

Response to Reviewer #2

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

Title: “Synergetic formation of secondary inorganic and organic aerosol: Influence of SO₂ and/or NH₃ in the heterogeneous process”

Revised Title: “Synergetic formation of secondary inorganic and organic aerosol: Effect of SO₂ and NH₃ 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 important revisions for the manuscript.** The line numbers in the response are from the revised manuscript.

The manuscript reports data related to the effect of SO₂ and NH₃ on aerosol formation from the oxidation of toluene in the presence on NO_x. 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 NH₃ or SO₂. This assumption is actually not true. In the presence of NH₃/SO₂, more inorganic aerosol (higher mass proportion) was generated than the experiment in the absence of NH₃/SO₂. The density of inorganic aerosol, mainly sulfate, nitrate and ammonium, is about 1.7 g/cm³, while it is about 1.4 g/cm³ for SOA. Therefore, the assumption of a same aerosol density would under estimate the increase effect of NH₃ or SO₂ 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 SO₂ and NH₃ 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 NH₃ 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 °C. 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, SO₂ and NH₃ were directly injected into the chamber from standard gas bottles using mass flow controllers. Before adding NH₃ into the chamber, NH₃ gas was passed through the inlet pipeline for about 15 minutes to reduce absorption within the line. The concentrations of NH₃ were estimated according to the amount of NH₃ introduced and the volume of the reactor. These experiments with NH₃ added to the chamber were referred to as NH₃-rich experiments in this study, since the concentrations of NH₃ were not measured and it was difficult to estimate the uncertainty of the calculated NH₃ concentration.”

Lines 205-209, Add: “The experiments were carried out at 30 °C with an initial RH of 50%. During the reaction, the temperature was kept nearly constant (30±0.5 °C) 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 NH₃ or SO₂ 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 SO₂ are needed. More information about SO₂ and a simple comparison between SO₂ and NH₃ 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 SO₂ 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 SO₂ in the world due to a large proportion of energy supply from coal combustion (Bauduin et al., 2016). Surface concentrations of SO₂ 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 SO₂ have decreased in most regions of China in recent years (Lu et al., 2010; Wang et al., 2015b), but high concentrations of SO₂ are still frequently observed. For example, the SO₂ concentration was as high as 43 ppb in the winter of 2013 in Jinan city (Wang et al., 2015a), while over 100 ppb SO₂ was observed in winter haze days during 2012 in Xi’an city (Zhang et al., 2015).”

Lines 83-85, Add: “Unlike SO₂, the emission of NH₃ 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 NO₂, O₃, 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 NH₃ is an important problem in this study. Due to the lack of analytical instruments, we were not able to measure the concentrations of NH₃ in the chamber. Alternatively, we used a mass flow controller and a stopwatch to control the added amount of NH₃ in the chamber. Then, we estimated the initial concentrations of NH₃ 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 NH₃ in the inlet pipeline (Before adding NH₃ into the chamber,

NH₃ 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 NH₃ 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 NH₃ gas in the chamber (As we mentioned in the manuscript, there was NH₃ 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 NH₃ added), the amount of NH₃ that contributed to NH₄ salt was calculated to be about 4.8 ppb. Besides, according to the equilibrium between aerosol (NH₄NO₃+(NH₄)₂SO₄) and gas phase (NH₃+HNO₃+H₂SO₄), the gas phase NH₃ 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 NH₃ 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, SO₂ and NH₃ were directly injected into the chamber from standard gas bottles with mass flow controllers. Before adding NH₃ into the chamber, NH₃ gas was passed the inlet pipeline for about 15 minutes to reduce the absorption. The concentrations of NH₃ were then estimated according to the introduced amount of NH₃ and the volume of the reactor. These experiments with NH₃ added to the chamber were referred as NH₃-rich experiments in this study since the concentrations of NH₃ were not measured and it was difficult to estimate the uncertainty of the calculated NH₃ 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 SO₂ and/or NH₃ in the heterogeneous process”

To: “Synergetic formation of secondary inorganic and organic aerosol: Effect of SO₂ and NH₃ 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, SO_2 reacted, NH_3 reacted and NO reacted, NO_x 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. These Figures has been added in the revised Supporting information.

