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Synergetic formation of secondary inorganic and organic aerosol: Influence of SO_2 and/or NH_3 in the heterogeneous process

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Abstract

The effects of SO_2 and NH_3 on secondary organic aerosol formation have rarely been investigated together, while the interactive effects between inorganic and organic species under highly complex pollution conditions remain uncertain. Here we studied the effects of SO_2 and NH_3 on secondary aerosol formation in the photooxidation system of toluene/NO_x in the

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presence or absence of Al_2O_3 seed aerosols in a 2 m^3 smog chamber. The presence of SO_2 increased new particle formation and particle growth significantly, regardless of whether NH_3 was present or not. Sulfate, organic aerosol, nitrate and ammonium were all found to increase linearly with increasing SO_2 concentrations. The increases in these four species were more obvious under NH_3-rich conditions, and the generation of nitrate, ammonium and organic aerosol increased more significantly than sulfate with respect to SO_2 concentration, while sulfate was the most sensitive species under NH_3-poor conditions. The synergistic effects between SO_2 and NH_3 in the heterogeneous process contributed greatly to secondary aerosol formation. Specifically, the generation of NH_4NO_3 was found to be highly dependent on the surface area concentration of suspended particles, and increased most significantly among the four species with respect to SO_2 concentration under ammonia-rich conditions. Meanwhile, the absorbed NH_3 might provide a liquid surface layer for the absorption and subsequent reaction of SO_2 and organic products, and therefore, enhance sulfate and secondary organic aerosol (SOA) formation. This effect mainly occurred in the heterogeneous process and resulted in a significantly higher growth rate of seed aerosols compared to that without NH_3. By applying positive matrix factorization (PMF) analysis to the AMS data, two factors were identified for the generated SOA. One factor, assigned to less-oxidized organic aerosol and some oligomers, increased with increasing SO_2 under NH_3-poor conditions, mainly due to the well-known acid catalytic effect of the acid products on SOA formation in the heterogeneous

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process. The other factor, assigned to the highly oxidized organic component and some nitrogen-containing organics (NOC), increased with SO_2 under a NH_3-rich environment, with NOC (organonitrates and NOC with reduced N) contributing most of the increase.

Introduction

With the recent rapid economic development and urbanization, the associated emissions from coal combustion, motor vehicle exhaust and various industrial emissions have led to highly complex air pollution in China. Besides the high concentrations of fine particles ($PM_{2.5}$), high concentrations of NO_x, SO_2, NH_3, and volatile organic compounds (VOCs) were observed in haze pollution episodes (Liu et al., 2013; Ye et al., 2011; Zou et al., 2015; Wang et al., 2015). For example, the SO_2 concentration in Jinan, a city in North China, can be as high as 43 ppb in the winter season (Wang et al., 2015). The high concentrations of precursors resulted in high concentrations of secondary inorganic and organic species in $PM_{2.5}$ during haze formation (Yang et al., 2011; Zhao et al., 2013; Dan et al., 2004; Duan et al., 2005; Wang et al., 2012). There has been no extensive measurement of NH_3 in China despite its extensive emission and increasing trend (Fu et al., 2015). A few studies reported high concentrations of NH_3 (maximum concentration higher than 100 ppb) in the North China Plain (Meng et al., 2015; Wen et al., 2015) and many observation data indicated NH_3-rich conditions for secondary aerosol formation, and strong correlations between peak levels of fine particles and large increases in NH_3

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concentrations in China (Ye et al., 2011; Liu et al., 2015a). Under this complex situation, studying the synergistic effects of SO_2 and NH_3 among pollutants in secondary aerosol formation is crucial in order to understand the formation mechanism of heavy haze pollution.

Interactions between inorganic pollutants in secondary aerosol formation have been investigated extensively. For example, NO_2 was found to increase the oxidation of SO_2 in aqueous aerosol suspensions (Tursic and Grgic, 2001) and on a sandstone surface (Bai et al., 2006). The synergistic reaction between SO_2 and NO_2 on mineral oxides was reported (Liu et al., 2012a) and proposed to explain the rapid formation of sulfate during heavy haze days (He et al., 2014). The presence of NH_3 was also found to enhance the conversion of SO_2 to sulfate in aerosol water and on the surface of mineral dust or $PM_{2.5}$ (Tursic et al., 2004; Behera and Sharma, 2011; Yang et al., 2016).

Secondary aerosol formation from coexisting inorganic and organic pollutants is far more complicated. There have been a few studies that investigated the effects of SO_2 or NH_3 on secondary organic aerosol (SOA) formation. SO_2 has been found to enhance SOA yield from isoprene (Edney et al., 2005; Kleindienst et al., 2006; Lin et al., 2013), α-pinene (Kleindienst et al., 2006; Jaoui et al., 2008), and anthropogenic precursors (Santiago et al., 2012) due to its acidic aerosol products, which were thought to either take up organic species (Liggio and Li, 2008, 2006) or result in the formation of high molecular weight compounds in acid-catalytic reactions (Liggio et al., 2007; Kleindienst et al., 2006; Santiago

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et al., 2012). Besides, sulfate esters were also confirmed as major players in SOA formation (Schmitt-Kopplin et al., 2010). The effects of NH_3 on SOA formation are relatively poorly understood. In previous studies, disparate effects of NH_3 on secondary aerosol formation were reported. It was found that the presence of NH_3 increased SOA formation in the reaction of α-pinene or cyclohexene with ozone (Na et al., 2007), but had little effect on SOA mass in isoprene ozonolysis (Na et al., 2007; Lin et al., 2013) and even decreased SOA production from the reaction of styrene and ozone (Na et al., 2006). NH_3 was reported to react with some organic acids and contribute to secondary aerosol formation (Na et al., 2007; Lin et al., 2013), while nucleophilic NH_3 might attack and decompose trioxolane and hydroxyl-substituted esters (Na et al., 2006), and therefore decrease SOA mass. Updyke et al. (2012) studied brown carbon formation via reactions of ammonia with SOA from various precursors and emphasized that aging by NH_3 is not a unique mechanism of SOA browning. It was found that the degree of browning had a positive correlation with the carbonyl products, which may react with NH_3 and generate hemiaminal (Amarnath et al., 1991), while the form of ammonia (NH_3 gas or NH_4^+ ion) had little influence on the browning processes.

The effects of SO_2 and NH_3 on SOA formation have rarely been investigated together, while the interactive effects between inorganic and organic species under highly complex pollution conditions remain uncertain. This study investigated secondary aerosol formation in the photooxidation of toluene/NO_x with varied concentrations of SO_2 under

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120 NH_3-poor and NH_3-rich conditions. Some synergetic effects in the
121 heterogeneous process that contributed to both secondary inorganic and
122 organic aerosol formation were explored.

