Response to Reviewer 2's comments:

We thank the reviewer for the comments. Below are our responses to the comments and corresponding modifications to the manuscript.

1. OS vs. inorganic sulfate. OS and oligomers analyses are not quantitative, it is not easy to rely on their peak identifications to explain the difference in yields under wet and dry conditions.

We agree with the reviewer that the organosulfate and oligomer analyses based on the ESI mass spectra may not be quantitative. As mentioned in the manuscript, the negative mode in ESI is sensitive only to acidic species. Therefore, the effects of SO_2 on relative signal fractions and oxidation states observed in this work may only be valid for these species. Though we observed increased total signal fraction of organosulfate ions with increased SO_2 concentration, since no authentic standards were available for quantification, no conclusions can be drawn about the difference in organosulfate amounts between the two experiments.

However, our qualitative analyses by linking the ion drift time and the Kendrick mass defect to the molecular formula of each peak in the ESI spectra highlights the formation of organosulfates. And the number of the organosulfates that were identified increased with increasing SO_2 injection.

2. Aerosol acidity has been used heavily to explain the results. Need better, at least, semi-quantitative discussions, on aerosol acidity. Dissociation of H_2SO_4 under dry condition and influence of organics/SOAs on DRH of AS need to be discussed.

For aerosol acidity, please refer to the response to Comment 4 and Comment 7.

With regards to the influence of α-pinene and limonene SOA on the hygroscopicity of ammonium sulfate particles, Takahama et al. (2007) observed that SOA from α-pinene and limonene ozonolysis has negligible effect on the efflorescence transitions of ammonium sulfate particles. Smith et al. (2011) demonstrated that both the deliquescence and efflorescence of ammonium sulfate were minimally affected by SOA from α-pinene ozonolysis.

As discussed in Section 2.1 in the manuscript, under dry conditions, ammonium sulfate particles were generated from atomizer, followed by drying with silica gel diffusion dryers. The RH used in the experiments under dry conditions (~10%) were below the efflorescence relative humidity of ammonium sulfate. Therefore, we expect that particles remain in a solid phase with limited water content present. However, under humid conditions (~50%), no diffusion dryer was used before injecting ammonium sulfate particles, suggesting that those particles are in a liquid form with higher liquid water content compared to those seeds under dry conditions.

3. Line 230

For all the experiments in Figure 2, when all the limonene was consumed, the particle volume concentration seemed kept increasing, i.e., Exp.#7, dark blue markers vertically stacked at 30 ppb limonene. Does that mean that particle volume concentration kept increasing after limonene was completely consumed? This is inconsistent with Figure 1 that when all the limonene was consumed, the particle volume concentration reached a plateau.

Thanks for the comment. The particle volume concentration continued to increase even when the majority of limonene was consumed. Fig. 1R plots the formation of particles as a function of limonene consumption shown in Fig. 1 (during the first limonene injection). Increased particle formation was observed even when the consumption of limonene was close to completion. This continued increase of particle mass concentration was also observed in studies by Ng et al. (2006) and Zhang et al. (2006) and was attributed to the multi-generation (first- and second-generation) oxidation and significantly slower (rate-limiting) oxidation of the exocyclic double bond in limonene. However, it should be noted that both the first- and the second-generation reactions took place over the course of the experiment. The second-generation reaction of limonene SOA did not solely exist after limonene was completely consumed (i.e. after 30 ppb shown in Fig. 1R). The enhancement of particle volume concentration after the complete consumption of limonene varied slightly from experiment to experiment due to factors such as chamber mixing, and/or particle wall loss correction and/or varied experimental conditions. However, this difference could be minimized by calculating the overall SOA yields. As shown in Table 1, the overall SOA yields increased with increasing SO_2 concentrations.

