



Enhanced trimethylamine-containing particles during fog events detected by single particle aerosol mass spectrometry in urban Guangzhou, China

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ABSTRACT

Trimethylamine (TMA) plays an important role in atmospheric chemistry, yet its pathway towards aerosol is not clear. We report in this study the measurement of TMA in submicron particles using a single particle aerosol mass spectrometer (SPAMS) in urban Guangzhou, China for the period of 30 April through 22 May, 2010. The number fraction of TMA-containing particles relative to total detected particle number dramatically increased within the occurrence of fogs. It changed from an average of ~7% for clear days to ~35% for the fog events. For particles with size larger than 0.5 μm , the fraction could even account up to ~60%. Averaged relative intensity of TMA was correlated well with relative humidity, indicating the important role of aerosol water content in the gas-to-particle partitioning of TMA. During the fog events, number based size distribution of TMA-containing particles shifted towards larger mode, peaking at droplet mode (0.5–1.2 μm), corresponding to the build-up of aerosol mass, suggesting the significant mass transfer of TMA and other semi-volatile species from gas to aerosol. Results also reveal that most of TMA-containing particles also contained signals from ammonium, nitrate and sulfate. A much larger fraction of TMA-containing particles was found to contain nitrate during the fog events than on clear days. During the fog events, nitrate and sulfate were more strongly associated with TMA compared to ammonia, which was oppositely observed on clear days. These results indicate that gas-to-particle partitioning of TMA in urban Guangzhou occurs preferentially during fog processing. The study could help improve our understanding in fog processing and potential roles of TMA-containing particles in urban Guangzhou.

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1. Introduction

Amines are ubiquitous in the atmospheric environment, and have been detected in marine, urban and rural atmosphere in the gas and particle phases as well as aqueous fog and rain water (Facchini et al., 2008; Müller et al., 2009; Rehbein et al., 2011; Zhang and Anastasio, 2003). Recent measurements by Silva et al. (2008) showed that amines could account up to 20% of organic matter mass in fine aerosol during some wintertime periods in Utah, USA. Angelino et al. (2001) reported that up to 80% of single particles contained amine signals during some episodes in Riverside, CA. To our best knowledge, amines in particulate phase were scarcely reported in China (Wang et al., 2010a).

Amines could be emitted from various sources, including animal husbandry (Rabaud et al., 2003; Schade and Crutzen, 1995), waste

incineration and sewage treatment (Abalos et al., 1999; Leach et al., 1999), marine environment (Facchini et al., 2008; Sorooshian et al., 2009), biomass burning (Lobert et al., 1991), industrial processes (Moffet et al., 2008; Reinard et al., 2007), and vehicle exhaust (Cadle and Mulawa, 1980). In particular, animal husbandry is a major source, where the mass concentration of amine aerosol could even represent up to 23% of that of ammonium (Sorooshian et al., 2008). Schade and Crutzen (1995) estimated that trimethylamine (TMA) was the highest contributor of amines to the global input of N from animal husbandry.

TMA can react with gas phase acid (e.g., sulfuric acid and nitric acid) in the atmosphere to form particulate salts through acid–base reactions (Kurtén et al., 2008; Murphy et al., 2007; Silva et al., 2008), and it is even more important than ammonia in enhancing atmospheric nucleation (Erupe et al., 2011; Kurtén et al., 2008; Smith et al., 2010). Through laboratory experiments and ambient observations using an aerosol time-of-flight mass spectrometer

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(ATOFMS), Rehbein et al. (2011) demonstrated that cloud/fog processing could enhance gas-to-particle partitioning of TMA, which is highly dependent on aerosol water content, and that TMA prefers to accumulate in acidic particles. TMA could also undergo heterogeneous reactions to form aminium salts, with faster rate in smaller particles (Bzdek et al., 2010a, b; Lloyd et al., 2009; Qiu et al., 2011; Wang et al., 2010b,c). Besides, TMA can also participate in the formation of secondary organic aerosol. Several studies have shown that gas-phase TMA could form non-salt organic aerosol products through reaction with oxidizing agents such as O₃, OH, and NO₃ radical (Murphy et al., 2007; Silva et al., 2008). The relative importance of atmospheric behaviors of TMA in different regions is not yet clear.