123 ## Methods

124 A series of smog chamber experiments were carried out to simulate
125 secondary aerosol formation in the photooxidation of VOC/NO_x in the
126 presence or absence of SO_2 and/or NH_3. The chamber is a 2 m^3 cuboid
127 reactor constructed with 50 μm-thick FEP-Teflon film (Toray Industries,
128 Inc., Japan). The chamber was described in detail in Wu *et al.* (2007). A
129 temperature-controlled enclosure (SEWT-Z-120, Escpec, Japan) provides
130 a constant temperature (30 ±0.5 ℃), and 40 black lights (GE F40T12/BLB,
131 peak intensity at 365 nm, General Electric Company, USA) provide
132 irradiation during the experiments. The hydrocarbon concentration was
133 measured by a gas chromatograph (GC, Beifen SP-3420, Beifen, China)
134 equipped with a DB-5 column (30 m ×0.53 mm ×1.5 mm, Dikma, USA) and
135 flame ionization detector (FID), while NO_x, SO_2 and O_3 were monitored
136 by an NO_x analyzer (Model 42C, Thermo Environmental Instruments,
137 USA), an SO_2 analyzer (Model 43I, Thermo Environmental Instruments,
138 USA) and an O_3 analyzer (Model 49C, Thermo Environmental Instruments,
139 USA), respectively. A scanning mobility particle sizer (SMPS) (TSI 3936,
140 TSI Incorporated, USA) was used to measure the size distribution of
141 particulate matter (PM) in the chamber, and also employed to estimate the
142 volume and mass concentration. The chemical composition of aerosols was

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measured by an aerosol chemical speciation monitor (ACSM, Aerodyne Research Incorporated, USA) or high resolution time of flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Incorporated, USA). ACSM is a simplified version of aerosol mass spectrometry (AMS), with similar principles and structure. Ng *et al.* (2011) presented a detailed introduction to this instrument and found that the measurement results agreed well with the AMS. Wall deposition of particles in the chamber was similarly corrected using a regression equation to describe the dependence of deposition rate on the particle size (Takekawa et al., 2003). Detailed information on this equation was given in our previous studies (Chu et al., 2012; Chu et al., 2014).

Alumina seed particles were produced on-line via a spray pyrolysis setup, which has been described in detail elsewhere (Liu et al., 2010). Liquid alumisol (AlOOH, Lot No. 2205, Kawaken Fine Chemicals Co., Ltd., Japan) with an initial concentration of 1.0 wt%, was sprayed to droplets by an atomizer. After that, the droplets were carried through a diffusion dryer and a corundum tube embedded in a tubular furnace with the temperature maintained at 1000 ℃ to generate alumina particles. The obtained alumina particles were γ-Al_2O_3 as detected by X-ray diffraction measurements, and spherical-shaped according to electron micrograph results. Before being introduced into the chamber, the particles were carried through a neutralizer (TSI 3087, TSI Incorporated, USA). In addition, toluene was injected into a vaporizer and then carried into the chamber by purified air, while NO_x, SO_2 and NH_3 were directly injected

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into the chamber from standard gas bottles. The concentrations of NH_3 were estimated according to the introduced amount of NH_3 and the volume of the reactor.

Results and discussion

Particle formation and growth in different inorganic gas conditions

The effects of SO_2 and NH_3 on secondary aerosol formation were qualitatively studied first in the photooxidation system of toluene/NO_x without the presence of a seed aerosol. Experiments were carried out in the absence of SO_2 and NH_3, in the presence of SO_2 or NH_3, and coexistence of SO_2 and NH_3, respectively. Experimental details are listed in Table 1. The letter codes used for the experiments represent a combination of the initial letters of the precursors for each experiment. For example, experiment "ASTN" is an experiment with presence of ammonia gas (A), sulfur dioxide (S), toluene (T) and nitrogen oxides (N). Two experiments (ATN1 and ATN2) were carried out under similar conditions to test the reproducibility of the experiments.

Secondary aerosol formation in these photooxidation experiments was measured by the SMPS, and the results are displayed in Fig. 1. Assuming the same aerosol density in these experiments, the presence of either NH_3 or SO_2 enhanced secondary aerosol formation markedly. Compared to toluene/NO_x photooxidation, the secondary aerosol volume concentration rose 1.5 times in the presence of SO_2, and was more than tripled in the

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189 presence of the NH_3. The volume of secondary aerosol showed an obvious
190 peak in the toluene/NO_x/NH_3 system at about 2.3 hours of photooxidation.
191 With the wall deposition accounted for, the decrease of the volume
192 concentration after that point was unexpected, but could be reproduced
193 (Experiment ATN1 and ATN2). Such a decrease was not observed with
194 coexisting NH_3 and SO_2, indicating interactions between NH_3 and SO_2 in
195 the photooxidation system. The reason for this phenomenon will be
196 discussed in the following analysis of the chemical composition of the
197 generated particles.

198 Table 1 Initial experimental conditions of toluene/NO_x photooxidation in the
199 presence or absence of SO_2 and/or NH_3

Experiment	**Hydrocarbon**	**NO**	**NO_x-NO**	**SO_2**	**NH_3***	**RH**	**T**
No.	*ppm*	*ppb*	*ppb*	*ppb*	*ppb*	*%*	*K*
TN	1.05	54	49	0	0	50	303
STN	1.05	55	50	137	0	50	303
ATN1	1.06	47	48	0	264	50	303
ATN2	0.98	48	54	0	264	50	303
ASTN	1.02	49	53	134	264	50	303

200 *The concentrations of NH_3 were calculated according to the introduced amount of NH_3
201 and the volume of the reactor.
202

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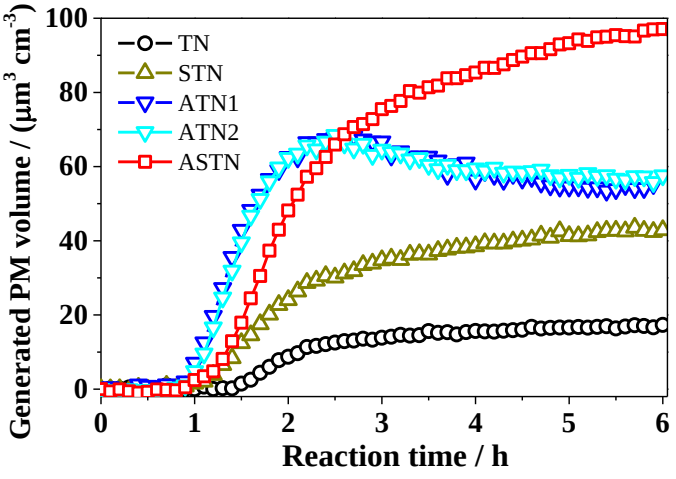

Fig. 1 Secondary aerosol formation in photooxidation of toluene/NO_x in the presence or absence of NH_3 and/or SO_2. The letters codes for the experiments indicate the introduced pollutants, i.e. "A" for ammonia, "S" for sulfur dioxide, "T" for toluene and "N" for nitrogen dioxide. Experimental details are listed in Table 1.

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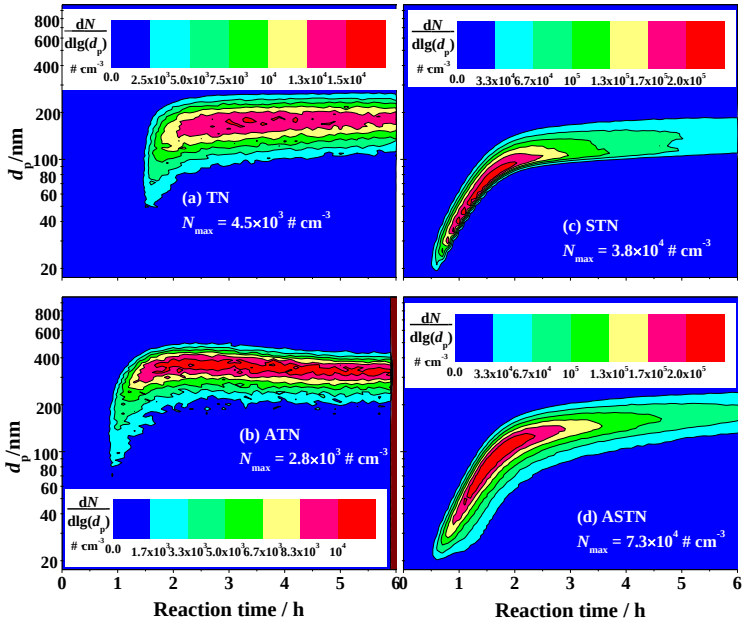

Fig. 2 Size distributions of the suspended particles as a function of time during the reaction in photooxidation of toluene/NO_x in the presence or absence of NH_3 and/or SO_2. N_{max} shows the maximal particle number concentration during the reaction for each experiment. Experimental details are listed in Table 1.

