Response to Reviewers

Ms. Ref. No.: acp-2016-486

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

Revised Title: “Synergetic formation of secondary inorganic and organic aerosol: Effect of SO_2 and NH_3 on particle formation and growth”

We appreciate the comments from the reviewers on this manuscript. We have answered them in the following paragraphs (the text in italics is the reviewer comments, followed by our response) point by point. The text in blue is some revisions for the manuscript. The line numbers in the response are from the revised manuscript.

Response for Reviewer #1

The authors investigated the effect of sulphur dioxide and ammonia on the secondary organic aerosol formation in the photooxidation of toluene/NOx with or without Al_2O_3 *seed particles. They presented new experimental results and showed that the synergistic effects between* SO_2 *and* NH_3 *in the heterogeneous process can greatly enhance the aerosol formation. While the authors presented valuable experimental data, they should provide detailed explanations to support their arguments and observations made in the manuscript.*

Comments

One main question is: How much toluene is being reacted under different experimental conditions? This information is not given in the manuscript. If the amount of the toluene reacted is known, what are the aerosol mass yields in these experiments? How do the measured aerosol mass yields compare with literature results, if any?

Response: Thanks for the reviewer’s comments. Time variations of gas-phase compounds in photooxidation of toluene/NO_x in the presence or absence of NH_3 and/or

SO_2 are displayed in Figure R1 and Figure R2. These Figures has been added in the revised Supporting information. The reacted amount of toluene was calculated and has been added in the revised manuscript. The presence of SO_2/NH_3 had no obvious effect on the reacted amount of toluene, as shown in Table R1 and Table R2. SOA yields were also calculated. In Figure R3, the SOA yields in this study are compared with literature results. SOA yields in in photooxidation of toluene/NO_x in the presence or absence of NH_3 and/or SO_2 were similar as that reported by Odum, J. R., et. al.. A closer inspection revealed that experiment TN had SOA yield a little lower than the curve in the study of Odum, J. R., et. al., experiment STN and ATN had SOA yields quite close to the curve, while experiment ASTN had a little higher yield than the curve. For SOA yields in photooxidation of toluene/NO_x with different concentrations of SO_2, SOA yields were higher in NH_3-rich condition compare to NH_3-poor condition. And there is a trend that SOA yield increased with increasing SO_2 concentrations. The presence of SO_2/NH_3 increased SOA yield.

Table R1. The consumption of gas precursors, the formation of ozone and SOA, and SOA yield 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.

Experiment No.	**Δtoluene** ppm	**ΔNO_x** ppb	**ΔSO_2** ppb	**ΔO_3** ppb	**SOA** μg/m^3	**SOA yield** %
TN	0.19	89	NA	179	8.0	1.1
STN	0.18	90	25	176	27.7	4.1
ATN	0.16	82	NA	159	17.2	2.9
ASTN	0.15	90	42	166	37.4	6.8

Table R2. The consumption of gas precursors, the formation of ozone and SOA, and SOA yield in photooxidation of toluene/NO_x with different concentrations of SO_2 under NH_3-poor and NH_3-rich conditions.

	Δtoluene ppb	**ΔNO_x** ppb	**ΔSO_2** ppb	**ΔO_3** ppb	**SOA** μg/m^3	**SOA yield** %
NH_3-poor	41	73	NA	22	0.6	0.4

	40	61	6	22	1.4	1.0
	39	62	12	20	1.5	1.1
NH_3-rich	47	79	NA	27	3.5	2.0
	45	81	6	26	5.1	3.1
	44	75	11	27	6.7	4.1

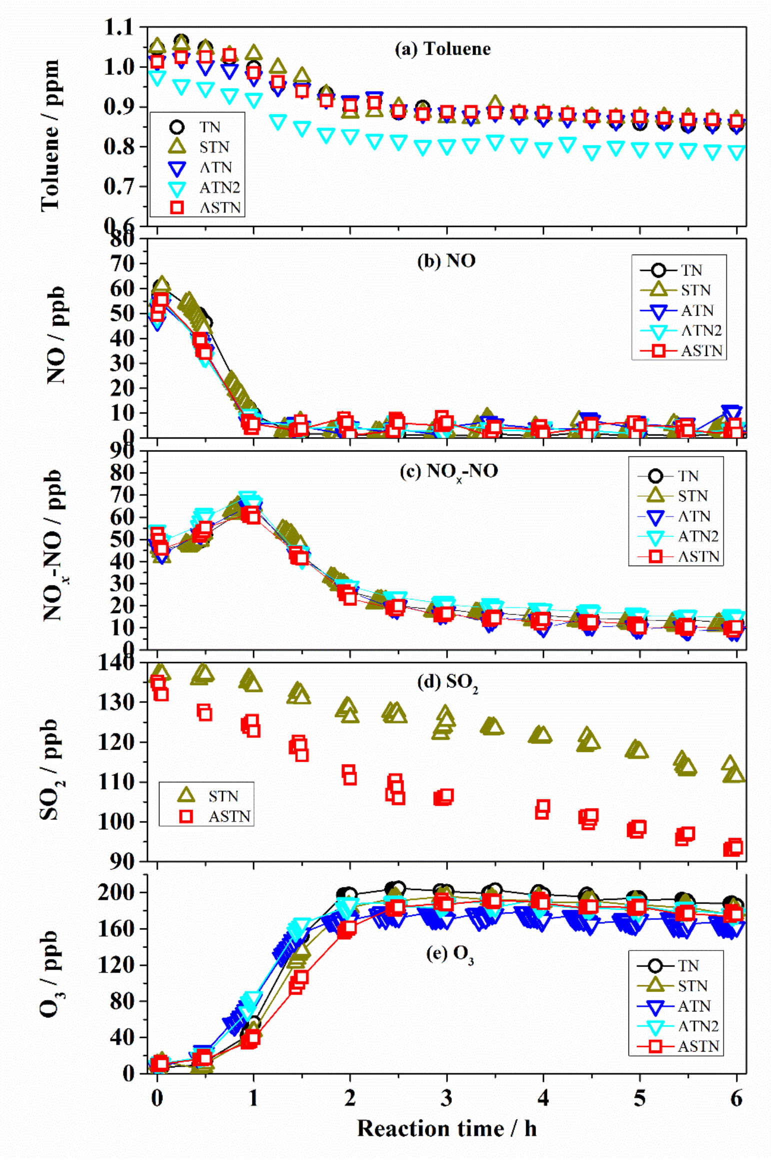

Figure R1. Time variations of gas-phase compounds in photooxidation of toluene/NO_x in the presence or absence of NH_3 and/or SO_2. The letters codes for the experiments indicate the introduced pollutants, i.e. “A” for ammonia, “S” for sulfur dioxide, “T” for toluene and “N” for nitrogen dioxide.

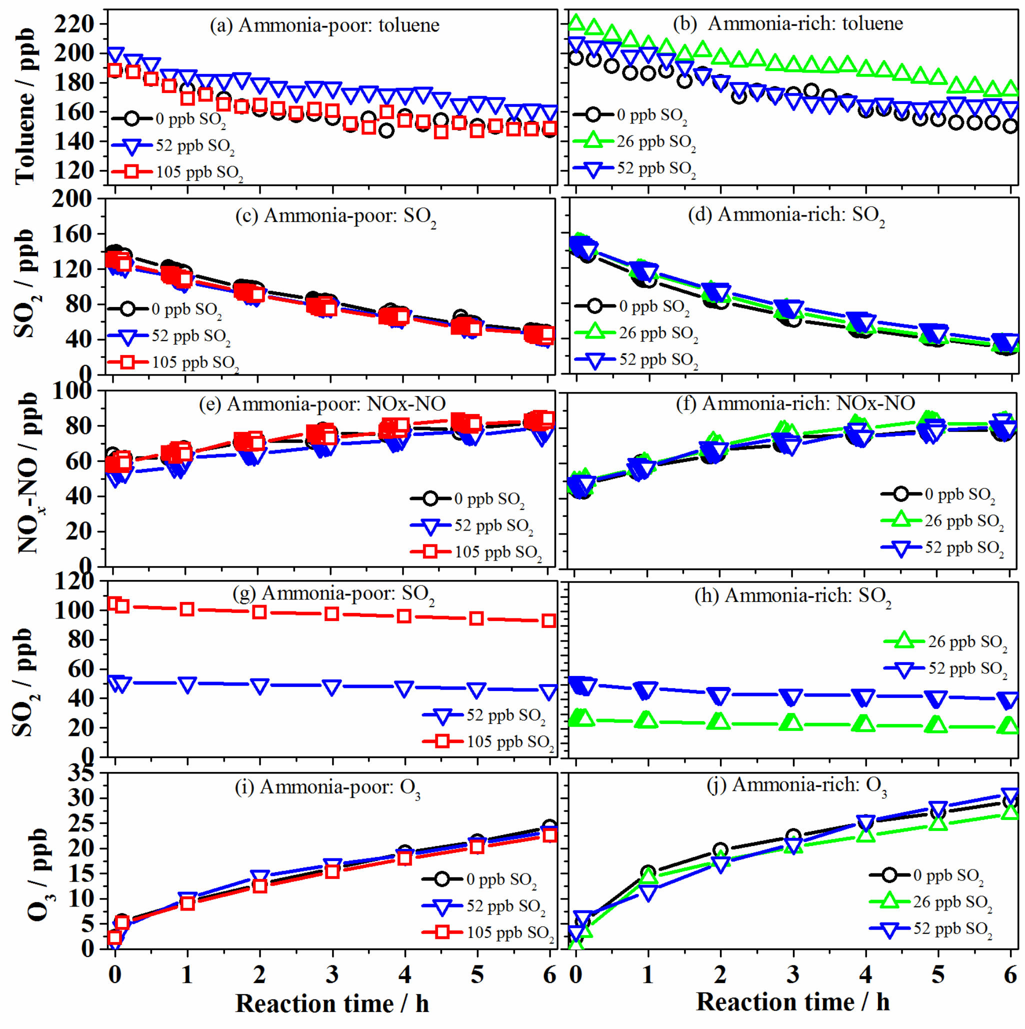

Figure R2. Time variations of gas-phase compounds in photooxidation of toluene/NO_x with different concentrations of SO_2 under NH_3-poor and NH_3-rich conditions

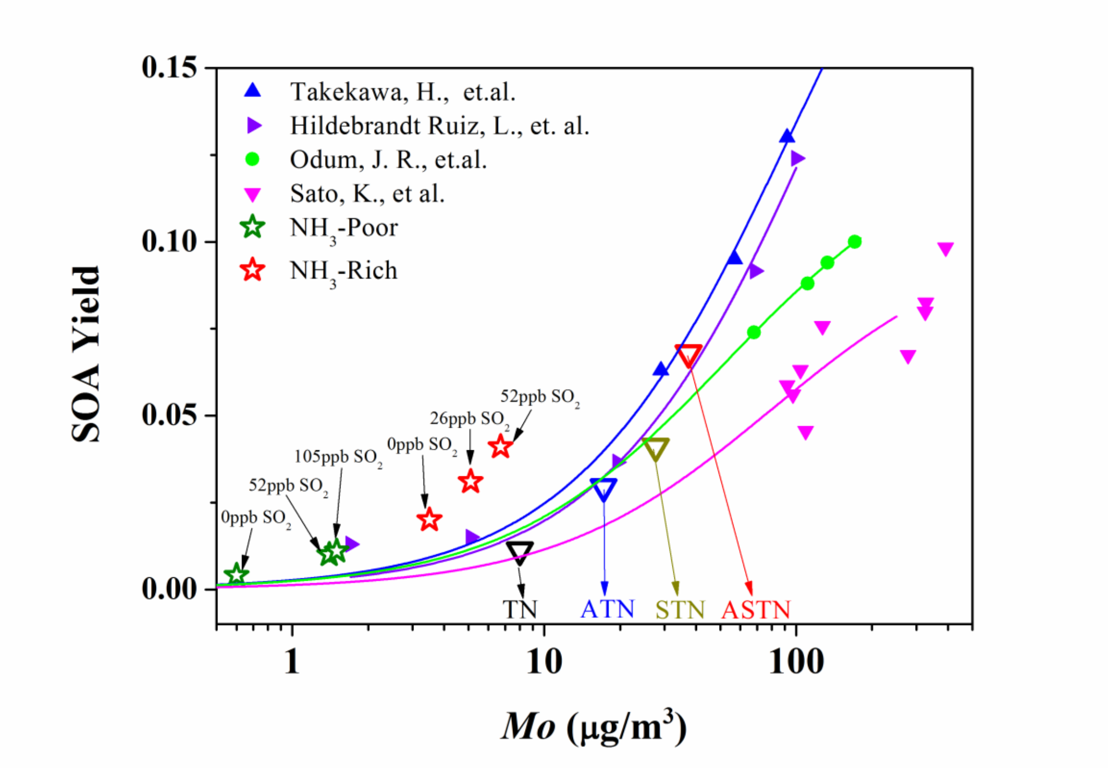

Figure R3. SOA yields in the experiments in this study and the comparison with literature results (Takekawa et al., 2003;Hildebrandt Ruiz et al., 2015;Odum et al., 1997;Sato et al., 2007)

Revision in the manuscript:

Lines 222-225, Add: “Time variations of gas phase compounds of these experiments are shown in Fig. S1 in the supporting information. 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.”

Add Table R1 and Table R2 in the supporting information

Add Fig. R1, Fig. R2 and Fig. R3 in the supporting information

Lines 428-430, Add: “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 supporting information.”

Line 184, “Assuming the same aerosol density in these experiments, the presence of either NH_3 or SO_2 enhanced secondary aerosol formation markedly” Can the authors provide justification for this assumption?

Response: This assumption is actually not true. In the presence of NH_3/SO_2, more inorganic aerosol (higher mass proportion) was generated than the experiment in the absence of NH_3/SO_2. The density of inorganic aerosol, mainly sulfate, nitrate and ammonium, is about 1.7 g/cm^3, while it is about 1.4 g/cm^3 for SOA. Therefore, the assumption of a same aerosol density would under estimate the increase effect of NH_3 or SO_2 on secondary aerosol formation. To keep things simple and to avoid misunderstanding, this sentence has been deleted in the revised manuscript.

Revision in the manuscript:

Lines 229-231, Delete: "Assuming the same aerosol density in these experiments, the presence of either NH_3 or SO_2 enhanced secondary aerosol formation markedly."

Line 217, "A significant increase in new particle formation was observed in the presence of SO_2." Can the authors provide an explanation for this observation?

Response: The new particle formation was not directly measured in this study. The comparison about new particle formation was made based on the number concentrations of particles. In the two experiments in the presence of SO_2, the maximum number concentration of particles are 3.8×10^4 particles/cm^3 and 7.3×10^4 particles/cm^3. This was one magnitude higher than that in the experiments in the absence of SO_2, in which the maximum number concentration of particles are 4.5×10^3 particles/cm^3 and 2.8×10^3 particles/cm^3, as shown in Fig. 2 in the manuscript. This explanation has been added in the revised manuscript.

Revision in the manuscript:

Lines 261-265, Change: "A significant increase in new particle formation was observed in the presence of SO_2."

To: "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."

Line 232, "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 NH4NO3 might partition back into the gas phase as reaction goes on." Can the authors preform any calculations or model simulations to support this hypothesis? What the concentration of the NH3, SO2 and NOx as a function of time in these experiments?*

Response: The partition of NH_4NO_3 has been simulated using the AIM Aerosol Thermodynamics Model. The detail of the model is available at http://www.aim.env.uea.ac.uk/aim/aim.php, and was described elsewhere (Clegg and Brimblecombe, 2005;Clegg et al., 1998;Carslaw et al., 1995). The simulation results are summarized in Fig. R4. This figure has been added in the supporting information. The results showed that the concentrations of NH_3 gas and coexisted $(NH_4)_2SO_4$ both influenced the partition balance between NH_4NO_3 and HNO_3+NH_3 in the gas phase. The deposition of NH_3 gas and $(NH_4)_2SO_4$ were likely to shift balance to the gas phase and reduce the concentration of NH_4NO_3 salt. While the concentration of NH_4NO_3 salt seemed not to be affected by the deposition of NH_4NO_3, as long as the wall loss was corrected accurately. As we mentioned in the manuscript, the deposition correction was introduced in our previous studies (Chu et al., 2012;Chu et al., 2014). We measured the deposition rates of $(NH_4)_2SO_4$ aerosol with different sizes and fitted them into an empirical function. Then, the deposition of aerosols was corrected based on the function and the size distribution of aerosols measured by the SMPS. According to these results, some revision has been made in the revised manuscript.