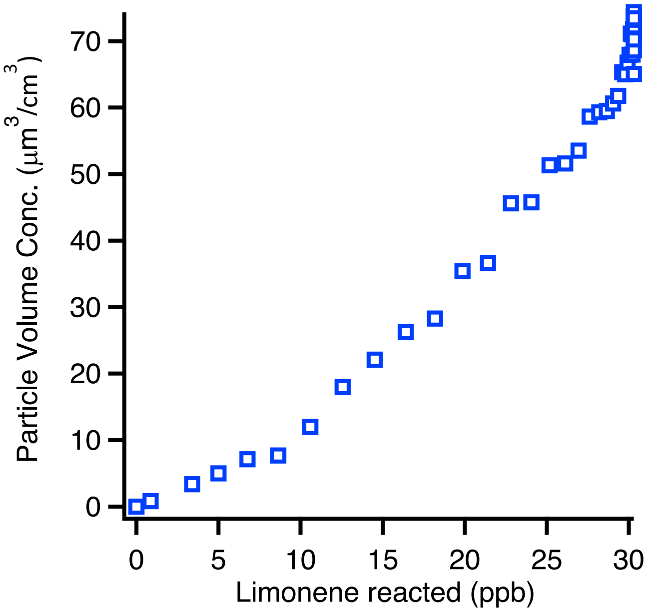

Figure R1 The relationship between particle volume concentration and limonene consumption shown in Fig. 1 (for the first limonene injection only). Increased particle volume concentration was observed even when limonene was completely consumed.

4. Line 235 & Line 245

The authors attribute the increased SOA formation to increased particle acidity. Experiments #1 - #10 were performed at RH below 16 %, where the particles might have less water. I'm not sure particle acidity is increased as it is a reflection of hydrogen activity, where aerosol water is needed. See comments earlier.

Enhanced SOA formation have been observed in the presence of acidic seeds under dry conditions (RH <= 20%) (Czoschke et al., 2003; Czoschke and Jang, 2006; Jang et al., 2002; Northcross and Jang, 2007). SOA yields from monoterpene ozonolysis were found to increase with increasing particle acidity.

We agree with the reviewer that under dry conditions, the particles might have less water. However, it should be noted that sulfuric acid is highly hydroscopic and it takes up water even at very low RH (Biskos et al., 2009; Seinfeld and Pandis, 2006). Condensation of sulfuric acid increases the liquid water content in the particle phase. This amount of water helps the dissociation of sulfuric acid and increases hydrogen ion activity in the particle phase, which enables acid-catalyzed reactions. Under humid conditions, though increased liquid water content may potentially increase the dissociation of sulfuric acid, it may also dilute the molarity of hydrogen ion in the particle phase. As for the hydrogen ion activity and the pH value under dry conditions, please refer to Comment 7 for detailed discussion.

5. Line 270

SO_2 can dissolve into the aqueous droplets, what is its contribution to the measured SO_2 gas consumption?

Dissolution of SO_2 into the particles is governed by Henry's law. We calculated the dissolved SO_2 in two scenarios (acidic and neutral). pH = 5 is used for the calculation in acidic scenario because the pH for pure ammonium sulfate particle was estimated to be ~5 according to E-AIM Aerosol Thermodynamics Model (Model II, Clegg et al., 1998).

The effective SO_2 Henry's law constants $H^*_{S(IV)}$ under these two scenarios are taken to be 1×10^3 M atm^{-1} (pH = 5) and 2×10^5 M atm^{-1} (pH = 7), respectively (Seinfeld and Pandis, 2006). Assuming an initial SO_2 concentration of 600 ppb (the maximum SO_2 concentration used in this study), the concentrations of dissolved sulfur [S(IV)] in the aqueous phase can be calculated as 0.60 mM (pH = 5) and 120 mM (pH = 7). Assuming that the entire particle is aqueous, the aqueous mass concentration would be ~100 µg/m^3, and dissolution of SO_2 would only result in a decrease of 1.5×10^{-3} ppb (pH = 5) and 0.3 ppb (pH = 7) gaseous SO_2, which is at least one order of magnitude less than observed. Therefore, we conclude that the loss of SO_2 into particle phase solely due to dissolution is negligible.

6. I understand the authors conducted flow tube experiments in order to collect more products for analysis. But I'm not sure the flow tube experiments are exactly comparable to the chamber ones. The key issue is that OH scavenger is not added in the flow tube experiments. It is more efficient in producing peroxides in OH system than in O_3 system due to the RO_2 + HO_2 reactions. Therefore, the bulk experiments using the LSOA extracts without scavenger will bias the absorption of SO_2 high compared with the real chamber SOA material where OH scavenger is present.

Thanks for the comment. OH scavenger was used in all the experiments, both in the flow tube and the chamber experiments. Therefore, the effect of OH on SOA formation in the flow tube was minimal. We apologize for not mentioning it clearly in the manuscript.