The size distributions of the secondary aerosol in the photooxidation, with a range of 17-1000 nm, were analyzed and are shown in Fig. 2. A significant increase in new particle formation was observed in the presence of SO_2. The maximal particle number concentrations in experiments ASTN and STN were one order of magnitude higher than those in experiments ATN and TN. The presence of NH_3 also contributed substantially to the particle growth in photooxidation of toluene/NO_x. Comparing Fig. 2(c) to Fig. 2(a), the total number concentration of particles in experiment ATN was a little lower than that in experiment TN, but the mode diameter of the

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particles was much larger.

Secondary inorganic aerosol formation

Some synergetic effects were observed in secondary inorganic aerosol formation besides the generation of ammonium and sulfate from NH_3 and SO_2. For example, nitrate formation was not only enhanced by NH_3, due to conversion of nitric acid into ammonia nitrate, but also was markedly affected by SO_2. The chemical compositions of the generated aerosols in the photooxidation of toluene/NO_x were analyzed with an ACSM, and their time variations are displayed in Fig. 3. In experiment ATN, the concentrations of ammonium and nitrate decreased after about 2.3 hours of reaction, as shown in Fig. 3, which was consistent with the decreasing trend of particle concentration shown in Fig. 1. The reason for this phenomenon is unknown but we speculate that the generated NH_4NO_3 might partition back into the gas phase as reaction goes on. In Fig. 2, we observed that the particle size was larger in experiment ATN than the other three experiments. The larger diameter resulted in more significant wall deposition, reduced the surface area of the suspended particles, and shifted the partition equilibrium to the gas phase. Adding SO_2 to the system resulted in a lower peak concentration but a higher final concentration of nitrate. In the presence of SO_2, higher concentrations of sulfate and organic species were generated and mixed with nitrate in the aerosol, which may shift the partition balance of NH_4NO_3 to the aerosol phase. In addition, the presence of organic matter might accelerate the deliquescence of generated

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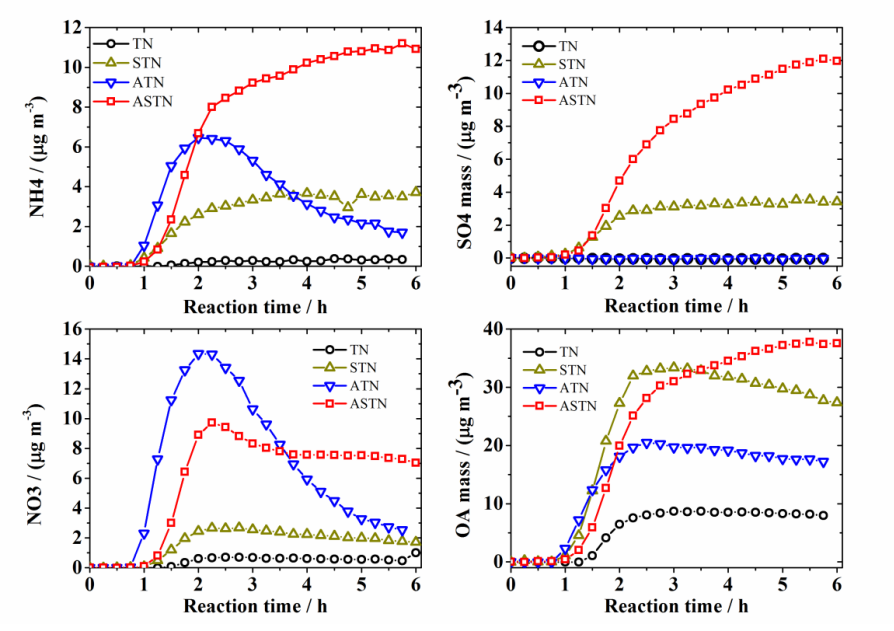
247 inorganic particles (Meyer et al., 2009;Li et al., 2014), and provide moist
248 surfaces for heterogeneous hydrolysis of N_2O_5, contributing to nitrate
249 formation (Pathak et al., 2009).



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251 Fig. 3 Time variations of the chemical species in the secondary aerosol generated
252 from the photooxidation of toluene/NO_x in the presence or absence of NH_3 and
253 SO_2. Letter codes for experiments indicate the introduced pollutants, i.e. "A" for
254 ammonia, "S" for sulfur dioxide, "T" for toluene and "N" for nitrogen dioxide.
255 Experimental details are listed in Table 1.

256 In Fig. 3, the generation of ammonium salt can be observed in the
257 photooxidation of toluene/NO_x/SO_2 without introducing NH_3 gas. This
258 indicated there was NH_3 present in the background air in the chamber, and
259 also indicated that the effects of NH_3 on secondary aerosol formation might
260 be underestimated in this study. The background NH_3 was derived from the

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partitioning of the deposited ammonium sulfate and nitrate on the chamber wall when humid air was introduced (Liu et al., 2015b). Unfortunately, due to the lack of appropriate instrumentation, we were not able to measure the exact concentration of NH_3 in the background air in the chamber. With this in mind, the experiments carried out without introducing NH_3 gas were considered "NH_3-poor" experiments in this study, while experiments with the introduction of NH_3 gas were considered "NH_3-rich" experiments, in which the concentrations of NH_3 were more than twice the SO_2 concentrations and the oxidation products of SO_2 and NO_x were fully neutralized by NH_3.

To further quantify the effect of SO_2 on secondary aerosol formation, different concentrations of SO_2 were introduced under NH_3-poor and NH_3-rich conditions. The details of the experimental conditions are shown in Table 2. In these experiments, the concentrations of toluene were reduced compared to the experiments in Table 1, and monodisperse Al_2O_3 seed particles with mode diameter about 100 nm were introduced into the chamber. As shown in Fig. 4, similar to the seed-free experiments, the presence of SO_2 and NH_3 clearly increased secondary aerosol formation in toluene/NO_x photooxidation in the presence of Al_2O_3 seed aerosols. In the experiments carried out in the presence of Al_2O_3 seed aerosols, the decrease of NH_4NO_3 was not obvious in the experiment carried out in the absence of SO_2 under NH_3-rich conditions, indicating that generation of NH_4NO_3 was highly dependent on the surface area concentration of the particles, which decreased the partitioning of NH_4NO_3 back to the gas

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phase, as discussed above.

Under both NH_3-poor and NH_3-rich conditions, all the detected chemical species in the generated aerosol, including sulfate, organic aerosol, nitrate and ammonium, increased linearly with increasing SO_2 concentrations, as shown in Fig. 5. The increase was more significant in a NH_3-rich environment than that under NH_3-poor conditions, indicating a synergistic effect of SO_2 and NH_3 on aerosol generation. Among the four chemical species, nitrate generation increased most significantly with respect to SO_2 concentration under NH_3-rich conditions, followed by ammonium and organic aerosol, while sulfate was the least sensitive species. Under NH_3-poor conditions, the sensitivity of these species followed a different sequence, in which sulfate > nitrate > organic aerosol > ammonium. A better correlation was found between secondary aerosol formation and particle surface area than that with particle volume, with details introduced in Fig. S1 in the supporting information, indicating an enhancement effect in the heterogeneous process rather than in bulk reactions. The different sequences under NH_3-rich and NH_3-poor conditions indicated that the presence of SO_2 and NH_3 not only contributed aerosol surface for partitioning, but also enhanced the heterogeneous process for secondary aerosol formation.

