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

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18 **Abstract:** Trimethylamine (TMA) enters the atmosphere from a variety of sources and
19 is a ubiquitous atmospheric organic base. The atmospheric reaction mechanism of
20 TMA with key atmospheric oxidants is important to predict its distribution and
21 environmental behavior in the particle phase. While previous studies have extensively
22 focused on the production of particle amine salts (i.e. trimethylamine-N-oxide
23 (TMAO)) using chamber experiments, the atmospheric behavior of TMAO in the
24 environment is still poorly understood. Ambient fine particulate matter (PM_{2.5}) was
25 collected at two sampling sites in Beijing from March 10 to May 10, 2012. We
26 analyzed the samples for water-soluble ions, crystal metals, TMA, and TMAO.
27 Water-soluble ions (e.g. SO₄²⁻, NO₃⁻, NH₄⁺), TMA, and TMAO were measured using
28 ion chromatography, while crystal metal (e.g. Al, Fe, Mn) in PM_{2.5} was quantified by
29 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.

Keywords: trimethylamine-N-oxide, $PM_{2.5}$, dust storm, density functional theory

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 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; Zhang et al., 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 SO₂, NO₂, 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-hour 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 S₁ (latitude: N 39°9'91"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 S₂ 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 hours PM_{2.5} aerosol samples were collected onto 90 mm diameter quartz microfiber filters (QMA, Whatman) at sites S₁ and S₂ 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. De-ionized 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 hours at 550°C and conditioned in desiccators for 2 hours prior to air sampling. Filters were changed daily at 10:00am. 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) (Figure 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 hours at 550°C and preserved in desiccators for 24 hours; then, pre-sampling weights were taken with a balance (CP225D, with accuracy of 0.01mg, 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-hour 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 cm² 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 minutes and vortexed (3000 rpm) for 5 minutes. Major ions—chlorine, sulfate, nitrate, sodium, potassium, calcium, magnesium, and ammonium—were analyzed by an ion chromatography system (Dionex ICS-2000). Sample concentrations were calibrated with a series of mixed standards of known concentrations (0.01-10 µg mL⁻¹). The repeatability, which is expressed as relative standard deviation (RSD) and is measured at a 50 ng mL⁻¹ level, was in the range of 4.3-5.6% for ions (n=7). Based on the RSDs measured at 50 ng mL⁻¹, the calculated detection limits (S/N=3) for chlorine, sulfate, nitrate, sodium, potassium, calcium, and ammonium were 2.5, 4.4, 5.4, 3.5, 4.7, 4.2, 3.8, and 6.2 ng mL⁻¹, respectively. Non-filter/filter and reagent blanks were also conducted to ensure analytical precision.

One quarter of each filter sample (area of 15 cm²) was digested with HNO₃+H₂O₂ (2:0.5) using a microwave assisted decomposition equipment (CEM Co., MARS). Elements (Zn, Cu, Mn, Al, and Fe) in the PM HNO₃ digestion solution were quantified using inductively coupled plasma mass spectrometry (Agilent 7500a). Filter and reagent blanks were also analyzed to ensure analytical precision. Recoveries of the samples were 98%. The RSDs measured for 5 ng mL⁻¹ metal solutions were in the range of 2.4-6.5% (n=7); the calculated detection limits (S/N=3) were in the range of 0.2-1.5 ng mL⁻¹. The metal concentrations were determined by calculating the difference between PM samples and blanks.

