

## Response to comments from referee #2

We thank the reviewer for the constructive comments, with which we have addressed point-by-point and modified the manuscript accordingly as below.

### General comments

Wang et al. ran a series of laboratory experiments to explore the uptake of SO<sub>2</sub> onto aerosols containing organic peroxides. They systematically explored several factors, including RH, peroxide types, peroxide content, and aerosol pH. This study addresses an important topic, and the experiments provide insights into the factors that control the heterogenous conversion of SO<sub>2</sub> to sulfate. This study is well within scope of the journal. My comments are below.

### Major comments:

1. How good was the reproducibility of the experiments (data shown in Figure 2-6)? I am a little concerned about the small statistics in these experiments that the authors used to conclude any trend. Were there any replicate experiments done?

### Response:

Thank you for the comments. Exp.10-12 (Table S1) were performed under similar conditions, and a standard deviation of 26% was found among the three different measurements. The trends of  $\gamma_{SO_2}$  reported in Figure 4-6 were based on a log scale. The measured deviation is less likely to change our conclusions.

As for the accuracy,  $\gamma_{SO_2}$  was solved from equation (1)  $-\frac{d[SO_2]}{dt} = \frac{1}{4}\gamma_{SO_2}A\bar{c}[SO_2]$ , where the uncertainties in measured  $y_{SO_2}$  can be propagated from estimated instrument accuracy in both A (particle surface area) and [SO<sub>2</sub>]. The SO<sub>2</sub> analyzer (Model 43i, Thermo Fisher Scientific) was calibrated using a Multi-Gas Calibrator (Model 146i, Thermo Fisher Scientific) and a standard gas mixture (32 ppm SO<sub>2</sub>, 610 ppm CO and 10.06% CO<sub>2</sub> balanced in N<sub>2</sub>, Linde) with the accuracy estimated to be 1% of full scale. We have propagated the uncertainties for each experiment with corresponding updates in table S1 and Figure 2-6.

### Minor comments:

1. Were the experiments conducted in a dark chamber? Could peroxides undergo photolysis?

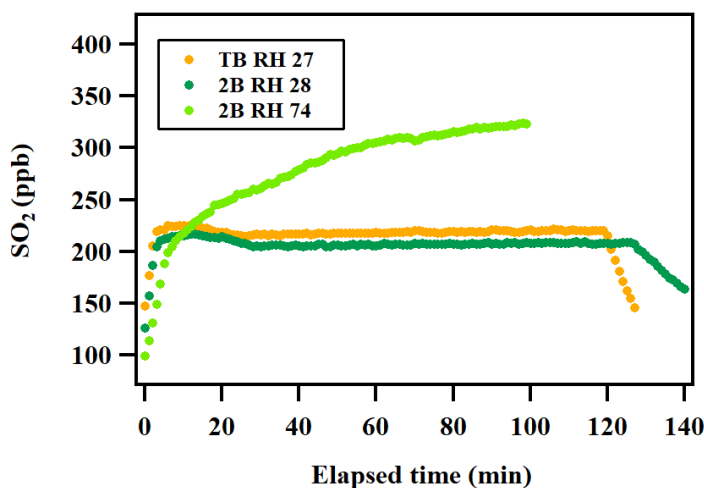
**Response:**

Experiments in the current study were performed in the 1 m<sup>3</sup> chamber located in our lab, which is covered with a piece of black fabric. Thus, our experiments were performed under dark conditions with negligible effects from photolysis on peroxides.

2. Line 187: Does the repartitioning of SO<sub>2</sub> from the wall depend on the type of organic peroxide in the chamber?

**Response:**

Thanks for the comments. Different types of organic peroxides have different vapour pressures and reactivities towards SO<sub>2</sub>, which might influence the repartitioning rate of SO<sub>2</sub> from the chamber wall during our experiments. We believe different types of organic peroxides might impact the repartitioning of SO<sub>2</sub> from the chamber wall, but it also depends on the amount of peroxides available during the experiments. We have performed SO<sub>2</sub>-organic peroxide vapour experiments under similar RH conditions (TB peroxide, RH 27%; 2B peroxide, RH 28%). As shown in the figure below, the SO<sub>2</sub> repartitioning rate for 2B peroxide and TB peroxide have no significant difference under similar RH conditions/initial SO<sub>2</sub> mixing ratios.



However, a significant enhancement of the SO<sub>2</sub> repartitioning rate was observed when the relative humidity increased from 28% to 74% for 2B peroxide (similar initial mixing ratios). As a result, the potential effects coming from peroxide types on the SO<sub>2</sub> repartitioning rate could be much less significant than that from relative humidity under the experimental conditions in the current study.