Table 2 Experimental conditions of the toluene/NO_x photooxidation in the presence of different concentrations of SO_2 and Al_2O_3 seed particles under NH_3-poor and NH_3-rich conditions

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	Toluene$_0$	**NO$_0$**	**NO$_x$-NO**	**SO$_2$**	**Al$_2$O$_3$**	**NH$_3$***	**RH**	**T**
	ppb	*ppb*	*ppb*	*ppb*	*particle/cm^3*	*ppb*	*%*	*K*
	188	147	60	0	2400	0	50	303
NH$_3$-poor	200	126	51	52	3100	0	50	303
	188	130	58	105	2100	0	50	303
	197	142	46	0	3300	105	50	303
NH$_3$-rich	220	147	50	26	3300	105	50	303
	207	145	49	52	3200	105	50	303

309 Calculated according to the introduced amount of NH_3 and the volume of the reactor.

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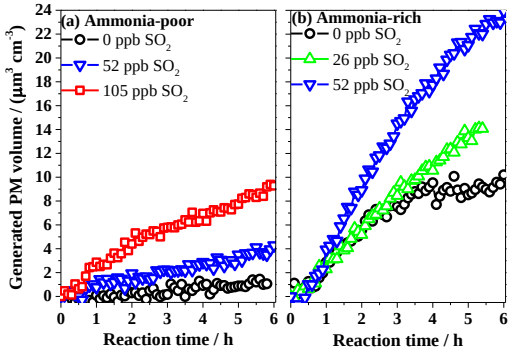

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312 Fig. 4 Secondary aerosol formation as a function of time with different

313 concentrations of SO_2 in the photooxidation of toluene/NO_x under NH_3-poor (a)

314 and NH_3-rich (b) conditions. Experimental details are listed in Table 1.

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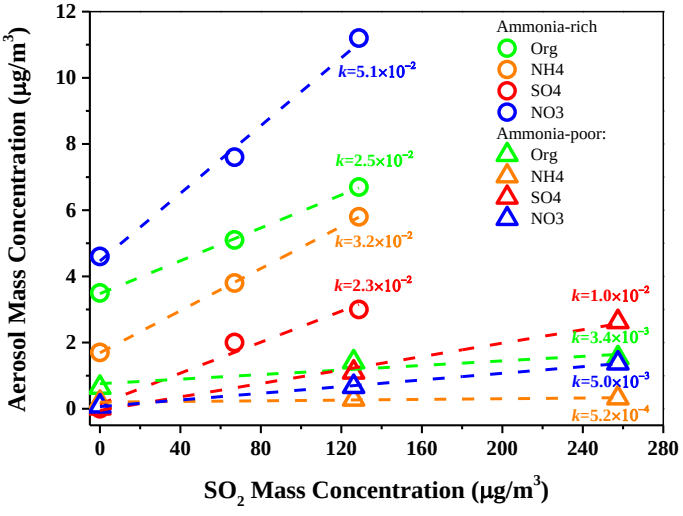

Fig. 5 Formation of nitrate (blue), organic aerosol (green), sulfate (red), and ammonium salt (orange) as functions of SO_2 concentration in the photooxidation of toluene/NO_x under NH_3-rich (circles) or NH_3-poor (triangles) conditions. The *k* values are the slopes of the fitted lines for each species. Experimental details are listed in Table 1.

Another synergetic effect we found in secondary inorganic aerosol formation was that sulfate formation was enhanced by the presence of NH_3. In both seed-free experiments and experiments in the presence of Al_2O_3 seed aerosols, the sulfate mass concentration was more than tripled under NH_3-rich conditions compared to an NH_3-poor environment. This is consistent with previous studies on the reactions of SO_2, NO_2 and NH_3 in smog chambers (Behera and Sharma, 2011) and the heterogeneous reaction between NH_3 and SO_2 on particle surfaces (Yang et al., 2016; Tursic et al.,

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2004). According to the consumption of toluene, OH concentrations in the photooxidation experiments were estimated to range from 1.6 $\times 10^6$ molecules/cm^3 to 2.7 $\times 10^6$ molecules/cm^3. The reaction between these OH radicals and SO_2 contributed 35%-50% of the total SO_2 degradation in NH_3-poor experiments, while this ratio was reduced to 25%-30% in NH_3-rich experiments. This indicated that the heterogeneous process was an important pathway for inorganic aerosol formation in the photooxidation system, and the heterogeneous process was enhanced by the presence of NH_3. This result is consistent with the finding that failure to include the heterogeneous process in the model caused an underestimation of SO_2 decay in the chamber (Santiago et al., 2012). According to previous studies, NH_3 might provide surface Lewis basicity and liquid surface layers for SO_2 absorption and subsequent oxidation, and therefore, enhance sulfate formation (Yang et al., 2016; Tursic et al., 2004).

Secondary organic aerosol formation

The presence of NH_3 and SO_2 caused significant formation of secondary inorganic aerosol, and meanwhile, enhanced SOA formation. In previous studies, Kleindienst et al. (2006) found that the presence of SO_2 did not disturb the dynamic reaction system of α-pinene or isoprene in the presence of NO_x. In the present study, no obvious difference was found in the OH concentration in experiments with different concentrations of SO_2 and NH_3. Therefore, it could be also assumed that the presence of SO_2 and NH_3 in this study did not significantly impact the gas phase oxidation of

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hydrocarbons and mainly played a role in the aerosol phase.

The presence of NH_3 markedly increased aerosol formation in the photooxidation of toluene/NO_x. In the seed-free toluene/NO_x photooxidation experiments, the presence of NH_3 caused similar additional amounts of organic aerosol mass and resulted in increases of 116% and 36% in the absence or presence of SO_2, respectively. In the experiments carried out in the presence of Al_2O_3 seed aerosols, the increase caused by NH_3 was more significant, with the organic aerosol quantity increasing by a factor of four to five. NH_3 may react with the ring opening oxycarboxylic acids from toluene (Jang and Kamens, 2001), resulting in products with lower volatility. The presence of NH_3 might also change the surface properties of the aerosol and enhance heterogeneous oxidation of organic products. As mentioned earlier in this study, there was NH_3 present in the background air in the chamber, so the effects of NH_3 on secondary aerosol formation might be underestimated in this study. Detecting the concentration of NH_3 gas as a function of time and quantifying the effects of NH_3 on secondary aerosol are meaningful, and are expected to be studied in the future.

The enhancing effect of NH_3 on secondary aerosol formation in toluene photooxidation was further attributed to its influence in heterogeneous reactions. In the presence of Al_2O_3 seed particles, no obvious new particle formation was detected in experiments without SO_2, as shown in Fig. 6(a) and Fig. 6(c). The presence of NH_3 caused a more noticeable particle growth of the Al_2O_3 seed particles. The increase mainly took place after 0.5 hours of irradiation, and lasted for about an hour, with an average

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diameter growth of about 12 nm. In the two experiments carried out in the presence of 52 ppb SO_2 in Fig. 7(b) and Fig. 7(d), significant but similar new particle formation occurred. The maximum particle number concentrations detected by the SMPS were about 33000 particle/cm^3 and 34000 particle/cm^3 under NH_3-poor and NH_3-rich conditions, respectively. However, the growth of the seed aerosol in these two experiments was quite different. Under an NH_3-poor condition, the mode diameter of the seed aerosols grew from 100 nm to about 130 nm, while under an NH-rich condition it grew to about 220 nm. These results indicated that elevated NH_3 concentrations mainly affected secondary aerosol formation in the heterogeneous process.

