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# Characteristics of dimethylaminium and trimethylaminium in atmospheric particles ranging from supermicron to nanometer sizes over eutrophic marginal seas of China and oligotrophic open oceans

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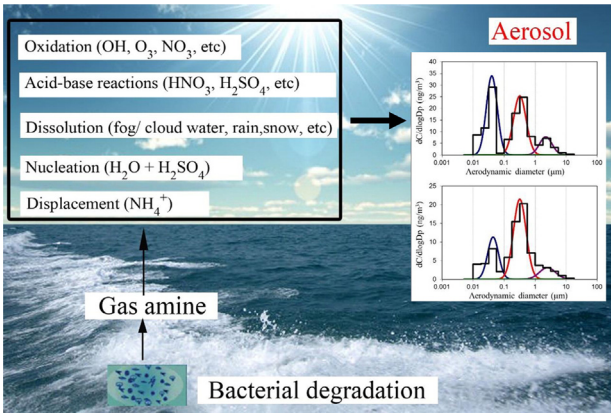
## HIGHLIGHTS

- Concentrations of $DMA^+$ and $TMA^+$ were investigated in marine atmospheric particles
- $DMA^+$ and $TMA^+$ in most samples dominantly existed in the size range of 0.1-1.8 μm
- Enrichment of $DMA^+$ and $TMA^+$ in 0.01-0.1 μm existed in different marine atmospheres

## GRAPHICAL ABSTRACT

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## ABSTRACT

In this study, we characterized dimethylaminium ($DMA^+$) and trimethylaminium ($TMA^+$) in size-segregated atmospheric particles during three cruise campaigns in the marginal seas of China and one cruise campaign mainly in the northwest Pacific Ocean (NWPO). An 14-stage nano-MOUDI sampler was utilized for sampling atmospheric particles ranging from 18 μm to 0.010 μm. Among the four cruise campaigns, the highest concentrations of $DMA^+$ and $TMA^+$ in $PM_{10}$ were observed over the South Yellow Sea (SYS) in August 2015, i.e., 0.76 ± 0.12 nmol $m^{-3}$ for $DMA^+$ (average value ± standard deviation) and 0.93 ± 0.13 nmol $m^{-3}$ for $TMA^+$. The lowest values were observed over the NWPO in April 2015, i.e., 0.28 ± 0.16 nmol $m^{-3}$ for $DMA^+$ and 0.22 ± 0.12 nmol $m^{-3}$ for $TMA^+$. In general, size distributions of the two ions exhibited a bi-modal pattern, i.e., one mode at 0.01–0.1 μm and the other at 0.1–1.8 μm. The two ions' mode at 0.01–0.1 μm was firstly observed. The mode was largely enhanced in samples collected over the SYS in August 2015, leading to high mole ratios of $(DMA^+ + TMA^+)/NH_4^+$ in $PM_{0.1}$ (0.4 ± 0.8, median value ± standard deviation) and the ions' concentrations

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$NH_4^+$
The Pacific Ocean

in $PM_{0.1}$ accounting for ~10% and ~40% of their corresponding concentrations in $PM_{10}$. This implied that ($DMA^+ + TMA^+$) likely played an important role in neutralizing acidic species in the smaller particles. Using $SO_4^{2-}$, $NO_3^-$ and $NH_4^+$ as references, we confirm that the elevated concentrations of $DMA^+$ and $TMA^+$ in the 0.01–0.1 μm size range were probably real signals rather than sampling artifacts.



## 1. Introduction

In the atmosphere, amines are highly hydrophilic basic gases like ammonia. The most common atmospheric amines are low molecular aliphatic amines which carbon numbers are under six and their concentrations generally vary from pg to ng per $m^3$ (Cornell et al., 2003; Ge et al., 2011a, 2011b). Recently, many attentions were paid to atmospheric amines because of their potential importance in the formation and growth of newly formed atmospheric particles (Smith et al., 2010; Wang et al., 2010; Kirkby et al., 2011; Kulmala et al., 2013). For example, Kirkby et al. (2011) proposed that the presence of ammonia and amines may greatly enhance nucleation of sulfuric acid-water system. Kulmala et al. (2013) found that dimethylamine (DMA) played an important role in newly formed particles in the sub–2 nm size range. Smith et al. (2010) reported that protonated amines may explain 10%–50% positive ions in 8–10 nm atmospheric particles, indicating that aminium salts yielded a significant contribution to the growth of atmospheric particles. Modeling results showed that amines may also contribute to the growth of >10 nm particles in the atmosphere (Yu and Luo, 2014). However, quantitative measurements of aminium ions in different sized atmospheric particles between 10 and 100 nm are still very limited. This restrains our understanding about this issue.

