during Campaign A (Fig. 3c). However,

the 25$^{th}$ percentile values were as low as 0.21 µg m$^{-3}$, suggesting low marine background values. The 50$^{th}$ percentile value was

also only 1.2 µg m$^{-3}$, which was considerably smaller than the average owing to the presence of strong peaks in $NH_4^+$

concentrations. The increased $NH_4^+$ concentrations associated with $NO_3^-$ and nss-$SO_4^{2-}$ during Campaign A were likely due to

the long-range transport from the upwind continents.

225    **4. Discussion**

**4.1 Effects of temperature on the observed basic gases in the marine atmosphere**

As mentioned above, the observed $TMA_{gas}$ likely originated from marine sources. We plotted the concentrations of $TMA_{gas}$

against the ambient air temperature (T) in Fig. 4a, which generally increased with increasing T. We further separated the

average hourly wind speeds (WS) into three categories: WS $\leq$ 5.0, $5.0 <$ WS $\leq 9.0$, and WS $> 9.0$ m s$^{-1}$. At WS $> 9.0$ m s$^{-1}$, the

230    data obtained from 15:00 on December 16 to 01:00 on December 19, including peaks 3 and 4, were separately considered as

half-full symbols in Fig. 4a. The concentrations of $TMA_{gas}$ (half-full symbols) generally exceeded those of the other gases at

the same T, with which they exhibited a moderately good exponent correlation ($[TMA_{gas}] = 0.03 \times e^{0.04T}$ with R$^2$=0.72). From

15:00 on December 16 to 01:00 on December 19, stronger emission potentials of $TMA_{gas}$ to the marine atmosphere were

expected in the corresponding marine zone. However, the measured concentrations of $TMAH^+$ and seawater pH in surface

235    seawater are required to confirm this.

Following the same approach, the $DMA_{gas}$ and $NH_{3gas}$ concentrations were plotted against T, as shown in Figs. 4b & c,

respectively. These values generally increased with increasing T. The $NH_{3gas}$ concentrations (half-full symbols) were strongly

correlated with T ($[NH_{3gas}] = 0.05 \times e^{0.3T}$ with R$^2$=0.96). As lower concentrations of nss-$SO_4^{2-}$, $NH_4^+$, and $SO_2$ were generally

observed simultaneously, the continental transport of $NH_{3gas}$ was greatly reduced; therefore, the observed $NH_{3gas}$ was mainly

240    derived from the seas. Therefore, the seas were the net source of $NH_{3gas}$ at the time of measurement. However, at the same T,

the $NH_{3gas}$ concentrations (half-full symbols) were generally lower than those during other periods in this study. The

concentrations of $NH_4^+$ in surface seawater may have been lower at the time of measurement. However, this may not be the

case, as higher concentrations of $TMAH^+$ were expected. Alternatively, the continental transport of $NH_{3gas}$ may have made an

important contribution to the observed $NH_{3gas}$ during most other periods when the seas were the net $NH_{3gas}$ sink.

245     $DMA_{gas}$ exhibited an extremely good exponent correlation with T (half-full symbols) at the measurement time ([$DMA_{gas}$] = $0.001 \times e^{0.3T}$ with $R^2$=0.91). At the same T, the $DMA_{gas}$ concentrations (half-full symbols) were not always higher or lower than the others. We considered these two hypotheses: In hypothesis 1, the observed $DMA_{gas}$ concentrations exceeded those predicted by the regression equation using the ambient T as the input; the seas were the net sinks of $DMA_{gas}$. In hypothesis 2, including all others, measurements of $DMAH^+$ in the surface seawater were required to confirm whether the seas were net

250     sources or sinks of $DMA_{gas}$.

## 4.2 Estimating the sea-derived $DMA_{gas}$ and $NH_{3gas}$ in the marine atmosphere

To estimate the sea-derived $DMA_{gas}$ and $NH_{3gas}$ concentrations in the marine atmosphere, we plotted the $DMA_{gas}$ and $NH_{3gas}$ concentrations against $TMA_{gas}$, as shown in Figs. 5a and b. The purple-red and dark-green markers represent the data obtained, with increasing concentrations of the three species from 10:00 on December 14 to 23:00 on December 16 (increasing period),

255     and with decreasing concentrations from 23:00 on December 16 to 19:59 on December 17 (decreasing period) during peak 3, respectively; these were analyzed separately. A good correlation was obtained between $DMA_{gas}$ and $TMA_{gas}$ during the increasing period ([$DMA_{gas}$] = 0.64×[$TMA_{gas}$] - 0.01, $R^2$=0.86, and P<0.01). The good correlation suggested that $DMA_{gas}$ was likely released with $TMA_{gas}$ from the seawater and facilitated the estimation of non-sea-derived $DMA_{gas}$ ($DMA_{gas}^{\#}$) concentrations using the regression equation. We assumed that any data beyond the purple-red dashed line reflected the non-

260     sea-derived $DMA_{gas}$, which can be attributed to continental transport. Therefore, we assumed that the $DMA_{gas}^{\#}$ concentrations were equal to the observed values of $DMA_{gas}$ minus the predicted values obtained using [$DMA_{gas}$] = 0.64×[$TMA_{gas}$] - 0.01; the calculated $DMA_{gas}^{\#}$ values are shown in Fig. 5c. During peak 1, the calculated $DMA_{gas}^{\#}$ contributed to over 40% of the observed $DMA_{gas}$ for 12 h. Similar calculated results for $DMA_{gas}^{\#}$ were obtained during peak 2.

