Impacts of crystal metal on secondary aliphatic amine aerosol formation during dust storm episodes in Beijing

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HIGHLIGHTS

- We detected the trimethylamine-N-oxide in fine particle matter in Beijing.
- Trimethylamine-N-oxide concentration was highly associated with Al.
- We applied the DFT method to investigate the formation mechanism of TMAO.

ABSTRACT

Trimethylamine (TMA) enters the atmosphere from a variety of sources and is a ubiquitous atmospheric organic base. The atmospheric reaction mechanism of TMA with key atmospheric oxidants is important to predict its distribution and environmental behavior in the particle phase. While previous studies have extensively focused on the production of particle amine salts (i.e. trimethylamine-N-oxide (TMAO)) using chamber experiments, the atmospheric behavior of TMAO in the environment is still poorly understood. Ambient fine particulate matter (PM$_{2.5}$) was collected at two sampling sites in Beijing from March 10 to May 10, 2012. We analyzed the samples for water-soluble ions, crystal metals, TMA, and TMAO. Water-soluble ions (e.g. SO_4^{2-}, NO_3^-, NH_4^+), TMA, and TMAO were measured using ion chromatography, while crystal metal (e.g. Al, Fe, Mn) in PM$_{2.5}$ was quantified by inductively coupled plasma mass spectrometry (ICP-MS). Two dust storms (DS) occurred during the sampling period on March 28 and April 28. Mineral dust impacted PM$_{2.5}$ mass and composition greatly during dust storm days, as it contributed approximately 1.2–4.0 times greater on dust storm days versus non-dust storm days. We found TMAO concentrations were highly associated with aluminum in PM$_{2.5}$. Further, we applied the density functional theory (DFT) method to confirm that aluminum plays a catalytic effect in the reaction of TMA with ozone (O$_3$). Our work improves understanding of the effect of crystal metals on secondary aliphatic amine aerosol formation in the atmosphere.

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1. Introduction

Among the organic compounds relevant in the atmosphere, amines are unique in their acid-neutralizing capability (Silva et al., 2008). Amines are derivatives of ammonia in which an alkyl or aryl group has replaced at least one hydrogen atom (Ge et al., 2011a,b).

Much attention has been devoted to the environmental behavior of low-molecular weight amines, such as dimethylamine (DMA) and trimethylamine (TMA) (Ge et al., 2011a,b). Schade and Crutzen (1995) estimated that TMA was the greatest contributor of amines to the global input of nitrogen from animal husbandry. TMA can be a strong base even in the presence of ammonia, with concentrations as much as 20% of the volume of ammonia, and it is even more important than ammonia in enhancing atmospheric nucleation (Tang et al., 2014). Further, TMA can also participate in the formation of secondary organic aerosol. Several studies have shown that gas-phase TMA can form non-salt organic aerosol

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products through reactions with oxidizing agents such as O_3, OH, and NO_3 radicals (Erupe et al., 2010; Murphy et al., 2007; Silva et al., 2008; Tang et al., 2013; Price et al., 2014). Trimethylamine-N-oxide (TMAO) has been confirmed as the reaction product of TMA in several smog chamber studies using aerosol time-of-flight mass spectrometry (ATOFMS) (Erupe et al., 2010; Murphy et al., 2007; Zhang et al., 2012). However, the concentration and environmental particle behavior of TMAO in different regions is still unclear.

Asian dust (yellow sand) storms commonly originate from arid areas in China and Mongolia, where strong surface winds uplift mineral particles into the middle troposphere (Liu et al., 2014a,b; Gross et al., 2015). Springtime trade winds carry a portion of this dust across China's mainland to East Asia and North America, which increases ambient particulate matter (PM) concentrations (Cao et al., 2015). According to a number of studies, the chemical characteristics of the dust involved in storm events is responsible for the feedback effects on climate and human health during periods of increased PM concentration (Wang et al., 2011; Srivastava et al., 2014; Liu et al., 2014a; Zhang et al., 2010). The heterogeneous reactions that occur on the large surface area of dust particles alter radioactive transfer and rates of photolysis (Manktelow et al., 2010; Sullivan et al., 2007; Erel et al., 2006). Mineral dust particles can become internally mixed with secondary species such as ammonium sulfate, ammonium nitrate, hydrochloric acid, sea salt, and particles produced by biomass burning through coagulation, cloud processing, and heterogeneous reactions (Usher et al., 2003). Mineral dust mixed with secondary acids can increase the solubility and bioavailability of iron, which is an important pathway for the fertilization of remote oceans with subsequent climate impacts (Shi et al., 2011). Nitrate on dust particle is also an important vector for nitrogen fertilization of oceans (Wang et al., 2013; Manktelow et al., 2010; Zhang et al., 2010). Aluminum is a major component of mineral dust in the atmosphere (Zhang et al., 2003, 2010). Input fluxes of dissolved dust aluminum from the Gobi desert region could result in phytoplankton blooms in the Southern Yellow Sea of China (Ren et al., 2011). Furthermore, several chamber experiments have confirmed that the presence of aluminum on dust particles could enhance the photo-oxidation rates of SO_2, NO_2, α-pinene, and m-xylene, resulting in the significant increases in secondary aerosol formation (Liu et al., 2013; Loza et al., 2012; Ma et al., 2008; Kroll and Seinfeld, 2008), which is one of the largest contributors to ambient PM during haze episodes in China (Huang et al., 2014; Liu et al., 2016). Currently, several quantum models, including density functional theory (DFT) (Xu et al., 2010; Zhang et al., 2014) and master chemical mechanism (MCM) (Wang et al., 2015), have been used to predict the chemical compositions of gas-phase oxidation products in the atmosphere, as those observed by the chamber experiments (Xu et al., 2010; Zhang et al., 2014; Wang et al., 2015). These models can provide more detail about the thermodynamic and kinetic analyses for oxidative reactions, but they require much less experimental effort (Xu et al., 2005; Zhang et al., 2014). Because DFT has computational advantages, it has successfully been used to study atmospheric reactions such as secondary formation of polycyclic aromatic hydrocarbons (PAHs) (Zhang et al., 2014) and dioxin formation from phenoxy radicals with 2-chlorophenoxy radicals (Xu et al., 2010).