We have added the following content into Section 2.2:

"To collect sufficient SOA mass for offline chemical analysis, SOA was also produced in a quartz flow tube by reacting limonene or α-pinene with ozone (~3 ppm) in the presence or absence of SO_2 under dry (10-13% RH) and humid (55-60% RH) conditions. The flow tube has a diameter of 10.2 cm and length of 120 cm, and the residence time in the flow tube is 4 min. Cyclohexane was used as OH scavenger. Limonene/cyclohexane (1:1500 v/v) and α-pinene/cyclohexane solution (1:500 v/v) was prefilled in a 1mL syringe (Hamilton) and injected into the flow tube using a syringe pump (Legato 100, KDS)."

7. Line 300

Even H_2SO_4 can be formed, I'm not sure in terms of the fate of "Sulfur", which is formed more significantly H_2SO_4 and OS? This is related to the mechanism/yield of SOA formation under dry condition. The authors stated aerosol acidity increased SOA yield but what is the acidity of aerosols in dry condition? And the authors did observe quite some OS molecules, will this be the major reason for increased SOA yield? Please clarify.

Thanks for the comments. In this study, the formation of both sulfuric acid and organosulfates were observed, as displayed in the ESI spectra in Fig. S5 and the peak assignments of sulfur-containing ions in Table S1. For example, m/z 96.96 (HSO_4^-) and m/z 194.93 ($H_2SO_4 \cdot HSO_4^-$) show the evidence of the formation of sulfuric acid. This observation is consistent with the results from Sipilä et al. (2014) who also observed efficient sulfuric acid formation from monoterpene ozonolysis with SO_2.

With regards to the contribution of organosulfates to SOA mass, Iinuma et al. (2007) demonstrated that organosulfates produced from limonene ozonolysis under acidic conditions contribute at least as much as the first- and second-generation oxidation products to SOA mass. However, to what extent organosulfates contribute to the total particle-phase sulfur and SOA mass in this study is unknown without authentic standards. Further study is in progress in this group to quantify organosulfate formation using synthetic standards.

In terms of aerosol acidity under dry conditions in this study, we did a simple estimation taking Exp. #6 as an example (both of SO_2 injection concentration and seed particle loading in Exp. #6 are in the middle range of all the experiments). Assuming all the consumed SO_2 resulting in sulfuric acid formation in the particle phase, the formed sulfuric acid in the particle phase is calculated to be 0.24 $\mu mol/m^3$. Ammonium sulfate seed concentration in Exp. #6 is 0.88 $\mu mol/m^3$ with a density of 1.77 g/cm^3. Based on the results from E-AIM Aerosol Thermodynamics Model (Model II; Clegg et al., 1998), the pH was then calculated using the following equations without considering the partitioning of NH_3 between the gas phase and the aqueous phase (Clegg et al., 1998):

$$pH = -\log [M_{H^+} \cdot \gamma_{H^+}]$$

where M_{H^+} and γ_{H^+} are the molarity and molarity-based activity coefficient of hydrogen ion in the aqueous phase, respectively.

Without taking the contribution of organic acids into account, the pH value was estimated to be ~1.2 at 10% RH, which is very acidic. And it is noted that if the partitioning of NH_3 is considered, the pH value will be even lower (i.e., even higher acidity).

8. Line 345

As the author said, aqueous reaction of SO_2 with O_3 in forming sulfate is proved to be quite efficient. What is the reason that SO_2 is not reacted efficiently with O_3 in these experiments? Any estimates for the rate constant of SO_2+O_3 in this experiment?

With regards to the effect of ozone, we have conducted control experiment by adding SO_2, ozone, formic acid and ammonium sulfate into the chamber, as shown in Fig. S4A in the Supporting Information. No significant decrease of SO_2 was observed, indicating that dissolved ozone in the aqueous phase is not an important sink of SO_2 under the conditions in this study. This is likely because that ammonium sulfate seed is slightly acidic (pH ~ 5) that is less favorable for SO_2 oxidation by ozone in the aqueous phase. According to Seinfeld and Pandis (2006), the rate of SO_2 and ozone reaction in the aqueous phase at pH = 4-5 is at the level of 10^6 M^{-1} s^{-1}. In addition, unlike SO_2 oxidation in a cloud droplet, the liquid water content in ammonium sulfate particles is limited. Therefore, little SO_2 depletion was observed.

