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Synergetic formation of secondary inorganic and organic aerosol: effect of SO_2 and NH_3 on particle formation and growth

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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 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. 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 with SO_2 concentration among the four species under NH_3-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 without NH_3. By applying positive matrix factorisation (PMF) analysis to the AMS data, two factors were identified for the generated SOA. One factor, assigned to less-oxidised 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 process. The other factor, assigned to the highly oxidised 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.

1 Introduction

With the recent rapid economic development and urbanisation, 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; L. Wang et al., 2015). China has the highest concentration of SO_2 in the world due to a large proportion of energy supply from coal combustion (Bauduin et al., 2016). Surface concentrations of SO_2 in the range of a few ppb to over 100 ppb have been observed in northern China (Sun et al., 2009; Li et al., 2007). The total emission and concentrations of SO_2 have decreased in most regions of China in recent years (Lu et al., 2010; S. W. Wang et al., 2015), but high concentrations of SO_2 are still frequently observed. For example, the SO_2 concentration was as high as 43 ppb in the winter of 2013 in Jinan city (L. Wang et al., 2015), while over 100 ppb SO_2 was observed in winter haze days during 2012 in Xi'an city (Zhang et al., 2015). High concentrations of precursors have 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 systematic measurement of NH_3 in China despite its extensive emission and increasing trend (Fu et al., 2015). A few studies have 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 observational data indicated NH_3-rich conditions for secondary aerosol formation, strong correlations between peak levels of fine particles and large increases in NH_3 concentrations in China (Ye et al., 2011; X. G. Liu et al., 2015). Unlike SO_2, the emission of NH_3 is mainly from non-point sources, which are difficult to control, and show an increasing trend in China (Dong, 2010). Under this complex situation, studying the synergistic effects of SO_2 and NH_3 in secondary aerosol formation is crucial for understanding the formation mechanism for 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). Synergistic reaction between SO_2 and NO_2 on mineral oxides was reported (C. Liu et al., 2012a) and was proposed to explain the rapid formation of sulfate in heavy haze days (He et al., 2014). The presence of NH_3 could also 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). The enhancing effect is mainly due to the fact that the acidic aerosol products of SO_2 can either take up organic species (Liggio

and Li, 2006, 2008) or increase the formation of high molecular weight compounds in acid-catalysed reactions (Liggio et al., 2007; Kleindienst et al., 2006; Santiago et al., 2012). Besides, sulfate esters can also contribute to 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. NH_3 increased SOA formation from ozonolysis of α-pinene or cyclohexene (Na et al., 2007), but had little effect on SOA mass from ozonolysis of isoprene (Na et al., 2007; Lin et al., 2013) and even decreased SOA production from ozonolysis of styrene (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 its nucleophilic attack might decompose trioxolane and hydroxyl-substituted esters and decrease SOA mass (Na et al., 2006). Updyke et al. (2012) studied brown carbon formation via reactions of ammonia with SOA from various precursors. It was found that the degree of browning had a positive correlation with the carbonyl products, which may react with NH_3 or NH_4^+ ion and generate hemiaminal (Amarnath et al., 1991).

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

2   Methods

A series of smog chamber experiments were carried out to simulate secondary aerosol formation in the photooxidation of toluene/NO_x in the presence or absence of SO_2 and/or NH_3. The chamber is a $2\,m^3$ cuboid reactor constructed with $50\,\mu m$-thick FEP-Teflon film (Toray Industries, Inc., Japan). The chamber was described in detail in Wu et al. (2007). A temperature-controlled enclosure (SEWT-Z-120, Escpec, Japan) provides a constant temperature ($30 \pm 0.5°$), and 40 black lights (GE F40T12/BLB, peak intensity at 365 nm, General Electric Company, USA) provide irradiation during the experiments. The hydrocarbon concentration was measured by a gas chromatograph (GC, Beifen SP-3420, Beifen, China) equipped with a DB-5 column ($30\,m \times 0.53\,mm \times 1.5\,mm$, Dikma, USA) and flame ionisation detector (FID), while NO_x, SO_2, and O_3 were monitored by an NO_x analyser (Model 42C, Thermo Environmental Instruments, USA), an SO_2 analyser (Model 43I, Thermo Environmental Instruments, USA), and an O_3 analyser (Model 49C, Thermo Environmental Instruments, USA). A scanning mobility particle sizer (SMPS; TSI 3936,