However, the equation for the decreasing period was as follows: [$DMA_{gas}$] = 1.4×[$TMA_{gas}$] - 0.05, $R^2$=0.84, and P<0.01. The

265     decreasing $R^2$ value and the increasing slope suggest that the $TMAH^+$ in the surface seawater may decompose into $DMAH^+$ to different extents (Lidbury et al., 2015a; Lidbury et al., 2015b; Xie et al., 2018). The two regression curves (purple-red and dark-green dashed lines in Figs. 5a and b) created a large triangular zone that likely reflected the different ratios of

DMA$_{gas}$/TMA$_{gas}$ in primary marine emissions on the cruise route. Based on the triangular zone in Fig. 5a, the aforementioned calculations should be considered as the lower limit of DMA$_{gas}$[#].

270    The same approach was employed to analyze the NH$_{3gas}$ results, as shown in Figs. 5b and d. During peak 1, the calculated non-sea-derived NH$_{3gas}$ (NH$_{3gas}$[#]) contributed to over 40% of the observed NH$_{3gas}$ for 17 h. During peak 2, the calculated NH$_{3gas}$[#] contributed to over 40% of the observed NH$_{3gas}$ for 24 h.

Overall, the DMA$_{gas}$[#] and NH$_{3gas}$[#] concentrations varied at approximately 0.001±0.002 and 0.18±0.39 µg m$^{-3}$, respectively. The calculated average DMA$_{gas}$[#] and NH$_{3gas}$[#] values accounted for 16% and 34% of the observed averages of each species,

275    respectively. The estimations suggested an appreciable continental contribution to the observed DMA$_{gas}$ and NH$_{3gas}$ during Camping A.

## 4.3 Estimation of non-sea-spray particulate DMAH$^+$ in the marine atmosphere

We plotted the concentrations of DMAH$^+$ against those of TMAH$^+$ in PM$_{2.5}$ (Fig. 6a) using the data obtained from 15:00 on

280    December 16 to 01:00 on December 19 ([DMAH$^+$]$_{PM2.5}$ =0.13 × [TMAH$^+$]$_{PM2.5}$, R$^2$=0.91, P<0.01). During this period, largely increased concentrations of DMAH$^+$ and TMAH$^+$ were observed under high wind speeds of 9-13 m s$^{-1}$. The good correlation suggested that the observed DMAH$^+$ was likely released with TMAH$^+$ as amines-contained sea spray aerosols in the atmosphere, and facilitated the calculation of sea-derived DMAH$^+$ using TMAH$^+$ as a tracer of sea-spray aerosols. Thus, the non-sea-derived DMAH$^+$ concentrations in PM$_{2.5}$, marked as DMAH$^{+\#}$, were assumed to be equal to the observed DMAH$^+$

285    values minus the predicted values (sea-derived DMAH$^+$) using the regression equation. The calculated DMAH$^{+\#}$ values are shown in Fig. 6b. The DMAH$^{+\#}$ concentrations varied at approximately 0.042±0.070 µg m$^{-3}$ throughout Campaign A, during which the calculated average DMAH$^{+\#}$ accounted for 65% of the observed average. Additionally, the calculated DMAH$^{+\#}$ values accounted for over 80% of the observed values in 26% of the Campaign A period. The estimations suggested that the observed DMAH$^+$ originated predominantly from long-range continental transport and/or secondary formation in the marine

290    atmosphere. The analysis was supported by the good correlation between the concentrations of DMAH$^{+\#}$ and those of NH$_4^+$; namely, [DMAH$^{+\#}$]$_{PM2.5}$ = 0.0089× [NH$_4^+$]$_{PM2.5}$, (R$^2$=0.82, P<0.01; Fig. 6c). The slope of 0.0089 was approximately 50% larger

than that obtained in the coastal atmosphere (0.0059), suggesting more $DMA_{gas}$ partitioning in $PM_{2.5}$ in the marine atmosphere than in the coastal atmosphere (Pankow, 2015; Xie et al., 2018).

Moreover, the decomposition of $TMAH^+$ to $DMAH^+$ may have occurred in surface seawater and/or the marine atmosphere, to an extent, and the estimated $DMAH^{+\#}$ should be considered as the upper limit. Notably, the $NH_4^+$ and $TMAH^+$ concentrations were negatively correlated during Campaign A, and no primary particulate $NH_4^+$ from sea-spray aerosols were identified.