The concentrations of trimethylamine and trimethylamine-N-oxide in PM were measured using methods described elsewhere (Erupe et al., 2010). For three 15 minute intervals, 15 cm² sections of the filters were ultrasonicated with 18.2 MΩ cm⁻¹ Milli-Q water and methanol (3/1, v/v). The extract was concentrated to a ~0.5 mL methanol solution using a C18 solid phase extraction column (AccuBOND, Agilent, USA) to minimize the interface from cationic ions. The C18 solid phase extraction procedure was tested with a model solution containing 10 ng mL⁻¹ aliphatic amine

(dimethylamine, trimethylamine, methylamine, and trimethylamine-N-oxide) with cationic ions (e.g. K^+ , Ca^{2+} , Na^+ , Mg^{2+} , Al^{3+} , and NH_4^+) before application to real samples, and the recoveries were in the range of 95-98% (n=7). Instead of a solvent, 2 mL of de-ionized water was added to the 0.5 mL methanol solution, and the mixed liquor was injected into ion chromatography equipment (Dionex ICS-2000), which included a binary pump and a non-suppressed detection. An automatic sampler with a 100 μ L loop (Rheodyne, USA) and a 250 mm $\times$ 4 mm id PRP X-200 (Hamilton, USA) guard column were used for injection and separation of analytes (Liu., 2010). The mobile phase was a mixture of 3% (v/v) acetonitrile solution and 5mM nitric acid, and the flow rate was kept at 1.0 mL min⁻¹. Mixed working standard solutions were prepared by dissolving methylamine (MMA), dimethylamine (DMA), trimethylamine (TMA), and trimethylamine-N-oxide (TMAO) in 18.2 M Ω cm⁻¹ Milli-Q water. A typical chromatogram of MMA, DMA, TMA, and TMAO at 100 μ g L⁻¹ is shown in Figure S2. The four aliphatic amine species were fully resolved and the separations were completed within 30 minutes. Standards for calibration were prepared by diluting the stock solution with Millipore water. The linearity of the four compounds ranged from 20 to 100 μ g L⁻¹; the RSDs measured for 50 μ g L⁻¹ of aliphatic amine solutions were in the range of 4.8-6.8% (n=7). The detection limits based on three levels of the background were 5 μ g L⁻¹ for MMA, 6 μ g L⁻¹ for DMA, 5 μ g L⁻¹ for TMA, and 8 μ g L⁻¹ for TMAO.

2.3 Computational modeling

Density functional theory is a quantum mechanical modeling approach that expresses the total energy of a system as a function of electron density. The electron density ($\rho(r)$) that defines the ground-state properties of a molecular system is the basis for DFT. In DFT, the energy function ($E(\rho)$) is written as a sum of four terms:

$$E[\rho(r)] = -\sum_{A=1}^M \int \frac{Z_A}{r-R_A} \rho(r) dr + \sum_{i=1}^N \int \psi_i(r) \left(-\frac{\nabla^2}{2} \right) \psi_i(r) dr + \frac{1}{2} \iint \frac{\rho(r_1)\rho(r_2)}{r_1-r_2} dr_1 dr_2 + E_{xc}[\rho(r)]$$

(1)

where Z_A is the charge on nucleus A, r is a position vector, R_A is the position vector of nucleus A, M is the number of nuclei, N is the number of electrons, ψ_i is the spatial orbital occupied by electron i , and $E_{xc}[\rho(\mathbf{r})]$ is the exchange-correlation energy functional. From utilization of Becke's 1988 gradient-corrected exchange functional, DFT calculations can give transition state geometries and barrier heights of reactions to determine whether the reaction proceeds. Therefore, geometrical parameters of the reactants, transition states, and products were fully optimized at the B3LYP level with a standard basis set at 6-311G (d, p). The position of stationary points and the zero-point energy (ZPE) were determined by the vibrational frequency calculation at the same level. For each transition state, the intrinsic reaction coordinate (IRC) calculation was performed using the same electronic structure theory to confirm that it was connected to the right minima along the reaction pathway (Bei et al., 2012; Sun et al., 2012).