The time variations of NO_x and SO_2 are shown in Fig. R1 as mentioned earlier. However, the concentrations of NH_3 were not measured in this study due to the lack of analytical instruments. We noticed the concentration of NH_3 is crucial for a quantitative study about the effects of NH_3 on secondary aerosol formation. This problem is expected to be solved in a future study.

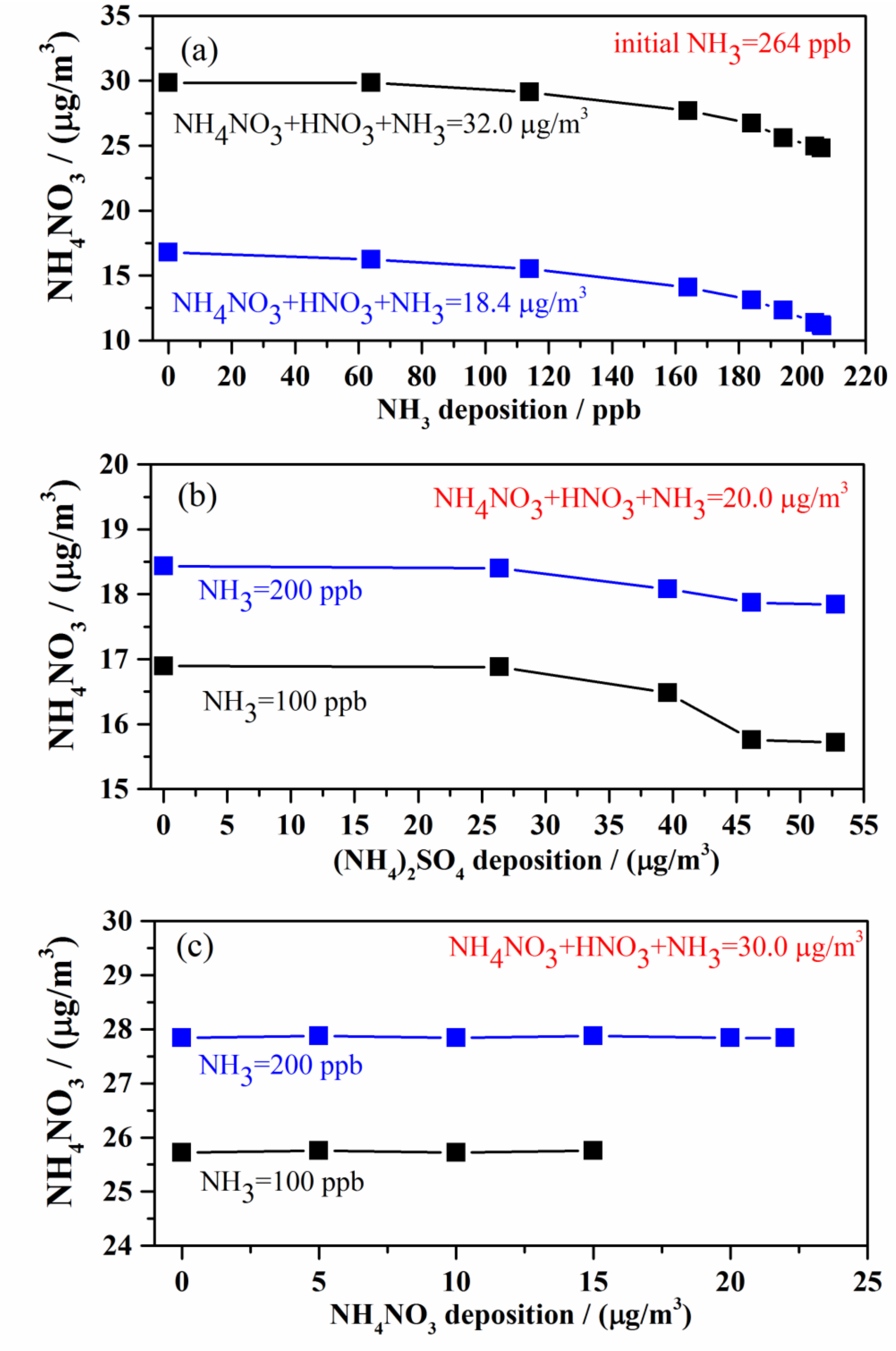

Figure R4. Concentrations of NH_4NO_3 salt as a function of the wall deposition of NH_3, $(NH_4)_2SO_4$ and NH_4NO_3 based on the simulation results of the AIM Aerosol Thermodynamics Model

Revision in the manuscript:

Lines 289-302, Change: "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."

To: "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 in the supporting information. 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;Chu et al., 2014)."

Add Fig. R4 in the supporting information

Lines 305-308, Add: "Some simulation results using the AIM Aerosol Thermodynamics Model with different concentrations of sulfate are also shown in Fig. S3 in the supporting information."

Line 245, "In addition, the presence of organic matter might accelerate the deliquescence of generated inorganic particles (Meyer et al., 2009;Li et al., 2014), and provide moist surfaces for heterogeneous hydrolysis of N2O5, contributing to nitrate formation (Pathak et al., 2009)." What is the meaning of "the deliquescence of generated inorganic particles"? Please elaborate. Does the N2O5 form under the experimental conditions?

Response: In the presence of organic compounds, $(NH_4)_2SO_4$ was reported to deliquesce at RH lower than pure $(NH_4)_2SO_4$. (Meyer et al., 2009;Li et al., 2014). To avoid misunderstanding, the description was revised.

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. Under the experimental conditions, the maximum formation velocity was calculated to be about 13 ppb/hour from gas phase reaction between NO_2 and O_3. The concentrations of NO_2 and O_3 are shown in Fig. R1. The reaction constant was summarized by Atkinson et al. (2004). The uptake coefficient of N_2O_5 on particle surface was reported to be about 10^{-2} on ammonium sulfate (Hallquist et al., 2003;Hu and Abbatt, 1997), but would decrease when organics coated on the sulfate (Anttila et al., 2006). The particle surface area concentration in experiment ASTN ranged from 0 to 0.1 m^2/m^3. Assuming a concentration of N_2O_5 of 0.1 ppb and an uptake coefficient of 10^{-3} for N_2O_5, the heterogeneous hydrolysis of N_2O_5 on 0.05 m^2/m^3 suspended particles would generate 6 $\mu g/m^3$ nitrate per hour in the reactor. Thus we speculated the heterogeneous hydrolysis of N_2O_5 might be important in the experiment. Some of these explanations have been added in the revised manuscript.

Revision in the manuscript:

Lines 308-317, Change: "In addition, the presence of organic matter might accelerate the deliquescence of generated inorganic particles (Meyer et al., 2009;Li et al., 2014), and provide moist surfaces for heterogeneous hydrolysis of N_2O_5, contributing to nitrate formation (Pathak et al., 2009)."

To: "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."

Line 256, "In Fig. 3, the generation of ammonium salt can be observed in the photooxidation of toluene/NOx/SO2 without introducing NH3 gas. This indicated there was NH3 present in the background air in the chamber, and also indicated that the effects of NH3 on secondary aerosol formation might be underestimated in this study." As stated, in order to better access the impact of NH3 on the aerosol formation, it is important to know the background NH3 concentration. The authors should give a reasonable guess or estimate on the background NH3 concentration in their experiments. Could the authors estimate background NH3 concentration based on their experimental results (e.g. STN data)?

Response: Thanks for the good suggestion! Based on the results of experiment STN, the amount of NH_3 (about 4.8 ppb) that contributed to NH_4 salt was calculated. Besides, according to the equilibrium between aerosol (NH_4NO_3+$(NH_4)_2SO_4$) and gas phase (NH_3+HNO_3+H_2SO_4), the gas phase NH_3 concentration was estimated to be about 3.0 ppb using the AIM Aerosol Thermodynamics Model. Therefore, the background NH_3 was estimated to be around 8 ppb. This information has been added in the revised manuscript.

Revision in the manuscript:

Lines 334-336, Add: "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."

Line 267, "in which the concentrations of NH3 were more than twice the SO2 concentrations and the oxidation products of SO2 and NOx were fully neutralized by NH3." Any experimental data or calculations to support this argument.

Response: As we mentioned earlier, the concentration of NH_3 was not measured in this study due to the lack of appropriate instruments. The initial concentration of NH_3 was estimated according to the amount of NH_3 added into the chamber and the volume of the reactor. The chemical composition of the aerosols was measured by the AMS. The concentrations of sulfate, nitrate, and ammonium salt could be used to calculate the acid-base balance. Some data are shown in Fig. R5. This figure has been added in the supporting information. As indicated in the figure, the sulfate and nitrate was fully neutralized by ammonium. The redundant ammonium was due to the formation of organic ammonium, which was discussed in the section "Secondary organic aerosol formation" and the supporting information about estimating concentrations of nitrogen-containing organics (NOC).

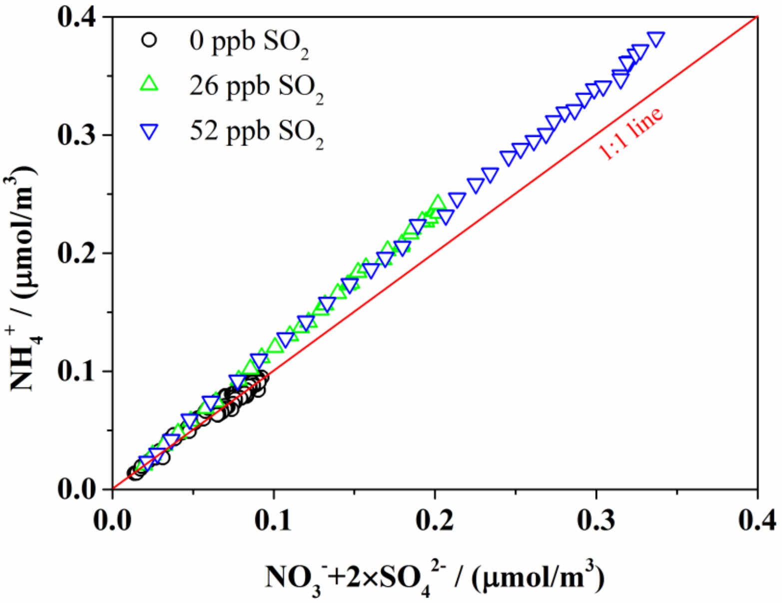

Figure R5. Evaluation of acid-base balance of the aerosols according to the concentrations of sulfate, nitrate, and ammonium salt measured by the AMS in NH_3-rich experiments. The line in the figure indicated an acid-base balance.

Revision in the manuscript:

Lines 339-344, Change: "in which the concentrations of NH_3 were more than twice the SO_2 concentrations and the oxidation products of SO_2 and NOx were fully neutralized by NH_3."

To: "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 neutralized by NH_3, according to the chemical composition of aerosols measured by the AMS. The details of the acid-base balance in the aerosols are shown in Fig. S4 in the supporting information."

Add Fig. R5 in the supporting information

Line 274, "In these experiments, the concentrations of toluene were reduced compared to the experiments in Table 1, and monodisperse Al2O3 seed particles with mode diameter about 100 nm were introduced into the chamber." Any reason why a lower concentration of toluene is used for the Al2O3 seed particle experiments.

Response: For experiments in Table 1, the concentrations of toluene were designed to be high to generate enough high concentration of secondary aerosol to reduce the experimental error for a qualitative study. For experiments in Table 2, in the presence of Al_2O_3 seed particles, secondary aerosol would be generated on their surface and would be easier to be detected by the AMS due to a larger diameter, so lower concentrations of toluene was used to simulate secondary aerosol formation under experimental conditions closer to real ambient conditions. Some of these explanations have been added in the revised manuscript.

Revision in the manuscript:

Lines 349-351, Add: "to simulate secondary aerosol formation under experimental conditions closer to real ambient conditions"

Line 279, "In the experiments carried out in the presence of Al2O3 seed aerosols, the decrease of NH4NO3 was not obvious in the experiment carried out in the absence of SO2 under NH3-rich conditions, indicating that generation of NH4NO3 was highly dependent on the surface area concentration of the particles, which decreased the partitioning of NH4NO3 back to the gas phase, as discussed above". In addition to describe the results in text, can the authors show the time variation of the chemical species in the SOA generated from the toluene oxidation in the presence of Al2O3 seed aerosols to support their argument?

Response: Time variations of chemical species for the secondary aerosol are shown in Fig. R6. This picture has also been added in the supporting information, and corresponding description had been added in the revised manuscript. As shown in Fig. R6(b), the decrease of NH_4NO_3 was less than 25%, which was less obvious than experiment ATN (decrease 75%). As we mentioned earlier, based on the simulation results for the partition of NH_4NO_3 using the AIM Aerosol Thermodynamics Model, the concentrations of NH_3 gas and coexisted $(NH_4)_2SO_4$ both influenced the partition balance between NH_4NO_3 and HNO_3+NH_3 in the gas phase. The deposition of NH_3 gas and $(NH_4)_2SO_4$ were likely to shift balance to the gas phase and reduce the concentration of NH_4NO_3 salt. While the concentration of NH_4NO_3 salt seemed not to be affected by the deposition of NH_4NO_3, as long as the wall loss was corrected accurately. We has revised the argument about the partition of NH_4NO_3 in the revised manuscript.

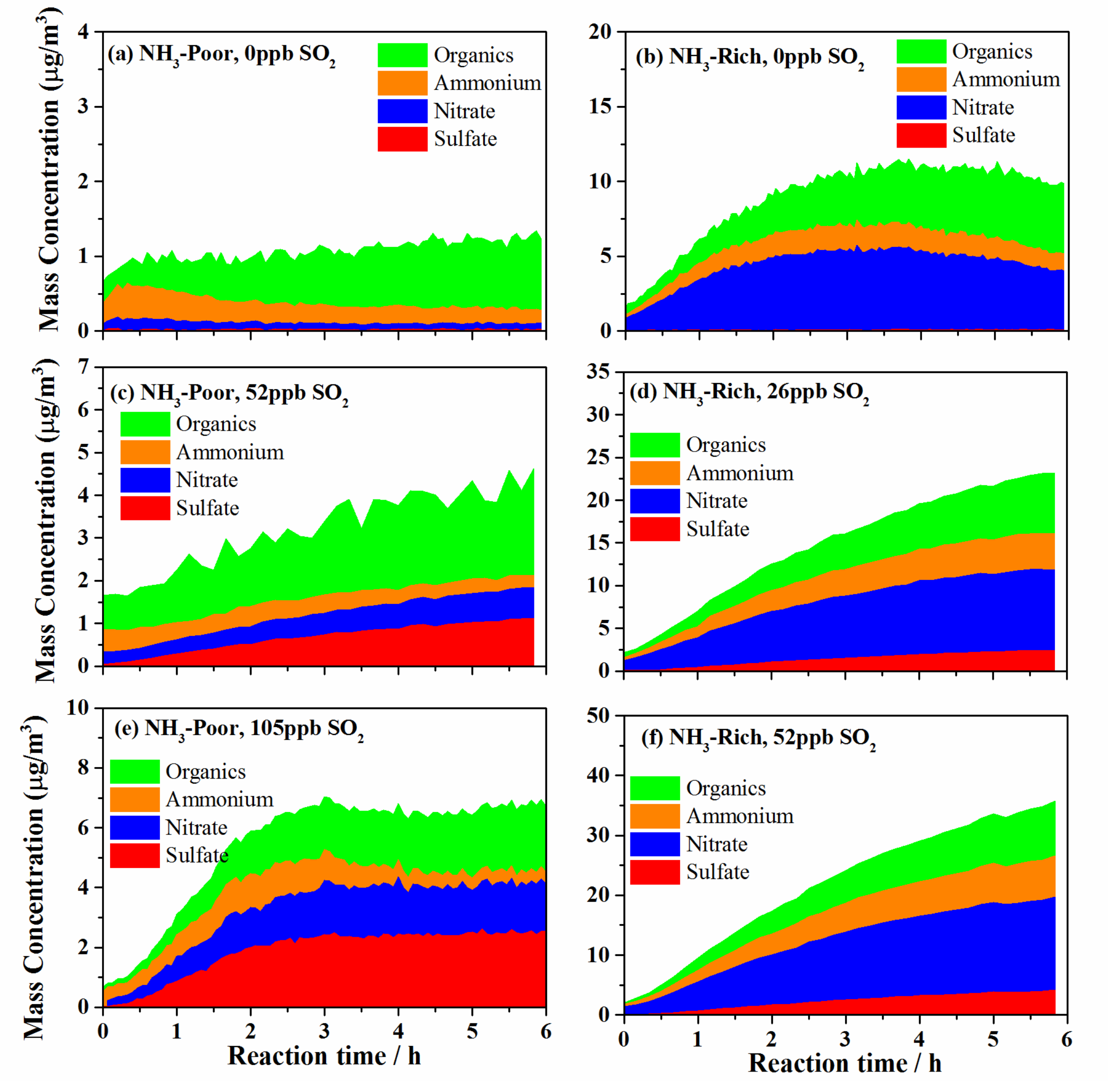

Figure R6. Time variations of sulfate, nitrate, and ammonium and organics measured by the AMS in the photooxidation of toluene/NO_x with different concentrations of SO_2 under NH_3-poor and NH_3-rich conditions

Revision in the manuscript:

Lines 354-362, Change: “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 phase, as discussed above.”