TSI Incorporated, USA) was used to measure the size distribution of particulate matter (PM) in the chamber and also employed to estimate the volume and mass concentration. The chemical composition of aerosols was 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 those of AMS. The chamber was run as a batch reactor in this study. Deposition of particles and gas compounds on the wall was considered to be a first-order process. The deposition rates of particles with different sizes (40–700 nm) were measured under dark conditions. Then, wall losses 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, 2014). The depositions of gas phase compounds were determined to be 0.0025, 0.0109, 0.0023, and 0.006 h^{-1} for NO_2, O_3, NO, and toluene, respectively. In this study, the wall loss of aerosol mass was about 30–50 % of total secondary aerosol mass, while the deposition of gas phase compounds was less than 5 % of their maximum concentrations in the experiments.

Prior to each experiment, the chamber was flushed for about 40 h with purified air at a flow rate of 15 L min^{-1}. In the first 20 h, the chamber was exposed to UV light at 34°. In the last several hours of the flush, humid air was introduced to obtain the target RH, which was 50 % in this study. After that, alumina seed particles were added into the chamber. Alumina seed particles were produced online via a spray pyrolysis set-up, 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 into droplets by an atomiser. 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 °C to generate alumina particles. The obtained alumina particles were γ-Al$_2$O$_3$, 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 neutraliser (TSI 3087, TSI Incorporated, USA). Then, toluene was injected into a vaporiser and carried into the chamber by purified air, while NO$_x$, SO$_2$, and NH$_3$ were directly injected into the chamber from standard gas bottles using mass flow controllers. Before adding NH$_3$ into the chamber, NH$_3$ gas was passed through the inlet pipeline for about 15 min to reduce absorption within the line. The concentrations of NH$_3$ were estimated according to the amount of NH$_3$ introduced and the volume of the reactor. These experiments with NH$_3$ added to the chamber were referred to as NH$_3$-rich experiments in this study, since the concentrations of NH$_3$ were not measured and it was difficult to estimate the uncertainty of the calculated NH$_3$ concentration. The experiments were carried out at 30° with an initial RH of 50 %. During the reaction, the temperature was kept nearly constant (30 ± 0.5°) in the temperature-controlled enclosure, while the RH decreased to 45–47 % at the end of the experiment.

3 Results and discussion

3.1 Particle formation and growth in different inorganic gas conditions

First, the effects of SO$_2$ and NH$_3$ on secondary aerosol formation were qualitatively studied 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$_3$. 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, ASTN is an experiment with the presence of ammonia gas (A), sulfur dioxide (S), toluene (T), and nitrogen oxides (N). Two experiments (ATN and ATN2) were carried out under similar conditions to test the reproducibility of the experiments. Time variations of gas phase compounds of these experiments are shown in Fig. S1 in the Supplement. The presence of SO$_2$ and/or NH$_3$ had no obvious effect on the gas phase compounds, including toluene, NO$_x$, SO$_2$, and O$_3$.

Secondary aerosol formation in these photooxidation experiments was measured by the SMPS, and the results are displayed in Fig. 1. 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 presence of NH$_3$. The volume of secondary aerosol showed an obvious peak in the toluene/NO$_x$/NH$_3$ system at about 2.3 h of photooxidation. With the wall deposition accounted for, the decrease of the volume concentration after that point was unexpected, but could be reproduced (experiments ATN and ATN2). Such a decrease was not observed with coexisting NH$_3$ and SO$_2$, indicating interactions between NH$_3$ and SO$_2$ in the photooxidation system. The reason for this phenomenon will be discussed in the following analysis of the chemical composition of the generated particles.