The following content has been modified into Section 3.3.3:

"…suggesting that reactions between SO_2 and ozone either in the gas or particle phase have negligible effects on SO_2 consumption. This is likely because that ammonium sulfate seed is slightly acidic. The pH value calculated based on the E-AIM Aerosol Thermodynamic Model for ammonium sulfate at 50% RH is ~5 (Clegg et al., 1998; Wexler and Clegg, 2002). Under this pH condition, SO_2 oxidation by ozone is slow and less favorable in the aqueous phase. It is noted that the pH value was estimated without considering the partitioning of trace gases (i.e. NH_3). Even lower pH (i.e. higher acidity) would be yielded if taking into account this effect. In addition, unlike SO_2 oxidation in a cloud droplet, the liquid water content in ammonium sulfate particles is limited. Therefore, little SO_2 depletion was observed."

9. Line 370
What is the resolution of the mass spectrometers? I wonder if it can give four decimals for the detected m/z.

The resolution of the time-of-flight mass spectrometer is around 3500–4000 FWHM at m/z 250. When performing mass calibration, the accuracy of each calibrated mass and the overall calibration was constrained within 5 ppm. For example, if an ion of calculated m/z 250 is observed at m/z 250.001, the mass accuracy is 4 ppm. Therefore, the mass detected by our instrument can be accurate to the third decimal place, with the fourth decimal point estimated.

This information of the mass spectral resolution and mass accuracy has been updated in the manuscript in Section 2.3:

"Particle composition was analyzed using electrospray ionization-ion mobility spectrometry-high resolution time-of-flight mass spectrometry (ESI-IMS-ToF, TOFWERK, hereafter referred to as IMS-TOF) with a mass spectral resolution of 3500-4000 FWHM at m/z 250. Mass calibration was performed before each measurement with a mass accuracy within 5 ppm of each calibration chemical. Details of the IMS-TOF technique are described in recent publications by Krechmer et al. (2016) and Zhang et al., (2016)."

10. Line 420
"first generation of oxidation products from alpha-pinene ozonolysis may be too volatile to condense…"
There are quite some studies (i.e., Ehn et al., Nature, 2014) showing that first generation of oxidation products were supposed to be HOMs, which are of extremely low vapor pressures and can condense easily. Please explain.

Thanks for the comment.

We have corrected the statements in the manuscript (Section 3.6):

"Limonene has two double bonds. If SO_2 prevents oligomerization of the first-generation products, these products can still react further with ozone to add another oxidized functional groups to form condensable products. As a comparison, α-pinene only have one double bond. The presence of SO_2 reduces oligomerization and limits enhancements in SOA yields."

11. Line 455

"We present evidence to suggest that HSO3- can further react with organic peroxides produced from monoterpene ozonolysis" I don't think the authors give any explanation before line 455 about reaction between HSO3- with organic peroxides. The authors only show the evidence that organic peroxides decreased when bubbling SO2 into the solution. Please explain the reaction mechanism of HSO3- with organic peroxides.

Thanks for the comment. It is well known that dissolved SO_2 can be oxidized by peroxides (e.g., H_2O_2, methylhydroxyperoxide and peroxyacetic acid) to form sulfate (Lind et al., 1987), as also shown in the following equations:

$$HSO_3^- + H_2O_2 + H^+ \longrightarrow SO_4^{2-} + 2H^+ + H_2O$$

$$HSO_3^- + CH_3OOH + H^+ \longrightarrow SO_4^{2-} + 2H^+ + CH_3OH$$

$$HSO_3^- + CH_3C(O)OOH + H^+ \longrightarrow SO_4^{2-} + 2H^+ + CH_3COOH$$

The bubbling experiments conducted in this study have shown significant depletion of the total peroxide content when bubbling SO_2 into either limonene SOA extract or pure organic peroxide, suggesting that peroxides in SOA are reactive to dissolved SO_2. This is consistent with our experimental observations that greater SO_2 depletion was observed under humid conditions where more dissolved SO_2 was present. Further investigation is undertaken in this group to elucidate the mechanisms and kinetics of SO_2/peroxide reaction.