TMA might have potential impact on the physical and chemical properties of atmospheric particles and fog droplets since TMA is a stronger base than ammonia and could substantially affect aerosol acidity (Sorooshian et al., 2008), which is regarded as an important factor in chemical reactions involving the formation of secondary organic aerosols (Jang et al., 2002; Pathak et al., 2011; Surratt et al., 2007). Moreover, TMA-containing particles might also impact on ecosystems (e.g., the buffering of soil and waters) after they are scavenged and delivered to ecosystems through atmospheric deposition. This study focuses on TMA-containing particles in the submicron size range (0.2–1.2 μm). Individual particles were analyzed by a single particle aerosol mass spectrometer (SPAMS) in urban Guangzhou, China, during late spring of 2010. We present here the number fraction and mixing state of TMA-containing particles during both the fog events and clear days, aiming to probe the potential pathway for particulate TMA in urban Guangzhou.

2. Experimental section

2.1. Ambient single particle analysis

Single particle measurement was carried out at the Guangzhou Institute of Geochemistry (GIG), Chinese Academy of Sciences, between 30 April and 21 May 2010 using a SPAMS manufactured by Hexin Analytical Instrument Co., Ltd. (Guangzhou, China). Measurement site and the meteorological conditions during sampling period have been described elsewhere (Bi et al., 2011).

The SPAMS system was installed in an air-conditioned room located on the first floor. Sample air was fed from a platform (about 10 m above ground on a three-story building at the sampling site) to the SPAMS through a copper tube. An additional pump was used to shorten the residence time of particles in the sampling tube. A PM_{2.5} cyclone was installed upstream the sample inlet to exclude coarse particles. Single particle detection procedure with SPAMS was described in detail by Li et al. (2011). Briefly, aerosol particles are drawn into aerodynamic lens of SPAMS through a 0.1 mm critical orifice at a flow of 80 mL min⁻¹. Velocities of individual particles are subsequently determined by the two continuous diode Nd:YAG laser beams (532 nm). The particles are then desorbed/ionized by a pulsed Nd:YAG laser (266 nm) triggered exactly based on the velocity of the specific particle. The positive and negative fragments generated are obtained. The energy of desorption/ionization laser in this study was kept relatively low, with power density at about 1.06E + 08 W cm⁻². To minimize the effects of size dependent detection efficiency for SPAMS (Allen et al., 2000; Su et al., 2004), the particle counts in small size bins (100 nm in width) were examined and merged if they were of similar temporal trends.

2.2. Single particle data analysis

The sampling in this study covered particles with vacuum aerodynamic diameters (Da) between 0.2 and 1.2 μm. A total of

696,465 single-particle mass spectra were collected over the course of the campaign. Particles sizes and mass spectra information were firstly used to create the peak lists with a minimum area threshold of 20 arbitrary units (the peaks for background noise were generally lower than 5 units) by using TSI MS-Analyze software. The peak lists were subsequently imported into MATLAB 7.1 (The Mathworks Inc.) and analyzed using YAADA 2.1 (www.yaada.org), a MATLAB-based software toolkit used for processing the single-particle mass spectral data. Peak identification described in this paper corresponds to the most probable assignments for each specific mass-to-charge ratio (*m/z*), and more details can be found in the published work by Liu et al. (2003) and Murphy and Thomson (1997a, b).

2.3. Scanning mobility particle sizer with a condensation particle counter (SMPS + C)

Particle size distribution measurements were performed continuously with a cylindrical scanning differential mobility analyzer upstream of a condensation particle counter (SMPS + C 5.401, GRIMM Aerosol Technik GmbH & Co. KG). It took about 7 min to complete a logarithmic scan from a mobility diameter of 11.1 nm–1083.3 nm. The sheath and excess flows of 3.0 L min⁻¹ were used, with a 10:1 flow rate ratio of sheath-to-aerosol. No drying procedure was run prior to the measurement.