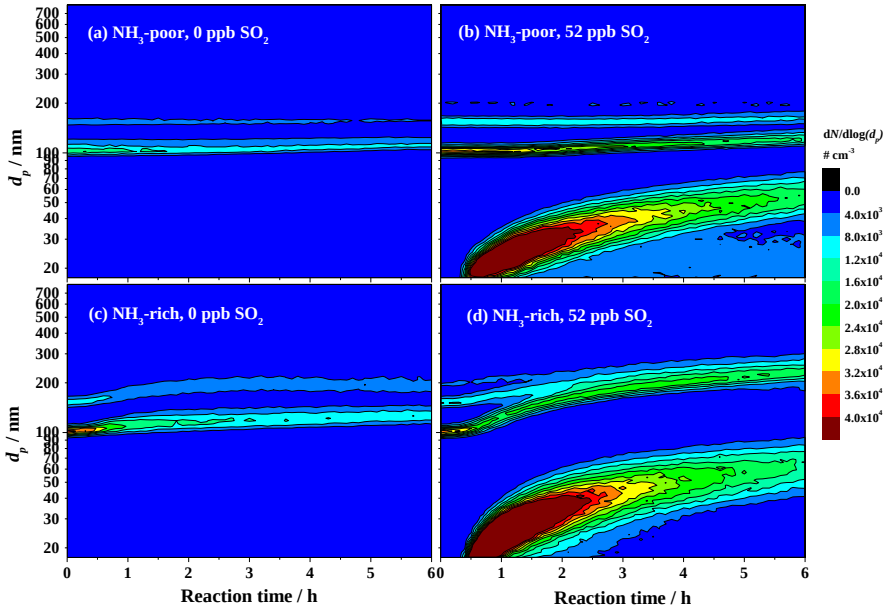

Fig. 6 Size distributions of the suspended particles as a function of time during the reaction in photooxidation of toluene/NO_x in the presence of Al_2O_3 seed particles.

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391 Experimental details are listed in Table 1.

392

393 The chemical properties of the generated SOA under different
394 conditions of NH_3 and SO_2 were compared by applying PMF analysis to
395 the AMS data. Two factors were identified from the analysis, with average
396 elemental composition of $CH_{0.82}O_{0.75}N_{0.051}S_{0.0014}$ for Factor 1 and
397 $CH_{1.05}O_{0.55}N_{0.039}S_{0.0017}$ for Factor 2. The difference mass spectra between
398 the two factors are shown in Fig. 7. The abundance of C_xH_y fragments was
399 higher in Factor 2 than Factor 1, while oxygen and nitrogen content in
400 Factor 1 were higher than Factor 2. Meanwhile, as indicated in the red box
401 in Fig. 7, fragments with high *m/z* were more abundant in Factor 2. Thus
402 we assigned Factor 1 to the highly oxidized organic component and some
403 nitrogenous organic compounds, while Factor 2 was assigned to less-
404 oxidized organic aerosol and some oligomers.

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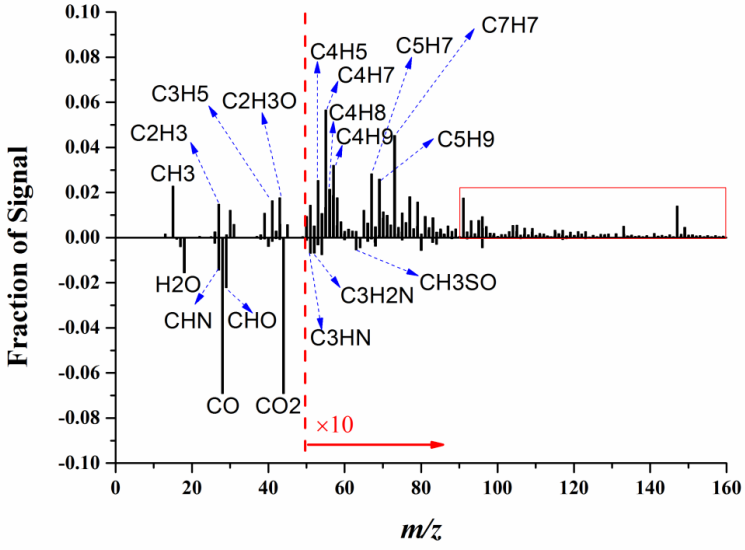

405

406 Fig. 7 The difference mass spectra (Factor 2 – Factor 1) between the two factors of
407 the generated organic aerosol identified by applying PMF analysis to the AMS
408 data

409 These two factors had different temporal variations during the reaction.
410 As indicated in Fig. 8, Factor 2 always increased at the beginning of the
411 reaction but decreased after reaching a peak with 1 or 2 hours of irradiation.
412 Factor 1 was generated later than Factor 2, while it continuously increased
413 during the reaction. Comparing experiments with different concentrations
414 of SO_2, the production of Factor 2 increased with increasing SO_2 under
415 NH_3-poor conditions, while Factor 1 increased with increasing SO_2 under
416 an NH_3-rich environment. Similar results can also be found in Fig. 9. The
417 higher production of Factor 2 with higher SO_2 under an NH_3-poor
418 environment could be probably attributed to the well-known acid-catalysis

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effects of the oxidation product of SO_2, i.e. sulfuric acid, on heterogeneous aldol condensation (Offenberg et al., 2009; Jang et al., 2002; Gao et al., 2004). Under NH_3-rich conditions, however, Factor 1, which has higher contents of oxygen and nitrogen than Factor 2, dominated in the SOA formation. Meanwhile, the production of Factor 2 increased significantly with increasing SO_2 concentration in NH_3-rich conditions. This indicated that the formation of highly oxidized organic compounds and nitrogenous organic compounds was increased with higher concentrations of SO_2 under NH_3-rich conditions. By inference and from the results of AMS measurements, aerosol water increased as the initial concentration of SO_2 increased, since more inorganic aerosol was generated. Liggio and Li (2013) suggest that dissolution of primary polar gases into a partially aqueous aerosol contributed to the increase of organic mass and oxygen content on neutral and near-neutral seed aerosols, which would also take place in the NH_3-rich experiments and contribute to the generation of Factor 1.

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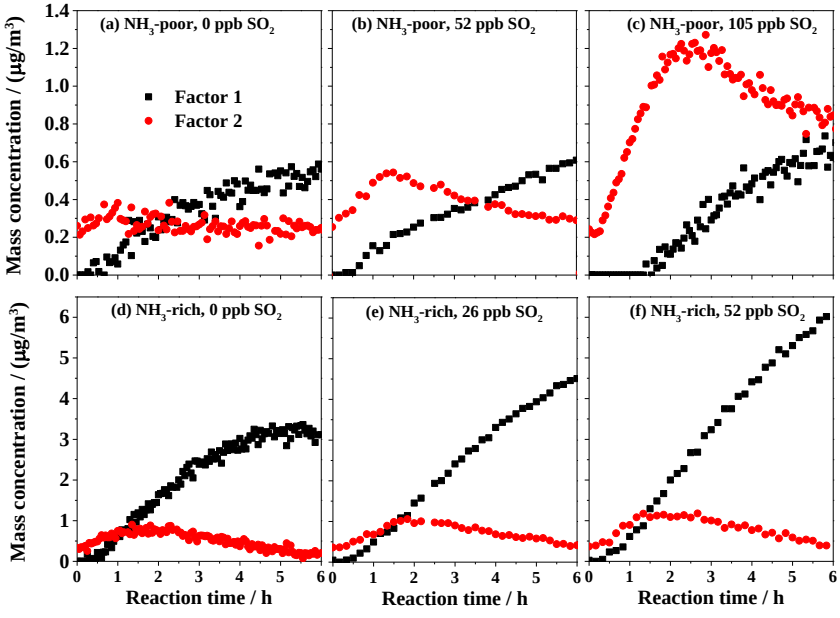

Fig. 8 Temporal variations of Factor 1 and Factor 2 in the presence of different concentrations of SO_2 under NH_3-poor and NH_3-rich conditions.