We collected 24-h ambient $PM_{2.5}$ samples during dust storm episodes at two sampling sites in Beijing, and measured their TMAO concentrations. We also combined experimental and DFT methods to confirm the secondary formation reaction of TMA on particles. This study provides new information to increase understanding of the factors that control secondary aliphatic amine aerosol formation in the atmosphere.

2. Methods

2.1. Aerosol samplings

The sampling site S_1 (latitude: N 39°97′91″0; longitude: E116°21′30″0) was located on the roof of an office building 20 m above ground within an urban area at the Institute of Botany of the Chinese Academy of Sciences. The site was 30 km away from the city center, it was surrounded by unused land, and the nearest source of anthropogenic pollution was a lightly trafficked road about 500 m away. The sampling site S_2 was located near a busy traffic line (latitude: N 39°56′50″7; longitude: E116°18′10″8) on the roof of a 30 m tall office building about 30 m away from major highways. 24 h $PM_{2.5}$ aerosol samples were collected onto 90 mm diameter quartz microfiber filters (QMA, Whatman) at sites S_1 and S_2 in spring 2012 (March 10-May 10) using medium volume sampling equipment at a flow rate of 100 L min^{-1}, as recommended by China's $PM_{2.5}$ standard method guidelines (HJ93-2013). The internal surfaces of the samplers were coated in high-density Teflon. Deionized water (18.2 MΩ cm^{-1} resistance), hexane, and acetone were used to clean the stainless steel tweezers used for filter and filter substrate handling in order to prevent sample contamination. The quartz filters were baked for 4 h at 550 °C and conditioned in desiccators for 2 h prior to air sampling. Filters were changed daily at 10:00 am. On average, one filter blank was collected for every 6 samples collected throughout the measurement period. After each measurement period, the samples were individually sealed into an aluminum foil package and stored at −18 °C prior to gravimetric and chemical analysis. Daily temperature, wind speed, and relative humidity (RH) were recorded using a Kestrel 3000 meteorological station (Kestrel Instrument, USA) (Fig. S1).

2.2. PM mass and chemical analysis

Details of PM gravimetric analysis, chemical analysis, and related quality assurance and control practices are described elsewhere (Liu et al., 2014a,b; Liu et al., 2016). $PM_{2.5}$ mass concentration was calculated as the filter mass difference before and after sampling at unit sampling volume. Filters were heated for 4 h at 550 °C and preserved in desiccators for 24 h; then, pre-sampling weights were taken with a balance (CP225D, with accuracy of 0.01 mg, made in Sartorius, Germany) in a weighing room, which had a controlled relative humidity of approximately 35% and a temperature of 20 ± 2 °C. Each filter was weighed 3 times, and the average of these readings was used for statistical analysis. All procedures followed the U.S. Environmental Protection Agency's (EPA) standard operating procedure for PM gravimetric analysis in order to avoid any possible contamination (Liu et al., 2014a). Blank corrections were calculated based on the weight differences between samples and blanks, which provide accurate results that are not affected by background values. The final PM mass concentration was determined by calculating the difference in filter weight before and after PM sampling, minus the average blank concentration, and divided by the standard air volume that passed through the filter during the 24-h measurement period. Total uncertainties were propagated using the square root of the sum of squares method, which accounts for both analytical uncertainties and uncertainties arising from field handling, shipping and storage, and the experimental instruments.

The quartz fiber filters were cut into 15 cm^2 pieces and extracted with 20 mL Milli-Q 18 MΩ cm^{-1} water (Dubuque, IA, USA) into Eppendorf vials. Then, they were sonicated for 30 min and vortexed (3000 rpm) for 5 min. Major ions—chlorine, sulfate, nitrate, sodium, potassium, calcium, magnesium, and ammonium—were analyzed by an ion chromatography system (Dionex ICS-2000).