3. Results and discussion

3.1. Detection of TMA-containing particles with SPAMS

TMA-containing particles are queried with an absolute peak area at mass-to-charge ratio (*m/z*) +59 ([N(CH₃)₃]⁺) greater than 20. Mass-to-charge ratio +59 is recognized as the dominant peak for TMA since it could not be produced from any other common amine species (Angelino et al., 2001; Rehbein et al., 2011). A total of 126,918 mass spectra for TMA-containing particles were obtained, which contributed approximately 18% on average to the total detected submicron particles by number. The average digitized positive and negative mass spectra of TMA-containing particles are displayed in Figure S1 of supplementary material. In addition to the peak at mass-to-charge +59 corresponding to the TMA, dominant peaks in the positive ion mass spectrum are potassium/organics (39K⁺/39[C₃H₃]⁺), organics (27[C₂H₃]⁺, 43[C₂H₃O]⁺), ammonium (18[NH₄]⁺) and carbon cluster ions ([C]⁺, [C₂]⁺, ..., [C_n]⁺). It is necessary to point out that ~77% of TMA-containing particles also contain signals for ammonium, implying their similar formation pathway. The negative ion spectrum exclusively consists of sulfate (−97[HSO₄][−] or −80[SO₃][−]) and nitrate (−46[NO₂][−] or −62[NO₃][−] or −125[H(NO₃)₂][−]), which suggests that TMA most likely occurs in the form of TMA-nitrate/sulfate salts in individual particles. The presence of [H(NO₃)₂][−] is an indication of large contribution from nitrate in particles (Dall'Osto et al., 2009a; Moffet et al., 2008). In this study, no evidence showed the presence of non-salt organic products of TMA in particles because no fragments of common secondary organic products for TMA such as trimethylamine-N-oxide at *m/z* 76 [TMAOH]⁺, dimethylnitramine at *m/z* −90 [CH₃N₂O₂][−] and *m/z* −74 [CH₃N₂O][−] were observed through the whole sampling period (Angelino et al., 2001; Silva et al., 2008).

Fig. 1 shows the temporal profiles of TMA-containing particles in two size ranges (200–500 nm and 500–1200 nm, respectively), the variations of local temperature and relative humidity, and the number count of hydroxymethanesulfonate (HMS) in detected particles. Several fog events were obtained during the whole sampling period, three of which corresponded to the spikes of TMA-containing particles. The three fog events (Fog 1, 20:00 07/05/

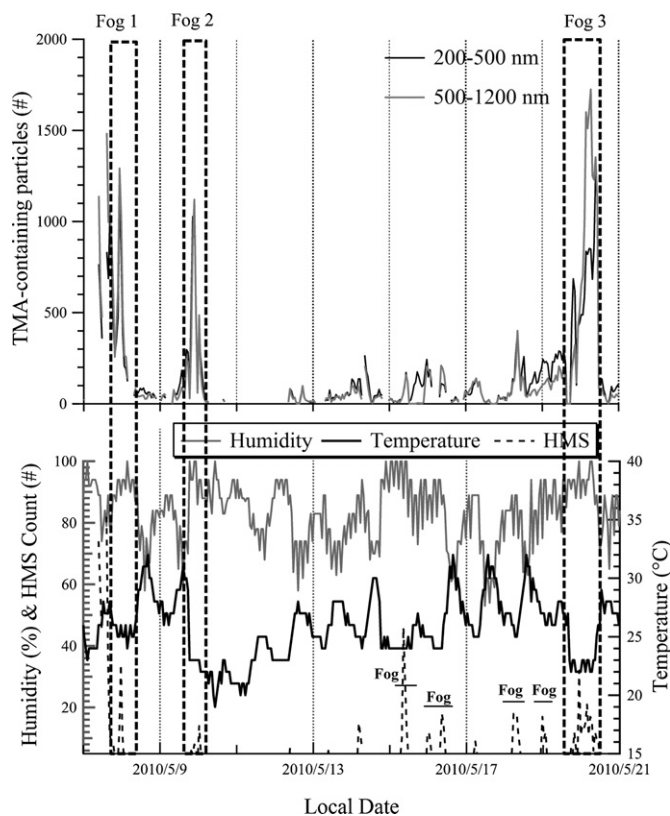


Fig. 1. The temporal profiles of TMA-containing particles (upper) in different size bins (200–500 nm and 500–1200 nm in width, respectively), and the variations of local temperature and relative humidity and the number count of hydroxymethanesulfonate (HMS) (bottom) during sampling days. Fog 1, Fog 2, Fog 3 were marked with dash lines in black rectangles. The other 4 fog events were marked with short black lines at the bottom part.