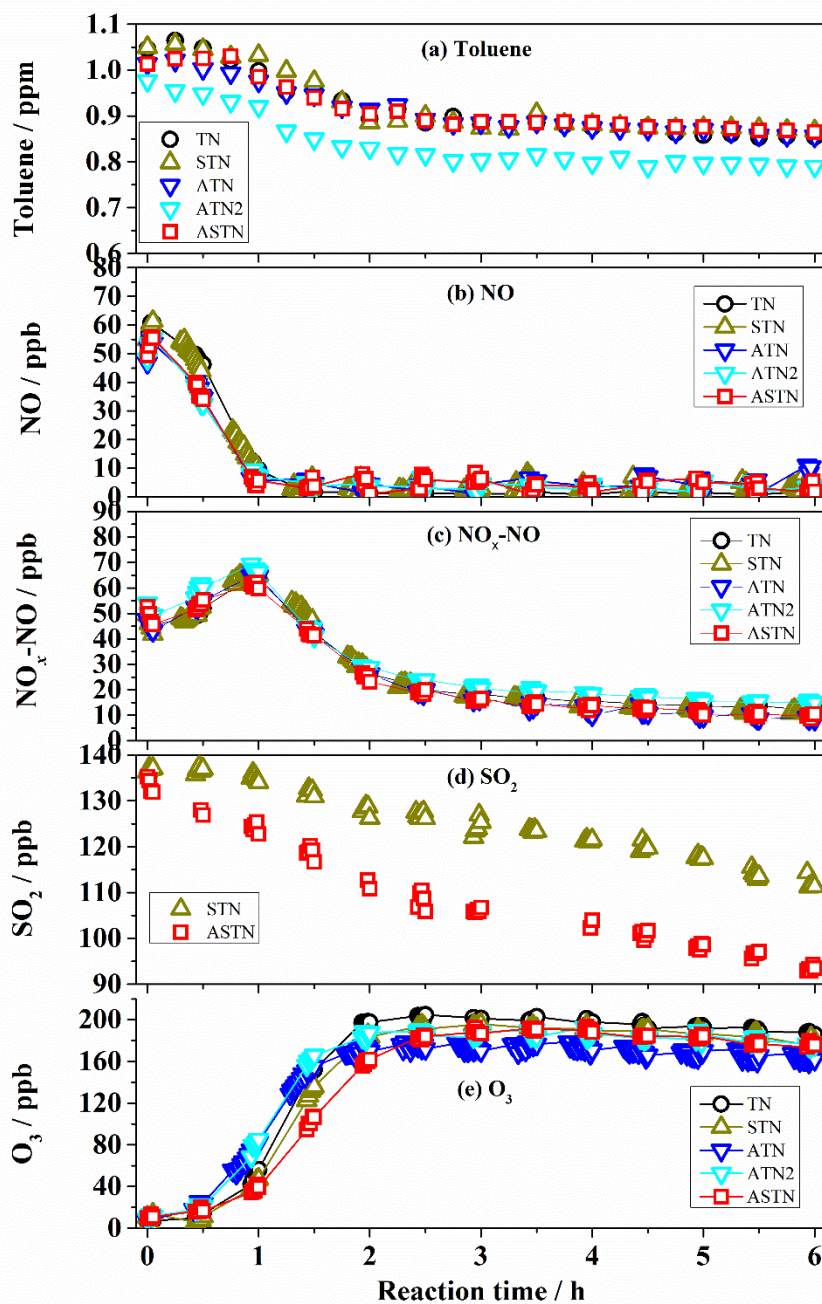


Figure R1. Time variations of gas-phase compounds in photooxidation of toluene/NO_x in the presence or absence of NH₃ and/or SO₂. The letters codes for the experiments indicate the introduced pollutants, i.e. “A” for ammonia, “S” for sulfur dioxide, “T” for toluene and “N” for nitrogen dioxide.

