Response for Reviewer #1

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 reviewer 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.

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

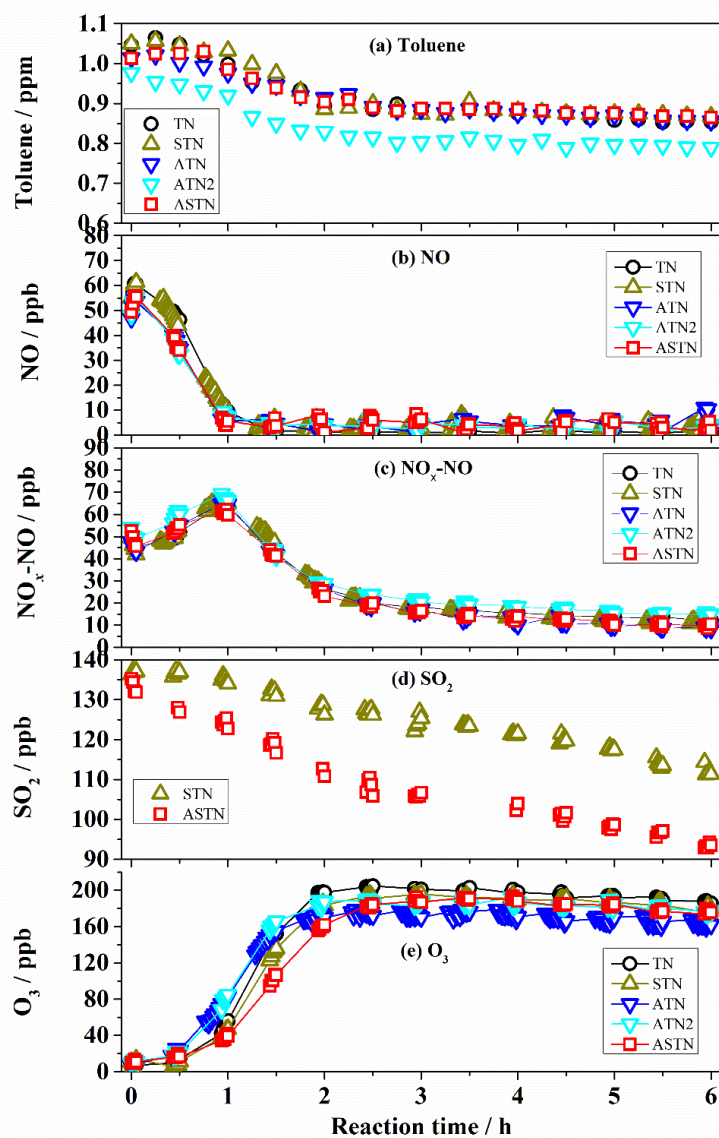|					
	40	61	6	22	1.4	1.0
	39	62	12	20	1.5	1.1
NH$_3$-rich	47	79	NA	27	3.5	2.0
	45	81	6	26	5.1	3.1
	44	75	11	27	6.7	4.1