**4.4 Formation and chemical conversion of aminium ions in the transported and self-vessel $SO_2$ plumes**

When the sea-spray particulate $DMAH^+$ was deducted, the increased concentrations of $DMAH^{+\#}$ were generally associated with increased $nss$-$SO_4^{2-}$ and $SO_2$ concentrations. Combining this with the moderate correlation between $DMAH^{+\#}$ and $NH_4^+$, we inferred that $DMAH^{+\#}$ likely originated from concurrent secondary formation with $NH_4^+$. However, we separated the air pollutant plumes into two groups. Group 1 represented an increase in $nss$-$SO_4^{2-}$ and $NH_4^+$ together with $SO_2$, while group 2 represented an increase in $SO_2$ without increases in $nss$-$SO_4^{2-}$ and $NH_4^+$. Group 1 likely reflected the transport of aged air pollutant plumes from the continents, while group 2 may reflect self-vessel $SO_2$ plumes. As shown in Figs. 6b and 3b-c, the concentrations of $DMAH^{+\#}$ and $NH_4^+$ in the self-vessel $SO_2$ plumes did not increase in the intervals between peaks 1 and 2 and between peaks 2 and 3. Therefore, no fresh formation of $DMAH^{+\#}$ and $NH_4^+$ in the self-vessel emissions was detected. However, the concentrations of $TMAH^+$ decreased in some self-vessel $SO_2$ plumes. The $TMAH^+$ concentrations were approximately one order of magnitude higher than those of $TMA_{gas}$ in the marine atmosphere. Assuming that the decreased $TMAH^+$ was released from $PM_{2.5}$ to the gas phase, a simultaneous large spike in $TMA_{gas}$ should be observed. However, this was not the case, as shown in Fig. 1c. The decreased $TMAH^+$ may persist in $PM_{2.5}$, but could not be detected by AIM-IC.

**5. Conclusion and Implication**

In continental China upwind of the Yellow Sea, the $TMA_{gas}$ and $TMAH^+$ concentrations in $PM_{2.5}$ were extremely low $(0.001\pm0.001~\mu g~m^{-3})$, mostly below the detection limit of the AIM-IC. Considering the observations as a reference, the largely increased $TMA_{gas}$ $(0.031\pm0.009~\mu g~m^{-3})$ and particulate $TMAH^+$ $(0.28\pm0.18~\mu g~m^{-3})$ concentrations in the marine atmosphere were attributed to marine emissions. Therefore, $TMA_{gas}$ and particulate $TMAH^+$ can be used as unique tracers to quantify the

marine emissions of $DMA_{gas}$, $NH_{3gas}$, and particulate $DMAH^+$, as well as the long-range transport from upwind continental China.

Through comprehensive comparison and correlation analyses, the high concentrations of $TMAH^+$ in $PM_{2.5}$ observed over the Yellow and Bohai seas, with episodic hourly averages exceeding 1 $\mu g \ m^{-3}$, were inferred to originate from strong primary sea-spray aerosol emissions. Moreover, the $TMA_{gas}$ concentrations generally increased with increasing ambient temperature and sea surface wind speeds, suggesting that the observed $TMA_{gas}$ was likely released from the surface seawater. However, the $TMA_{gas}$ concentrations were substantially lower than those of particulate $TMAH^+$, and were not significantly correlated. Although different mechanisms have been reported in the literature for the release of $TMA_{gas}$ and particulate $TMAH^+$ from the seas, the lack of a significant correlation between them was surprising and was explored in the companion study.

The $DMA_{gas}$ and $NH_{3gas}$ concentrations varied at approximately $0.006\pm0.006$ and $0.53\pm0.53$ $\mu g \ m^{-3}$ during Campaign A, wherein at least 16% and 34% of the observational values were derived from continental transport, respectively. The sea-derived $DMA_{gas}$ and $NH_{3gas}$ were likely released with $TMA_{gas}$ as they peaked simultaneously. The $DMAH^+$ concentrations in $PM_{2.5}$ varied at approximately $0.065\pm0.068$ $\mu g \ m^{-3}$ during Campaign A, 65% of which was derived from continental transport. Our analysis results did not support the occurrence of photolysis of marine organic nitrogen to generate $NH_{3gas}$ in the marine atmosphere during winter, as there was no correlation between the sea-derived $NH_{3gas}$ and particulate $TMAH^+$ concentrations. Additionally, peaks 2 and 3 of $NH_{3gas}$ persisted for dozens of hours under strong winds and were therefore unlikely to be derived from seabird emissions. A good exponent correlation was observed between the observed $NH_{3gas}$ concentrations and T during the period without continental air pollutant transport, suggesting that the observed $NH_{3gas}$ was released from seawater. $NH_3$ emissions from seabirds were unlikely contributors to the observed $NH_{3gas}$ in the marine atmosphere during winter; however, this may not have been the case during other seasons.

Additionally, no formation of particulate $NH_4^+$ and $DMAH^+$ in the self-vessel $SO_2$ plume was observed in the marine atmosphere. However, the particulate $TMAH^+$ concentration clearly decreased in the self-vessel $SO_2$ plume without a simultaneous increase in the $TMA_{gas}$ concentration. Chemical conversion of particulate $TMAH^+$ likely occurred in the plume, while AIM-IC could not detect the products. This requires further investigation.

**Data availability.** The datasets related to this work can be accessed via https://data.mendeley.com//datasets/3kpnkkr55c/1.

**Author contributions**. XY designed the research. DC carried out the field measurements and analyzed the data. XY helped to interpretation of the results. All authors wrote the paper and contributed toward improving the paper.