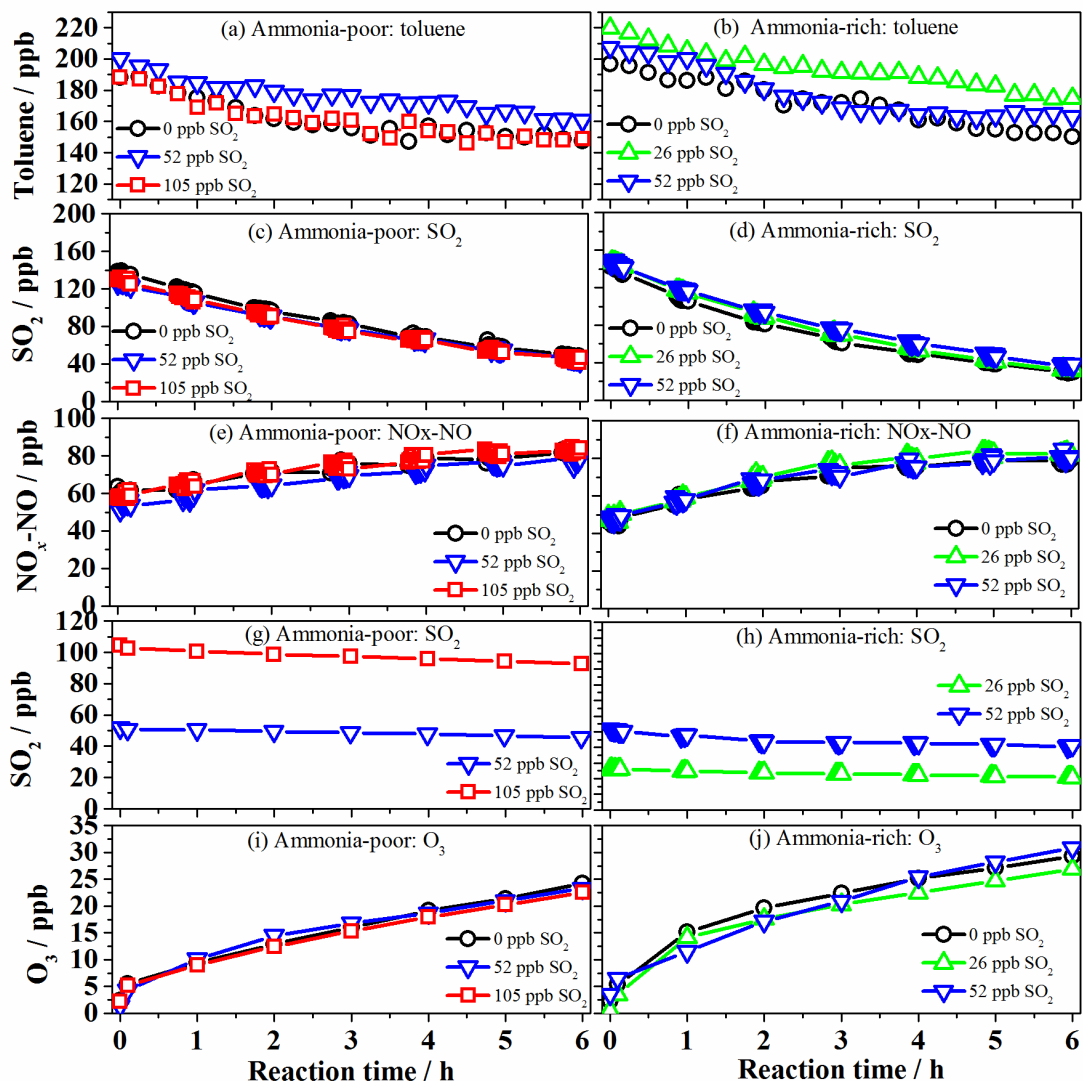


Figure R2. Time variations of gas-phase compounds in photooxidation of toluene/ NO_x with different concentrations of SO_2 under NH_3 -poor and NH_3 -rich conditions

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 over 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 °C. 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 °C with an initial RH of 50%. During the reaction, the temperature was kept nearly constant (30 ± 0.5 °C) 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: NH₃ 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 NH₃ in the chamber. Then, we estimated the initial concentrations of NH₃ based on the volume of the reactor. The solenoid three-way valve was placed on the inlet next to the chamber. Before adding NH₃ into the chamber, NH₃ gas was passed the inlet pipeline for about 15 minutes (not into the chamber through the valve) to reduce the absorption when adding NH₃ into the chamber.

Revision in the manuscript:

Lines 196-204, Add: "NO_x, SO₂ and NH₃ were directly injected into the chamber from standard gas bottles using mass flow controllers. Before adding NH₃ into the chamber, NH₃ gas was passed through the inlet pipeline for about 15 minutes to reduce absorption within the line. The concentrations of NH₃ were estimated

according to the amount of NH₃ introduced and the volume of the reactor. These experiments with NH₃ added to the chamber were referred to as NH₃-rich experiments in this study, since the concentrations of NH₃ were not measured and it was difficult to estimate the uncertainty of the calculated NH₃ 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. SOA yields were also calculated. The presence of SO₂/NH₃ had no obvious effect on the reacted amount of toluene. In Fig. 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 NH₃ and/or SO₂ 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 SO₂, SOA yields were higher in NH₃-rich condition compare to NH₃-poor condition. And there is a trend that SOA yield increased with increasing SO₂ concentrations. The presence of SO₂/NH₃ 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 NH₃ and/or SO₂. 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 SO₂ under NH₃-poor and NH₃-rich conditions