To: “In the experiments carried out in the presence of Al_2O_3 seed aerosols, the decrease of NH_4NO_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 Fig.S5 in the supporting information and Fig.3. This might also indicate that generation of NH_4NO_3 was dependent on the surface area concentration of the particles, which decreased the partitioning of NH_4NO_3 back to the gas phase, as discussed above concerning the effects of co-existing $(NH_4)_2SO_4$."

Add Fig. R6 in the supporting information

Line 297, "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". From the Figure S1, the authors argue that there is a significant correlation between the aerosol formation and aerosol surface area. From that point, they suggest that the heterogeneous processes is important than the bulk reactions. However, a strong conclusion cannot be easily drawn from the simple correlation method and limited data points. Furthermore, a nice correlation between the aerosol formation and aerosol volume is observed. Can the authors further elaborate this point?

Response: We also notice that argue the heterogeneous reactions is important form the correlation is not convictive. The statement about heterogeneous and bulk reactions has been deleted in the revised manuscript. The possible importance of heterogeneous process was discussed in Page 22 based on Figure 6.

Revision in the manuscript:

Lines 375-379, Delete: "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."

Line 330, "According to the consumption of toluene, OH concentrations in the photooxidation experiments were estimated to range from 1.6x106 molecules/cm3 to

2.7 x106 molecules/cm3. The reaction between these OH radicals and SO2 contributed 35%-50% of the total SO2 degradation in NH3-poor experiments, while this ratio was reduced to 25%-30% in NH3-rich experiments" Again, what is the amount of toluene and SO2 reacted in the experiments? What the time variations of the toluene and SO2 and other gas phase species (e.g. NOx) in these experiments?

Response: As mentioned earlier, the time variations of toluene and SO_2, O_3 and NO_x are shown in Fig. R2, while the reacted amount of toluene and SO_2 are shown in Table R2. This figure has been added in the supporting information. We estimated OH radical concentrations according to the decay of toluene, and then calculated the decay of SO_2 in the reaction between OH radical and SO_2 using the known reaction constant and the measured time variations of SO_2 concentrations, and finally calculated the ratios mentioned in the text.

Revision in the manuscript:

Add Fig. R2 in the supporting information

Line 341, "According to previous studies, NH3 might provide surface Lewis basicity and liquid surface layers for SO2 absorption and subsequent oxidation, and therefore, enhance sulfate formation (Yang et al., 2016; Tursic et al., 2004)." What is the physical state of the aerosols in the experiments? Aqueous droplets or solid particles?

Response: Al_2O_3 seed aerosols were used in this study. It is quite hydrophobic and would be solid in the experiments. Yang et al. reported that the coexistence of NH_3 would enhance the heterogeneous oxidation of SO_2 on Al_2O_3 surface(Yang et al., 2016). During the reaction, secondary aerosol would be generated on the surface of the seed aerosols or as new particles. The deliquescence relative humidity of NH_4NO_3 and $(NH_4)_2SO_4$ were reported to be about 60% and 80%, which were higher than the RH of 50% in the experiments. However, as we mentioned earlier, inorganic aerosol might deliquesce at a RH lower than the DRH for pure salt (Meyer et al., 2009;Li et al., 2014). Tursic et al. found the presence of NH_3 would significantly increase the amount of condensed water and enhance the conversion of SO_2 to sulfate(Tursic et al., 2004). Thus we speculated that there might be liquid surface layers on the secondary aerosols.

Revision in the manuscript:

Lines 419-424, Change: "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)."

To: "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)"

Line 416, "The higher production of Factor 2 with higher SO2 under an NH3-poor environment could be probably attributed to the well-known acid-catalysis effects of the oxidation product of SO2, i.e. sulfuric acid, on heterogeneous aldol condensation (Offenberg et al., 2009; Jang et al., 2002; Gao et al., 2004)" What is the pH or acidity of the aerosols in these experiments?

Response: Based on the chemical compositions of aerosols measured by the AMS, the mole concentrations of species are shown in Table R3. As shown in the table, the concentration of H^+ increased with the increasing of SO_2 in NH_3-poor condition.

Table R3. The mole concentrations of chemical species in the NH_3-poor experiments in the chamber (μmol/m^3)

	H^+	NH_4^+	SO_4^{2-}	NO_3^-
0ppb SO_2	0.000	0.0020	0.0003	0.0015
52ppb SO_2	0.018	0.016	0.011	0.011
105ppb SO_2	0.059	0.018	0.027	0.022

Using the AIM model as we mentioned earlier, the concentrations of these species in the aqueous phase was calculated. The results for the two experiments in the presence of SO_2 are shown in Table R4. The pH of the aerosols was calculated to be -0.5 and -0.7 in the two experiments, respectively. With this acidity, the aerosol was likely to enhance SOA formation due to acid-catalytic effects on heterogeneous aldol condensation.

Table R4. The concentrations of inorganic species in the aqueous phase in the two NH_3-poor experiments in the presence of SO_2

(a) 52 ppb SO_2

Species	Moles	Grams	Molality	Mole Frac.	Act. Coeff.
H(aq)	7.63E-09	7.69E-09	6.54E+00	6.88E-02	1.05E+01
NH_4(aq)	1.60E-08	2.89E-07	1.37E+01	1.44E-01	2.63E-01
HSO_4(aq)	1.04E-08	1.01E-06	8.89E+00	9.35E-02	3.77E+00
SO_4(aq)	1.13E-09	1.08E-07	9.67E-01	1.02E-02	7.80E-03
NO_3(aq)	1.10E-08	6.82E-07	9.43E+00	9.92E-02	3.84E-01
OH(aq)	1.68E-26	2.85E-25	1.44E-17	1.51E-19	2.13E+01
H_2O(aq)	6.48E-08	1.17E-06	5.55E+01	5.84E-01	8.56E-01
NH_3(aq)	4.90E-20	8.34E-19	4.20E-11	4.42E-13	1.71E+00

The density of the aqueous phase is 1.39289 g per cm^3, and its total volume is 2.34095E-06 cm^3.

(b) 105 ppb SO_2

Species	Moles	Grams	Molality	Mole Frac.	Act. Coeff.
H(aq)	3.50E-08	3.53E-08	8.93E+00	1.09E-01	8.35E+00
NH_4(aq)	1.80E-08	3.25E-07	4.59E+00	5.62E-02	1.85E-01
HSO_4(aq)	2.40E-08	2.33E-06	6.12E+00	7.49E-02	1.00E+01
SO_4(aq)	3.51E-09	3.37E-07	8.95E-01	1.10E-02	1.22E-02
NO_3(aq)	2.20E-08	1.36E-06	5.61E+00	6.87E-02	8.43E-01
OH(aq)	5.31E-25	9.03E-24	1.35E-16	1.66E-18	1.54E+00
H_2O(aq)	2.18E-07	3.92E-06	5.55E+01	6.80E-01	7.35E-01
NH_3(aq)	3.57E-20	6.07E-19	9.09E-12	1.11E-13	1.47E+00

The density of the aqueous phase is 1.34747 g per cm^3, and its total volume is 6.16843E-06 cm^3.

Revision in the manuscript:

Lines 505-508, Add: "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."

Line 427 "By inference and from the results of AMS measurements, aerosol water increased as the initial concentration of SO2 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 NH3-rich experiments and contribute to the generation of Factor 1." What is the amount of aerosol phase water and how the aerosol water content change with reactions in these experiments?

Response: The aerosol water concentrations measured by AMS are shown in Figure R7. First, we have to point out that there is high uncertainty about the aerosol water measured by AMS. But there is a tendency than aerosol water increased with reaction time. Besides, higher concentrations of aerosol water were observed in NH_3-rich experiment compare to that in the NH_3-poor experiment.

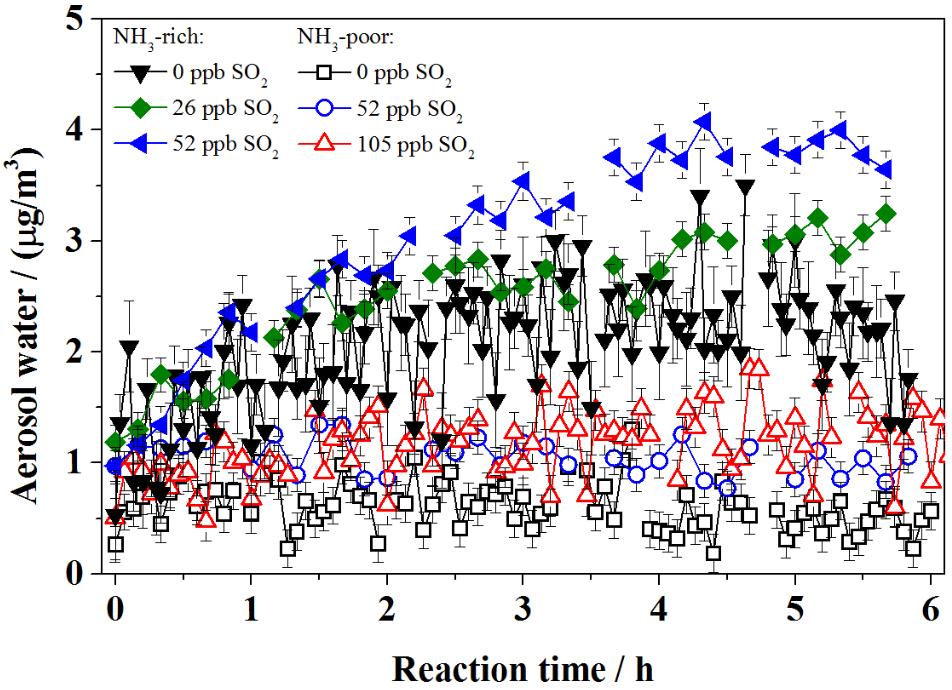

Figure R7. Time variations of aerosol water measured by the AMS in the photooxidation of toluene/NO_x with different concentrations of SO_2 under NH_3-poor and NH_3-rich conditions

Response for Reviewer #2

The manuscript reports data related to the effect of SO2 and NH3 on aerosol formation from the oxidation of toluene in the presence on NOx. The experimental study was conducted in the presence or absence of inorganic seed aerosol: AL2O3. NH3 and SO2 are two species emitted into the atmosphere and can have a large effect on atmospheric chemistry. The data analysis show aerosol formation and growth increased in the presence of SO2 regardless of the presence of NH3. This study and its topic is of great interest and appropriate to ACPD journal. This study is worth to be published since it present an important set of data that can be useful for the atmospheric communities. However, I feel that the text and the scientific discussion (interpretation of experimental data) (see my comments below) need to be addressed before publication.

The experimental part needs to be addressed and clearly state how the experiments were run. Toluene as well other gas phase species need to be reported vs time in this study. The role of OH radicals should be discussed? The wall loss of gas phase and particles should be addressed also? The errors and uncertainties need to be addressed since assumptions were made in this study. Yield should be reported in this study for the different systems studied.

Response: Thanks for the reviewer’s comments. Here we response to some of the comments, while the other questions (including gas compounds, OH radicals, wall loss and yield) would be answered later in the following paragraphs point by point.

Some additional information about how we run the experiments has been added in the methods section. We introduced how we wash the chamber, how we control the humidity, how we adding gas and particles into the chamber and so on.

Several assumptions were made in this study due to the limitation of analytical instruments. In Line 184 in the original manuscript, we assumed a same aerosol density in experiments in the presence or absence of NH_3 or SO_2. This assumption is actually not true. In the presence of NH_3/SO_2, more inorganic aerosol (higher mass proportion) was generated than the experiment in the absence of NH_3/SO_2. The density of inorganic aerosol, mainly sulfate, nitrate and ammonium, is about 1.7 g/cm^3, while it is about 1.4 g/cm^3 for SOA. Therefore, the assumption of a same aerosol density would under estimate the increase effect of NH_3 or SO_2 on secondary aerosol formation. To keep things simple and to avoid misunderstanding, this sentence has been deleted in the revised manuscript. In Line 184 in the original manuscript, we assumed that the presence of SO_2 and NH_3 did not significantly impact the gas phase oxidation of hydrocarbons and mainly played a role in the aerosol phase. This is actually not an assumption but a corollary based on previous studies and experimental data in this study. Some revision about these sentences has been made in the revised manuscript. The assumption and uncertainties about NH_3 concentrations would be discussed later in this file.

Revision in the manuscript:

For how the experiments were run:

Lines 179-183, Add: "Prior to each experiment, the chamber was flushed for about 40 h with purified air at a flow rate of 15 L/min. 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."

Lines 194-204, Add: "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 minutes 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."

Lines 205-209, Add: "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."

For the errors and uncertainties:

Lines 192-194, Delete: "Assuming the same aerosol density in these experiments, the presence of either NH_3 or SO_2 enhanced secondary aerosol formation markedly."

Line 426, Change: "assumed"

To: "speculated"

As I mentioned, the manuscript reports a set of great data important to scientist interested in atmospheric organic and inorganic aerosol formation and the effect of NH3 and SO2!

Response: Thanks for the affirmation.

Comments:

In the introduction (1st paragraph), the authors report literature data for NH3 in China and almost no data was provided for SO2. I suggest SO2 should be provided also and a comparison should be reported between SO2 and NH3. The text in the manuscript should be edited for consistency. I found it very hard to follow the authors' ideas in the manuscript, although lot of information is provided. For example, sentences reported between lines 89 and 115 are very difficult to follow for me!!! This is true for most the manuscript!

Response: We agree with the reviewer that more literature data for SO_2 are needed. More information about SO_2 and a simple comparison between SO_2 and NH_3 has also been added in the introduction.

The introduction, the description about the results and the discussions were carefully amended in the revised manuscript. The manuscript was also revised by a native English to make it more readable. A lot of revisions have been made. These revisions are recorded in the revised manuscript, but are not listed one by one here.

Revision in the manuscript:

Lines 61-72, Change: “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., 2015a)”

To: “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 north 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; Wang et al., 2015b), 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 (Wang et al., 2015a), while over 100 ppb SO_2 was observed in winter haze days during 2012 in Xi’an city (Zhang et al., 2015).”

Lines 83-85, Add: “Unlike SO_2, the emission of NH_3 is mainly from non-point sources, which are difficult to control, and shows an increasing trend in China (Dong, 2010).”

Line 125: this study focusses on "toluene" and "VOC" should be deleted.

Response: Corresponding revision has been made in the revised manuscript.

Revision in the manuscript:

Line 141, Change: “VOC/NO_x”

To: “toluene/NO_x”

The chamber was a 2 m3 and the losses expected to be higher. The authors should give more information in this study about the wall losses of gas phase and particles.

Response: Yes, the wall deposition of particles was high in this study due to the small volume of the chamber. We measured the deposition rate of different gases, particles of different sizes. Deposition of particles and gas compounds on the wall was considered to be a first-order process for wall loss correction. Additional information has been added in the revised manuscript.

Revision in the manuscript:

Lines 165-169, Add: “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."

Lines 173-178, Add: "The deposition of gas phase compounds was determined to be 0.0025 h^{-1}, 0.0109 h^{-1}, 0.0023 h^{-1} 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."

How NH3 was estimated (line 168)? Needs errors and uncertainties?

Response: The concentration of NH_3 is an important problem in this study. Due to the lack of analytical instruments, we were not able to measure the concentrations of NH_3 in the chamber. Alternatively, we used a mass flow controller and a stopwatch to control the added amount of NH_3 in the chamber. Then, we estimated the initial concentrations of NH_3 based on the volume of the reactor. As the reviewer pointed out, there are many uncertainties for the estimated concentrations. The main uncertainties included:

(1) the absorption of NH_3 in the inlet pipeline (Before adding NH_3 into the chamber, NH_3 gas was passed through the inlet pipeline for about 15 minutes to reduce absorption within the line. This uncertainty is difficult to estimate.)