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

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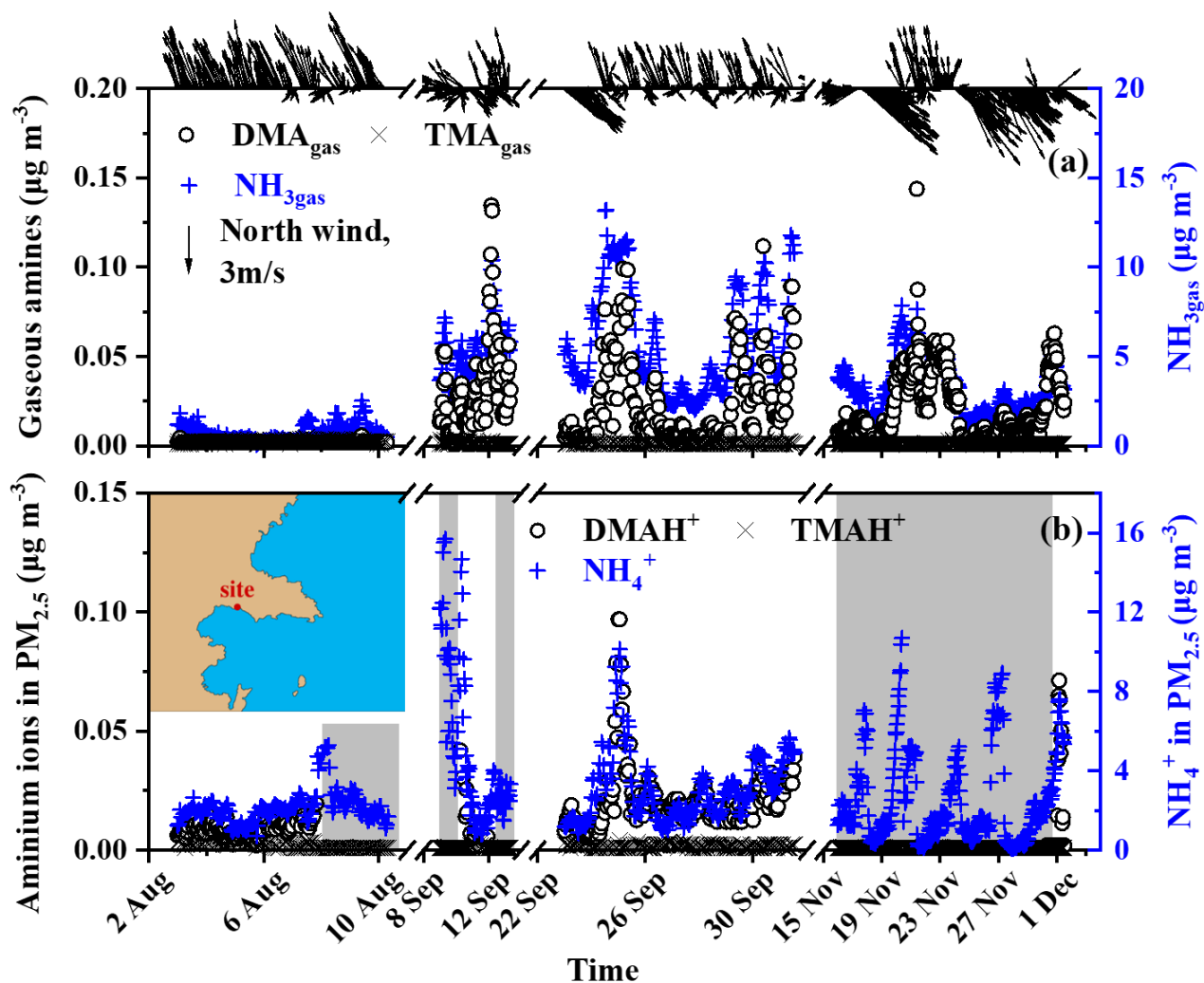


**Figure 1: Temporal variations in the concentrations of NH$_{3gas}$, gaseous amines, and their counterparts in PM$_{2.5}$ at a coastal site during three seasons of 2019 ((a) NH$_{3gas}$ and gaseous amines; (b) counterparts in PM$_{2.5}$; wind speed and direction superimposed on the top of (a); a map of the sampling site superimposed in (b); the missing data regarding aminium ions in the PM$_{2.5}$ shading in the gray shadow were due to occasional K$^+$ interference (b)).**