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.
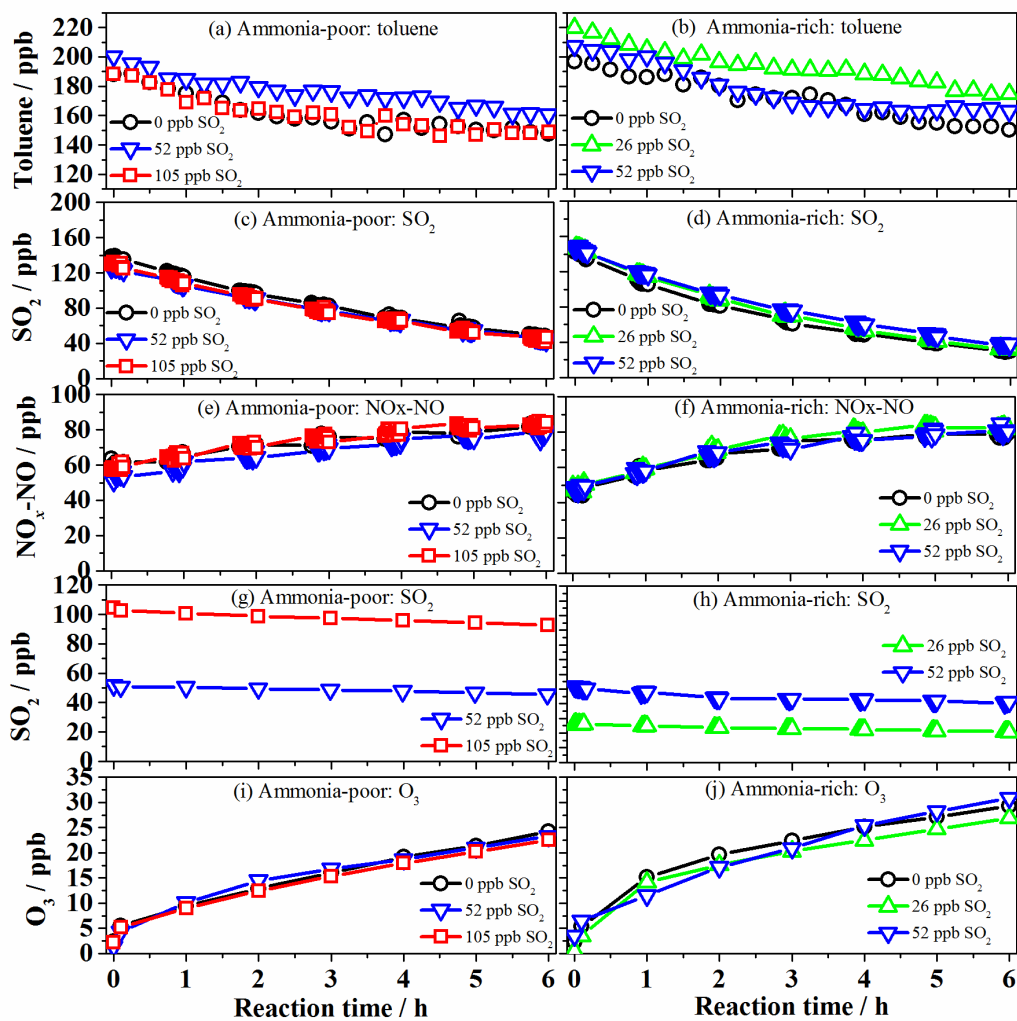
Figure R2. Time variations of gas-phase compounds in photooxidation of toluene/NO$_x$ with different concentrations of SO$_2$ under NH$_3$-poor and NH$_3$-rich conditions
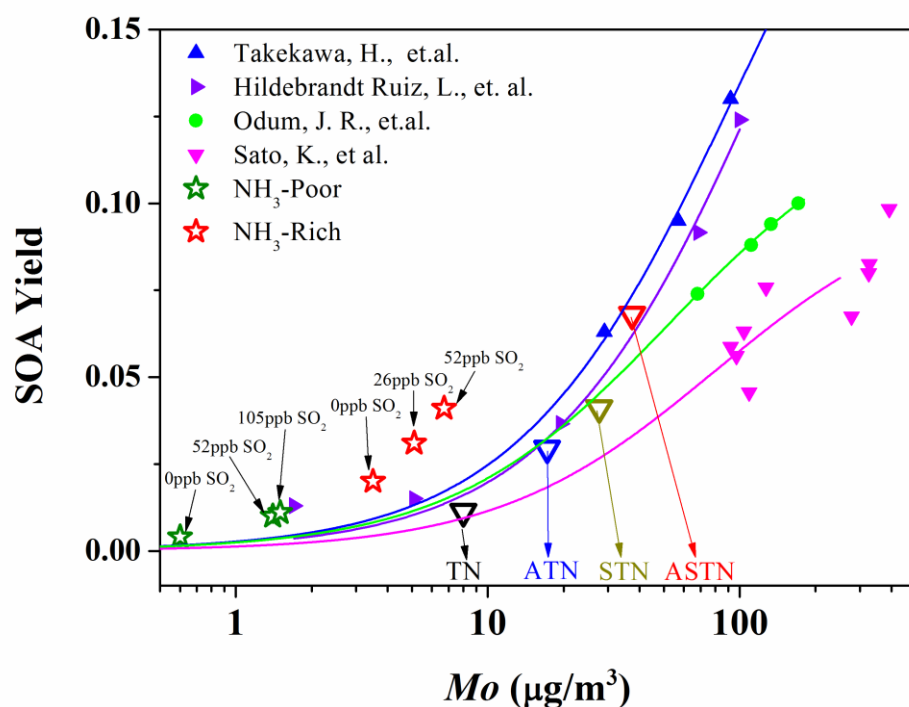
Figure R3. SOA yields in the experiments in this study and the comparison with literature results (Takekawa et al., 2003;Hildebrandt Ruiz et al., 2015;Odum et al., 1997;Sato et al., 2007)