The changes in thermodynamic functions, including entropy; enthalpy; free energies for reactants, transition states, and products; and the equilibrium constants of the reaction in the Eyring transition state theory were calculated at the B3LYP/6-311G (d, p) level. Reaction rate constants ($k(T)$), changes in the thermodynamic functions (ΔS , ΔH and ΔG), and equilibrium constants of the reactions were calculated using the B3LYP/6-311G (d, p)-optimized geometries, and the harmonic vibrational frequencies. The rate constant is given

$$k(T) = \frac{k_B T}{h} \exp\left(\frac{\Delta S}{R} - \frac{\Delta H}{RT}\right) \quad (2),$$

where k_B is the Boltzmann constant, h is the Planck constant, ΔH is the activation enthalpy, and ΔS is the activation entropy. The reaction equilibrium constant is

$$K = \exp\left(-\Delta G \times \frac{1000}{RT}\right) \quad (3),$$

where ΔG is the Gibbs free energies of the reaction. All the calculations were performed with the Gaussian 03 software package (Gaussian, Inc., Wallingford, CT, USA) (Frisch et al., 2003).

2.4 Statistical analysis

We present the summary statistics for PM mass and chemical components on dust storm and non-dust storm days (Table 1). Summary statistics for data are presented as the mean and standard deviation for each day of the study, based on the results from at least three independent experiments that used the ambient PM sample. Students' t-tests were used to estimate the mean differences in PM_{2.5} mass and components on dust storm versus non-dust storm days.

The correlation analysis assists in verification of the variables that could impact the concentrations of TMA and TMAO formation in PM_{2.5}. Correlations between variables (e.g. relative humidity, SO₄²⁻, NO₃²⁻) and the concentrations of TMA and TMAO on dust storm and non-dust storm days were tested using Pearson's correlation coefficients with statistical significances at $p < 0.001$ and $p < 0.05$ (2-tailed). The one-sample Kolmogorov-Smirnov test was used in testing the normal distribution for all variables (Mirabella, 2006). The results showed all 2-tailed p-values are greater than 0.05, which indicates the data is suitable for correlation analysis. All statistical analyses were performed using SPSS V13.0.

2.5 Backward trajectories analysis

Air mass backward trajectories were conducted using the National Oceanic and Atmospheric Administration's (NOAA) ARL Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) 4.8 model with meteorological data from the Global Data Assimilation System (GDAS) (<http://www.arl.noaa.gov/ready/hysplit4.html>) (Draxler and Hess, 1998). With Beijing as the starting point (39.97°N, 116.21°E), 24-hour backward trajectories were performed at 200 and 500 m levels.

3. Results

Two dust storm (DS) events occurred during the sampling period on March 28 and April 28. The storms spread over an area that encompassed both sampling sites S₁ and S₂. Lead isotopes, 24-hour backward trajectories, and meteorological factors (e.g. temperature, relative humidity, wind speed) were used to confirm the dust storm events and origins, which were described in detail in previous work (Liu et al., 2014b).

During the sampling period, PM_{2.5} mass peaked at 409 $\mu\text{g m}^{-3}$ at the peri-urban site (S₁) and 291 $\mu\text{g m}^{-3}$ at the central site (S₂); these values are 2.7-3.0 times higher than the mean concentrations at the S₁ (140) and S₂ (100) sites (Figure 1). Dust events are generally characterized as cold fronts with relatively dry conditions, low relative humidity, and high wind speed (Zhang et al., 2010). Higher PM_{2.5} mass concentrations were observed on March 28 and April 27-29—days with elevated wind speed and decreased relative humidity (Figure S1). These conditions are consistent with meteorological data that suggests a cold front was responsible for the dust storms that occurred over both sampling sites (Liu et al., 2014a, b).