Nitrogen-containing organics (NOC) are a potentially important aspect of SOA formation, and may have contributed to the increase of Factor 1 in this study. NOC might contain organonitrates, formed through reactions between organic peroxy radicals (RO_2) and NO (Arey et al., 2001), organic ammonium salts, generated in acid-base reactions between ammonia/ammonium and organic acid species (Liu et al., 2012b), and species with carbon covalently bonded to nitrogen, generated in reactions of ammonia/ammonium with carbonyl functional group organics (Wang et al., 2010). Although we were not able to measure NOC, some indirect estimation methods suggested by Farmer et al. (2010) could be applied. The details for estimation of the concentrations of organonitrates and NOC

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with reduced N are given in the supporting information. Despite the uncertainty, there is an obvious increasing trend of organonitrates and NOC with reduced N with increasing SO_2 concentration under NH_3-rich conditions, as shown in Fig. 9. The increase ratio of NOC is higher than that of the organic aerosol or Factor 1 as SO_2 concentration increases. The estimated NOC contributed most of the increase in Factor 1 in NH_3-rich conditions. These results provide some evidence that the formation of organonitrates and NOC with reduced N (organic ammonium salts, imines, imidazole, and so on) played an important role in the increasing trend of SOA with SO_2 in a NH_3-rich environment. It was speculated that the higher surface acidity of aerosol formed in the presence of a high concentration of SO_2 favors NOC formation through NH_3 uptake by SOA, as observed in a recent work (Liu et al., 2015b).

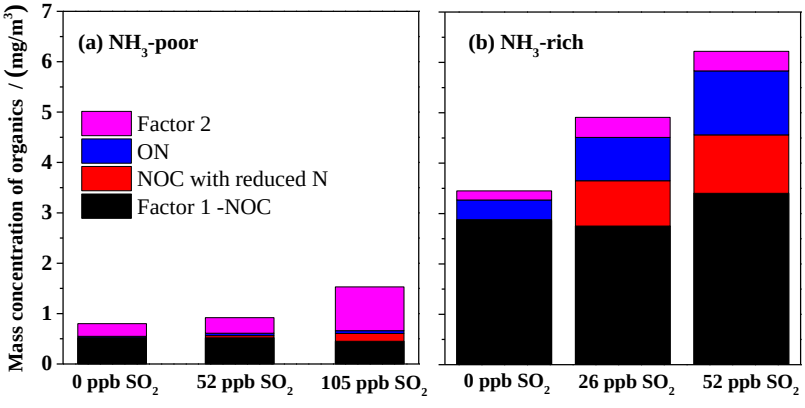

Fig. 9 The estimated concentrations of NOC (ON+NOC with reduced N) and the two factors (identified by PMF analysis) in SOA as a function of SO_2 concentration in photooxidation of toluene/NO_x under (a)

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467 NH_3-poor and (b) NH_3-rich conditions

468 ## Conclusions

469 In the photooxidation system of toluene/NO_x, the presence of SO_2
470 and/or NH_3 increased secondary aerosol formation markedly, regardless of
471 whether Al_2O_3 seed aerosol was present or not. Some synergetic effects in
472 the heterogeneous process were observed in secondary inorganic aerosol
473 formation in addition to the generation of ammonium and sulfate from NH_3
474 and SO_2. Specifically, the generation of NH_4NO_3 was found to be highly
475 dependent on the surface area concentration of suspended particles, and
476 was enhanced by increased SO_2 concentration. Meanwhile, sulfate
477 formation was also increased in the presence of NH_3. The absorbed NH_3
478 might provide liquid surface layers for the absorption and subsequent
479 reaction for SO_2 and organic products, and therefore, enhance sulfate and
480 SOA formation. NH_3 mainly influenced secondary aerosol formation in the
481 heterogeneous process, resulting in significant growth of seed aerosols, but
482 had little influence on new particle generation. In the experiments carried
483 out in the presence of Al_2O_3 seed aerosols, sulfate, organic aerosol, nitrate
484 and ammonium were all found to increase linearly with increasing SO_2
485 concentrations in toluene/NO_x photooxidation. The increase of these four
486 species was more obvious under NH_3-rich conditions, and the order of their
487 sensitivity was different from that under NH_3-poor conditions. A better
488 correlation between secondary aerosol formation and particle surface area
489 than that with particle volume indicated an enhancement effect in the

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heterogeneous process rather than in bulk reactions.

Two factors were identified in the PMF analysis of the AMS data. One factor assigned to less-oxidized organic aerosol and some oligomers increased with increasing SO_2 under NH_3-poor conditions, mainly due to the well-known acid catalytic effects of the acid products on SOA formation in the heterogeneous process. The other factor, assigned to the highly oxidized organic component and some nitrogenous organic compounds, increased with increasing SO_2 under an NH_3-rich environment, with NOC (organonitrates and NOC with reduced N) contributing most of the increase.

This study indicated that the synergistic effects between inorganic pollutants could substantially enhance secondary inorganic aerosol formation. Meanwhile, the presence of inorganic gas pollutants, i.e. SO_2 and NH_3, promoted SOA formation markedly. Synergistic formation of secondary inorganic and organic aerosol might increase the secondary aerosol load in the atmosphere. These synergistic effects were related to the heterogeneous process on the aerosol surface, and need to be quantified and considered in air quality models.

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516 Inc.

517 References

518 Amarnath, V., Anthony, D. C., Amarnath, K., Valentine, W. M., Wetterau, L. A., and
519 Graham, D. G.: Intermediates in the Paal-Knorr Synthesis of Pyrroles, J. Org. Chem.,
520 56, 6924-6931, DOI 10.1021/jo00024a040, 1991.
521 Arey, J., Aschmann, S. M., Kwok, E. S. C., and Atkinson, R.: Alkyl nitrate,
522 hydroxyalkyl nitrate, and hydroxycarbonyl formation from the NOx-air
523 photooxidations of C-5-C-8 n-alkanes, J. Phys. Chem. A, 105, 1020-1027, DOI
524 10.1021/jp003292z, 2001.
525 Bai, Y., Thompson, G. E., and Martinez-Ramirez, S.: Effects of NO_2 on oxidation
526 mechanisms of atmospheric pollutant SO2 over Baumberger sandstone, Building and
527 Environment, 41, 486-491, DOI 10.1016/j.buildenv.2005.02.007, 2006.
528 Behera, S. N., and Sharma, M.: Degradation of SO_2, NO_2 and NH_3 leading to formation
529 of secondary inorganic aerosols: An environmental chamber study, Atmos. Environ.,
530 45, 4015-4024, DOI 10.1016/j.atmosenv.2011.04.056, 2011.
531 Chu, B., Hao, J., Takekawa, H., Li, J., Wang, K., and Jiang, J.: The remarkable effect
532 of $FeSO_4$ seed aerosols on secondary organic aerosol formation from photooxidation of
533 α-pinene/NO_x and toluene/NOx, Atmos. Environ., 55, 26-34, DOI
534 10.1016/j.atmosenv.2012.03.006, 2012.
535 Chu, B., Liu, Y., Li, J., Takekawa, H., Liggio, J., Li, S.-M., Jiang, J., Hao, J., and He,
536 H.: Decreasing effect and mechanism of FeSO4 seed particles on secondary organic
537 aerosol in α-pinene photooxidation, Environ. Pollut., 193, 88-93, DOI
538 10.1016/j.envpol.2014.06.018, 2014.
539 Dan, M., Zhuang, G., Li, X., Tao, H., and Zhuang, Y.: The characteristics of
540 carbonaceous species and their sources in PM2.5 in Beijing, Atmos. Environ., 38, 3443-
541 3452, DOI 10.1016/j.atmosenv.2004.02.052, 2004.
542 Duan, F., He, K., Ma, Y., Jia, Y., Yang, F., Lei, Y., Tanaka, S., and Okuta, T.:
543 Characteristics of carbonaceous aerosols in Beijing, China, Chemosphere, 60, 355-364,
544 2005.