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.
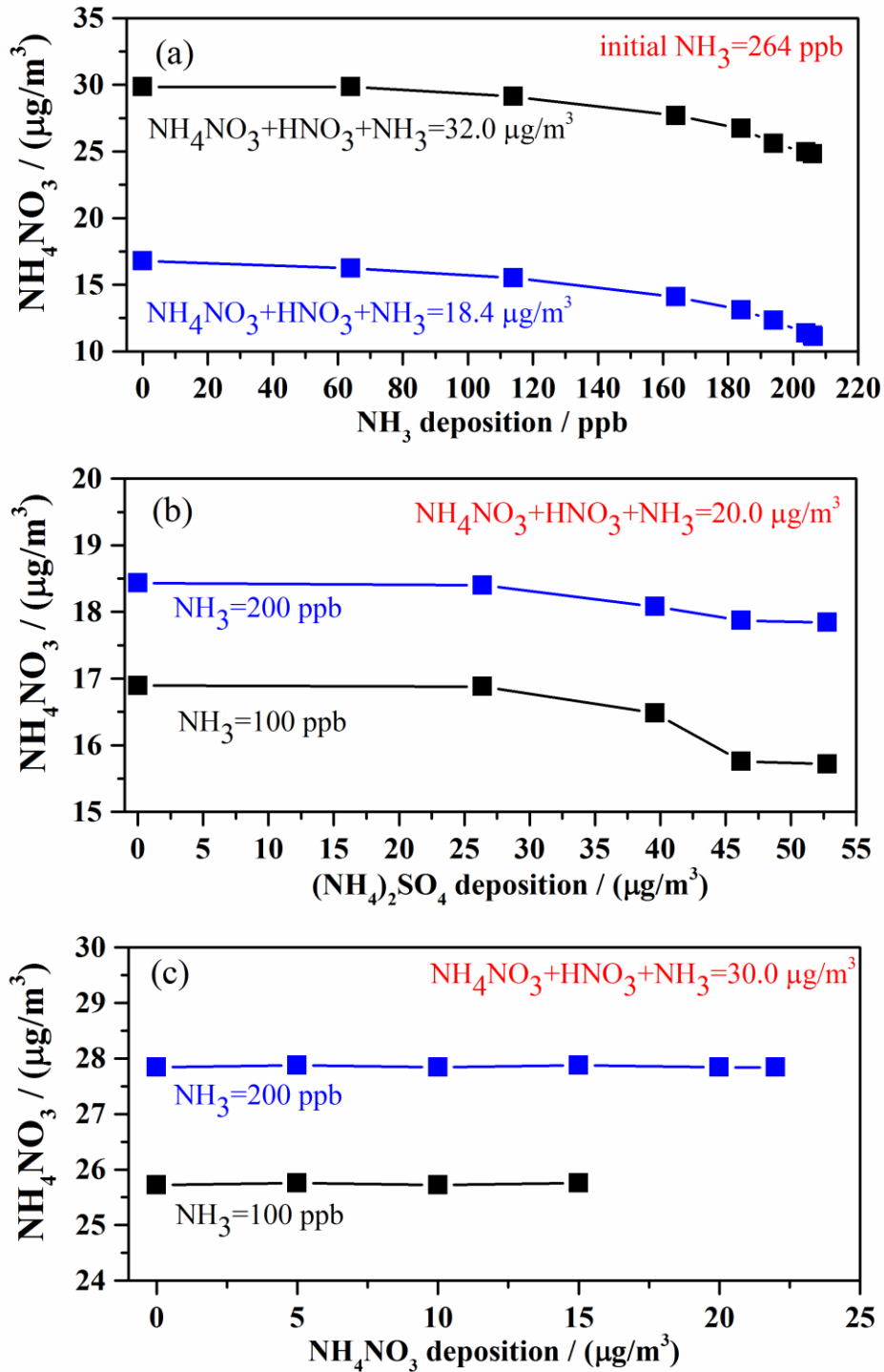
Figure R4. Concentrations of NH$_4$NO$_3$ salt as a function of the wall deposition of NH$_3$, (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ based on the simulation results of the AIM Aerosol Thermodynamics Model

Revision in the manuscript:

Lines 289-302, Change: "In 错误!未找到引用源。, 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, $(NH_{4)2}SO_4$ was reported to deliquesce at RH lower than pure $(NH_{4)2}SO_4$. (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).
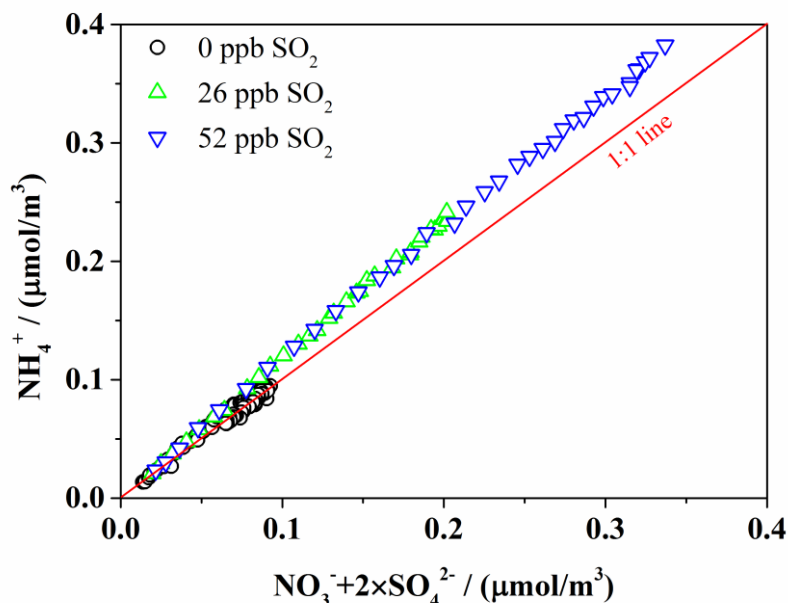
Figure R5. Evaluation of acid-base balance of the aerosols according to the concentrations of sulfate, nitrate, and ammonium salt measured by the AMS in NH₃-rich experiments. The line in the figure indicated an acid-base balance.

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.
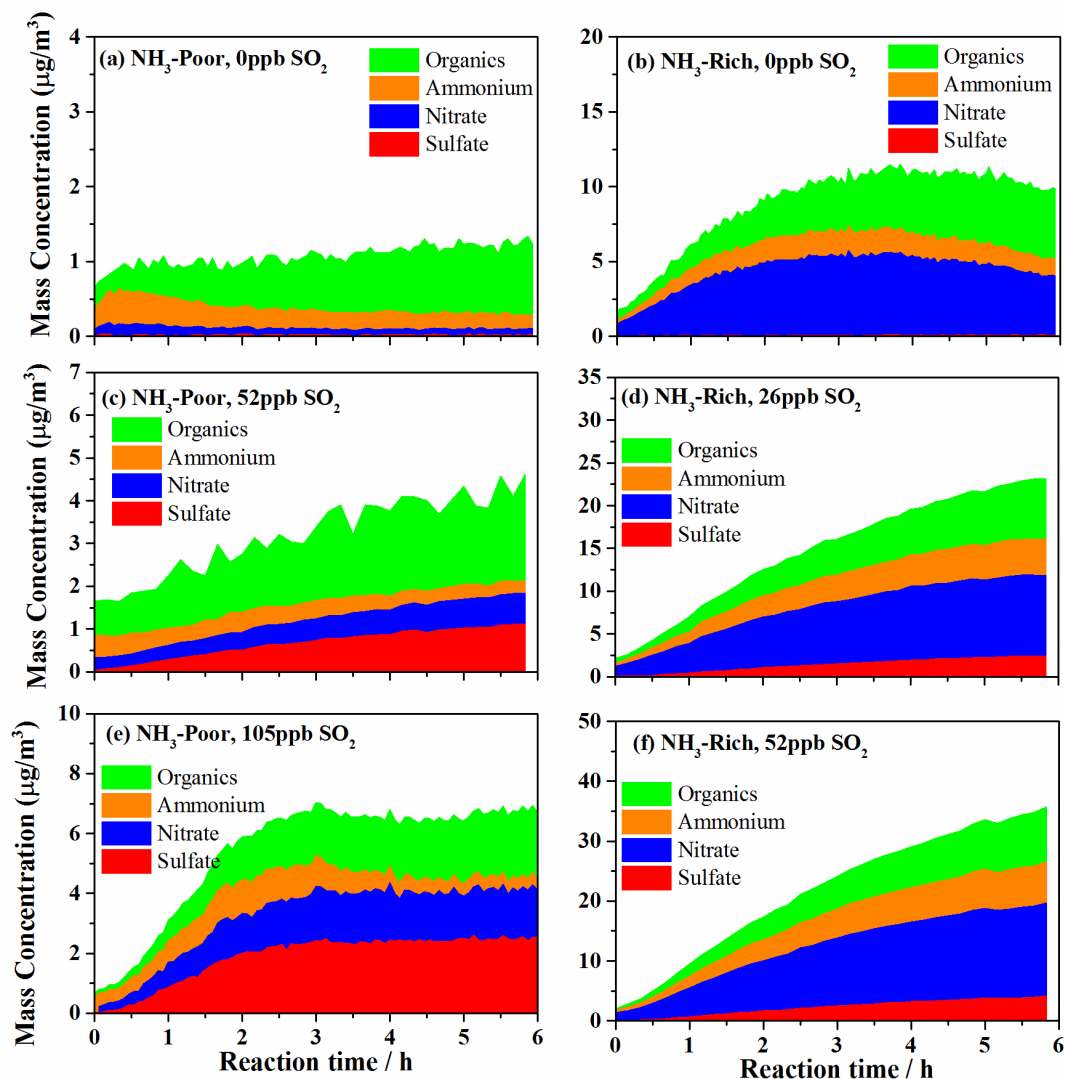