	Δ toluene ppb	Δ NO _x ppb	Δ SO ₂ ppb	Δ O ₃ ppb	SOA $\mu\text{g}/\text{m}^3$	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

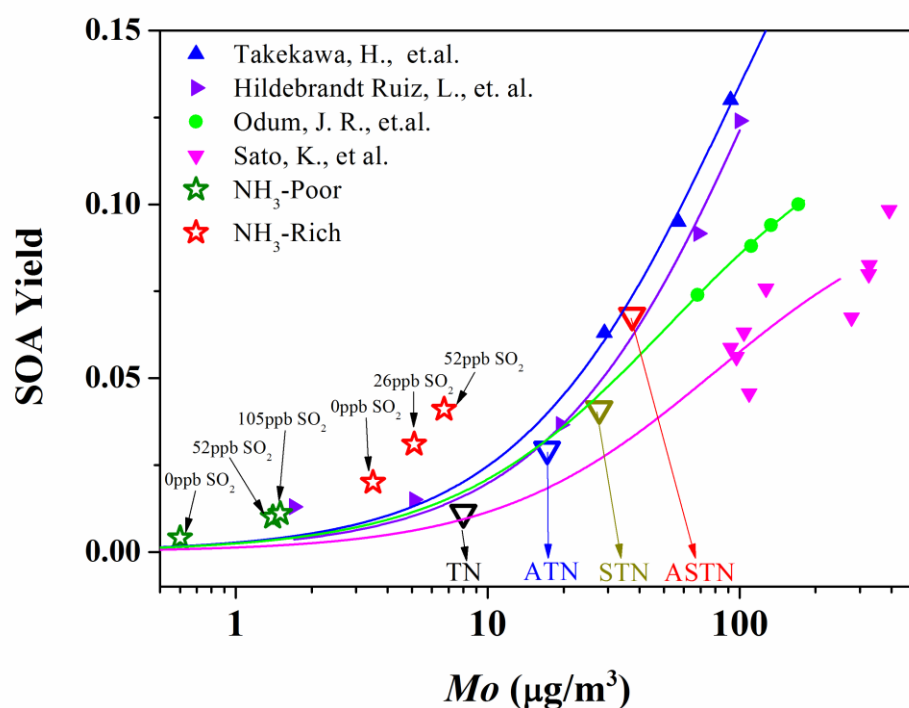


Figure R3. SOA yields in the experiments in this study and the comparison with literature results (Takekawa et al., 2003;Hildebrandt Ruiz et al., 2015;Odum et al., 1997;Sato et al., 2007)

Revision in the manuscript:

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 NH₃ and SO₂ 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°C 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 referring 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.

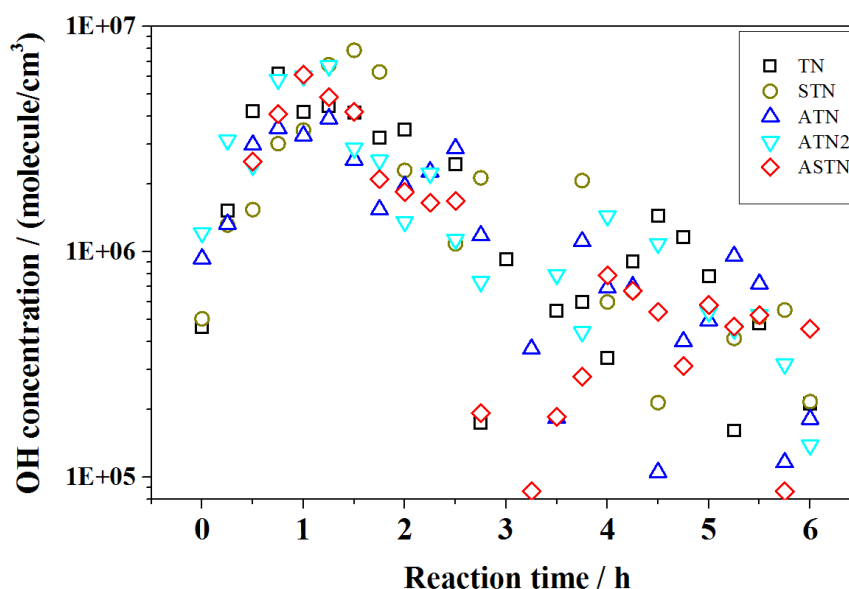


Figure R4. Time variations of OH radical concentrations in photooxidation of toluene/ NO_x in the

presence or absence of NH₃ and/or SO₂. 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.