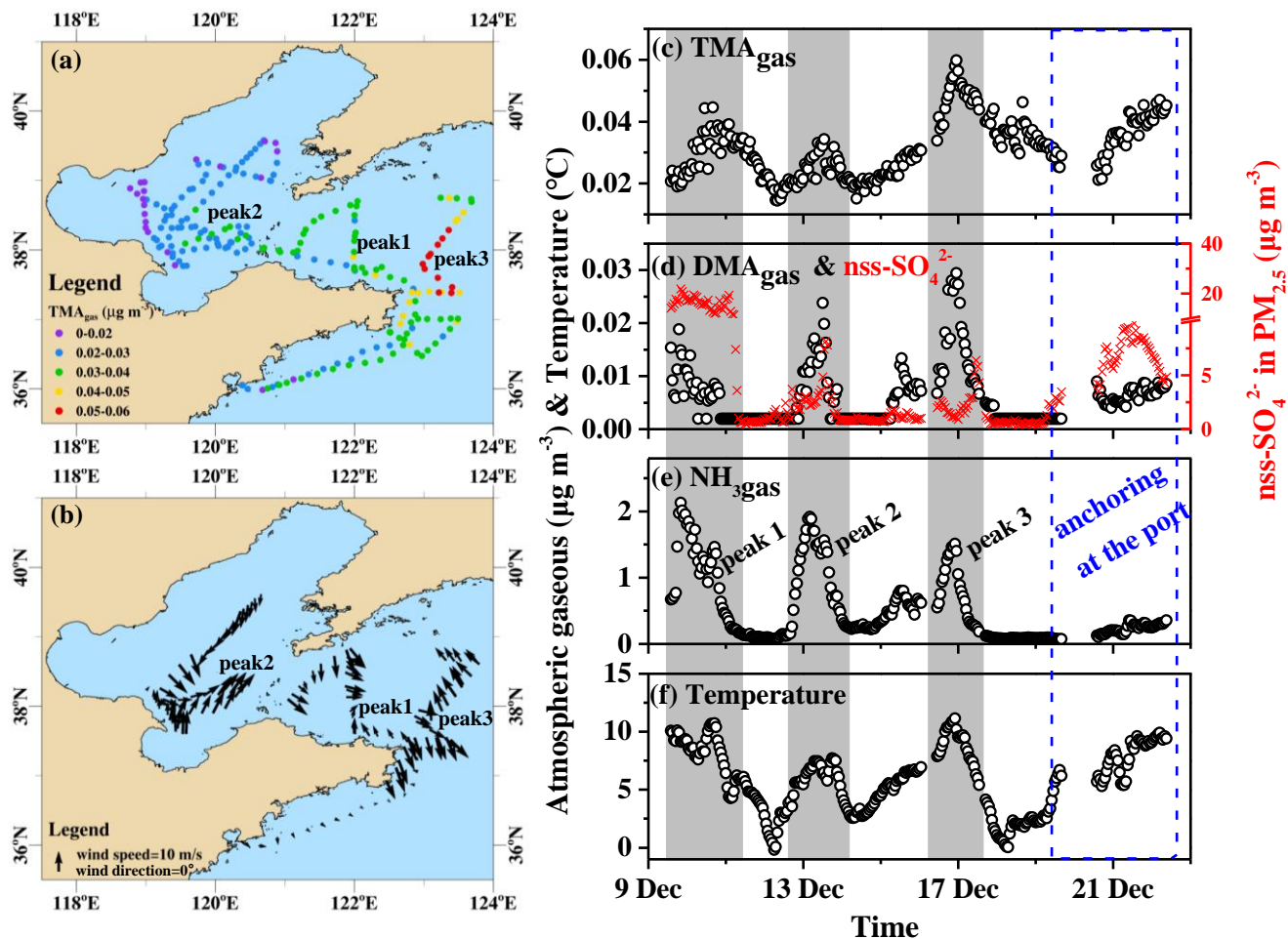



**Figure 2: Spatiotemporal variations in the concentrations of basic gases and other parameters during cruise campaigns in the Yellow and Bohai seas on December 9-22, 2019 ((a) mapping TMA_gas by concentration; (b) mapping onboard recorded wind speeds and directions; time-series of (c) TMA_gas, (d) DMA_gas, (e) NH_3gas, and (f) ambient air temperature recorded onboard. The time-series of nss-SO_4^{2-} in PM_2.5 were shown as indicators of anthropogenic air pollutants in (d); not all data were shown in (b) to avoid clustering).**