The average concentrations of Na⁺, Mg²⁺, Ca²⁺, K⁺, and Cl⁻ on dust storm days were 1-2 times higher than those on non-dust storm days (Table 1 and Figure S3), indicating relatively direct primary emissions during dust storm days (Geng et al., 2009; Srivastava et al., 2014). Concentrations of SO₄²⁻, NO₃⁻, and NH₄⁺ had similar trends, and the highest concentrations were observed during dust storm days—specifically April 28, when concentrations were 2-5 times greater than those of non-dust storm days. There were significant differences observed in the average concentration of SO₄²⁻, NO₃⁻, and NH₄⁺ between the dust storm and non-dust storm days (Table 1 and Figure S4). Several previous studies found these inorganic salts (i.e. SO₄²⁻, NO₃⁻, NH₄⁺) could be detected in the air of the Taklimakan desert and transported to Chinese mainland during dust storm days (Wu et al., 2014; Hatakeyama et al., 2014; Zhang et al., 2010). Moreover, SO₄²⁻, NO₃⁻, and NH₄⁺ could be more easily formed from the precursors SO₂, NO_x, and NH₃ on dust particles (Zhang et al., 2003; Zhang et al., 2010; Wang et al., 2015). Our results support results from a previous Beijing study in which increased concentrations of SO₄²⁻, NO₃⁻, and NH₄⁺ were attributed to long-range transport of emissions from the desert, as well as secondary formation on dust particles (Zhang et al., 2003; Wu et al., 2014; Hatakeyama et al., 2014). Average concentrations of Al and Fe showed a remarkable concentration elevation during dust storm days in comparison to those on normal days (Table 1 and Figure S5), suggesting that direct primary emissions were enhanced during dust storm days (Erel et al., 2006; Zhang et al., 2010).

Daily TMA concentrations were in the range of 0.015-0.084 $\mu\text{g m}^{-3}$ (mean: 0.029 $\mu\text{g m}^{-3}$) at the peri-urban site (S_1), and ranged from 0.011 to 0.035 $\mu\text{g m}^{-3}$ (mean: 0.020) at the central site (S_2) (Figure 2). Similarly, TMA concentrations on dust storm days were considerably higher than those of non-dust storm days (Table 1). Based on backward trajectories from the NOAA HYSPLIT model, the dust storms appear to be influenced by rural parts of northwestern China (Figures S6 and S7). The differences in TMA concentration on dust storm days versus non-dust storm days were associated with agricultural land northwest of the observation site, where agricultural activities are the major source of amines (Ge et al., 2011b). The average TMAO concentration during dust storm days was 0.060 $\mu\text{g m}^{-3}$ for S_1 and 0.026 $\mu\text{g m}^{-3}$ for S_2 , which is more than 1.3 times higher than concentration average for non-dust storm days (S_1 : 0.026 $\mu\text{g m}^{-3}$; S_2 : 0.019 $\mu\text{g m}^{-3}$) (Table 1 and Figure 2). The reaction of trimethylamine (TMA) with O_3 , OH, and NO_3 radicals produces TMAO, while TMA is emitted from chemical manufacturing, industry, automobiles, landfills, agricultural activities, and food waste/biomass burning (Price et al., 2014; Ge et al., 2011a, b). Zhang et al. (2012) found that fractions of TMA-containing particles increased dramatically during fog occurrences in Guangzhou and concluded that gas-to-particle partitioning of TMA occurs preferentially with increased air humidity. We did not find a significant correlation between increased TMA concentrations and relative humidity at either sampling site (S_1 : $r=0.23$, $p>0.05$; S_2 : $r=0.05$, $p>0.05$) (Figure S8), which does not agree with results by Zhang et al. (2012). Increased concentrations of particle TMA on dust storm days could be attributed to the primary emissions (i.e. agricultural activities), which may explain the low correlation between TMA concentration and relative humidity in our study. Tang et al. (2013) explored the effects of relative humidity (from 0.1% to 40%) on secondary aliphatic amine formation and concluded that secondary aerosols are formed in greater quantities under high relative humidity (RH) conditions. There was no difference in RH between dust storm versus non-dust storm days (S_1 : 25% vs. 27%, $p=0.09$; S_2 : 37% vs. 37%, $p=0.271$) (Table S1). In addition, concentrations of TMAO were not significantly associated with RH during the sampling period (S_1 : $-r=0.01$, $p>0.05$; S_2 : $r=-0.01$,

p>0.05) (Figure S9). It is important to observe that the predominant variable related to the increase in TMAO concentration during these dust storm episodes was not relative humidity.