The size distributions of the secondary aerosol in the photooxidation, with a range of 17–1000 nm, were analysed and are shown in Fig. 2. The new particle formation was not directly measured in this study, but the newly generated particles could be detected when the particles increased in size. According to the particle number concentrations, new particle formation appeared to increase a great deal in the presence of SO$_2$. The maximal particle number concentrations

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

Experiment No.	Toluene ppm	NO ppb	NO_x-NO ppb	SO_2 ppb	NH_3^* ppb	RH %	T K
TN	1.05	54	49	0	0	50	303
STN	1.05	55	50	137	0	50	303
ATN	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

* The concentrations of NH_3 were calculated according to the amount of NH_3 introduced and the volume of the reactor.
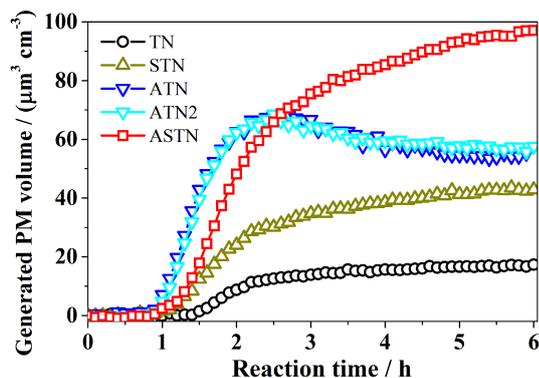
Figure 1. Secondary aerosol formation in photooxidation of toluene/NO_x in the presence or absence of NH_3 and/or SO_2. The letter codes for the experiments indicate the introduced pollutants, i.e. A for ammonia, S for sulfur dioxide, T for toluene, and N for nitrogen dioxide. Experimental details are listed in Table 1.

in the experiments ASTN and STN were 1 order of magnitude higher than in ATN and TN. The presence of NH_3 also contributed substantially to the particle growth in photooxidation of toluene/NO_x. Comparing Fig. 2c to a, the total number concentration of particles in experiment ATN was a little lower than in experiment TN, but the mode diameter of the particles was much larger.

3.2 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 (which may include both inorganic nitrate and organic nitrates) was not only enhanced by NH_3, but was also markedly affected by SO_2. The chemical compositions of the aerosols generated in the photooxidation of toluene/NO_x were analysed with an ACSM, and their time variations are displayed in Fig. 3. Since the ACM or AMS cannot distinguish organic salts and organic nitrates, the measured sulfate, nitrate, and ammonium were all considered secondary inorganic aerosol, while the organics were all considered secondary organic aerosol in this study. In experiment ATN, the concentrations of ammonium and nitrate decreased af-

ter about 2.3 h 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. Detailed simulation results based on the AIM aerosol thermodynamics model (Clegg and Brimblecombe, 2005; Clegg et al., 1998; Carslaw et al., 1995) are shown in Fig. S3. The deposition of NH_3 in the experiment was likely to shift the partition equilibrium to the gas phase and reduce the concentration of NH_4NO_3 salt. In addition, the wall deposition of aerosols might also introduce some error in the concentrations of NH_4NO_3 salt, although wall deposition was corrected using an empirical function based on deposition rates of $(NH_4)_2SO_4$ aerosol with different sizes (Chu et al., 2012, 2014). 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. Some simulation results using the AIM aerosol thermodynamics model with different concentrations of sulfate are also shown in Fig. S3. In addition, in the presence of organic matter, $(NH_4)_2SO_4$ aerosol might deliquesce at a RH lower than the deliquescence relative humidity (DRH; Meyer et al., 2009; Li et al., 2014). If this took place in the experiment, sulfate might provide moist surfaces for heterogeneous hydrolysis of N_2O_5, contributing to nitrate formation due to the high uptake coefficient of N_2O_5 on ammonium sulfate (Pathak et al., 2009; Hallquist et al., 2003; Hu and Abbatt, 1997). N_2O_5 was not measured in this study, but it was expected to be generated in the presence of NO_2 and O_3 in the experiments.