Ocean is one of the important sources of atmospheric amines (Ge et al., 2011a, 2011b; Hu et al., 2015). Previous modeling results showed that approximately 0.08 Tg amines were released from ocean to atmosphere per year, and the amines' contribution to marine secondary organic aerosols (SOA) reached up to 20%, second only to dimethylsulfide (DMS) (Myriokefalitakis et al., 2010). DMA and trimethylamine (TMA) are the two most common aliphatic amines in the atmosphere (Ge et al., 2011b). In marine environments, both DMA and TMA can be produced by organic degradation (Welsh, 2000; Carpenter et al., 2012). Recent studies also showed that TMA can be further oxidized to produce TMAO and then DMA in aerobic conditions (Chen et al., 2011). Several studies found that concentrations of $DMA^+$ and $TMA^+$ in marine atmospheric particles were associated with biological activities, e.g., Sorooshian et al. (2009) reported that increased concentrations of diethylaminium ($DEA^+$) and methanesulfonic acid (MSA) in atmospheric particles were well coincident with high concentrations of chlorophyll-*a* in surface seawater. Hu et al. (2015) reported a moderately good correlation between concentrations of $DMA^+$ (or $TMA^+$) in atmospheric particles and chlorophyll-*a* fluorescence values in surface seawater. However, these studies didn't measure the concentrations of $DMA^+$ or $TMA^+$ in <100 nm marine atmospheric particles.

In this paper, we conducted a comparative study of $DMA^+$ and $TMA^+$ in the size-segregated marine atmospheric particles measured during three cruise campaigns performing in the eutrophic marginal seas of China and one cruise campaign mainly in the oligotrophic open oceans of the northwest Pacific Ocean (NWPO). The objectives of this study include: 1) to determine the concentrations of particulate $DMA^+$ and $TMA^+$ in various marine atmospheres and to investigate their origins; 2) to study size distributions and formation pathways of $DMA^+$ and $TMA^+$ in atmospheric particles with the particular attention to the ions in atmospheric particles below 0.10 μm. Our results showed that $DMA^+$ and $TMA^+$ sometimes enriched in nanometer atmospheric particles, implying their important roles in the formation and growth of the smaller particles through neutralizing acidic species.

## 2. Experimental

In this study, we participated in four cruise campaigns. During 2–19 November 2012, 6–25 November 2013 and 18 August–September 2015, the research vessel (R/V) Dong Fang Hong II cruised in the marginal seas of China including the Bohai Sea (BS), the North Yellow Sea (NYS) and the South Yellow Sea (SYS). The vessel used general diesel fuel, in which the sulfur-content was 2000 ppm in 2012, but only 350 ppm after July 2013. In the spring campaign of 2015, the research vessel cruised in oligotrophic open oceans of the NWPO during 3 April and 3 May 2015 and in the SYS and the East China Sea (ECS) during 31 March −2 April and 4–5 May 2015. The marginal seas of China suffer from eutrophication to some extents, especially those zones including the Yangtze River Estuary, the BS and NYS and inshore seawater teeming with mariculture. The world's largest macroalgal bloom (green tide) occurs from May through August in the SYS every year because of the expanded seaweed mariculture (Liu et al., 2009).

An 14-stage Micro-Orifice Uniform Deposition Impactors (MOUDI) sampler was deployed on the upper deck of Dong Fang Hong II (~8 m above the sea surface) for collecting atmospheric particles. The MOUDI sampler was operated at a flow rate of 29.4 L $min^{-1}$ and had 50% cut-off points for particle aerodynamic diameters: 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.10, 0.056, 0.032, 0.018 and 0.010 μm. Teflon filters (47 mm, PALL Life Sciences) and Zefluor™ supported PTFE filters (90 mm, PALL Life Sciences) were used for collecting particles larger than 0.056 μm and particles below 0.056 μm, respectively. The sampling strategy is in effort to collect enough amount for analyzing interested species in different sized particles and enough samples for obtaining statistically significant results. However, the sampler had to be shut down during the vessel anchoring to avoid contamination from the smoke stack. The vessel was anchored frequently during the three cruise campaigns in the marginal seas of China, leading to sampling durations below 10 h. Occasionally, a few sampling durations lasted for only 3–4 h. During the cruise campaign in the NWPO, sampling durations usually lasted for 1–3 days because of low concentrations. 2–3 field blank samples were also collected in each cruise campaign, depending on the campaign length. Thus, we had 6–9 pieces of 90-mm filters and/or 22–33 pieces of 47-mm filters as field blank in each campaign. The collected samples were wrapped in pre-baked aluminum foil (450 °C, 6 h) and sealed in polyethylene bags with silica gel, then stored at −20 °C until chemical analysis.

All filters were extracted in the mixing solution of 0.5 mL anhydrous ethanol and 20 mL deionized water (18.2 MΩ·cm) using an ultrasonic bath at 0 °C for 20 min. The extract was then filtered through 0.45 μm PTFE syringe filters (25 mm, PALL Life Sciences) to remove insoluble materials (Hu et al., 2015). The ions in extracts were determined using an Ion Chromatography (Dionex 3000). The detected ions included aminium ions ($DMA^+$, $TMA^+$), inorganic ions ($Cl^-$, $SO_4^{2-}$, $NO_3^-$, $NH_4^+$, $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$) and dicarboxylic acids. Different analytic columns and leacheates were employed to determine these ions, i.e., CS17A (Dionex, 250 mm × 4 mm) and methylsulphonic acid (6 mmol $L^{-1}$) were used to determine amines, CS12A (Dionex, 250 mm × 4 mm) and methylsulphonic acid (18 mmol $L^{-1}$) were used to determine other cations and AS11 (Dionex, 250 mm × 4 mm) and NaOH (3–40 mmol $L^{-1}$, gradient) were used to determine anions and dicarboxylic acids. Column temperatures, in all cases, were

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