(2) the concentrations of NH_3 standard gas (Less than 1%, Beijing AP BAIF Gases Industry CO., Ltd)

(3) the volume of the reactor (Less than 5% according to our experiences and the concentrations of other pollutants)

(4) the background NH_3 gas in the chamber (As we mentioned in the manuscript, there was NH_3 present in the background air in the chamber derived from the partitioning of the deposited ammonium sulfate and nitrate on the chamber wall when humid air was introduced. Based on the results of experiment STN (without NH_3 added), the amount of NH_3 that contributed to NH_4 salt was calculated to be about 4.8 ppb. Besides, according to the equilibrium between aerosol (NH_4NO_3+$(NH_4)_2SO_4$) and gas phase (NH_3+HNO_3+H_2SO_4), the gas phase NH_3 concentration was estimated to be about 3.0

ppb using the AIM Aerosol Thermodynamics Model. The detail of the model is available at http://www.aim.env.uea.ac.uk/aim/aim.php, and was described elsewhere (Clegg and Brimblecombe, 2005;Clegg et al., 1998;Carslaw et al., 1995). Therefore, the background NH_3 was estimated to be around 8 ppb. This information has been added in the revised manuscript.)

Revision in the manuscript:

Lines 196-204, Add: "NO_x, SO_2 and NH_3 were directly injected into the chamber from standard gas bottles with mass flow controllers. Before adding NH_3 into the chamber, NH_3 gas was passed the inlet pipeline for about 15 minutes to reduce the absorption. The concentrations of NH_3 were then estimated according to the introduced amount of NH_3 and the volume of the reactor. These experiments with NH_3 added to the chamber were referred 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."

Lines 333-335, Add: "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. "

Line 171. title not clear to me? Be specific I would suggest: Effect of NH3 and SO2 on particle formation and growth

Response: Corresponding revision has been made in the revised manuscript.

Revision in the manuscript:

The title, Change: "Synergetic formation of secondary inorganic and organic aerosol: Influence of SO_2 and/or NH_3 in the heterogeneous process"

To: "Synergetic formation of secondary inorganic and organic aerosol: Effect of SO_2 and NH_3 on particle formation and growth"

Table 1 change "hydrocarbon" to "toluene"

Response: Corresponding revision has been made in the revised manuscript.

Revision in the manuscript:

Table 1, Change: "hydrocarbon"

To: "toluene"

Data provided in Table 1 are initial concentration? The authors need to specify how the chamber was run (as flow reactor or batch reactor). Based on fig 1, it seems to me it was conducted as a batch reactor. In this case the wall losses are important and need to be incorporated in the discussion and how toluene and SMPS data were analyzed to get to Figs 1, 2.. and tables 1, 2.

Response: Yes, the data provided in Table 1 are the initial concentrations. The chamber was run as a batch reactor. To make this clear, corresponding revisions have been made in the revised manuscript. For the wall losses, as we mentioned earlier, additional information about the deposition rates of gas phase compounds and contribution of particle deposition to Figs 1 and 2 have been added in the revised manuscript.

Revision in the manuscript:

Table 2, Change: "Experimental conditions"

To: "Initial experimental conditions"

(For Table 1, it is "Initial experimental conditions" in the manuscript.)

Lines 165-169 Add: "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."

Lines 173-178, Add: "The deposition of gas phase compounds was determined to be 0.0025 h^{-1}, 0.0109 h^{-1}, 0.0023 h^{-1} 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."

It is also very important to provide data for Toluene reacted, SO2 reacted, NH3 reacted and NO reacted, NOx reacted (vs. time) in the gas phase in a separate figure.

Response: Time variations of gas-phase compounds in photooxidation of toluene/NO_x

in the presence or absence of NH_3 and/or SO_2 are displayed in Figure R1 and Figure R2 in the "Response for Reviewer #1". These Figures has been added in the revised Supporting information.

Revision in the manuscript:

Lines 222-225, Add: "Time variations of gas phase compounds of these experiments are shown in Fig. S1 in the supporting information. 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."

Add Fig. R1 and Fig. R2 in the supporting information

The experiments were conducted under 50% RH. The authors didn't reported in the text until Table 1 was mentioned. This is a very important parameters that should be reported and discussed at list briefly. How it was measured and controlled in the chamber!!! Same thing for the temperature! I'm expecting the RH will change aver the run time and will be not constant?

Response: Thanks for the reviewer's reminding. As we mentioned above for how the experiment was run, some information about the temperature and RH have been added in the methods in the revised manuscript.

Revision in the manuscript:

Lines 179-183, Add: "Prior to each experiment, the chamber was flushed for about 40 h with purified air at a flow rate of 15 L/min. 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."

Lines 205-209, Add: "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."

How NH3 was introduced into the chamber? Please elaborate!

Response: NH_3 was introduced into the chamber using standard gas from high-pressure gas bottle. We used a mass flow controller, a stopwatch and a solenoid three-way valve to control the amount of NH_3 in the chamber. Then, we estimated the initial concentrations of NH_3 based on the volume of the reactor. The solenoid three-way valve was placed on the inlet next to the chamber. Before adding NH_3 into the chamber, NH_3 gas was passed the inlet pipeline for about 15 minutes (not into the chamber through the valve) to reduce the absorption when adding NH_3 into the chamber.

Revision in the manuscript:

Lines 196-204, Add: "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 minutes 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."

It's important to have the amount of toluene reacted in each case in order to see how much was oxidized. then measure the yield etc... The OH radicals present in the system can be reacted with different gas phase species (e.g. toluene, SO2,..) and then depending on the rate constant, it can affect the conclusion reported in this study.

Response: The reacted amounts of gas phase species were calculated and are displayed in Table R1 and Table R2 in "Response for Reviewer #1". SOA yields were also calculated. The presence of SO_2/NH_3 had no obvious effect on the reacted amount of toluene. In Fig. R3 in "Response for Reviewer #1", the SOA yields in this study are compared with literature results. SOA yields in in photooxidation of toluene/NO_x in the presence or absence of NH_3 and/or SO_2 were similar as that reported by Odum, J. R., et. al.. A closer inspection revealed that experiment TN had a SOA yield a little lower than the curve in the study of Odum, J. R., et. al., experiment STN and ATN had SOA yields quite close to the curve, while experiment ASTN had a yield a little higher than the curve. For SOA yields in photooxidation of toluene/NO_x with different concentrations of SO_2, SOA yields were higher in NH_3-rich condition compare to NH_3-poor condition. And there is a trend that SOA yield increased with increasing SO_2 concentrations. The presence of SO_2/NH_3 increased SOA yield.

Revision in the manuscript:

Add Table. R1 and Table. R2 in the supporting information

Add Fig. R3 in the supporting information

Lines 428-430, Add: "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 supporting information."

Line 225: How the authors distinguish between secondary organic aerosol and secondary inorganic aerosol in these experiments?

Response: The chemical composition of the aerosols was measured by the ACSM and AMS in this study. The measurement results of ACSM and AMS including the concentrations of sulfate, nitrate, ammonium salt and organics. In the ACSM or AMS, the aerosols were heated to about 600℃ and ionized by 70eV electrons. During the ionization, most secondary species were fragmented. There were some organic nitrates and organic acid ammonium in the aerosols, as we discussed in the section of "secondary organic aerosol formation", but they can't be identified from the ACSM or AMS data. Therefore, the measured sulfate, nitrate, ammonium salt (estimated from corresponding fragments) were all considered secondary inorganic aerosol, and the organics (estimated from organic fragments) were all considered secondary organic aerosol. Some explanation has been added in the revised manuscript.

Revision in the manuscript:

Lines 280-284, Add: "Since the ACM or AMS cannot distinguish organic salts and organic nitrates, the measured sulfate, nitrate, ammonium were all considered secondary inorganic aerosol, while the organics were all considered secondary organic aerosol in this study."

Line 228-230 How the authors come to this conclusion? It's speculation and not based on data reported here. How nitrate are measured in this study? Are you refering to inorganic or organic nitrates? It will be great if a distinction was made between SOA and secondary inorganic aerosol in this study?

Response: As we mentioned above, the chemical composition of the aerosols was measured by the ACSM and AMS in this study. The inorganic or organic nitrates were not distinguished. Here, the nitrate is the sum of inorganic or organic nitrates. Therefore, besides ammonia nitrate, organic nitrate might also contribute to the observed nitrate.

Revision in the manuscript:

Lines 276-279, Change: "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."

To: "For example, nitrate formation (which may include both inorganic nitrate and organic nitrates) was not only enhanced by NH_3, but also was markedly affected by SO_2."

It will be interesting to estimate the concentration of OH radicals vs time in these experiments?

Response: The time variations of OH radicals were calculated based on the time variations of toluene and the reaction rate between toluene and OH radical. The results are shown in the following two pictures. The concentrations are quite scattered due to the measurement error of the toluene in the GC-FID. As we can see in the two pictures, the estimated OH radical concentrations were higher at the beginning of the experiment than that at the end of the experiment.

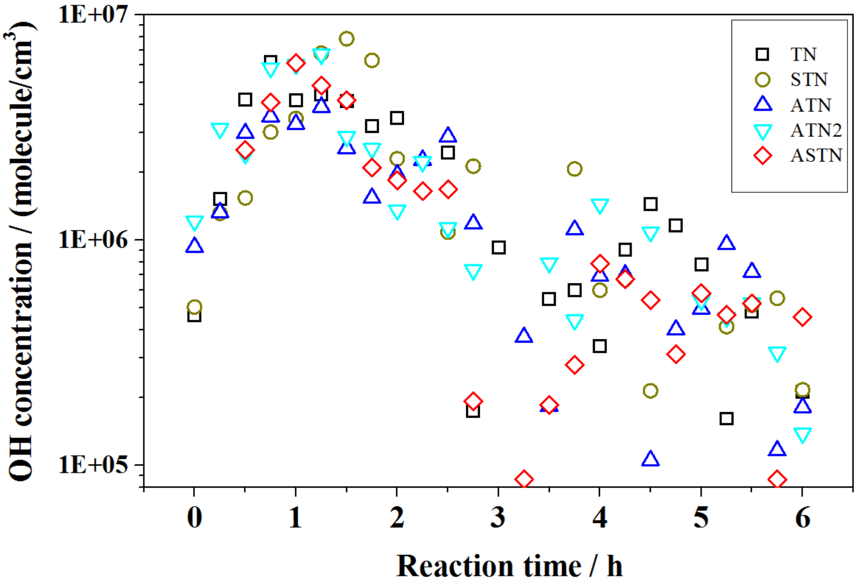

Figure R8. Time variations of OH radical concentrations in photooxidation of toluene/NO$_x$ in the presence or absence of NH_3 and/or SO_2. The letters codes for the experiments indicate the introduced pollutants, i.e. "A" for ammonia, "S" for sulfur dioxide, "T" for toluene and "N" for nitrogen dioxide.

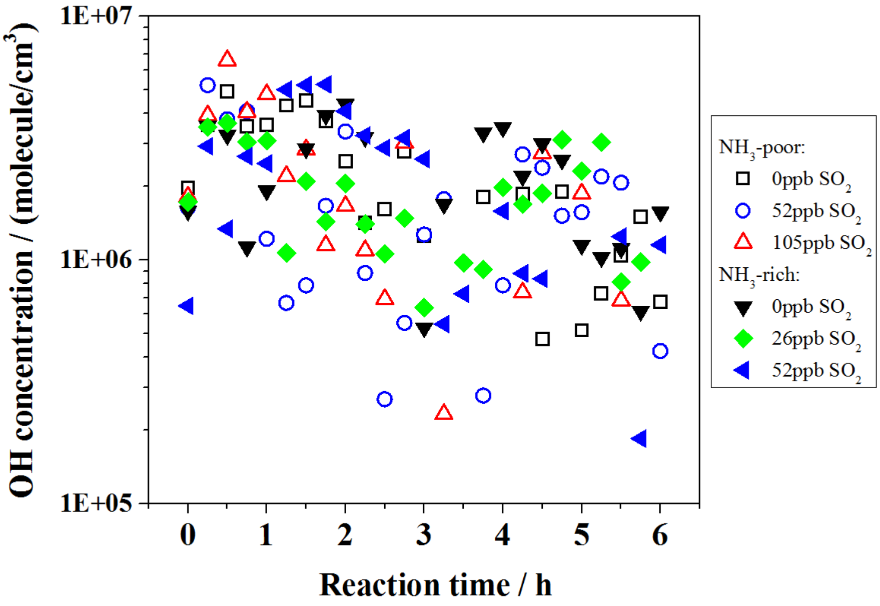

Figure R9. Time variations of OH radical concentrations in photooxidation of toluene/NO$_x$ with different concentrations of SO_2 under NH_3-poor and NH_3-rich conditions

Line 239. "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." Are the authors measured the wall losses at different size distribution or this only speculation?

Response: As we mentioned above, the deposition rates of particles with different sizes

(40-700nm) under dark conditions were measured. Additional information has been added in the revised manuscript. However, the reason for the decreasing of NH_4NO_3 was revised according to the simulation results from the AIM Aerosol Thermodynamics Model. The simulation results are summarized in Fig. R4 in "Response for Reviewer #1". This figure has been added in the supporting information. The results showed that the concentrations of NH_3 gas and coexisted $(NH_4)_2SO_4$ both influenced the partition balance between NH_4NO_3 and HNO_3+NH_3 in the gas phase. The deposition of NH_3 gas and $(NH_4)_2SO_4$ were likely to shift balance to the gas phase and reduce the concentration of NH_4NO_3 salt. While the concentration of NH_4NO_3 salt seemed not to be affected by the deposition of NH_4NO_3, as long as the deposition was corrected accurately. According to these results, some revision has been made in the revised manuscript.

Revision in the manuscript:

Lines 165-169, Add: "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."

Lines 290-302, Change: "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."

To: "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 in the supporting information. 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;Chu et al., 2014)."

Add Fig. R4 in the supporting information

Line 245 – 249. It seems to me that these were not based on data reported in these study. How N2O5 plays a role here? N2O5 was measured in this study? How it was formed in the chamber. Is ozone was measured in this study? If yes it should be reported vs time.

Response: In the presence of organic compounds, $(NH_4)_2SO_4$ was reported to deliquesce at RH lower than pure $(NH_4)_2SO_4$. (Meyer et al., 2009;Li et al., 2014). To avoid misunderstanding, the description was revised.

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. Under the experimental conditions, the maximum formation velocity was calculated to be about 13 ppb/hour from gas phase reaction between NO_2 and O_3. The concentrations of NO_2 and O_3 are shown in Fig. R1. The reaction constant was summarized by Atkinson et al. (2004). The uptake coefficient of N_2O_5 on particle surface was reported to be about 10^{-2} on ammonium sulfate (Hallquist et al., 2003;Hu and Abbatt, 1997), but would decrease when organics coated on the sulfate (Anttila et al., 2006). The particle surface area concentration in experiment ASTN ranged from 0 to 0.1 m^2/m^3. Assuming a concentration of N_2O_5 of 0.1 ppb and an uptake coefficient of 10^{-3} for N_2O_5, the heterogeneous hydrolysis of N_2O_5 on 0.05 m^2/m^3 suspended particles would generate 6 $\mu g/m^3$ nitrate per hour in the reactor. Thus we speculated the heterogeneous hydrolysis of N_2O_5 might be important in the experiment. Some of these explanations have been added in the revised manuscript.

Revision in the manuscript:

Lines 308-317, Change: "In addition, the presence of organic matter might accelerate the deliquescence of generated inorganic particles (Meyer et al., 2009;Li et al., 2014), and provide moist surfaces for heterogeneous hydrolysis of N_2O_5, contributing to nitrate formation (Pathak et al., 2009)."

To: "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."

Lines 256. Is ammonia salt was measured? How the authors come to the measured ammonia salt.

Response: As we mentioned earlier, the chemical composition of the aerosols were measured by the ACSM or AMS in this study. The measurement results of ACSM or AMS including the concentrations of sulfate, nitrate, ammonium salt and organics. These results were shown in Fig.3 in the manuscript.

NH3 was estimated in the chamber according to Table 2. Why NH3 was not measured experimentally vs time? This is very important (same for SO2). I suggest to use "experiment without NH3 added to the chamber" instead of "NH3 poor"? It's confusing and make it difficult for comparison with other data?