In Fig. 3, the generation of ammonium salt can be observed in the photooxidation of toluene/NO_x/SO_2 without introducing NH_3 gas. This indicated there was NH_3 present in the background air in the chamber, and also indicated that the effects of NH_3 on secondary aerosol formation might be underestimated in this study. The background NH_3 was derived from the partitioning of the deposited ammonium sulfate and nitrate on the chamber wall when humid air was introduced (Y. Liu et al., 2015). Unfortunately, due to the lack of appropriate instruments, we were not able to measure the exact concentration of NH_3 in the background air in the chamber. It was estimated to be around 8 ppb based on the amount of ammonium salt and the gas–aerosol equilibrium calculated using the AIM aerosol thermodynamics model. 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 estimated concentrations of NH_3 were more than twice the SO_2 concentrations and the oxidation products of SO_2 and NO_x were fully neutralised by NH_3, according to the chemical composition of aerosols measured by the AMS.
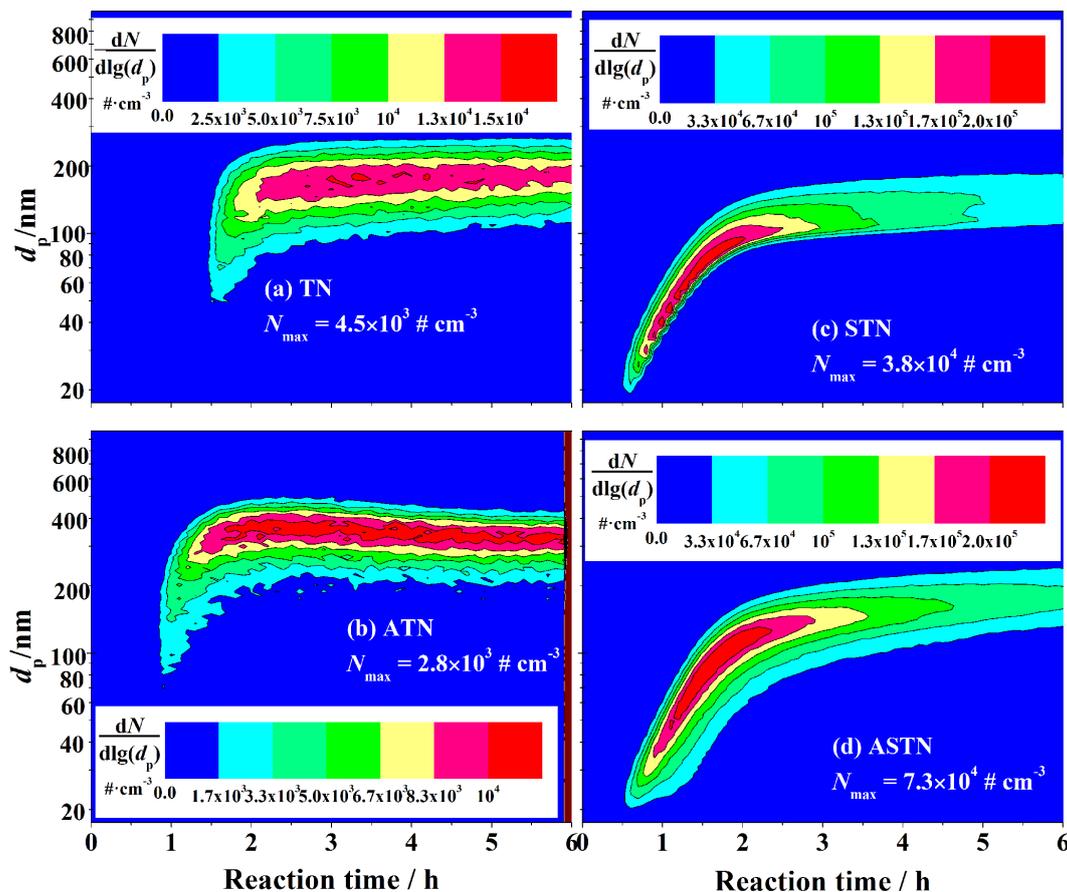
Figure 2. Size distributions of the suspended particles as a function of time during the reaction in photooxidation of toluene/NO$_x$ in the presence or absence of NH$_3$ and/or SO$_2$. N_{max} shows the maximal particle number concentration during the reaction for each experiment. Experimental details are listed in Table 1.