4. Discussion

We assessed the relationships between TMAO concentration and PM_{2.5} components at the two sampling sites using Pearson's correlation. We found moderate to strong correlations between increased TMAO concentration and sulfate/nitrate (S₁: r=0.528-0.629, p<0.001; S₂=0.370-0.436, p<0.001), which is consistent with the previous finding that nitrate and sulfate formation is highly associated with amine-containing particles (Figures S10, S11 and Table S2) (Zhang et al., 2012). TMAO concentration was significantly correlated with Al (r>0.370, p<0.001) for both sites (Figures S10 and S11). The Pearson's correlation coefficient for TMAO with Al in PM_{2.5} was considerably higher on dust storm days at both sites, indicating that catalytic effects of Al in TMAO formation may also have been more impactful on dust storm days (Table S3). Similar observation results are not found elsewhere. As suggested in previous studies, it is possible that TMAO formation and sulfate/nitrate formation in dust particles is similar (Usher et al., 2003; Geng et al., 2009; Wang et al., 2011; Zhang et al., 2010). Increased content of crystal metals (e.g. Al, Fe) in PM_{2.5} during dust days would favor sulfate and nitrate formation onto the particles (Usher et al., 2003). The concentration of TMAO was also highly associated with Cl in PM_{2.5}; thus, AlCl₃ can be used as a simple proxy in the DFT method to further investigate the catalytic effects of Al in the TMAO formation mechanism.

The calculation results at the B3LYP/6-311G (d, p) levels showed that there were two pathways for the reaction of TMA with O₃ in the presence of AlCl₃, as seen in Figure 3. They can be depicted as follows:

- (1) Reaction Al-O (14): the AlCl₃ attacked O₃ from the front of the TMA molecular;
- (2) Reaction Al-O (16): the AlCl₃ attacked O₃ from the back of the TMA molecule, which was far away from the nitrogen atom.

The geometries of the reactants, products, and transition states (TS) attacked by AlCl_3 on O_3 from different positions were optimized at the B3LYP/6-311G (d, p) level. The corresponding energies (including ZPE, ZPVE, and energies corrected by ZPVE) are listed in Table 2. In order to understand the reactions more precisely, the optimized parameters and energies for the ozonolysis reaction with TMA without AlCl_3 are listed in Tables 2 and S4, respectively.

The barrier heights calculated at the B3LYP/6-311G (d, p) level are $-102.9196 \text{ kJ mol}^{-1}$ for Al-O (14) and $-87.6917 \text{ kJ mol}^{-1}$ for Al-O (16), while the barrier height for the ozonolysis reaction with TMA is $-1.5753 \text{ kJ mol}^{-1}$ (Table 2). The latter ($-1.5753 \text{ kJ mol}^{-1}$) are much higher than the formers ($-102.9196 \text{ kJ mol}^{-1}$ for Al-O (14) and $-87.6917 \text{ kJ mol}^{-1}$ for Al-O (16)). Thus, we can conclude that aluminum is vital for the reaction of O_3 with TMA. Furthermore, we assessed the impacts of other metals (Cu, Zn, Fe) on the reaction of O_3 with TMA and did not find the right minima along the reaction pathway using the DFT method, indicating other metals may have no catalytic effect on the reaction.

Thermodynamic and kinetic analyses for reactions can quantitatively explain their reliability and possibility in the real atmosphere (Bei et al., 2012; Zhang et al., 2014; Yu et al., 2011). Based on calculations from equations (2) and (3), the rate and equilibrium constants of the reaction in the absence of AlCl_3 at 298 K are $1.09 \times 10^{-1} \text{ s}^{-1}$ and 1.63×10^{-1} , respectively; therefore, this reaction could not proceed at room temperature (Table 3). Tang et al. (2013) also confirmed that ozonolysis with TMA could produce negligible amounts of secondary aerosol in the chamber experiment. The respective rate and equilibrium constants at 298 K are $2.74 \times 10^6 \text{ s}^{-1}$ and 2.89×10^{18} for Al-O (14) and $1.25 \times 10^{10} \text{ s}^{-1}$ and 2.40×10^{14} for Al-O (16) (Table 3). These values are significantly higher than those for the reaction of O_3 with TMA, which support our field observation results that the formation of TMAO could occur faster when ambient particles of aluminum are present.