545 Edney, E. O., Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenberg, J. H., Wang,
546 W., and Claeys, M.: Formation of 2-methyl tetrols and 2-methylglyceric acid in
547 secondary organic aerosol from laboratory irradiated isoprene/NO_x/SO_2/air mixtures
548 and their detection in ambient $PM_{2.5}$ samples collected in the eastern United States,
549 Atmos. Environ., 39, 5281-5289, DOI 10.1016/j.atmosenv.2005.05.031, 2005.
550 Farmer, D. K., Matsunaga, A., Docherty, K. S., Surratt, J. D., Seinfeld, J. H., Ziemann,
551 P. J., and Jimenez, J. L.: Response of an aerosol mass spectrometer to organonitrates
552 and organosulfates and implications for atmospheric chemistry, Proc. Natl. Acad. Sci.
553 USA, 107, 6670-6675, DOI 10.1073/pnas.0912340107, 2010.
554 Fu, X., Wang, S. X., Ran, L. M., Pleim, J. E., Cooter, E., Bash, J. O., Benson, V., and
555 Hao, J. M.: Estimating NH_3 emissions from agricultural fertilizer application in China
556 using the bi-directional CMAQ model coupled to an agro-ecosystem model, Atmos.
557 Chem. Phys., 15, 6637-6649, DOI 10.5194/acp-15-6637-2015, 2015.
558 Gao, S., Ng, N. L., Keywood, M., Varutbangkul, V., Bahreini, R., Nenes, A., He, J. W.,
559 Yoo, K. Y., Beauchamp, J. L., Hodyss, R. P., Flagan, R. C., and Seinfeld, J. H.: Particle
560 phase acidity and oligomer formation in secondary organic aerosol, Environ. Sci. &
561 Technol., 38, 6582-6589, DOI 10.1021/es049125k, 2004.
562 He, H., Wang, Y., Ma, Q., Ma, J., Chu, B., Ji, D., Tang, G., Liu, C., Zhang, H., and Hao,
563 J.: Mineral dust and NOx promote the conversion of SO2 to sulfate in heavy pollution
564 days, Sci. Rep., 4, 04172, DOI 10.1038/srep04172, 2014.
565 Jang, M. S., and Kamens, R. M.: Characterization of secondary aerosol from the
566 photooxidation of toluene in the presence of NOx and 1-propene, Environ. Sci. &
567 Technol., 35, 3626-3639, DOI 10.1021/es010676+, 2001.
568 Jang, M. S., Czoschke, N. M., Lee, S., and Kamens, R. M.: Heterogeneous atmospheric
569 aerosol production by acid-catalyzed particle-phase reactions, Science, 298, 814-817,
570 2002.
571 Jaoui, M., Edney, E. O., Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., Surratt,
572 J. D., and Seinfeld, J. H.: Formation of secondary organic aerosol from irradiated alpha-
573 pinene/toluene/NOx mixtures and the effect of isoprene and sulfur dioxide, J. Geophys.
574 Res.- Atmos., 113, D09303, DOI 10.1029/2007jd009426, 2008.
575 Kleindienst, T. E., Edney, E. O., Lewandowski, M., Offenberg, J. H., and Jaoui, M.:
576 Secondary organic carbon and aerosol yields from the irradiations of isoprene and
577 alpha-pinene in the presence of NOx and SO2, Environ. Sci. & Technol., 40, 3807-3812,
578 DOI 10.1021/es052446r, 2006.
579 Li, W. J., Shao, L. Y., Shi, Z. B., Chen, J. M., Yang, L. X., Yuan, Q., Yan, C., Zhang, X.
580 Y., Wang, Y. Q., Sun, J. Y., Zhang, Y. M., Shen, X. J., Wang, Z. F., and Wang, W. X.:

581 Mixing state and hygroscopicity of dust and haze particles before leaving Asian
582 continent, J. Geophys. Res.- Atmos., 119, 1044-1059, DOI 10.1002/2013jd021003,
583 2014.
584 Liggio, J., and Li, S. M.: Reactive uptake of pinonaldehyde on acidic aerosols, J.
585 Geophys. Res.- Atmos., 111, DOI 10.1029/2005jd006978, 2006.
586 Liggio, J., Li, S. M., Brook, J. R., and Mihele, C.: Direct polymerization of isoprene
587 and alpha-pinene on acidic aerosols, Geophysical Research Letters, 34, DOI
588 10.1029/2006gl028468, 2007.
589 Liggio, J., and Li, S. M.: Reversible and irreversible processing of biogenic olefins on
590 acidic aerosols, Atmos. Chem. Phys., 8, 2039-2055, 2008.
591 Liggio, J., and Li, S. M.: A new source of oxygenated organic aerosol and oligomers,
592 Atmos. Chem. Phys., 13, 2989-3002, DOI 10.5194/acp-13-2989-2013, 2013.
593 Lin, Y. H., Knipping, E. M., Edgerton, E. S., Shaw, S. L., and Surratt, J. D.:
594 Investigating the influences of SO2 and NH3 levels on isoprene-derived secondary
595 organic aerosol formation using conditional sampling approaches, Atmos. Chem. Phys.,
596 13, 8457-8470, DOI 10.5194/acp-13-8457-2013, 2013.
597 Liu, C., Liu, Y., Ma, Q., and He, H.: Mesoporous transition alumina with uniform pore
598 structure synthesized by alumisol spray pyrolysis, Chem. Eng. J., 2010.
599 Liu, C., Ma, Q., Liu, Y., Ma, J., and He, H.: Synergistic reaction between SO_2 and NO_2
600 on mineral oxides: a potential formation pathway of sulfate aerosol, Phys. Chem. Chem.
601 Phys., 14, 1668-1676, DOI 10.1039/c1cp22217a, 2012a.
602 Liu, X. G., Li, J., Qu, Y., Han, T., Hou, L., Gu, J., Chen, C., Yang, Y., Liu, X., Yang, T.,
603 Zhang, Y., Tian, H., and Hu, M.: Formation and evolution mechanism of regional haze:
604 a case study in the megacity Beijing, China, Atmos. Chem. Phys., 13, 4501-4514, DOI
605 10.5194/acp-13-4501-2013, 2013.
606 Liu, X. G., Sun, K., Qu, Y., Hu, M., Sun, Y. L., Zhang, F., and Zhang, Y. H.: Secondary
607 Formation of Sulfate and Nitrate during a Haze Episode in Megacity Beijing, China,
608 Aerosol Air Qual. Res., 15, 2246-2257, DOI 10.4209/aaqr.2014.12.0321, 2015a.
609 Liu, Y., Ma, Q., and He, H.: Heterogeneous Uptake of Amines by Citric Acid and
610 Humic Acid, Environ. Sci. & Technol., 46, 11112-11118, 10.1021/es302414v, 2012b.
611 Liu, Y., Liggio, J., Staebler, R., and Li, S. M.: Reactive uptake of ammonia to secondary
612 organic aerosols: kinetics of organonitrogen formation, Atmos. Chem. Phys., 15,
613 13569-13584, DOI 10.5194/acp-15-13569-2015, 2015b.
614 Meng, Z., Xie, Y., Jia, S., Zhang, R., Lin, W., Xu, X., and Yang, W.: Characteristics of
615 Atmospheric Ammonia at Gucheng, a Rural Site on North China Plain in Summer of
616 2013, J. Appl. Meteor. Sci., 26, 141-150, 2015.