The details of the acid-base balance in the aerosols are shown in Fig. S4.

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 to simulate secondary aerosol formation under experimental conditions closer to real ambient conditions, and monodisperse Al$_2$O$_3$ 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$_2$O$_3$ seed aerosols. In the experiments carried out in the presence of Al$_2$O$_3$ seed aerosols, the decrease of NH$_4$NO$_3$ was less obvious in the experiment carried out in the absence of SO$_2$ under NH$_3$-rich conditions than in experiment ATN, as indicated in Figs. S5 and 3. This might also indicate that generation of NH$_4$NO$_3$ was dependent on the surface area concentration of the particles, which decreased the

partitioning of NH$_4$NO$_3$ back to the gas phase, as discussed above concerning the effects of co-existing (NH$_4$)$_2$SO$_4$.

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 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. 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. Initial experimental conditions for 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.

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

* Calculated according to the amount of NH_3 introduced and the volume of the reactor.
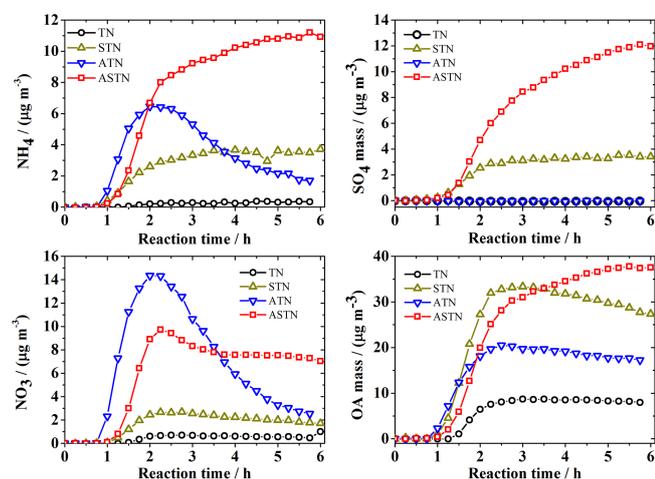
Figure 3. Time variations of the chemical species in the secondary aerosol generated from the photooxidation of toluene/NO_x in the presence or absence of NH_3 and SO_2. Letter codes for experiments indicate the introduced pollutants, i.e. A for ammonia, S for sulfur dioxide, T for toluene, and N for nitrogen dioxide. Experimental details are listed in Table 1.

Figure 4. Secondary aerosol formation as a function of time with different concentrations of SO_2 in the photooxidation of toluene/NO_x under NH_3-poor **(a)** and NH_3-rich **(b)** conditions. 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., 2004). According to the consumption of toluene, OH concentrations in the photooxidation experiments were estimated to range from 1.6×10^6 to 2.7×10^6 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 impor-

tant 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 the 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 for SO_2 absorption on Al_2O_3 aerosols (Yang et al., 2016) and increase the amount of condensed water on the secondary aerosols (Tursic et al., 2004) and, therefore, enhance sulfate formation (Yang et al., 2016; Tursic et al., 2004).