Reference

Biskos, G., Buseck, P. R. and Martin, S. T.: Hygroscopic growth of nucleation-mode acidic sulfate particles, J. Aerosol Sci., 40(4), 338–347, doi:10.1016/j.jaerosci.2008.12.003, 2009.

Clegg, S. L., Brimblecombe, P. and Wexler, A. S.: Thermodynamic model of the system $H^+-NH_4^+-SO_4^{2-}-NO_3^--H_2O$ at tropospheric temperatures, J. Phys. Chem. A, 102(12), 2137–2154, doi:10.1021/jp973042r, 1998.

Czoschke, N. M. and Jang, M.: Acidity effects on the formation of α-pinene ozone SOA in the presence of inorganic seed, Atmos. Environ., 40(23), 4370–4380, doi:10.1016/j.atmosenv.2006.03.030, 2006.

Czoschke, N. M., Jang, M. and Kamens, R. M.: Effect of acidic seed on biogenic secondary organic aerosol growth, Atmos. Environ., 37(30), 4287–4299, doi:10.1016/S1352-2310(03)00511-9, 2003.

Iinuma, Y., Müller, C., Böge, O., Gnauk, T. and Herrmann, H.: The formation of organic sulfate esters in the limonene ozonolysis secondary organic aerosol (SOA) under acidic conditions, Atmos. Environ., 41(27), 5571–5583, doi:10.1016/j.atmosenv.2007.03.007, 2007.

Jang, M., Czoschke, N. M., Lee, S. and Kamens, R. M.: Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions, Science, 298(5594), 814–817, doi:10.1126/science.1075798, 2002.

Lind, J. A., Lazrus, A. L. and Kok, G. L.: Aqueous phase oxidation of sulfur(IV) by hydrogen peroxide, methylhydroperoxide, and peroxyacetic Acid, J. Geophys. Res., 92(D4), 4171–4177, doi:10.1029/JD092iD04p04171, 1987.

Ng, N. L., Kroll, J. H., Keywood, M. D., Bahreini, R., Varutbangkul, V., Flagan, R. C., Seinfeld, J. H., Lee, A. and Goldstein, A. H.: Contribution of first- versus second-generation products to secondary organic aerosols formed in the oxidation of biogenic hydrocarbons, Environ. Sci. Technol., 40(7), 2283–2297, doi:10.1021/es052269u, 2006.

Northcross, A. L. and Jang, M.: Heterogeneous SOA yield from ozonolysis of monoterpenes in the presence of inorganic acid, Atmos. Environ., 41(7), 1483–1493, doi:10.1016/j.atmosenv.2006.10.009, 2007.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to climate change, 2nd Ed., Wiley: New York., 2006.

Sipilä, M., Jokinen, T., Berndt, T., Richters, S., Makkonen, R., Donahue, N. M., Mauldin III, R. L., Kurtén, T., Paasonen, P., Sarnela, N., Ehn, M., Junninen, H., Rissanen, M. P., Thornton, J., Stratmann, F., Herrmann, H., Worsnop, D. R., Kulmala, M., Kerminen, V.-M. and Petäjä, T.: Reactivity of stabilized Criegee intermediates (sCIs) from isoprene and monoterpene ozonolysis toward SO_2 and organic acids, Atmos. Chem. Phys., 14(22), 12143–12153, doi:10.5194/acp-14-12143-2014, 2014.

Smith, M. L., Kuwata, M. and Martin, S. T.: Secondary organic material produced by the dark ozonolysis of α-pinene minimally affects the deliquescence and efflorescence of ammonium sulfate, Aerosol Sci. Technol., 45(2), 244–261, doi:10.1080/02786826.2010.532178, 2011.

Takahama, S., Pathak, R. K. and Pandis, S. N.: Efflorescence transitions of ammonium sulfate particles coated with secondary organic aerosol, Environ. Sci. Technol., 41(7), 2289–2295, doi:10.1021/es0619915, 2007.

Zhang, J., Huff Hartz, K. E., Pandis, S. N. and Donahue, N. M.: Secondary organic aerosol formation from limonene ozonolysis: Homogeneous and heterogeneous influences as a function of NOx, J. Phys. Chem. A, 110(38), 11053–11063, doi:10.1021/jp062836f, 2006.