Response: As we mentioned earlier, the concentrations on NH_3 were not measured due to lack of analytical instruments. Besides, as we mentioned in the manuscript, there was NH_3 present in the background air in the chamber derived from the partitioning of the deposited ammonium sulfate and nitrate on the chamber wall when humid air was introduced. Based on the results of experiment STN, the background NH_3 was estimated to be around 8 ppb. With this in mind, the experiments carried out without NH_3 added were considered "NH_3-poor" experiments in this study, while experiments with NH_3 added were considered "NH_3-rich" experiments.

Line 314. Should be Table 2.

Response: Thanks for the reminding! Corresponding revision has been made in the revised manuscript.

Revision in the manuscript:

Fig. 4 caption: "Table 1"

To: “Table 2”

References

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Synergetic formation of secondary inorganic and organic aerosol: ~~Influence~~ Effect of SO_2 and~~/or~~ NH_3 ~~in the heterogeneous process~~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 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 with SO_2 concentration 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 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., 2015a). China has the highest concentration of SO_2 in the world due to a large proportion of energy supply ~~through~~from coal combustion (Bauduin et al., 2016). ~~The s~~Surface concentrations of SO_2 ~~were observed~~ in the range of a few ppb to over 100 ppb have been observed in north China (Sun et al., 2009; Li et al., 2007). The total emission and ~~the~~ concentrations of SO_2 have decreased in most regions of China in recent years (Lu et al., 2010; Wang et al., 2015b), but high concentrations of SO_2 ~~were~~are still frequently observed. For example, the SO_2 concentration ~~in Jinan, a city in North China, can be~~ was as high as 43 ppb in the winter ~~season~~of 2013 in Jinan city (Wang et al., 2015a), while over 100 ppb SO_2 was observed in winter haze days ~~of~~during 2012 in Xi'an city (Zhang et al., 2015). ~~The high~~ 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 ~~extensive~~ 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, and strong correlations between peak levels of fine particles and large increases in NH_3 concentrations in China (Ye et al., 2011;Liu et al., 2015a). Unlike SO_2, the emission of NH_3 ~~are~~is mainly from non-point sources, which ~~is~~are difficult to control, and ~~presented~~shows an increasing trend in China (Dong, 2010). 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~~ 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). ~~The synergistic~~ Synergistic reaction between SO_2 and NO_2 on mineral oxides was reported (Liu et al., 2012a) and was proposed to explain the rapid formation of sulfate ~~during~~ in heavy haze days (He et al., 2014). The presence of NH_3 ~~was also found to~~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 ~~its~~ the fact that the acidic aerosol products of SO_2~~, which were thought to~~ can either take up organic species (Liggio and Li, 2008, 2006) or ~~result in~~increase the formation of high molecular weight compounds in acid-catalytic reactions (Liggio et al., 2007; Kleindienst et al., 2006; Santiago et al., 2012). Besides, sulfate esters ~~were~~ ~~could~~can also ~~confirmed as major players in~~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. ~~It was found that the presence of~~ NH_3 increased SOA formation ~~in the reaction of~~from ozonolysis of α-pinene or cyclohexene~~ with ozone~~ (Na et al., 2007), but had little effect on SOA mass ~~in~~ from ozonolysis of isoprene ~~ozonolysis~~ (Na et al., 2007; Lin et al., 2013) and even decreased SOA production from ozonolysis~~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 its nucleophilic ~~NH$_3$ might~~ attack ~~and~~ might decompose trioxolane and hydroxyl-substituted esters and decrease SOA mass (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$_3$ or NH$_4^+$ ion 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 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.

Methods

A series of smog chamber experiments were carried out to simulate secondary aerosol formation in the photooxidation of ~~VOC~~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 μm-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 ±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 ×0.53 mm ×1.5 mm, Dikma, USA) and flame ionization detector (FID), while NO_x, SO_2 and O_3 were monitored by an NO_x analyzer (Model 42C, Thermo Environmental Instruments, USA), an SO_2 analyzer (Model 43I, Thermo Environmental Instruments, USA) and an O_3 analyzer (Model 49C, Thermo Environmental Instruments, USA), respectively. 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 ~~the~~ 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 ~~as~~to be a first~~-~~-order process. The deposition rates of particles with different sizes (40-700 nm) ~~under dark conditions~~ were measured under dark conditions. Then, ~~Wall~~ wall ~~deposition~~ 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; Chu et al., 2014). The deposition of gas phase compounds ~~were~~was ~~measured~~determined to be 0.0025 h^{-1}, 0.0109 h^{-1}, 0.0023 h^{-1} 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. 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 ~~is~~was 50% in this study. After that, alumina seed particles were added into the chamber. 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 into 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~~Then, 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 into the chamber from standard gas bottles using~~with~~ mass flow controllers. Before adding NH$_3$ into the chamber, NH$_3$ gas was passed through the inlet pipeline for about 15 minutes to reduce ~~the~~ absorption within the line. The concentrations of NH$_3$ were ~~then~~ estimated according to the ~~introduced~~ 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 ℃ ~~and~~ with an initial RH of 50%~~ in this study~~. During the reaction, the temperature ~~were~~was ~~controlled to be almost~~kept nearly constant (30±0.5 ℃) in the temperature-controlled enclosure, while the RH decreased to 45%-47% at the end of the experiment.

Results and discussion

Particle formation and growth in different inorganic gas conditions

~~The~~ First, 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 (ATN~~1~~ 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 supporting information. 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 Figure 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 presence of ~~the~~ NH_3. The volume of secondary aerosol showed an obvious peak in the toluene/NO_x/NH_3 system at about 2.3 hours 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~~1~~ 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.

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

Experiment **No.**	**~~Hydrocarbon~~Tolu~~n~~ene** *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~~	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 ~~introduced~~ amount of NH_3 introduced and the volume of the reactor.

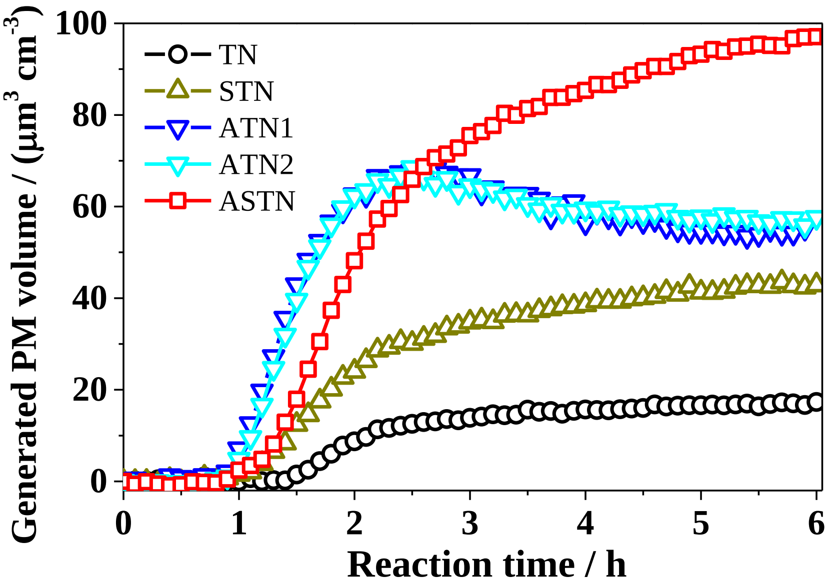

Figure 1. Secondary aerosol formation in photooxidation of toluene/NO_x in the presence or absence of NH_3 and/or SO_2. The letters codes for the experiments indicate the introduced pollutants, i.e. “A” for ammonia, “S” for sulfur dioxide, “T” for toluene and “N” for nitrogen dioxide. Experimental details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

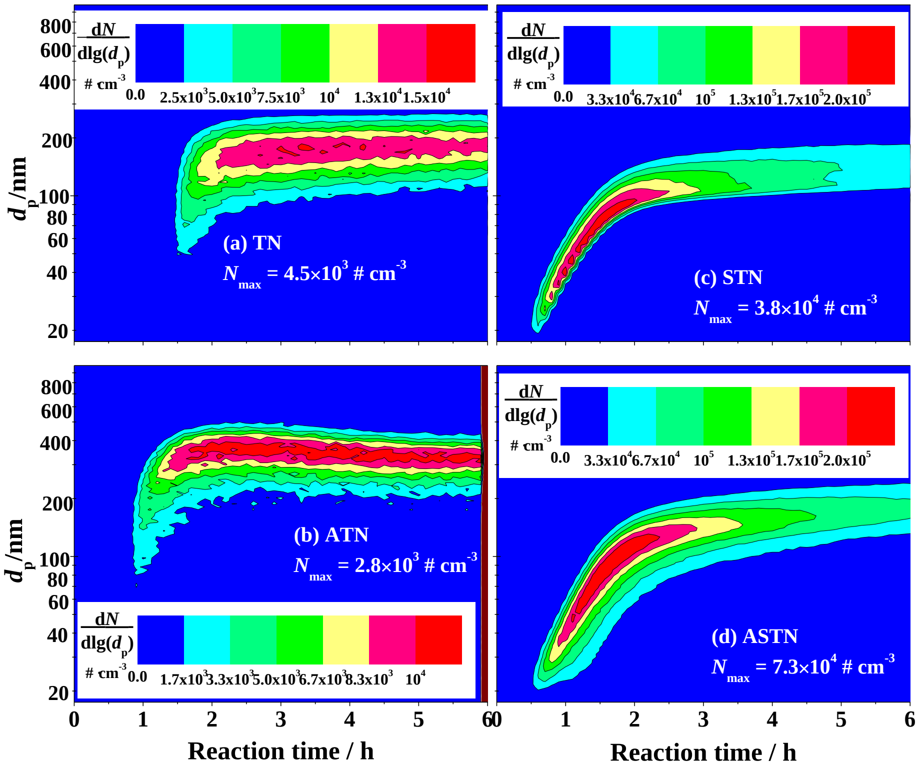

Figure 2. Size distributions of the suspended particles as a function of time during the reaction in photooxidation of toluene/NO_x in the presence or absence of NH_3 and/or SO_2. N_{max} shows the maximal particle number concentration during the reaction for each experiment. Experimental details are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

The size distributions of the secondary aerosol in the photooxidation, with a range of 17-1000 nm, were analyzed and are shown in Figure 2. The new particle formation was not directly measured in this study, but the newly generated particles could be detected when the particles ~~grow up~~increased in size. According to the particle number concentrations, ~~A significant increase in~~ new particle formation appeared to increase a great deal 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 Figure 2(c) to Figure 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 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 (which may include both inorganic nitrate and organic nitrates) 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 generated in the photooxidation of toluene/NO_x were analyzed with an ACSM, and their time variations are displayed in Figure 3. Since the ACM or AMS ~~can't~~cannot distinguish organic salts and organic nitrates, the measured sulfate, nitrate, ammonium were all considered ~~as~~ secondary inorganic aerosol, while the organics were all considered ~~as~~ secondary organic aerosol in this study. 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. 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 in the supporting information. The deposition of NH_3 in the experiment was likely to~~In~~ Figure 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~~ shift~~ed~~ the partition equilibrium to the gas phase and reduce the concentration of NH_4NO_3 salt. ~~Besides~~In addition, the wall deposition of aerosols might also introduce some error ~~to~~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; Chu et al., 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 ~~with different concentrations of sulfate~~ using the AIM Aerosol Thermodynamics Model with different concentrations of sulfate are also shown in Fig. S3 in the supporting information. In addition, in the presence of organic matter, $(NH_4)_2SO_4$ aerosol might ~~accelerate the~~ deliquesce~~nce of generated inorganic particles~~at a RH lower than the deliquescence relative humidity (DRH) (Meyer et al., 2009; Li et al., 2014). If this ~~happened~~took place in the experiment, ~~and~~ sulfate might provide moist surfaces for heterogeneous hydrolysis of N_2O_5, contributing to nitrate formation due to ~~a~~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.

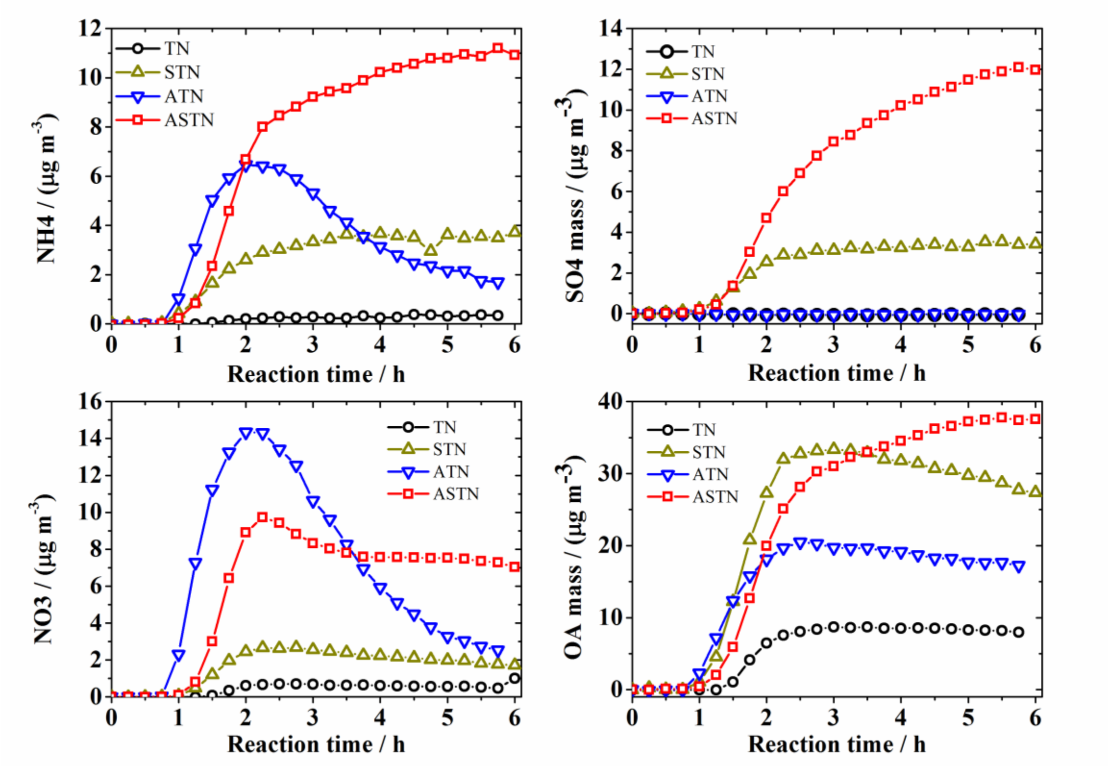

Figure 3. Time variations of the chemical species in the secondary aerosol generated from the photooxidation of toluene/NO_x in the presence or absence of NH_3 and SO_2. Letter codes for experiments indicate the introduced pollutants, i.e.

"A" for ammonia, "S" for sulfur dioxide, "T" for toluene and "N" for nitrogen dioxide. Experimental details are listed in Table 1.

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 (Liu et al., 2015b). Unfortunately, due to the lack of appropriate ~~instrumentation~~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 ~~calculated~~ 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 neutralized by NH_3, according to the chemical composition of aerosols measured by the AMS. The details of the acid-base balance in the aerosols ~~is~~are shown in Fig. S4 in the supporting information.

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 ~~more close~~closer to real ambient conditions, 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 less~~not~~ obvious in the experiment carried out in the absence of SO_2 under NH_3-rich conditions than in experiment ATN, as indicated in Fig.S5 in the supporting information and Fig.3. This might also ~~indicating~~ indicate~~d~~ 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 phase, as discussed above ~~about~~concerning the effects of ~~the~~ co-exist~~ed~~ing $(NH_4)_2SO_4$.

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 ~~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. Initial ~~E~~experimental conditions ~~of the~~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$_0$	**NO_0**	**NO_x-NO**	**SO_2**	**Al_2O_3**	**NH_3***	**RH**	**T**
	ppb	*ppb*	*ppb*	*ppb*	*particle/cm^3*	*ppb*	*%*	*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 ~~introduced~~ amount of NH_3 introduced and the volume of the reactor.

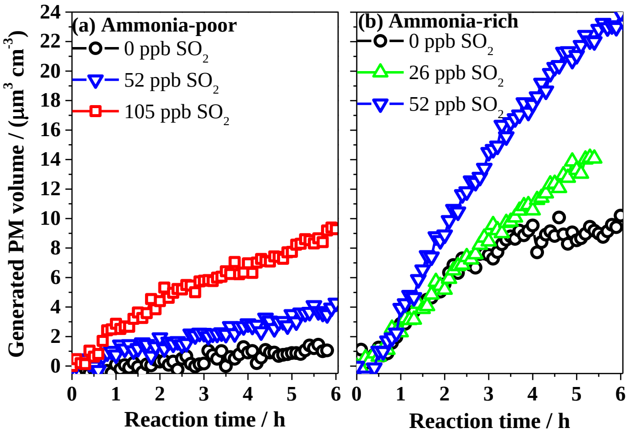

Figure 4. Secondary aerosol formation as a function of time with different concentrations of SO_2 in the photooxidation of toluene/NO_x under NH_3-poor (a) and NH_3-rich (b) conditions. Experimental details are listed in ~~Table 1~~Table 2.