3.3 Secondary organic aerosol formation

The presence of NH_3 and SO_2 caused significant formation of secondary inorganic aerosol and enhanced SOA formation. The increases of SOA mass in the presence of NH_3 and SO_2 are shown in Fig. 5. Similar trends for SOA yields can be found in the Supplement. In previous studies, Kleindienst et al. (2006) found that the presence of SO_2 did not disturb
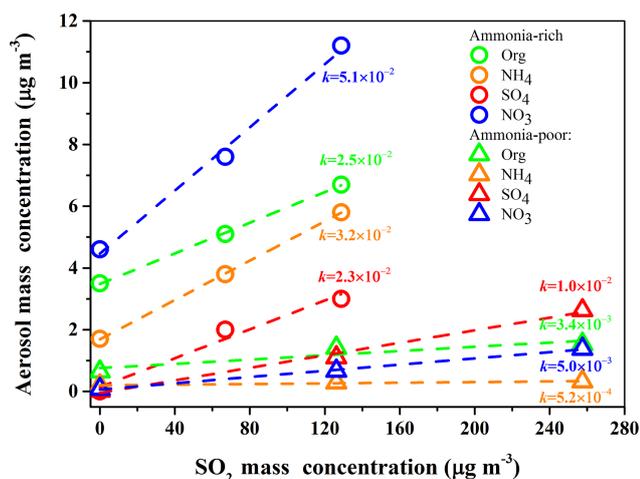
Figure 5. Formation of nitrate (blue), organic aerosol (green), sulfate (red), and ammonium salt (orange) as functions of SO_2 concentration in the photooxidation of toluene/NO_x under NH_3-rich (circles) or NH_3-poor (triangles) conditions. The k values are the slopes of the fitted lines for each species. Experimental details are listed in Table 1.

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 speculated that the presence of SO_2 and NH_3 in this study did not significantly impact the gas phase oxidation of 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 and 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 oxycarboxylic acids from ring-opening reactions in the photooxidation of 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. 6a and c. The presence of NH_3 caused a more noticeable growth in the size of the Al_2O_3 seed particles. The increase mainly took place after 0.5 h of irradiation, and lasted for about an hour, with an average diameter growth of about 12 nm. In the two experiments carried out in the presence of 52 ppb SO_2 in Fig. 6b and d, significant but similar new particle formation occurred. The maximum particle number concentrations detected by the SMPS were about 33 000 and 34 000 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.