2010–07:00 08/05/2010; Fog 2, 14:00 09/05/2010–03:00 10/05/2010; Fog 3, 23:00 19/05/2010–10:00 20/05/2010) are marked with dash lines in black rectangles. However, no obvious spike of TMA-containing particles was observed during other fog events from 15/05/2010 through 19/05/2010 as marked in Fig. 1. Back trajectory of the air mass originated from southeast or northeast during these fog events (Figure S2), which indicates that long range transport might be not the dominant factor that affected the difference between these events. Other factors (e.g., the emission strength of TMA from local sources) might be candidates. This remains to be verified in further research.

Relative humidity averaged at $93 \pm 3\%$, $88 \pm 11\%$ and $94 \pm 4\%$ during Fog 1, Fog 2 and Fog 3, and the corresponding temperature was $25 \pm 1^\circ\text{C}$, $25 \pm 3^\circ\text{C}$ and $23 \pm 1^\circ\text{C}$, respectively. The number of TMA-containing particles was significantly enhanced exclusively when fog formed, especially during Fog 1, Fog 2 and Fog 3. As a tracer for aqueous-phase fog processing, the number of particles containing HMS also sharply increased during these events, consistent with the earlier studies (Munger et al., 1986; Whiteaker and Prather, 2003). It provides evidence that fog processing assists the formation of TMA-containing particles since TMA preferentially resides in the gas phase due to its volatility (Rehbein et al., 2011). Elevated concentration of amines were also detected in fog water by Zhang and Anastasio (2003). Additionally, significant correlation ($r = 0.95$, $p < 0.01$) between relative intensity of TMA and relative humidity was observed in this study (Figure S3), and the most enhanced TMA in the particle phase was obtained during Fog 3 with the highest RH, which suggests that aerosol water content

might play an important role in mass transfer of TMA from gas to aerosol in urban Guangzhou during late spring. Theoretical calculation also supports the enhanced gas-to-particle partitioning of semi-volatile species such as TMA/ammonium nitrate under elevated relative humidity and lower temperature conditions (Ge et al., 2011; Hu et al., 2008). Theoretical calculation was performed by Ge et al. (2011) at 298.15 K and shows that it is possible to form TMA salt in aqueous aerosol. The increase of relative humidity and decrease of temperature were observed commonly at the beginning of fog events (Fig. 1).

3.2. Size distributions of TMA-containing particles during fog events and clear days

Comparisons were made for size distributions of TMA-containing particles during several episodes, including three fog events and four clear days with longer continuous measurement time in a day (> 12 h). Clear days had characteristic of lower relative humidity ($77 \pm 11\%$) and higher temperature ($27 \pm 2^\circ\text{C}$) versus fog events. The unscaled SPAMS count of TMA-containing particles as a function of Da for these episodes is presented in Fig. 2. The TMA-containing particles show dominant peaks in smaller sizes on clear days and shift to larger sizes during the fog events. The accumulation of TMA on the droplet mode particles (500–1200 nm) is in accordance to the considerable build-up of submicron particles mass in droplet mode during the episodes, which is derived from SMPS + C measurements (Figure S4). The result indicates that fog processes enhanced the growth of particles, directly contributed from water uptake due to the increase of RH and also the enhanced gas-to-particle partitioning of semi-volatile species (e.g., TMA and nitrate), which is consistent with the observations of a foggy event in London using ATOFMS by Dall'Osto et al. (2009b). It also agrees well with the mass size distribution of particles from SMPS + C, shifting toward the larger mode with the forming of fogs; and backward when fogs dissipated.