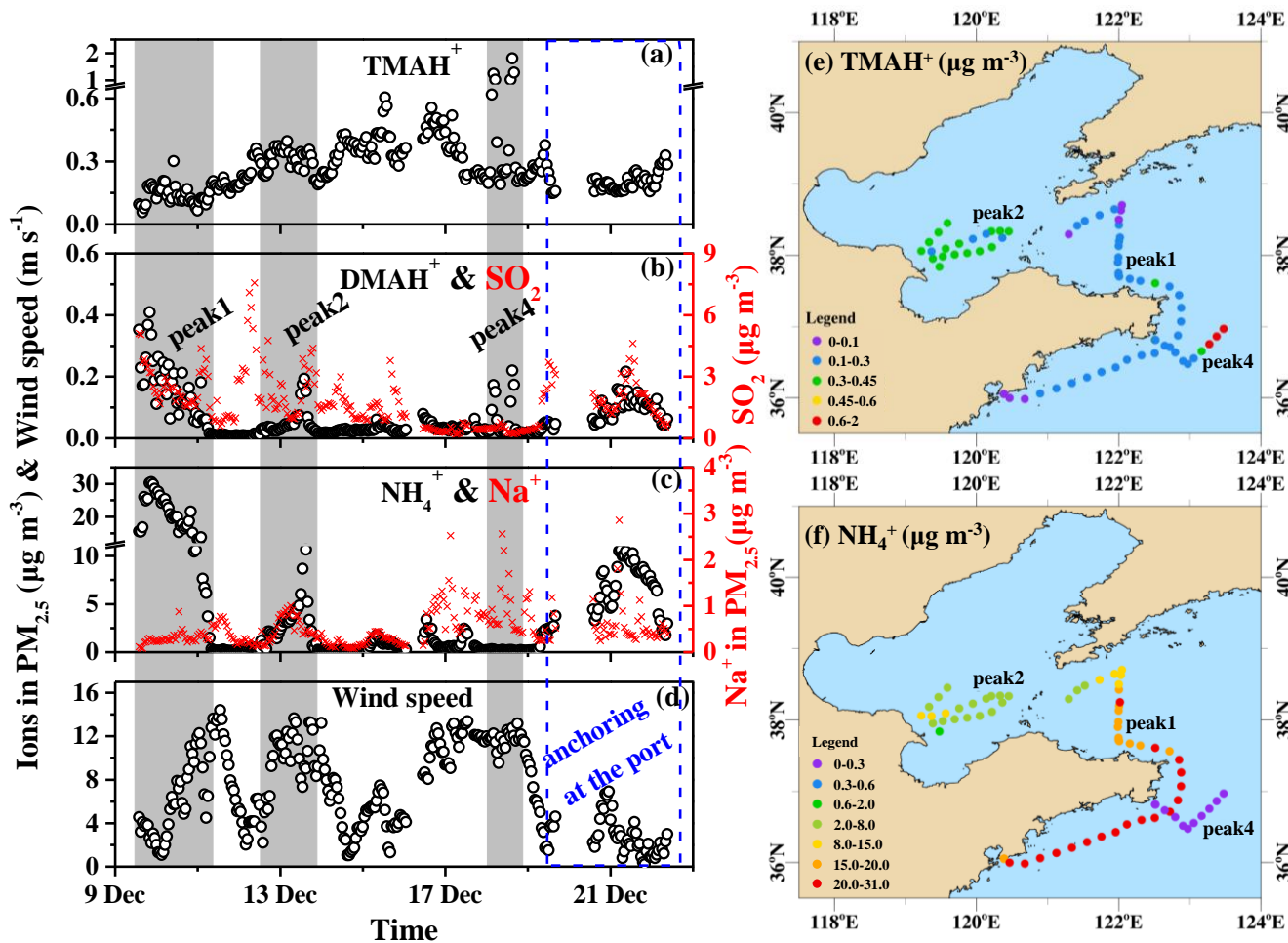



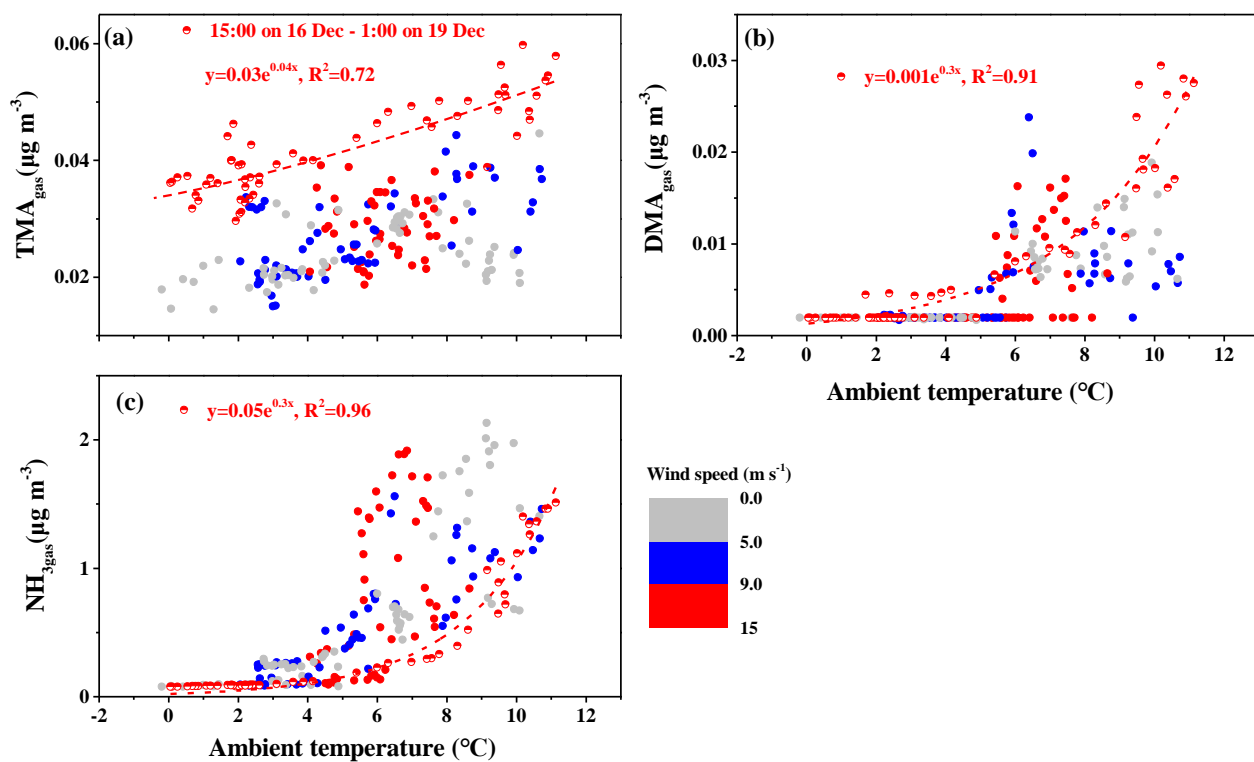
Figure 3: Spatiotemporal variations in the aminium ions and $NH_4^+$ concentrations of $PM_{2.5}$ and other parameters during cruise campaigns over the Yellow and Bohai seas on December 9-22, 2019 (time-series of (a) $TMAH^+$, (b) $DMAH^+$, and (c) $NH_4^+$ in $PM_{2.5}$; (d) wind speeds (WS); (e) mapping of the $TMAH^+$ in concentration; (f) mapping of the $NH_4^+$ concentration. The time-series of $SO_2$ is shown as an indicator in (b); that of $Na^+$ in $PM_{2.5}$ is shown as an indicator of sea-spray aerosols in (c). To better show the spatiotemporal distributions of $TMAH^+$ and $NH_4^+$ during peaks 1, 2, and 4, only the data during periods shaded in (a-d) were used in (e) and (f) to avoid clustering).