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

These two factors had different temporal variations during the reaction. As indicated in Fig. 8, Factor 2 always increased at the beginning of the reaction but decreased after reaching a peak at 1 or 2 hours of irradiation. Factor 1 was generated later than Factor 2, while it continuously increased during the reaction. Comparing experiments with different concentrations of SO_2, the production of Factor 2 increased with increasing SO_2 under NH_3-poor conditions, while Factor 1 increased with increasing SO_2 under an NH_3-rich environment. Similar results can also be found in Fig. 9. The higher production of Factor 2 with higher SO_2 under an NH_3-poor environment could probably be attributed to the well-known acid catalysis 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). This is consistent with the fact that the aerosols in the NH_3-poor environment were quite acidic according to the simulation results of the AIM model, based on the chemical compositions of aerosols measured by the AMS. 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 signif-
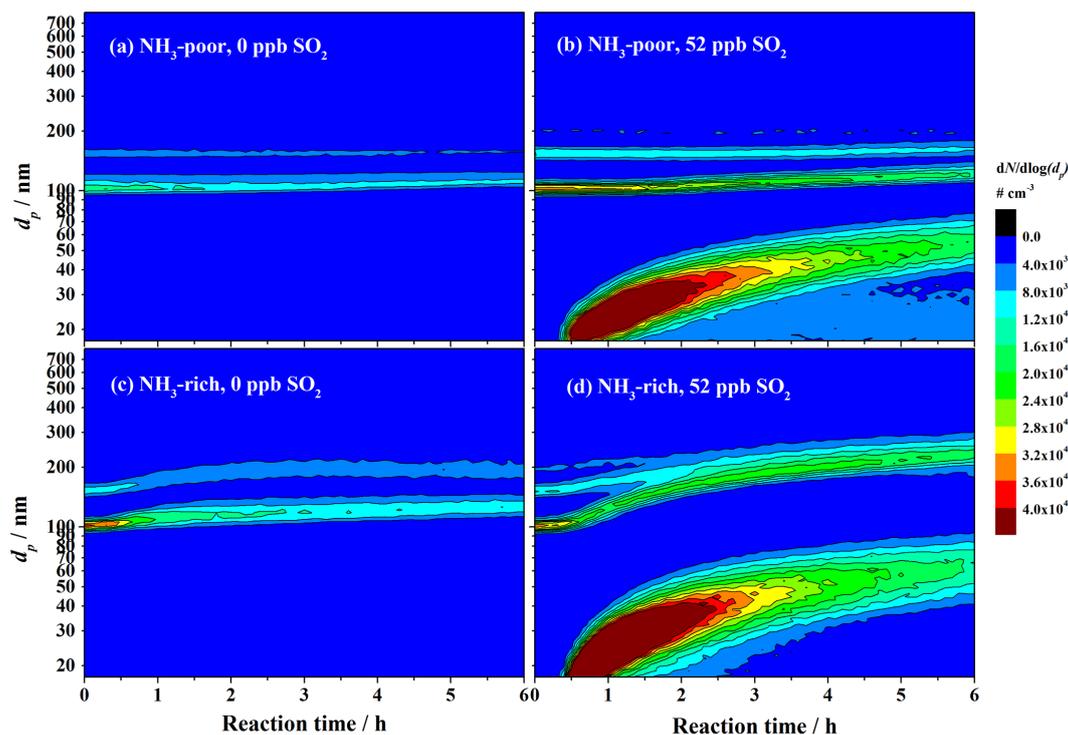
Figure 6. Size distributions of the suspended particles as a function of time during the reaction in photooxidation of toluene/NO_x in the presence of Al_2O_3 seed particles. Experimental details are listed in Table 1.
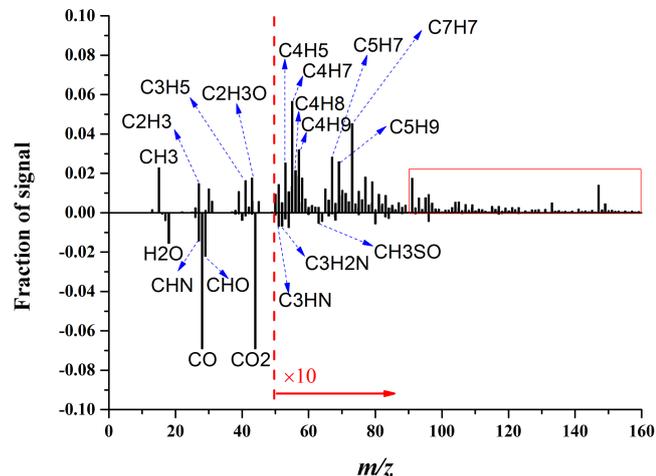
Figure 7. The difference mass spectra (Factor 2–Factor 1) between the two factors of the generated organic aerosol identified by applying PMF analysis to the AMS data.

icantly with increasing SO_2 concentration in NH_3-rich conditions. This indicated that the formation of highly oxidised 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 contributes 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.