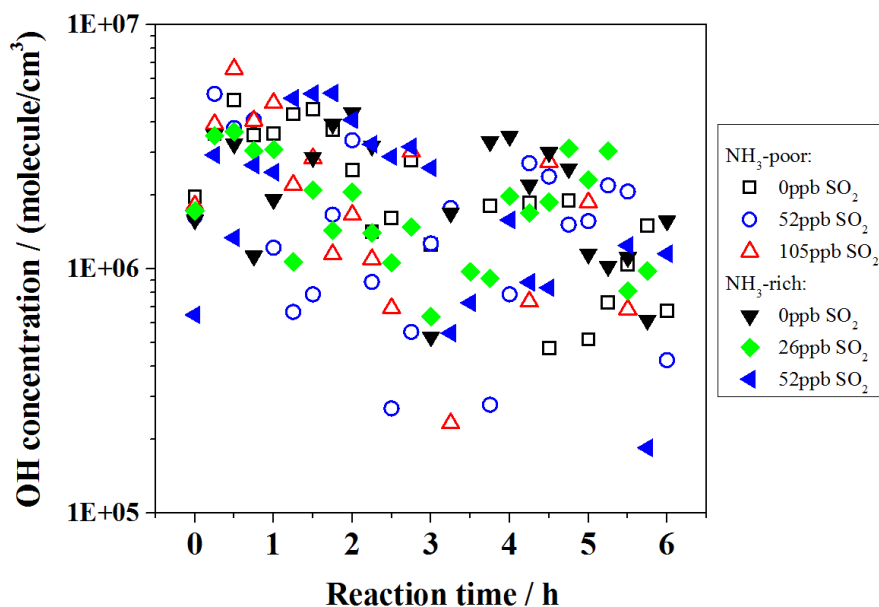


Figure R5. Time variations of OH radical concentrations in photooxidation of toluene/NO_x with different concentrations of SO₂ under NH₃-poor and NH₃-rich conditions

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 NH₄NO₃ was revised according to the simulation results from the AIM Aerosol Thermodynamics Model. The simulation results are summarized in Fig. R6. This figure has been added in the supporting information. The results showed that the concentrations of NH₃ gas and coexisted (NH₄)₂SO₄ both influenced the partition balance between NH₄NO₃ and HNO₃+NH₃ in the gas phase. The deposition of NH₃ gas and (NH₄)₂SO₄ were likely to shift balance to the gas phase and reduce the concentration of NH₄NO₃ salt. While the concentration of NH₄NO₃ salt seemed not to be affected by the deposition of NH₄NO₃, as long as the deposition was corrected

accurately. According to these results, some revision has been made in the revised manuscript.