The number fractions of TMA-containing particles relative to the total detected particles as a function of Da under different meteorological conditions are displayed in Fig. 3. During clear days, TMA-containing particles contributed only $7 \pm 3\%$ by number, ranging between 4% and 12% on average, depending on Da. However, the contribution of TMA-containing particles during the fog events was obviously larger, with $35 \pm 13\%$ for the three fog events on average, and it could represent even up to $\sim 60\%$ in particles with larger sizes. This result further demonstrates that fog processes enhance the gas-to-particle partitioning of TMA to the larger particles.

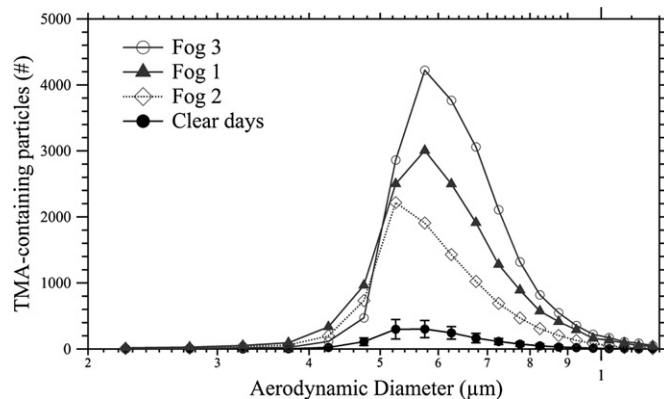


Fig. 2. Unscaled number size distributions of TMA-containing particles during both fog events and clear days.

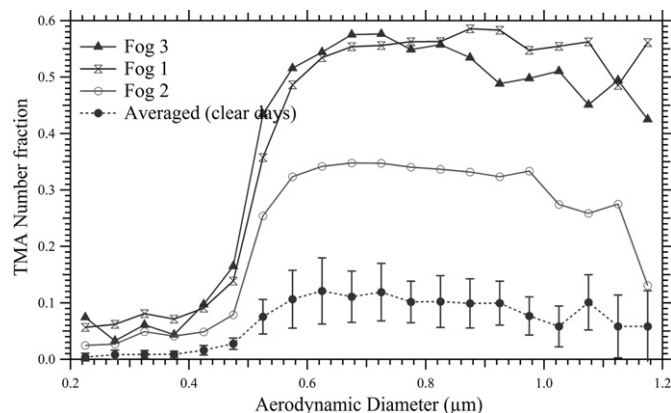


Fig. 3. TMA number fraction (relative to total detected particles) as a function of aerodynamic diameter (D_a) under different meteorological conditions.

3.3. Mixing state of TMA-containing particles with secondary inorganic species

The mixing state of TMA with ammonium, nitrate and sulfate is vital in understanding the acid–base chemistry of TMA in the atmosphere. As shown in Figure S1, considerable fraction of TMA-containing particles internally mixed with nitrate, sulfate and ammonium, approximate 66%, 76% and 77% on average in number

fraction, respectively. However, these fractions were changeable under different meteorological conditions as illustrated in Figure S5. The fraction of nitrate ranged between 69 and 90% during the fog events, while only ~53% on average during clear days, suggesting that fog processes probably enhance the gas-to-particle partitioning of nitrate, which was also observed for non-TMA-containing particles. The number fraction for sulfate in TMA-containing particles decreased from ~88% on clear days to ~70% during the fog events, although several studies demonstrate enhanced production of sulfate through fog/cloud processes (Minami and Ishizaka, 1996).

To further determine the specific relationships between TMA, ammonium, nitrate and sulfate in TMA-containing particles under different meteorological conditions, ternary plots of relative distributions of these species during Fog 3 and a clear day are displayed in Fig. 4, while the data for Fog 1 and Fog 2 are provided in Figure S6. It could be seen that the dots are distributed along TMA–nitrate and TMA–sulfate axes during the fog events, indicating that nitrate and sulfate are more strongly associated with TMA compared to ammonium, which is consistent with the previous observation by Pratt et al. (2009) during summer in Riverside, CA. While during clear days, the particles are mainly distributed along ammonium–nitrate and ammonium–sulfate axes, with extremely low TMA peak areas, indicating nitrate and sulfate are more strongly associated with ammonium. The low water content of particles during clear days would not be favorable for the diffusion of TMA onto the particles (Ge et al., 2011).