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 (Y. 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 with reduced N are given in the Supplement. 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 ratio of NOC increases to a higher level 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 re-
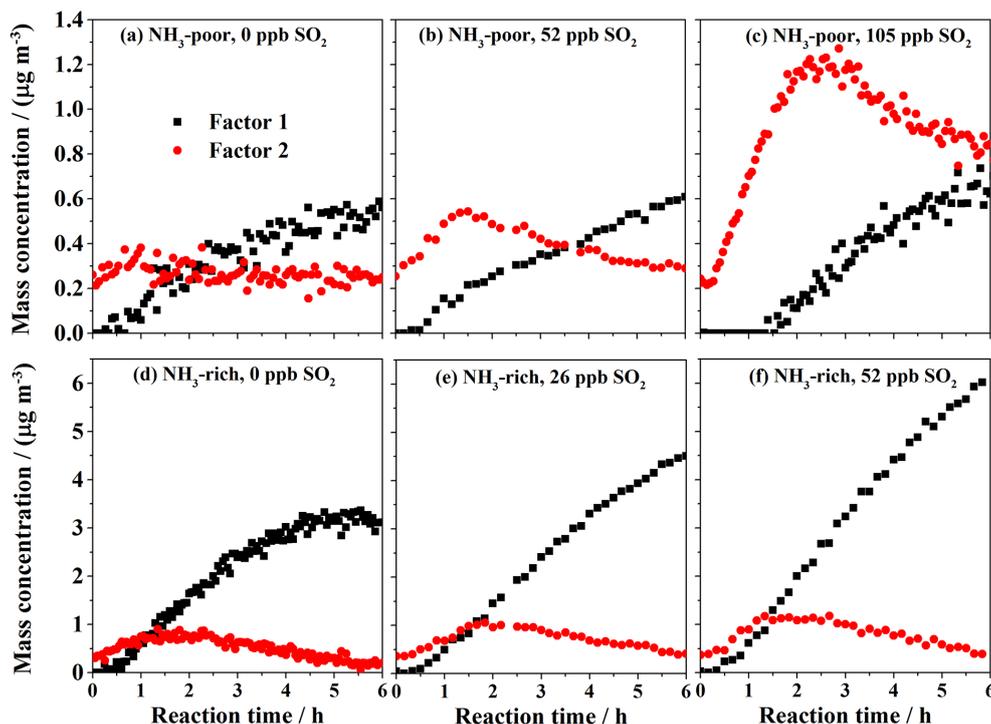
Figure 8. Temporal variations of Factor 1 and Factor 2 in the presence of different concentrations of SO_2 under NH_3-poor and NH_3-rich conditions.
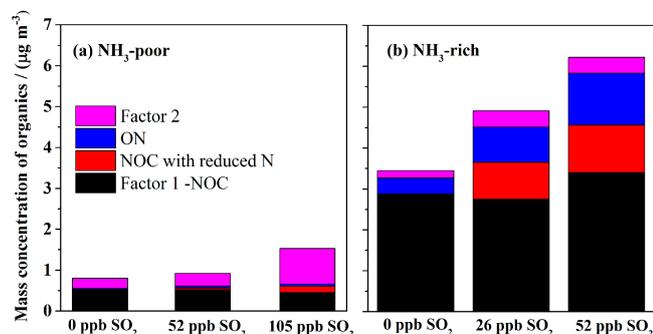
Figure 9. The estimated concentrations of NOC (ON and NOC with reduced N) and the two factors (identified by PMF analysis) in SOA as a function of SO_2 concentration in photooxidation of toluene/NO_x under **(a)** NH_3-poor and **(b)** NH_3-rich conditions.

sults 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 an 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 favours NOC formation through NH_3 uptake by SOA, as observed in a recent work (Y. Liu et al., 2015).

4 Conclusions

In the photooxidation system of toluene/NO_x, the presence of SO_2 and/or NH_3 increased secondary aerosol formation markedly, regardless of whether Al_2O_3 seed aerosol was present. Some synergetic effects in the heterogeneous process were observed in secondary inorganic aerosol formation in addition to the generation of ammonium and sulfate from NH_3 and SO_2. Specifically, the generation of NH_4NO_3 was found to be highly dependent on the surface area concentration of suspended particles and was enhanced by increased SO_2 concentration. Meanwhile, sulfate formation was also increased in the presence of NH_3. The absorbed NH_3 might provide liquid surface layers for the absorption and subsequent reaction for SO_2 and organic products and, therefore, enhance sulfate and SOA formation. NH_3 mainly influenced secondary aerosol formation in the heterogeneous process, resulting in significant growth of seed aerosols, but had little influence on new particle generation. In the experiments carried out in the presence of Al_2O_3 seed aerosols, sulfate, organic aerosol, nitrate, and ammonium were all found to increase linearly with increasing SO_2 concentration in toluene/NO_x photooxidation. The increase of these four species was more obvious under NH_3-rich conditions, and the order of their sensitivity was different to under NH_3-poor conditions.

Two factors were identified in the PMF analysis of the AMS data. One factor assigned to less-oxidised 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 oxidised 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.

5 Data availability

The datasets are available upon request to the contact author. Data for the consumption of gas-phase compounds and SOA yields are available in the Supplement.

The Supplement related to this article is available online at doi:10.5194/acp-16-14219-2016-supplement.

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