617 Meyer, N. K., Duplissy, J., Gysel, M., Metzger, A., Dommen, J., Weingartner, E.,
618 Alfarra, M. R., Prevot, A. S. H., Fletcher, C., Good, N., McFiggans, G., Jonsson, A. M.,
619 Hallquist, M., Baltensperger, U., and Ristovski, Z. D.: Analysis of the hygroscopic and
620 volatile properties of ammonium sulphate seeded and unseeded SOA particles, Atmos.
621 Chem. Phys., 9, 721-732, 2009.
622 Na, K., Song, C., and Cocker, D. R.: Formation of secondary organic aerosol from the
623 reaction of styrene with ozone in the presence and absence of ammonia and water,
624 Atmos. Environ., 40, 1889-1900, DOI 10.1016/j.atmosenv.2005.10.063, 2006.
625 Na, K., Song, C., Switzer, C., and Cocker, D. R.: Effect of ammonia on secondary
626 organic aerosol formation from alpha-Pinene ozonolysis in dry and humid conditions,
627 Environ. Sci. & Technol., 41, 6096-6102, DOI 10.1021/es061956y, 2007.
628 Ng, N. L., Herndon, S. C., Trimborn, A., Canagaratna, M. R., Croteau, P. L., Onasch,
629 T. B., Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L., and Jayne, J. T.: An Aerosol
630 Chemical Speciation Monitor (ACSM) for routine monitoring of the composition and
631 mass concentrations of ambient aerosol, Aerosol Sci. Technol., 45, 770-784, DOI
632 10.1080/02786826.2011.560211, 2011.
633 Offenberg, J. H., Lewandowski, M., Edney, E. O., Kleindienst, T. E., and Jaoui, M.:
634 Influence of Aerosol Acidity on the Formation of Secondary Organic Aerosol from
635 Biogenic Precursor Hydrocarbons, Environ. Sci. & Technol., 43, 7742-7747, DOI
636 10.1021/es901538e, 2009.
637 Pathak, R. K., Wu, W. S., and Wang, T.: Summertime $PM_{2.5}$ ionic species in four major
638 cities of China: nitrate formation in an ammonia-deficient atmosphere, Atmos. Chem.
639 Phys., 9, 1711-1722, 2009.
640 Santiago, M., Garcia Vivanco, M., and Stein, A. F.: SO_2 effect on secondary organic
641 aerosol from a mixture of anthropogenic VOCs: experimental and modelled results,
642 International Journal of Environment and Pollution, 50, 224-233, 2012.
643 Schmitt-Kopplin, P., Gelencser, A., Dabek-Zlotorzynska, E., Kiss, G., Hertkorn, N.,
644 Harir, M., Hong, Y., and Gebefuegi, I.: Analysis of the Unresolved Organic Fraction in
645 Atmospheric Aerosols with Ultrahigh-Resolution Mass Spectrometry and Nuclear
646 Magnetic Resonance Spectroscopy: Organosulfates As Photochemical Smog
647 Constituents, Anal. Chem., 82, 8017-8026, DOI 10.1021/ac101444r, 2010.
648 Takekawa, H., Minoura, H., and Yamazaki, S.: Temperature dependence of secondary
649 organic aerosol formation by photo-oxidation of hydrocarbons, Atmos. Environ., 37,
650 3413-3424, DOI 10.1016/s1352-2310(03)00359-5, 2003.
651 Tursic, J., and Grgic, I.: Influence of NO_2 on S(IV) oxidation in aqueous suspensions
652 of aerosol particles from two different origins, Atmos. Environ., 35, 3897-3904, DOI

10.1016/s1352-2310(01)00142-x, 2001.

Tursic, J., Berner, A., Podkrajsek, B., and Grgic, I.: Influence of ammonia on sulfate formation under haze conditions, Atmos. Environ., 38, 2789-2795, DOI 10.1016/j.atmosenv.2004.02.036, 2004.

Updyke, K. M., Nguyen, T. B., and Nizkorodov, S. A.: Formation of brown carbon via reactions of ammonia with secondary organic aerosols from biogenic and anthropogenic precursors, Atmos. Environ., 63, 22-31, DOI 10.1016/j.atmosenv.2012.09.012, 2012.

Wang, L., Wen, L., Xu, C., Chen, J., Wang, X., Yang, L., Wang, W., Yang, X., Sui, X., Yao, L., and Zhang, Q.: HONO and its potential source particulate nitrite at an urban site in North China during the cold season, Sci. Total Environ., 538, 93-101, DOI 10.1016/j.scitotenv.2015.08.032, 2015.

Wang, X. F., Gao, S., Yang, X., Chen, H., Chen, J. M., Zhuang, G. S., Surratt, J. D., Chan, M. N., and Seinfeld, J. H.: Evidence for High Molecular Weight Nitrogen-Containing Organic Salts in Urban Aerosols, Environ. Sci. & Technol., 44, 4441-4446, DOI 10.1021/es1001117, 2010.

Wang, Z., Wang, T., Guo, J., Gao, R., Xue, L. K., Zhang, J. M., Zhou, Y., Zhou, X. H., Zhang, Q. Z., and Wang, W. X.: Formation of secondary organic carbon and cloud impact on carbonaceous aerosols at Mount Tai, North China, Atmos. Environ., 46, 516-527, DOI 10.1016/j.atmosenv.2011.08.019, 2012.

Wen, L. A., Chen, J. M., Yang, L. X., Wang, X. F., Xu, C. H., Sui, X. A., Yao, L., Zhu, Y. H., Zhang, J. M., Zhu, T., and Wang, W. X.: Enhanced formation of fine particulate nitrate at a rural site on the North China Plain in summer: The important roles of ammonia and ozone, Atmos. Environ., 101, 294-302, DOI 10.1016/j.atmosenv.2014.11.037, 2015.

Wu, S., Lu, Z. F., Hao, J. M., Zhao, Z., Li, J. H., Hideto, T., Hiroaki, M., and Akio, Y.: Construction and characterization of an atmospheric simulation smog chamber, Advances in Atmospheric Sciences, 24, 250-258, DOI 10.1007/s00376-007-0250-3, 2007.

Yang, F., Tan, J., Zhao, Q., Du, Z., He, K., Ma, Y., Duan, F., Chen, G., and Zhao, Q.: Characteristics of $PM_{2.5}$ speciation in representative megacities and across China, Atmos. Chem. Phys., 11, 5207-5219, DOI 10.5194/acp-11-5207-2011, 2011.

Yang, W., He, H., Ma, Q., Ma, J., Liu, Y., Liu, P., and Mu, Y.: Synergistic formation of sulfate and ammonium resulting from reaction between SO_2 and NH_3 on typical mineral dust, Phys. Chem. Chem. Phys., 18, 956-964, DOI 10.1039/c5cp06144j, 2016.

Ye, X. N., Ma, Z., Zhang, J. C., Du, H. H., Chen, J. M., Chen, H., Yang, X., Gao, W.,

689 and Geng, F. H.: Important role of ammonia on haze formation in Shanghai, Environ.
690 Res. Lett., 6, Artn 024019, DOI 10.1088/1748-9326/6/2/024019, 2011.
691 Zhao, P. S., Dong, F., He, D., Zhao, X. J., Zhang, X. L., Zhang, W. Z., Yao, Q., and Liu,
692 H. Y.: Characteristics of concentrations and chemical compositions for $PM_{2.5}$ in the
693 region of Beijing, Tianjin, and Hebei, China, Atmos. Chem. Phys., 13, 4631-4644, DOI
694 10.5194/acp-13-4631-2013, 2013.
695 Zou, Y., Deng, X. J., Zhu, D., Gong, D. C., Wang, H., Li, F., Tan, H. B., Deng, T., Mai,
696 B. R., Liu, X. T., and Wang, B. G.: Characteristics of 1 year of observational data of
697 VOCs, NO_x and O_3 at a suburban site in Guangzhou, China, Atmos. Chem. Phys., 15,
698 6625-6636, DOI 10.5194/acp-15-6625-2015, 2015.

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