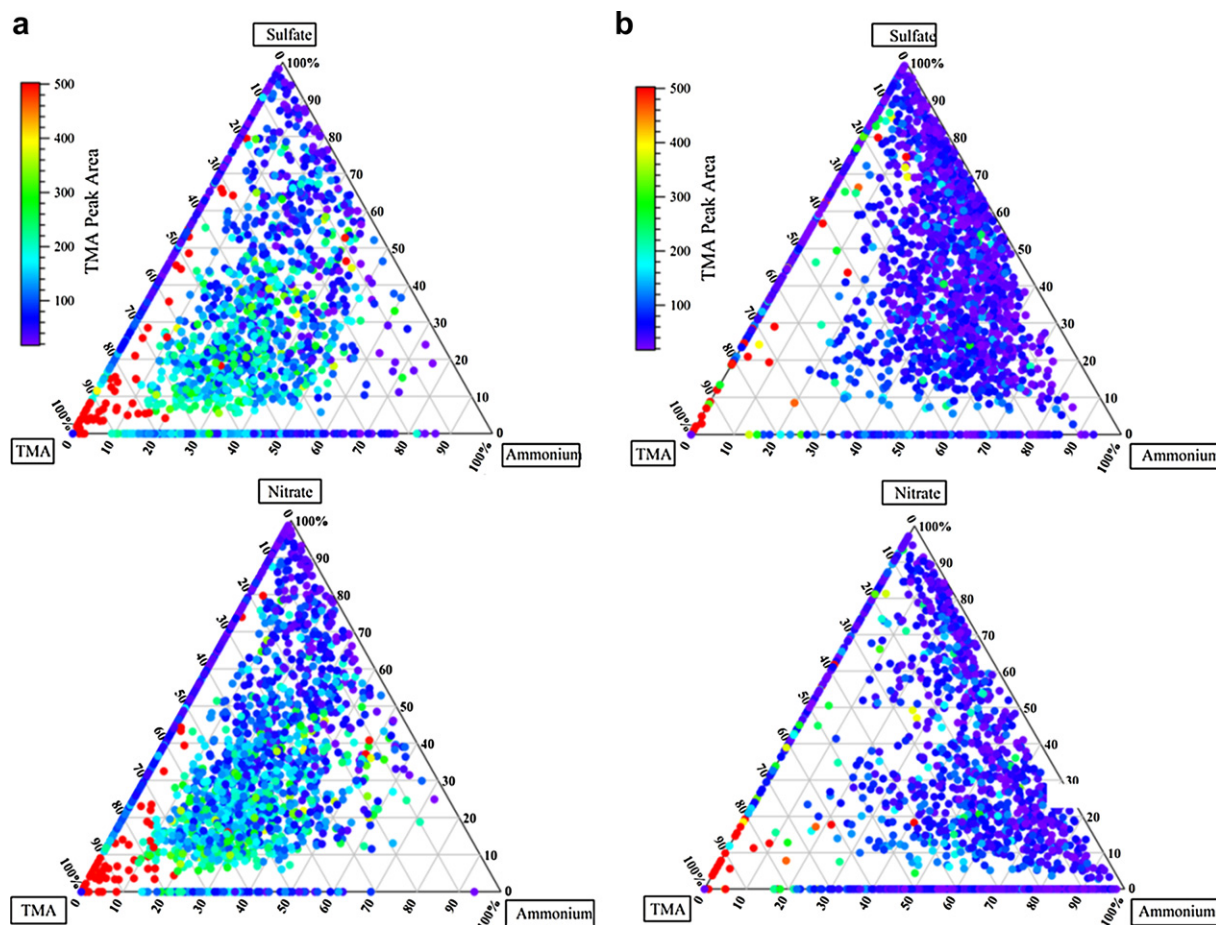
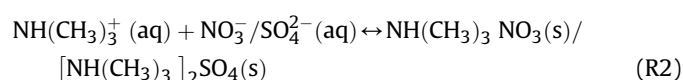
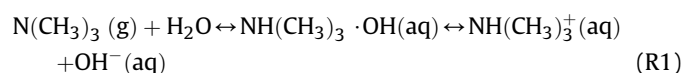