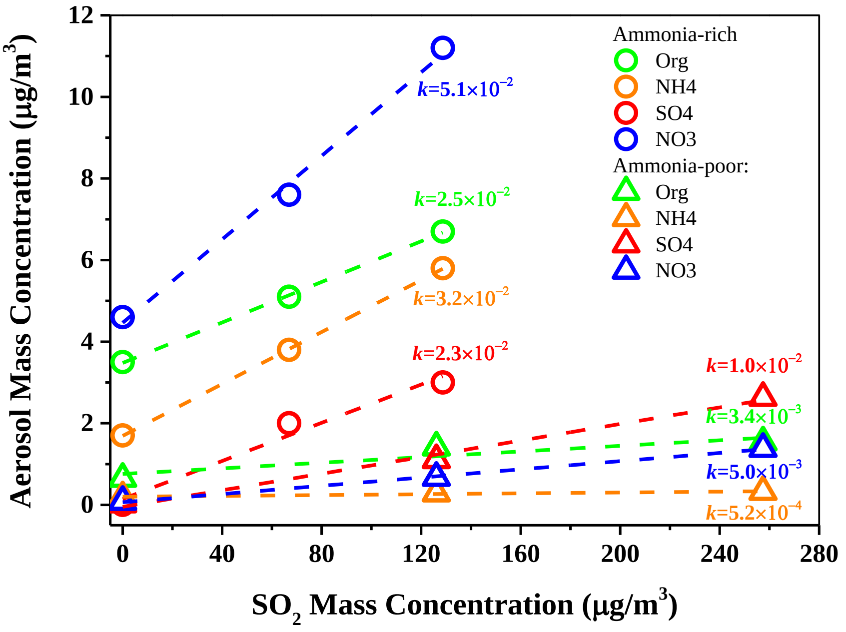

Figure 5. Formation of nitrate (blue), organic aerosol (green), sulfate (red), and ammonium salt (orange) as functions of SO_2 concentration in the photooxidation

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.

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 molecules/cm^3 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 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~~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)~~ (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,~~also 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 ~~could~~can be found in the supporting information. 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~~ 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 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 ring-opening reactions in the photo-oxidation 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. 6(a) and Fig. 6(c). The presence of NH_3 caused a more noticeable ~~particle~~ growth in the size 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 diameter growth of about 12 nm. In the two experiments carried out in the presence of 52 ppb SO_2 in Fig. ~~7~~6(b) and Fig. ~~7~~6(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.

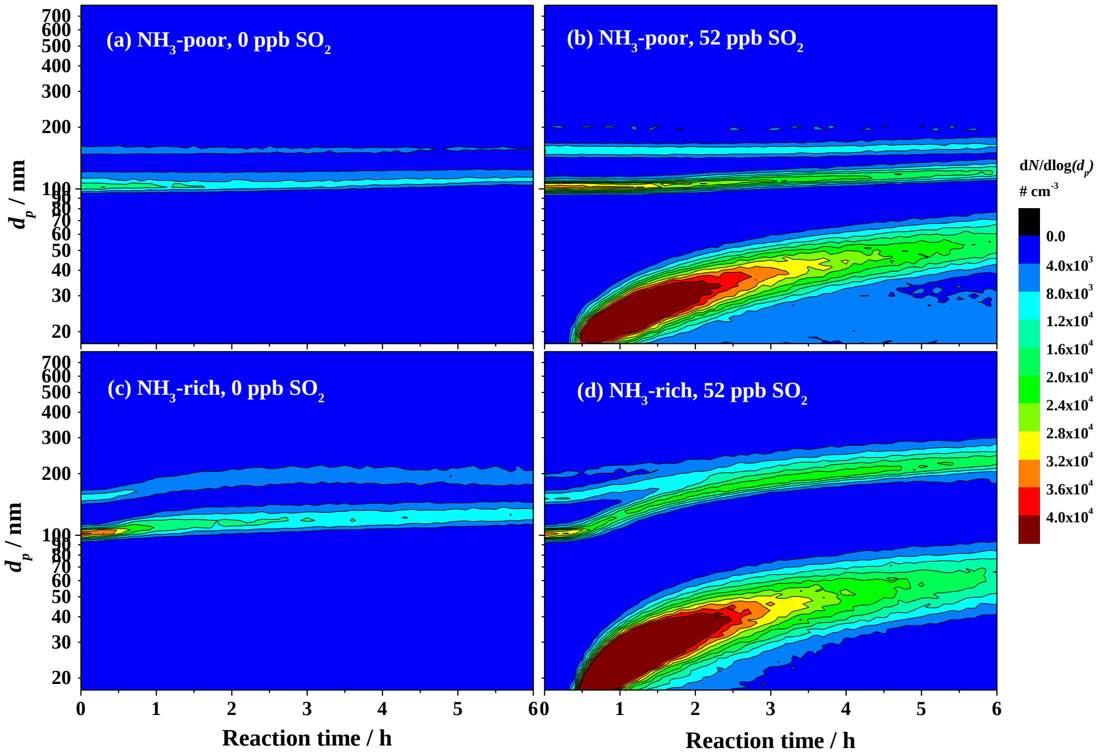

Figure 6. Size distributions of the suspended particles as a function of time during the reaction in photooxidation of toluene/NO_x in the presence of Al_2O_3 seed particles. Experimental details are listed in Table 1.

The chemical properties of the ~~generated~~ SOA generated under 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 oxidized organic component and some nitrogenous organic compounds, while Factor 2 was assigned to less-oxidized organic aerosol and some oligomers.

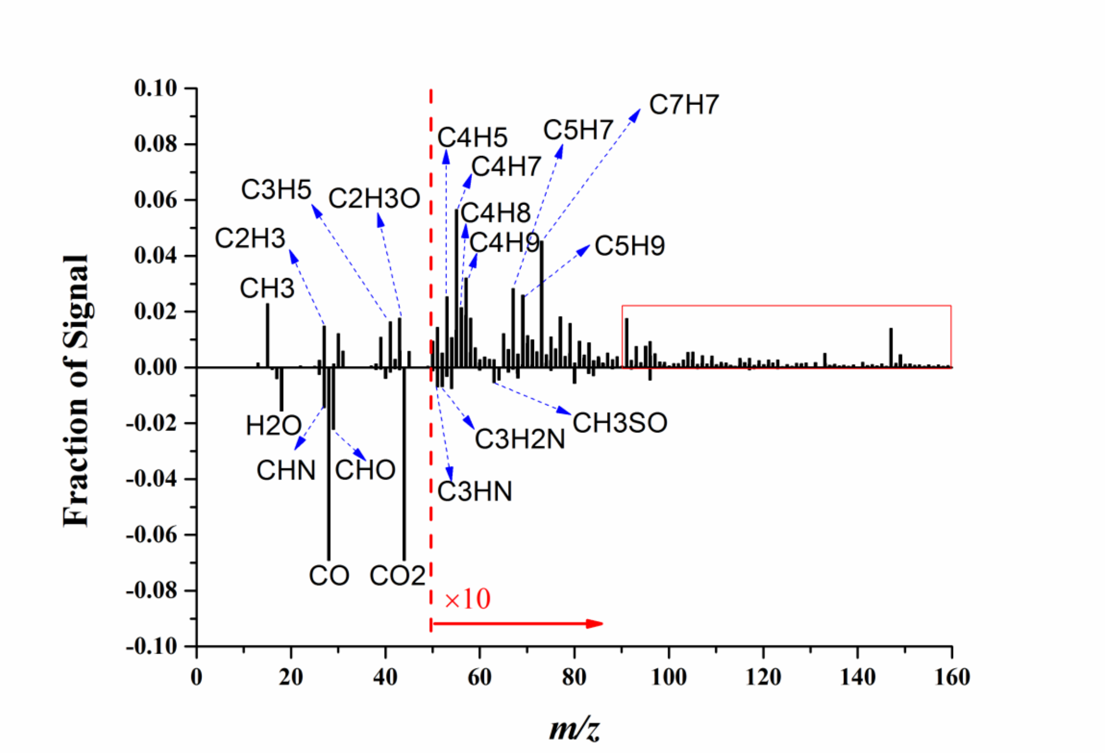

Figure 7. The difference mass spectra (Factor 2 – Factor 1) between the two factors of the generated organic aerosol identified by applying PMF analysis to the AMS data

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 ~~with~~ 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 be probably 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 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~~ 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.

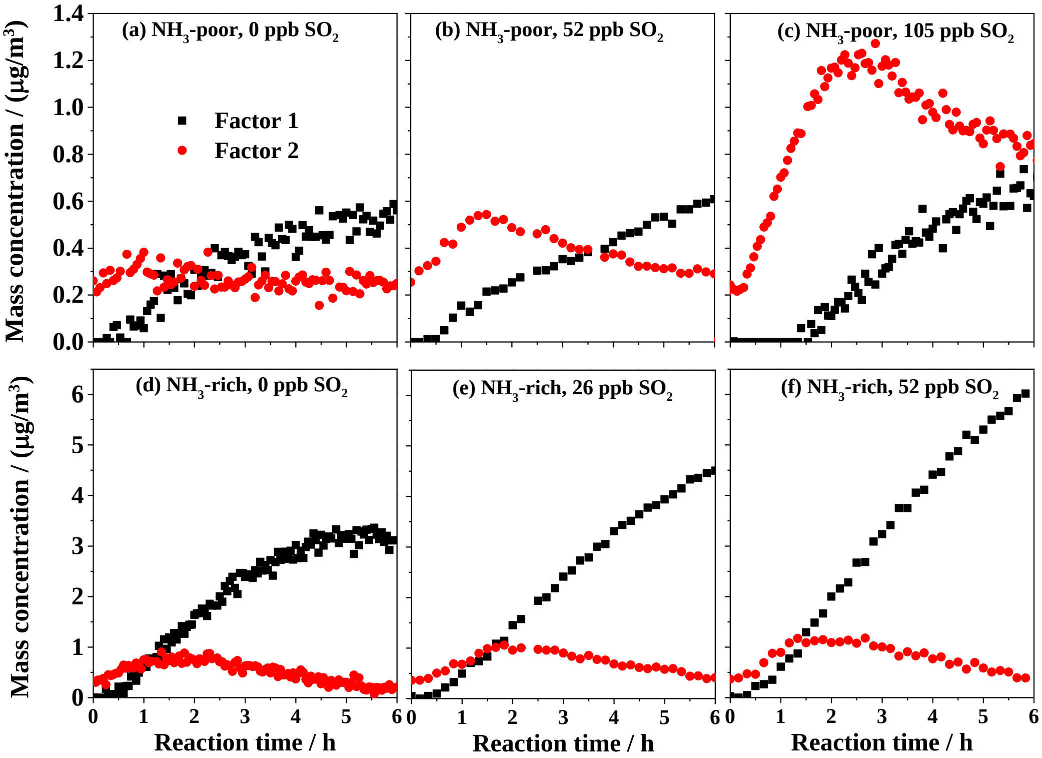

Figure 8. Temporal variations of Factor 1 and Factor 2 in the presence of different concentrations of SO_2 under NH_3-poor and NH_3-rich conditions.

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 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 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 favors NOC formation through NH_3 uptake by SOA, as observed in a recent work (Liu et al., 2015b).

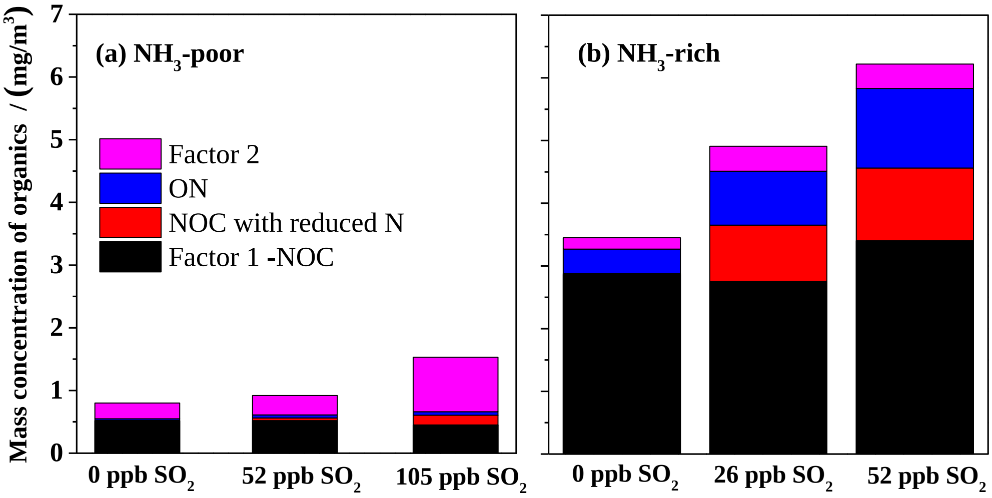

Figure 9. The estimated concentrations of NOC (ON+NOC with reduced N) and the two factors (identified by PMF analysis) in SOA as a function of SO_2 concentration in photooxidation of toluene/NO_x under (a) NH_3-poor and (b) NH_3-rich conditions

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 or not. 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~~s~~ 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 from that under NH_3-poor conditions. ~~A~~ The better correlation between secondary aerosol formation and particle surface area than that with particle volume indicated an enhancement effect in the 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.

Acknowledgments

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Synergetic formation of secondary inorganic and organic aerosol: ~~Influence~~ Effects of SO_2 and/or NH_3 ~~in the heterogeneous process~~on particle formation and growth

(Supporting information)

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The consumption of gas precursors, the formation of ozone and SOA, and SOA yield

Table R1. The consumption of gas precursors, the formation of ozone and SOA, and SOA yield 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.

Experiment No.	**Δtoluene** ppm	**ΔNO$_x$** ppb	**ΔSO$_2$** ppb	**ΔO$_3$** ppb	**SOA** μg/m^3	**SOA yield** %
TN	0.19	89	NA	179	8.0	1.1
STN	0.18	90	25	176	27.7	4.1
ATN	0.16	82	NA	159	17.2	2.9
ASTN	0.15	90	42	166	37.4	6.8

Table R2. The consumption of gas precursors, the formation of ozone and SOA, and SOA yield in photooxidation of toluene/NO$_x$ with different concentrations of SO$_2$ in the photooxidation of toluene/NO$_x$ under NH$_3$-poor and NH$_3$-rich conditions.