5. Conclusions

To the best of our knowledge, this study is the first to detect trimethylamine-N-oxide in ambient particle samples and assess the catalytic effects of metals on its formation mechanism during dust storm episodes. We found that significantly higher TMAO in dust particles was strongly associated with increased levels of sulfate, nitrate, and aluminum. The experimental and DFT results indicate that aluminum plays an important role in TMAO formation in the real atmospheric environment. Our results support previous studies that have shown secondary sources are enhanced during dust storm episodes, and provide important new information regarding the contribution of aluminum in secondary aliphatic amine aerosol formation in dust particles.

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Figure 1. Daily trends in **PM_{2.5}** mass concentration at a peri-urban (S₁) and a central site (S₂) in Beijing from March 10 to May 10, 2012.

Figure 2. The daily variations of TMA and TMAO in PM_{2.5} at a peri-urban site (S₁) and a central site (S₂) during the sampling time in Beijing. TMA: Trimethylamine, TMAO: Trimethylamine-N-oxide.

Figure 3. The geometries of the reactants (Re), transition states (TS) and final products (P) calculated at the B3LYP/6-311G (d, p) level.

Table 1.Concentration ($\mu\text{g m}^{-3}$) of mass and metals in PM_{2.5} at aperi-urban site (S₁) and a central Beijing site (S₂) during dust storm and non-dust storm days.

	Mean (SD) at S ₁	Mean (SD) at S ₂		Mean (SD) at S ₁	Mean (SD) at S ₂		Mean (SD) at S ₁	Mean (SD) at S ₂		Mean (SD) at S ₁	Mean (SD) at S ₂
Mass			Mg ⁺			SO ₄ ²⁻			Mn		
N	120±64	100±60	N	0.25±0.08	0.60±0.19	N	1.84±1.31	2.97±0.62	N	0.30±0.26	0.22±0.16
D	210±160	150±60	D	0.43±0.10	0.72±0.25	D	3.71±1.87	3.65±1.09	D	0.41±0.24	0.15±0.17
	(^a <i>p</i> <0.001)	(^a <i>p</i> <0.001)		(^a <i>p</i> <0.001)	(^a <i>p</i> <0.001)		(^a <i>p</i> <0.001)	(^a <i>p</i> <0.001)		(^a <i>p</i> <0.001)	(^a <i>p</i> =0.212)
Na ⁺			Ca ²⁺			TMAO			Fe		
N	1.06±0.48	1.57±0.52	N	5.14±0.88	4.73±1.04	N	0.026±0.005	0.019±0.004	N	4.32±1.88	0.69±0.19
D	1.83±0.52	1.79±0.52	D	8.99±1.75	6.65±1.41	D	0.060±0.027	0.026±0.002	D	11.00±6.37	1.12±0.18
	(^a <i>p</i> <0.001)	(^a <i>p</i> <0.001)		(^a <i>p</i> <0.001)	(^a <i>p</i> <0.001)		(^a <i>p</i> <0.001)	(^a <i>p</i> <0.001)		(^a <i>p</i> <0.001)	(^a <i>p</i> <0.001)
NH ₄ ⁺			Cl ⁻			TMA			Cu		
N	0.89±0.30	1.85±0.57	N	0.75±0.26	1.31±0.41	N	0.037±0.011	0.033±0.011	N	0.97±1.14	0.75±0.6
D	1.40±0.13	1.98±0.65	D	1.61±0.51	1.87±0.56	D	0.074±0.020	0.039±0.010	D	0.90±1.09	0.78±0.34
	(^a <i>p</i> <0.001)	(^a <i>p</i> <0.001)		(^a <i>p</i> <0.001)	(^a <i>p</i> <0.001)		(^a <i>p</i> <0.001)	(^a <i>p</i> <0.001)		(^a <i>p</i> =0.131)	(^a <i>p</i> =0.154)
K ⁺			NO ₃ ⁻			Al			Zn		
N	0.25±0.08	0.41±0.15	N	1.65±1.32	3.99±1.69	N	0.76±0.61	0.32±0.18	N	1.61±1.81	0.71±0.99
D	0.46±0.12	0.48±0.12	D	2.63±1.34	4.58±1.22	D	3.97±1.26.	0.65±0.22	D	1.58±1.94	0.62±0.35
	(^a <i>p</i> <0.001)	(^a <i>p</i> <0.001)		(^a <i>p</i> <0.001)	(^a <i>p</i> <0.001)		(^a <i>p</i> <0.001)	(^a <i>p</i> <0.001)		(^a <i>p</i> =0.118)	(^a <i>p</i> =0.098)