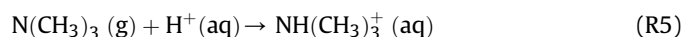
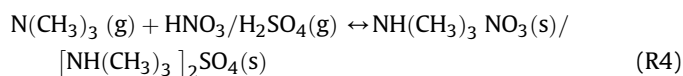
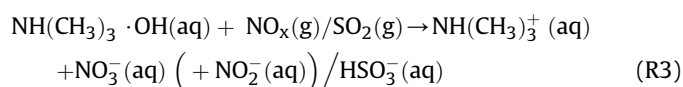
Fig. 4. Ternary plots showing the relative distributions of peak areas of TMA, ammonium, nitrate and sulfate for the TMA-containing particles during a typical foggy event (left half, a) And a typical clear day (right, b). 2000 TMA-containing particles are randomly selected for each analysis.

3.4. Possible formation mechanism of particulate TMA

In order to understand the roles of TMA in the atmosphere, the chemical processes involving TMA towards aerosol phase are illustrated as following although the evidence is still weak to determine the relative importance of these processes. Significant amount of particulate ammonium salts with sulfate and nitrate observed in this study indicates that acid–base chemistry and gas-to-particle partitioning might play a substantially important role in the atmosphere of urban Guangzhou, especially during foggy episodes. Gas-to-particle phase partitioning via direct dissolution (R1) should be extremely important for TMA due to its strong correlation with relative humidity and significantly enhanced intensity during fog processing (Rehbein et al., 2011).



TMA could further neutralize aqueous acids by the reaction of R2 after dissolution, which would further promote the accumulation of TMA (Ge et al., 2011). Previous theoretical calculation and experimental observation suggest that the gas-to-particle partitioning of TMA could be enhanced in acidic particles (R1 and R2) (Rehbein et al., 2011).



Heterogeneous uptake of acidic gas (e.g., NO, NO₂, N₂O₅ and SO₂) to the aqueous surface by TMA (R3) of alkaline nature might also occur. Tan et al. (2002) suggested that the presence of the TMA within aqueous surface on particles would promote the accumulation of sulfate and nitrate (R2 and R3). TMA also has the potential to undergo gas phase acid–base reactions (R4) with gaseous acids (e.g., HCl, HNO₃ and H₂SO₄) mimic ammonia to form inorganic salts (Angelino et al., 2001; Murphy et al., 2007). Additionally, heterogeneous reaction between gas-phase TMA and acid (R5) could take place as well. Uptake coefficients measured by Wang et al. (2010c) have suggested that heterogeneous reaction with TMA leads to efficient growth of acidic particles.

4. Conclusion

Single particle characterization of submicron TMA-containing particles using SPAMS was carried out in urban Guangzhou late spring, 2010. Mass spectra analysis shows that most of TMA in urban Guangzhou were internally mixed with ammonium, nitrate and sulfate, and no fragments of secondary organic products from TMA. The results indicate that acid–base chemistry and gas-to-particle partitioning might be more important rather than secondary oxidation processes for TMA in urban Guangzhou. Considerable number concentration and significantly enhanced peak areas of TMA in atmospheric submicron particles (especially particles larger than 0.5 μm) occurred during the fog events. Nitrate and sulfate were more strongly associated with TMA compared to

ammonium during the fog events. While on clear days, nitrate and sulfate were more strongly associated with ammonium. Other than the condensation of water vapor, elevated mass transfer from gas-to-particle of TMA and nitrate might also contribute to the size distribution shifting to larger mode. This study improves our understanding of the importance of fog processing and potential roles of TMA-containing particles in urban Guangzhou. Further work is needed to elucidate the specific chemistry of TMA and to determine the role TMA plays on regional air quality.

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Appendix A. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.atmosenv.2012.03.038.

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