Figure R6. Time variations of sulfate, nitrate, and ammonium and organics measured by the AMS in the photooxidation of toluene/NO_x with different concentrations of SO_2 under NH_3-poor and NH_3-rich conditions

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 ($\mu mol/m^3$)

	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$_2$O(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$_2$O(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.
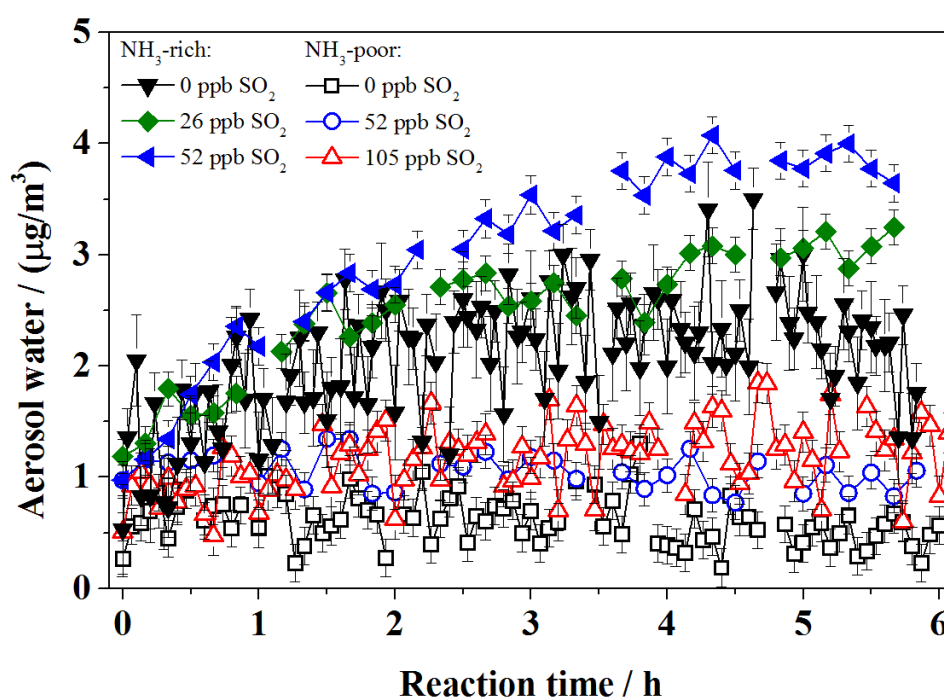

Figure R7. Time variations of aerosol water measured by the AMS in the photooxidation of

References

Anttila, T., Kiendler-Scharr, A., Tillmann, R., and Mentel, T. F.: On the reactive uptake of gaseous compounds by organic-coated aqueous aerosols: Theoretical analysis and application to the heterogeneous hydrolysis of N$_2$O$_5$, J. Phys. Chem. A, 110, 10435-10443, doi: 10.1021/jp062403c, 2006.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of Ox, HOx, NOx and SOx species, Atmos. Chem. Phys., 4, 1461-1738, doi: doi:10.5194/acp-4-1461-2004, 2004.