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**Figure 4: Correlations between the concentrations of basic gases and ambient temperature ((a) TMA$_{gas}$; (b) DMA$_{gas}$; (c) and NH$_3$. The colored bar represents different wind speeds; full symbols represent the data observed throughout the campaign excluding the period from 15:00 on December 16 to 01:00 on December 19, 2019).**
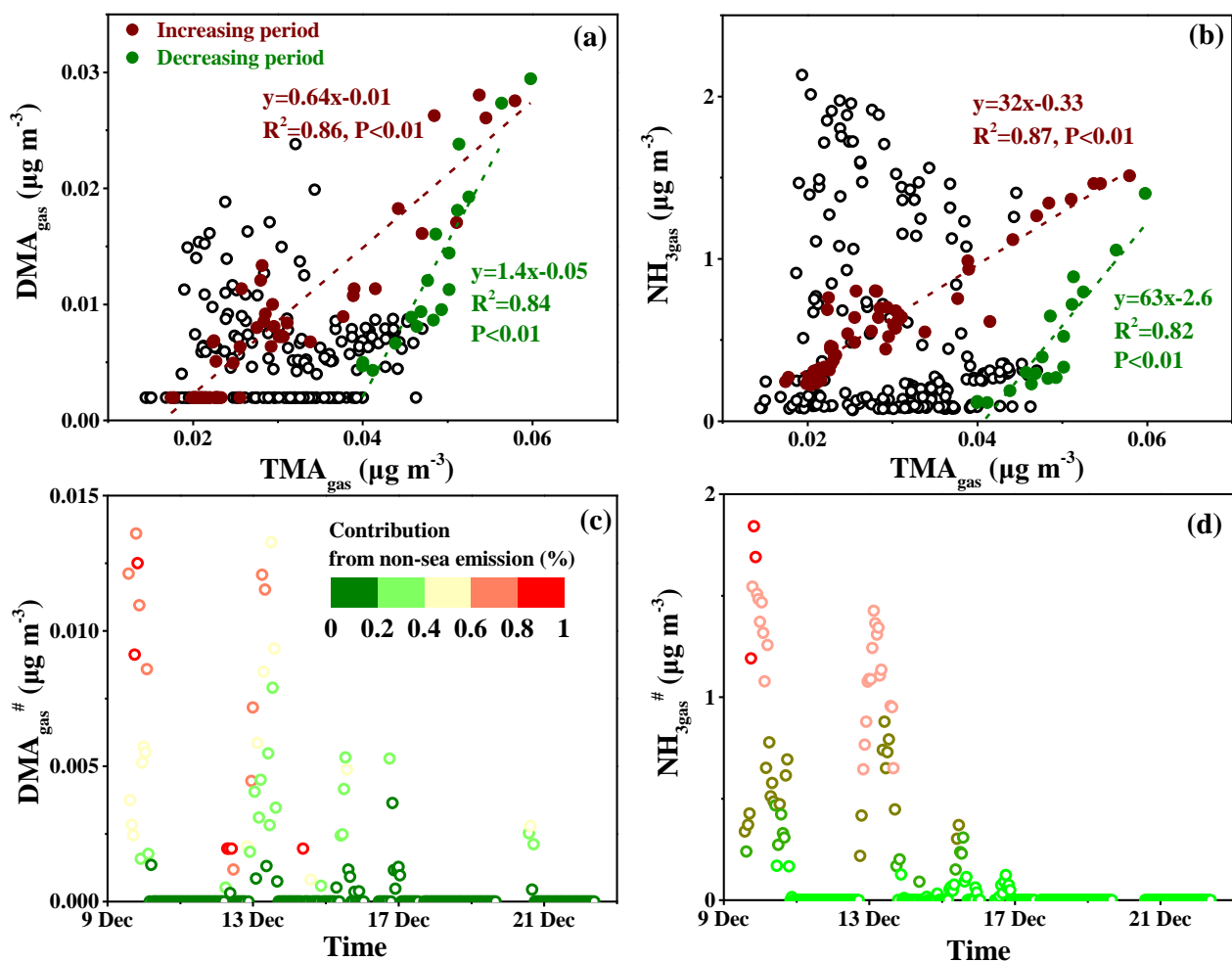
**Figure 5: Correlations of DMA$_{gas}$ and NH$_{3gas}$ with TMA$_{gas}$ and time-series of