N: Non-dust storm days (n=45), D: Dust storm days (n=9); TMAO: Trimethylamine-N-oxide; TMA:Trimethylamine; SD: standard deviation; PM_{2.5},;particulate matter with an aerodynamic diameter <2.5 microns. ^a*p*-value for the difference in arithmetic means of PM_{2.5} mass and chemical components, stratified by different sub-groups.

7 **Table 2.** Absolute energies, zero-point energies, and relative energies of reactants (Re),
8 intermediates, transition states (TS), and products (P) calculated at B3LYP/6-311G (d,
9 p).

Species	$E_{\text{ZPVE}}^*/$ (kJ mol ⁻¹)	$E^*/\text{a.u.}$	$E_{\text{T}}^*/\text{a.u.}$	$E_{\text{R}}^*/$ (kJ mol ⁻¹)
Re=N(CH ₃) ₃ +O ₃	337.4060	-400.0063	-399.8778	0.0
TS	338.5656	-399.9804	-399.8514	69.3132
P=NO(CH ₃) ₃ +O ₂	343.1204	-400.0091	-399.8784	-1.5753
Re (Al-14)=N(CH ₃) ₃ +O ₃ (14)+AlCl ₃	354.4050	-2023.3851	-2023.2501	0.0
TS(Al-14)	353.6153	-2023.3720	-2023.2373	33.6064
P(Al-14)=NO(CH ₃) ₃ -AlCl ₃ +O ₂	361.4655	-2023.4270	-2023.2893	-102.9196
Re(Al-16)=N(CH ₃) ₃ +O ₃ (16)+AlCl ₃	355.3078	-2023.3605	-2023.2252	0.0
TS(Al-16)	354.9135	-2023.3567	-2023.2215	9.7144
P(Al-16)=NO(CH ₃) ₃ +AlCl ₃ +O ₂	361.6422	-2023.3963	-2023.2586	-87.6917

10 * E_{ZPVE} : Zero-point vibrational energy correction; E_{T} : Energies corrected by zero-point
11 vibrational energy; E_{R} : Energies corrected by energies of reactants.
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13 **Table 3.** Rate constants $k(T)$ (298K) and equilibrium constants $K(T)$ (298K) calculated
 14 at B3LYP/6-311G (d, p).

Species	$k(T) / (s^{-1})$	$K(T)$
$R=N(CH_3)_3+O_3$	1.09×10^{-1}	1.63×10^{-1}
$R(Al-14)=N(CH_3)_3+O_3(14)+AlCl_3$	2.74×10^6	2.89×10^{18}
$R(Al-16)=N(CH_3)_3+O_3(16)+AlCl_3$	1.25×10^{10}	2.40×10^{14}

15 R: Trimethylamine-N-oxide reaction

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