	Δtoluene ppb	**ΔNO$_x$** ppb	**ΔSO$_2$** ppb	**ΔO$_3$** ppb	**SOA** μg/m^3	**SOA yield** %
NH$_3$-poor	41	73	NA	22	0.6	0.4
	40	61	6	22	1.4	1.0
	39	62	12	20	1.5	1.1
NH$_3$-rich	47	79	NA	27	3.5	2.0
	45	81	6	26	5.1	3.1
	44	75	11	27	6.7	4.1

Time variations of gas phase compounds

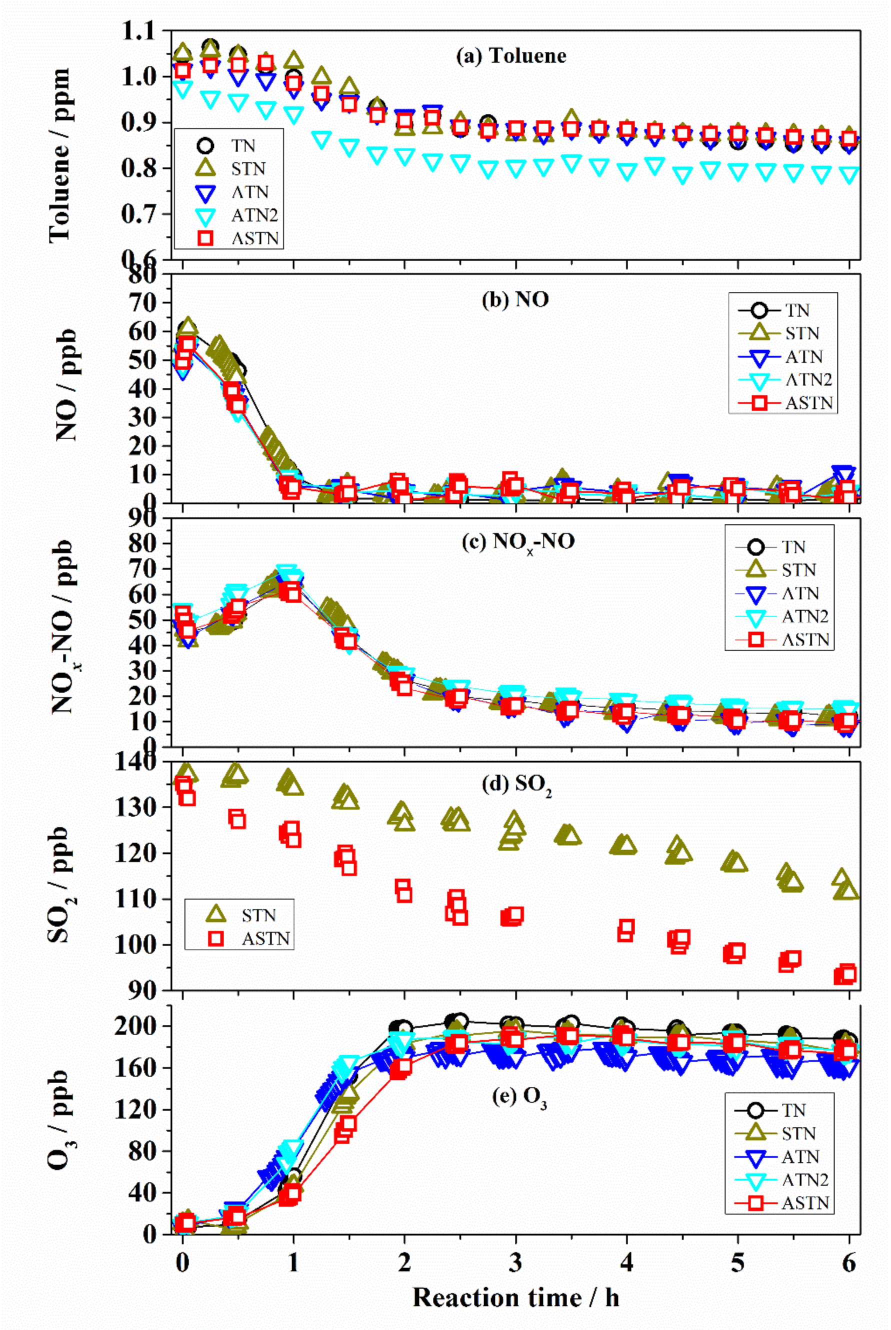


Figure S1. Time variations of gas-phase compounds in photooxidation of toluene/NO_x in the presence or absence of NH_3 and/or SO_2. The letters codes for the experiments indicate the introduced pollutants, i.e. “A” for ammonia, “S” for sulfur dioxide, “T” for toluene and “N” for nitrogen dioxide.

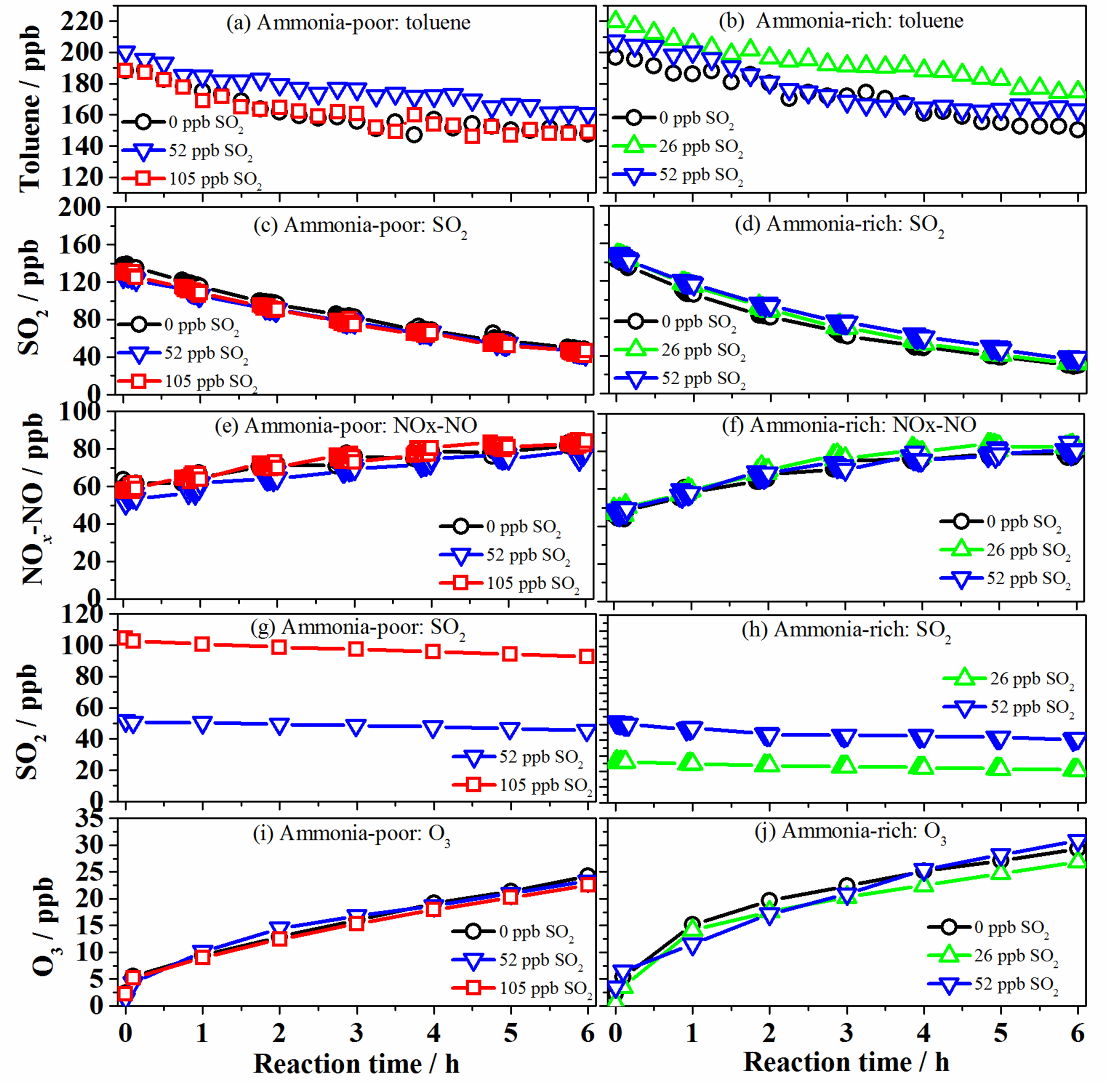


Figure S2. Time variations of gas-phase compounds in photooxidation of toluene/NO$_x$ with different concentrations of SO$_2$ under NH$_3$-poor and NH$_3$-rich conditions

Partition of NH_4NO_3 salt based on the simulation results of the AIM Aerosol Thermodynamics Model

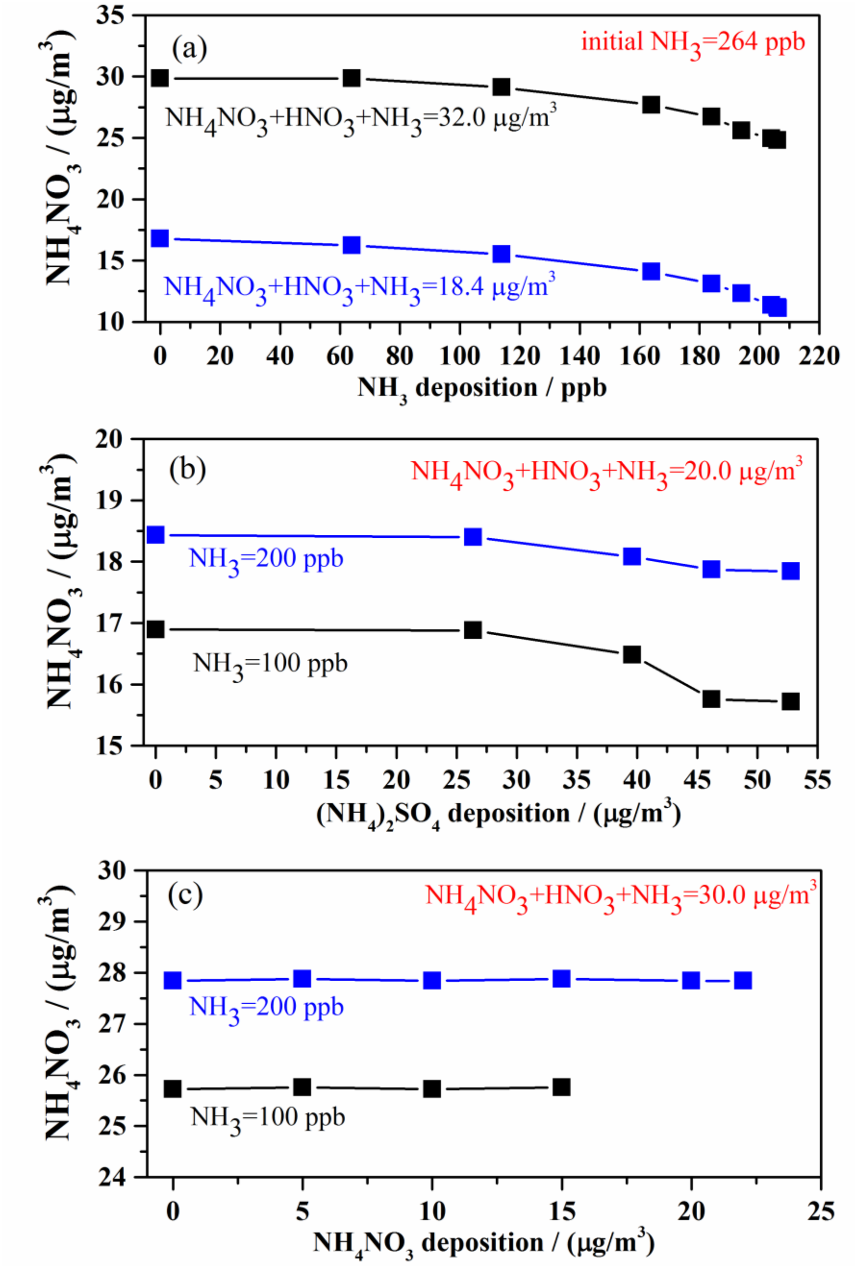


Figure S3. Concentrations of NH_4NO_3 salt as a function of the wall deposition of NH_3, $(NH_4)_2SO_4$ and NH_4NO_3 based on the simulation results of the AIM Aerosol Thermodynamics Model

Acid-base balance in the aerosols in NH_3-rich experiments

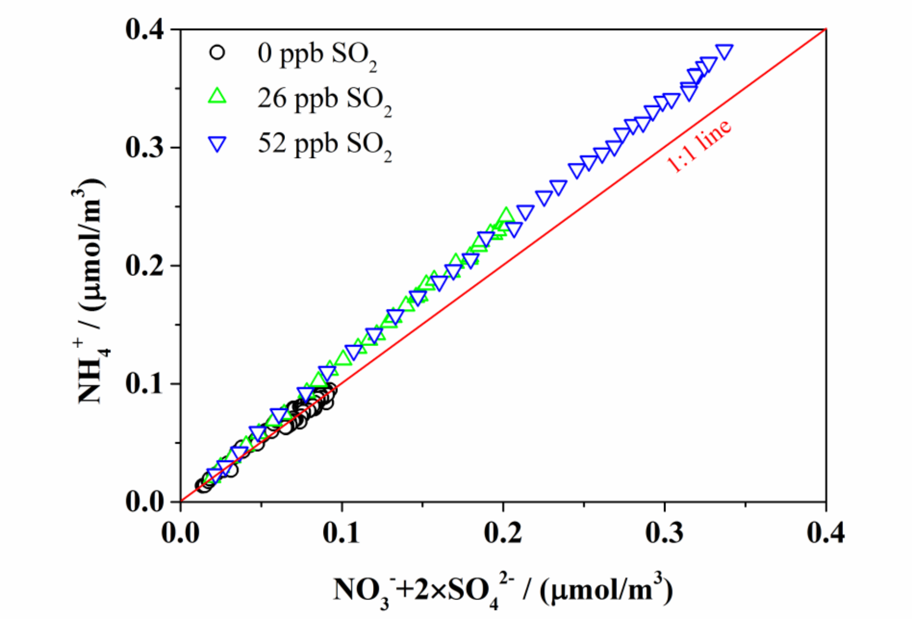


Figure S4. Evaluation of acid-base balance of the aerosols according to the concentrations of sulfate, nitrate, and ammonium salt measured by the AMS. The line in the figure indicated an acid-base balance.

Chemical compositions of aerosols in the photooxidation of toluene/NO_x with different concentrations of SO_2 under NH_3-poor and NH_3-rich conditions

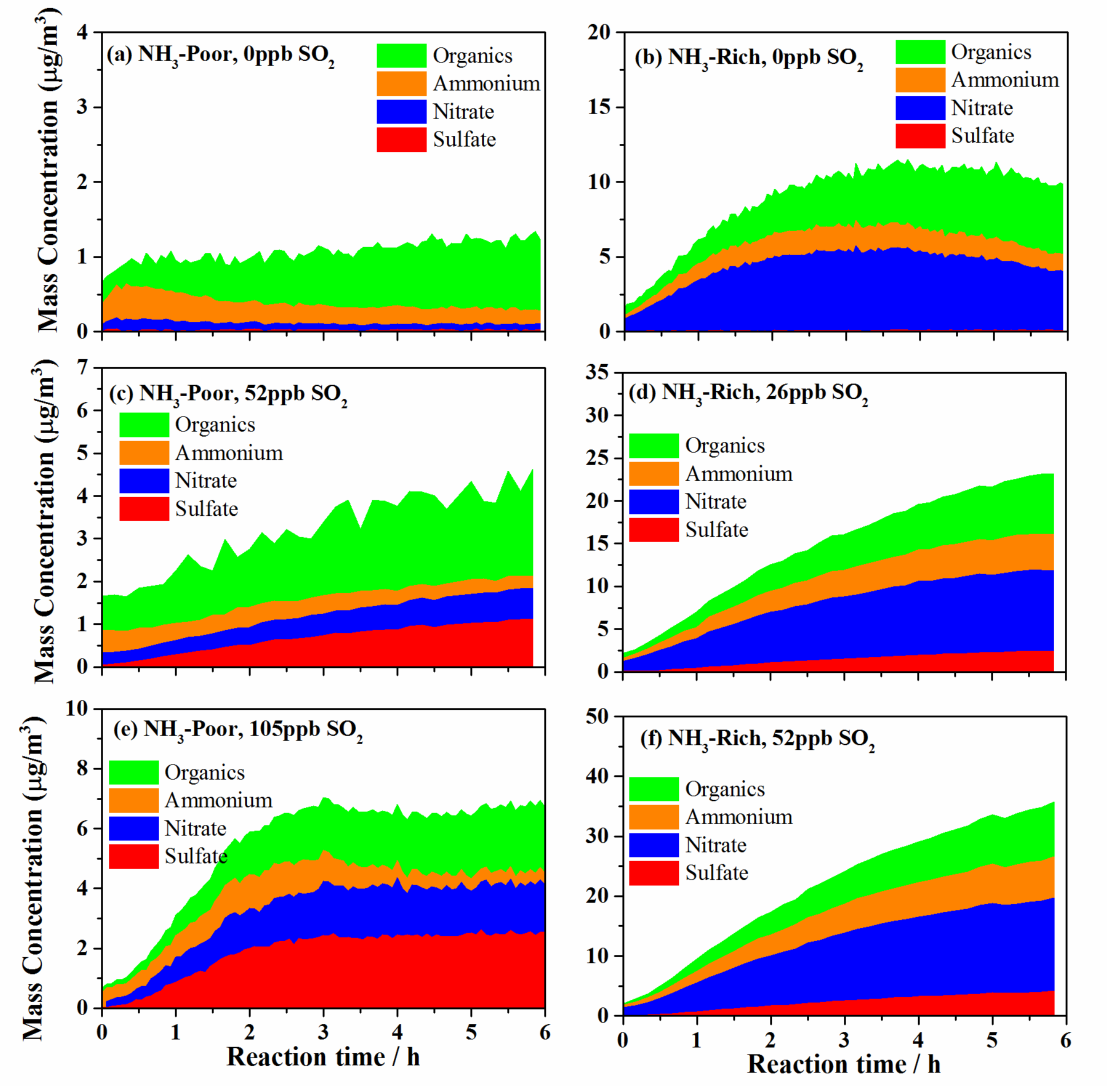


Figure S5. Time variations of sulfate, nitrate, and ammonium and organics measured by the AMS in the photooxidation of toluene/NO_x with different concentrations of SO_2 under NH_3-poor and NH_3-rich conditions