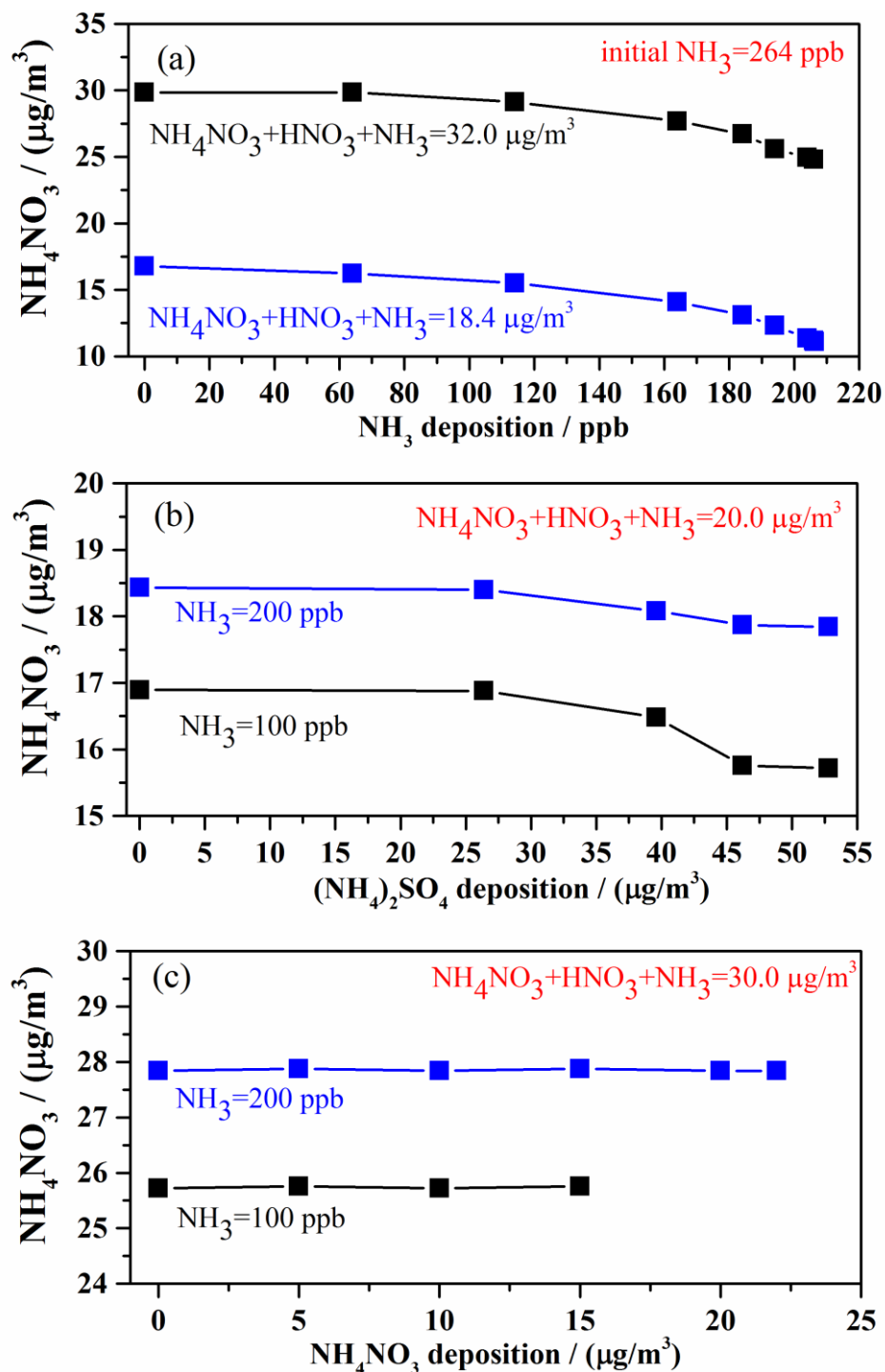


Figure R6. Concentrations of NH_4NO_3 salt as a function of the wall deposition of NH_3 , $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 based on the simulation results of the AIM Aerosol Thermodynamics Model

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 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 NH₃ in the experiment was likely to shift the partition equilibrium to the gas phase and reduce the concentration of NH₄NO₃ salt. In addition, the wall deposition of aerosols might also introduce some error in the concentrations of NH₄NO₃ salt, although wall deposition was corrected using an empirical function based on deposition rates of (NH₄)₂SO₄ aerosol with different sizes (Chu et al., 2012;Chu et al., 2014).”

Add Fig. R6 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, (NH₄)₂SO₄ was reported to deliquesce at RH lower than pure (NH₄)₂SO₄. (Meyer et al., 2009;Li et al., 2014). To avoid misunderstanding, the description was revised.

N₂O₅ was not measured in this study, but it was expected to be generated in the presence of NO₂ and O₃ in the experiments. Under the experimental conditions, the maximum formation velocity was calculated to be about 13 ppb/hour from gas phase reaction between NO₂ and O₃. The concentrations of NO₂ and O₃ 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 $0.1 \text{ m}^2/\text{m}^3$. 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 $0.05 \text{ m}^2/\text{m}^3$ suspended particles would generate $6 \text{ }\mu\text{g}/\text{m}^3$ 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, $(\text{NH}_4)_2\text{SO}_4$ 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 NH₃ were not measured due to lack of analytical instruments. Besides, as we mentioned in the manuscript, there was NH₃ 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 NH₃ was estimated to be around 8 ppb. With this in mind, the experiments carried out without NH₃ added were considered “NH₃-poor” experiments in this study, while experiments with NH₃ added were considered “NH₃-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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