Carslaw, K. S., Clegg, S. L., and Brimblecombe, P.: A thermodynamic model of the system HCl-HNO$_3$-H$_2$SO$_4$-H$_2$O, including solubilities of HBr, from less-than-200 to 328 K, J. Phys. Chem., 99, 11557-11574, doi:10.1021/j100029a039, 1995.

Chu, B., Hao, J., Takekawa, H., Li, J., Wang, K., and Jiang, J.: The remarkable effect of FeSO$_4$ seed aerosols on secondary organic aerosol formation from photooxidation of α-pinene/NOx and toluene/NOx, Atmos. Environ., 55, 26-34, doi:10.1016/j.atmosenv.2012.03.006, 2012.

Chu, B., Liu, Y., Li, J., Takekawa, H., Liggio, J., Li, S.-M., Jiang, J., Hao, J., and He, H.: Decreasing effect and mechanism of FeSO$_4$ seed particles on secondary organic aerosol in α-pinene photooxidation, Environ. Pollut., 193, 88-93, doi:10.1016/j.envpol.2014.06.018, 2014.

Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic model of the system H$^+$-NH$_4^+$-SO$_4^{2-}$-NO$_3^-$-H$_2$O at tropospheric temperatures, J. Phys. Chem. A, 102, 2137-2154, doi:10.1021/jp973042r, 1998.

Clegg, S. L., and Brimblecombe, P.: Comment on the "Thermodynamic dissociation constant of the bisulfate ion from Raman and ion interaction modeling studies of aqueous sulfuric acid at low temperatures", J. Phys. Chem. A, 109, 2703-2706, doi:10.1021/jp0401170, 2005.

Hallquist, M., Stewart, D. J., Stephenson, S. K., and Cox, R. A.: Hydrolysis of N2O5 on sub-micron sulfate aerosols, Phys. Chem. Chem. Phys., 5, 3453-3463, doi: 10.1039/b301827j, 2003.

Hildebrandt Ruiz, L., Paciga, A. L., Cerully, K. M., Nenes, A., Donahue, N. M., and Pandis, S. N.: Formation and aging of secondary organic aerosol from toluene: changes in chemical composition, volatility, and hygroscopicity, Atmos. Chem. Phys., 15, 8301-8313, doi:10.5194/acp-15-8301-2015, 2015.

Hu, J. H., and Abbatt, J. P. D.: Reaction probabilities for N$_2$O$_5$ hydrolysis on sulfuric acid and ammonium sulfate aerosols at room temperature, J. Phys. Chem. A, 101, 871-878, doi: 10.1021/jp9627436, 1997.

Li, W. J., Shao, L. Y., Shi, Z. B., Chen, J. M., Yang, L. X., Yuan, Q., Yan, C., Zhang, X. Y., Wang, Y. Q., Sun, J. Y., Zhang, Y. M., Shen, X. J., Wang, Z. F., and Wang, W. X.: Mixing state and hygroscopicity of dust and haze particles before leaving Asian continent, J. Geophys. Res.- Atmos., 119, 1044-1059, doi:10.1002/2013jd021003,

2014.

Meyer, N. K., Duplissy, J., Gysel, M., Metzger, A., Dommen, J., Weingartner, E., Alfarra, M. R., Prevot, A. S. H., Fletcher, C., Good, N., McFiggans, G., Jonsson, A. M., Hallquist, M., Baltensperger, U., and Ristovski, Z. D.: Analysis of the hygroscopic and volatile properties of ammonium sulphate seeded and unseeded SOA particles, Atmos. Chem. Phys., 9, 721-732, doi: 10.5194/acp-9-721-2009, 2009.

Odum, J. R., Jungkamp, T. P. W., Griffin, R. J., Forstner, H. J. L., Flagan, R. C., and Seinfeld, J. H.: Aromatics, reformulated gasoline, and atmospheric organic aerosol formation, Environ. Sci. & Technol., 31, 1890-1897, doi:10.1021/es960535l, 1997.

Sato, K., Hatakeyama, S., and Imamura, T.: Secondary organic aerosol formation during the photooxidation of toluene: NOx dependence of chemical composition, J. Phys. Chem. A, 111, 9796-9808, doi:10.1021/jp071419f, 2007.

Takekawa, H., Minoura, H., and Yamazaki, S.: Temperature dependence of secondary organic aerosol formation by photo-oxidation of hydrocarbons, Atmos. Environ., 37, 3413-3424, doi:10.1016/s1352-2310(03)00359-5, 2003.

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

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