SOA yields in the experiments in this study and the comparison with literature results

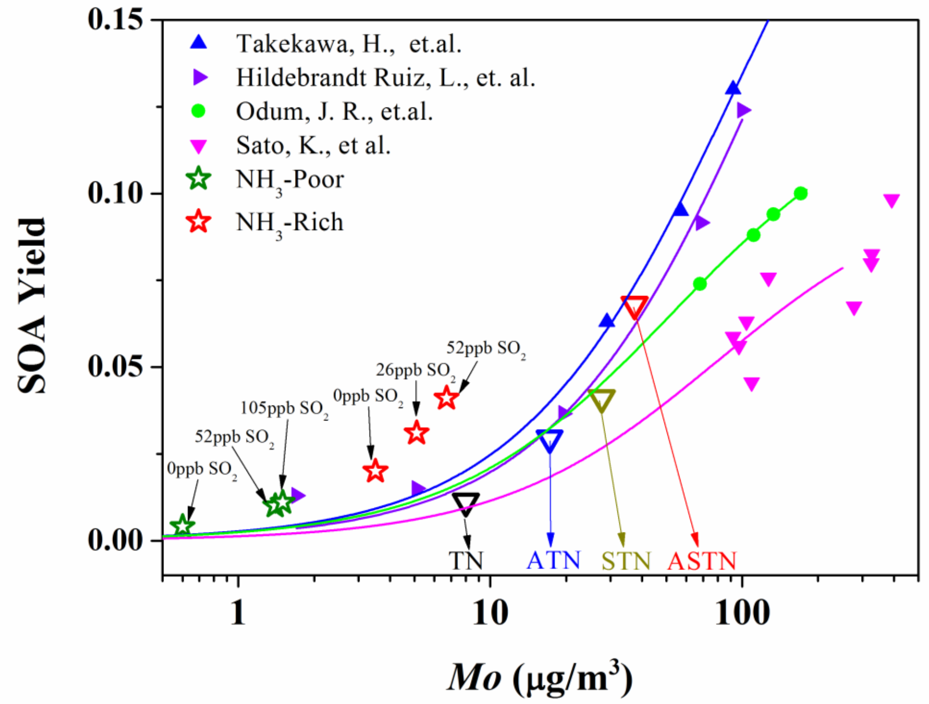


Figure S6. SOA yields in the experiments in this study and the comparison with literature results (Takekawa et al., 2003;Hildebrandt Ruiz et al., 2015;Odum et al., 1997;Sato et al., 2007)

Increase of secondary aerosol formation with SO_2 consumption, particle surface area, and particle volume

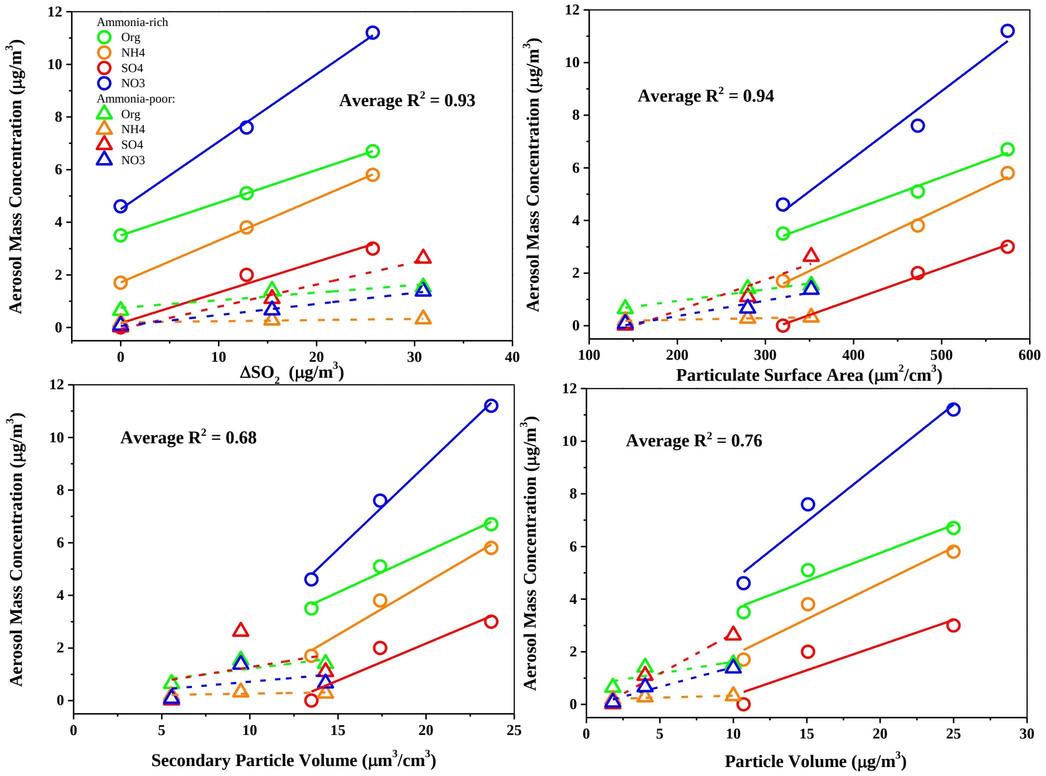


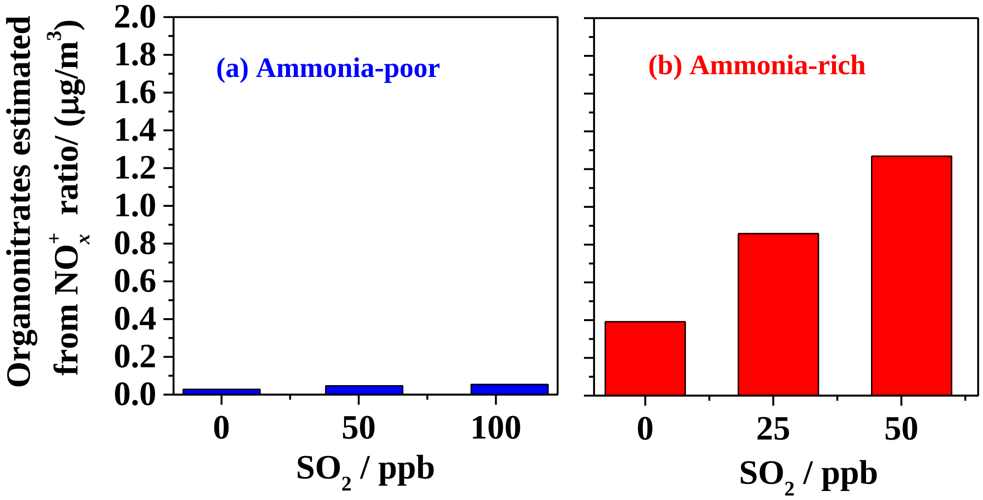
Figure S37.~~Fig. S1~~ Correlation of secondary aerosol formation with SO_2 consumption, particle surface area, and particle volume~~.~~

Estimating concentrations of nitrogen-containing organics (NOC)

Nitrogen-containing organics (NOC) might contain organonitrates, organic ammonium salts, and species with carbon covalently bonded to nitrogen. Organonitrates could be estimated using methods suggested by Farmer et al. (2010), one of which was using NO_x^+ ratios. The ratio of m/z 30 to m/z 46 for nitrate ($R_{NH_4NO_3}$) is lower than that of organonitrates ($R_{Organonitrates}$) in AMS measurement, so the observed ratio, R_{obs}, can be used to estimate the fraction of the total nitrate signal due to organonitrates (x) using the Equation S1:

$$x = \frac{\left(R_{obs} - R_{NH_4NO_3}\right)\left(1+R_{obs}\right)}{\left(R_{Organonitrates} - R_{NH_4NO_3}\right)\left(1+R_{Organonitrates}\right)} \qquad \text{(S1)}$$

where $R_{NH_4NO_3}$ was measured as 2.35 in the calibration of AMS, and $R_{Organonitrates}$ was assumed to be 15, which was highest value suggested by Farmer et al (2010), to avoid overestimation of organonitrates. The estimated concentrations of organonitrates are shown in Fig. ~~S2~~S8.



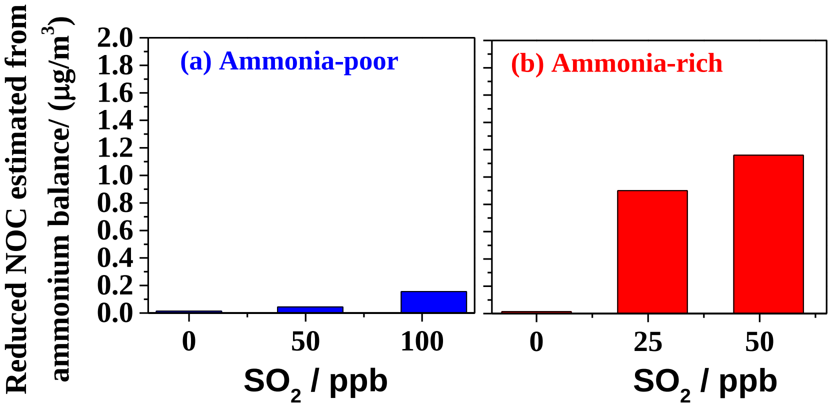
Figure~~.~~ ~~S2~~ S8 The estimated concentrations of organonitrates from NO_x^+ ratios as a function of SO_2 concentration in photooxidation of toluene/NO_x under (a) NH_3-poor and (b) NH_3-rich conditions

As suggested by Farmer et al. (2010), NH_4^+ is required to balance with the SO_4^{2-} and NO_3^- in the absence of NOC. In this study, the measured concentration of NH_4^+ was higher than the calculated concentration according to charge balance, especially in the NH_3-rich experiments. This result indicated the presence of NOC with reduced N

(Reduced NOC). The NH_3 present may react with the ring opening oxycarboxylic acids from toluene (Jang and Kamens, 2001) and carbonyl functional group organics (Wang et al., 2010), and result in organic ammonium salt products, imines, imidazole, and so on. The NH_4 balance considering the presence of NOC with reduced N is described by Equation S2:

$$\frac{c_{NH_4}}{18} - \frac{c_{Reduced\ NOC}}{M_{Reduced\ NOC}} = 2 \times \frac{c_{SO_4}}{96} + \left[\frac{c_{NO_3}}{62} - \frac{c_{Organonitrates}}{M_{Organonitrates}}\right] \qquad \text{(S2)}$$

where c_{NH_4} , c_{SO_4} and c_{NO_3} are the mass concentrations of ammonium and sulfate and nitrate in AMS measurement results, respectively; while $c_{Reduced\ NOC}$ and $c_{Organonitrates}$ are the estimated mass concentrations of NOC with reduced N and organonitrates, respectively. $M_{Reduced\ NOC}$ and $M_{Organonitrates}$ in Equation S2 are the molecular weights of NOC with reduced N and organonitrates, and are assumed to be 100 and 200, respectively. $M_{Reduced\ NOC}$ is assumed to have a smaller value than $M_{Organonitrates}$ to avoid overestimation of NOC with reduced N. Using the estimated concentration of organonitrates according to Equation S1, the estimated concentrations of the NOC with reduced N are calculated and displayed in Fig. ~~S3~~S9.



Figure~~.~~ ~~S3~~ S9 The estimated concentrations of NOC with reduced N as a function of SO_2 concentration in photooxidation of toluene/NO_x under (a) NH_3-poor and (b) NH_3-rich conditions

The uncertainty in the results in Fig. ~~S2~~ S8 and Fig. ~~S3~~ S9 might be large, since a lot of parameters are assumed and the measurement response of AMS to the NOC is still highly uncertain. We analyzed the organic fragments containing N in the AMS measurements. Farmer et al. (2010) suggested the estimation of concentrations of organonitrates using the sum of the signals of the five major $C_xH_yO_zN^+$ fragments in AMS measurement results. However, as pointed out by Farmer et al (2010) and other studies (Galloway et al., 2009;Laskin et al., 2014;Liu et al., 2015), NOC with reduced N could also produce these fragments. In this study, we used Equation S3 to provide an estimate of NOC:

$$c_{NOC}=\frac{CH_4NO^+ + C_2H_5NO^+ + C_3H_4NO^+ + CH_2NO_3^+ + CH_2NO_2^+}{R_{C_xH_yO_zN^+}} \qquad (S3)$$

where $R_{C_xH_yO_zN^+}$ is the fraction of these five major $C_xH_yO_zN^+$ fragments and accounts for the total oxidized N signal of the organonitrates samples, and was measured as 0.045 in the study of Farmer et al. (2010). The estimated concentrations of NOC using Equation S3 are shown in Fig. ~~S4~~S10. These results appear to be comparable to the sum of organonitrates in Fig. ~~S2~~ S8 and NOC with reduced N in Fig. ~~S3~~S9. Meanwhile, the concentrations of $C_xH_yN^+$ fragments are displayed in Fig. ~~S5~~S11. They also have similar change trends with SO_2 concentration as the estimated NOC concentrations.

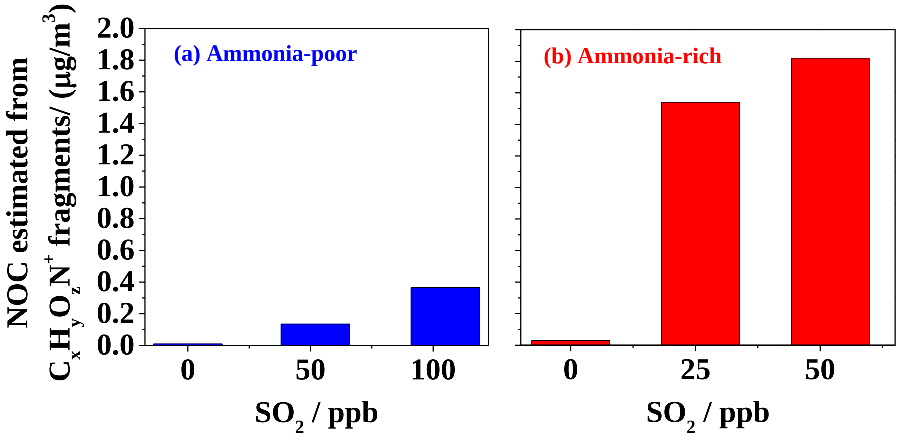
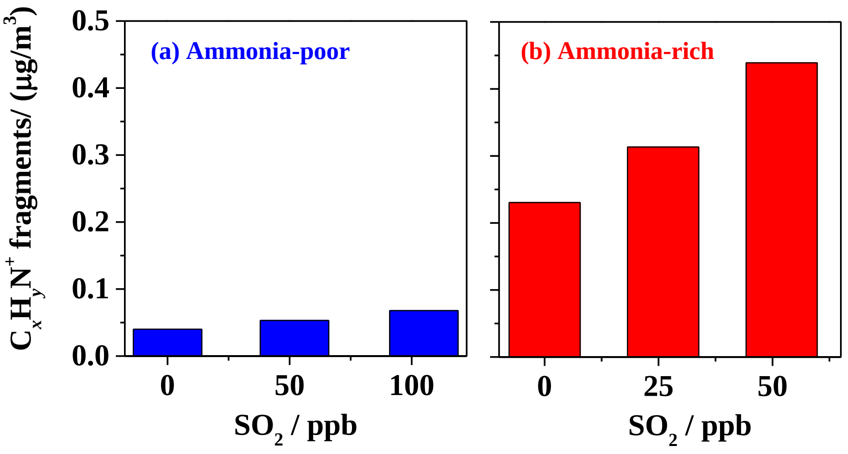


Fig. ~~S4~~ S10 The estimated concentrations of NOC from $C_xH_yO_zN^+$ fragments as a function of SO_2 concentration in photooxidation of toluene/NO_x under (a) NH_3-poor and (b) NH_3-rich conditions



Fig~~.~~ure ~~S5~~ S11 The concentrations of $C_xH_yN^+$ fragments as a function of SO_2 concentration in photooxidation of toluene/NO_x under (a) NH_3-poor and (b) NH_3-rich conditions

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