the calculated DMA$_{gas}$# and NH$_{3gas}$# ((a) DMA$_{gas}$ vs. TMA$_{gas}$; (b) NH$_{3gas}$ vs. TMA$_{gas}$; (c) DMA$_{gas}$#; and (d) NH$_{3gas}$#. The colored bars in (c) and (d) represent the percentages of transported DMA$_{gas}$# and NH$_{3gas}$# in each corresponding observed value).**
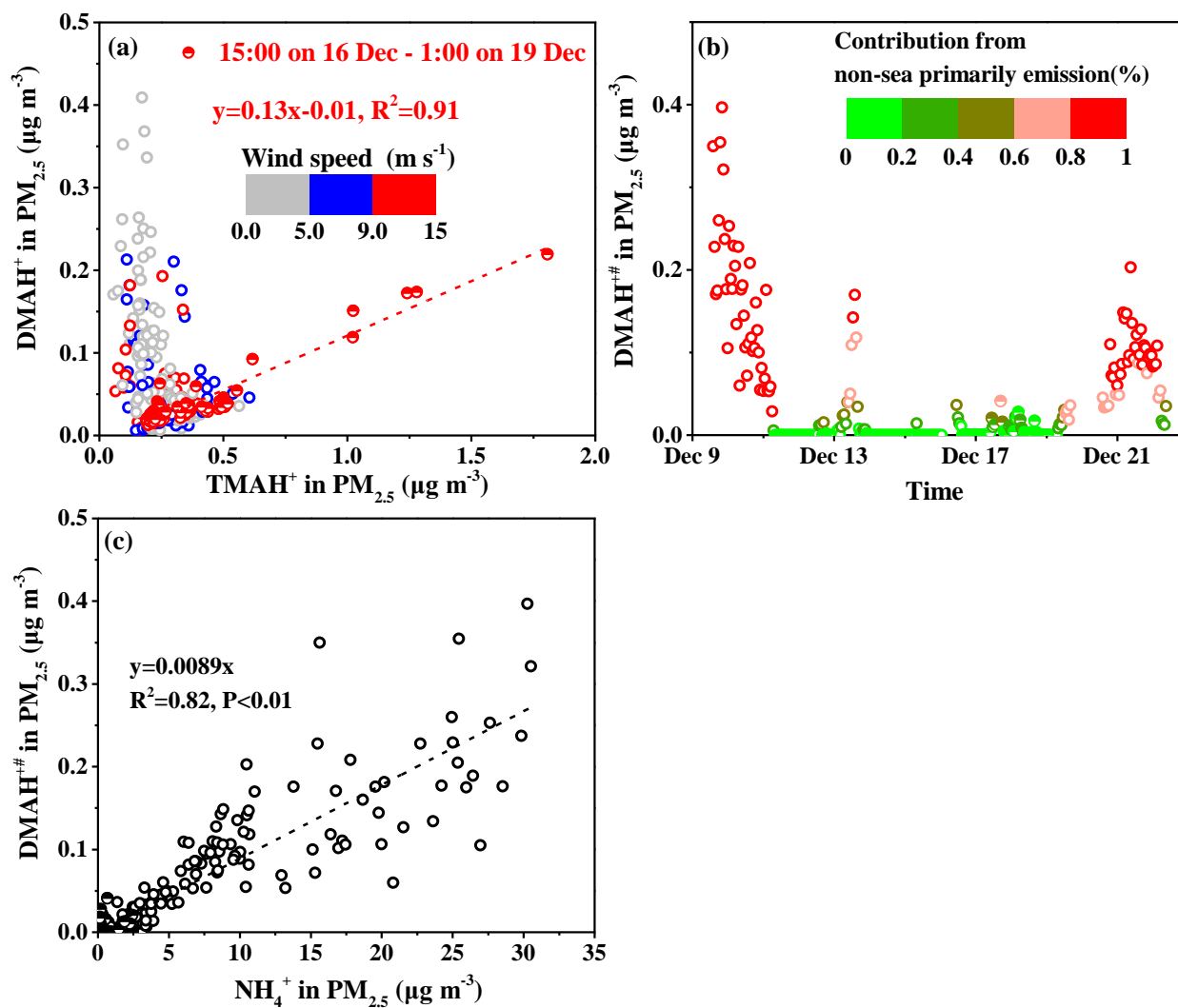
**Figure 6: Correlation analyses of different variables in PM₂.₅ and the time-series of the calculated DMAH⁺# in PM₂.₅ ((a) DMAH⁺ vs. TMAH⁺; (b) time-series of DMAH⁺#; (c) DMAH⁺# vs. NH₄⁺).**