3. Line 208-line 209: “The average molecular mass for aerosol was assumed based on the chemical composition in order to calculate the molar fraction of total peroxides”. The authors need to provide more details on how this was done, especially for the SOA particles. How were the chemical composition determined for SOA? What were the molar fractions of peroxides in the SOA particles?

**Response:**

Since the chemical composition of SOA is more complicated than the peroxide/ammonium sulfate aerosol, there exist large uncertainty in estimating the molar of total SOA molecules. As a result, the current study didn't measure the peroxide molar fraction in SOA samples. In this study, we measured the molar fraction of peroxides in the peroxide/ammonium sulfate mixed aerosol. Based on the initial mixing ratio (2:1) and the molecular mass of peroxide/ammonium sulfate, we can estimate the averaged molar of the aerosol as:

$$\text{Molar fraction of peroxide} = \frac{N_{\text{peroxide}}}{N_{\text{aerosol}}} = N_{\text{peroxide}} \frac{M_{(NH_4)_2SO_4} f_{(NH_4)_2SO_4} + M_{\text{peroxide}} f_{\text{peroxide}}}{m_{\text{aerosol}}}$$

where  $m_{\text{aerosol}}$  is the weighed aerosol mass on the filter;  $M_{(NH_4)_2SO_4}$  and  $M_{\text{peroxide}}$  are the molecular mass of ammonium sulfate and peroxide, respectively;  $f_{(NH_4)_2SO_4}$  and  $f_{\text{peroxide}}$  are the initial molar fraction of ammonium sulfate and peroxide;  $N_{\text{peroxide}}$  and  $N_{\text{aerosol}}$  are the measured peroxide molar and calculated aerosol molar, respectively. The corresponding information has been added the manuscript.

Line 215-224:

“...An average molecular mass for seed particles (SOA + ammonium sulfate) was assumed based on the chemical composition in order to calculate the molar fraction of total peroxides using the following equation:

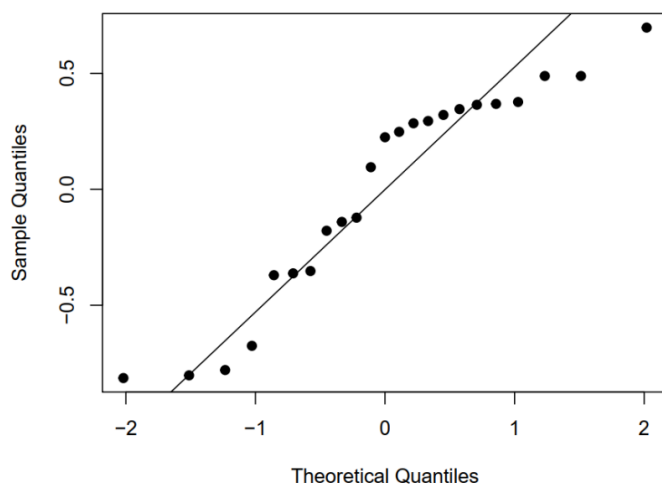
$$\text{Molar fraction of peroxide} = \frac{N_{\text{peroxide}}}{N_{\text{aerosol}}} = N_{\text{peroxide}} \frac{M_{(NH_4)_2SO_4} f_{(NH_4)_2SO_4} + M_{\text{peroxide}} f_{\text{peroxide}}}{m_{\text{aerosol}}}$$

where  $m_{\text{aerosol}}$  is the weighed aerosol mass on the filter;  $M_{(NH_4)_2SO_4}$  and  $M_{\text{peroxide}}$  are the molecular mass of ammonium sulfate and peroxide, respectively;  $f_{(NH_4)_2SO_4}$  and  $f_{\text{peroxide}}$  are the initial molar fraction of ammonium sulfate and peroxide;  $N_{\text{peroxide}}$  and  $N_{\text{aerosol}}$  are the measured peroxide molar and calculated aerosol molar, respectively...”

4. Figure S9: the residual distribution does not look like a normal distribution.

**Response:**

Thank you for the comment. A quantile-quantile plot can be made based on the multi-linear regression (MLR) built in the current study. The sample data should fall on the diagnostic line for an ideal normal distribution. An evenly distributed residual points can be found around the diagnostic line of the plot, indicating the normality of the residuals calculated from the MLR.



5. When using the SMPS to derive the average aerosol surface area, how well was the RH maintained in the SMPS flow? In other words, could there be a size change due to a change in RH in the SMPS that leads to an underestimation of the surface area?

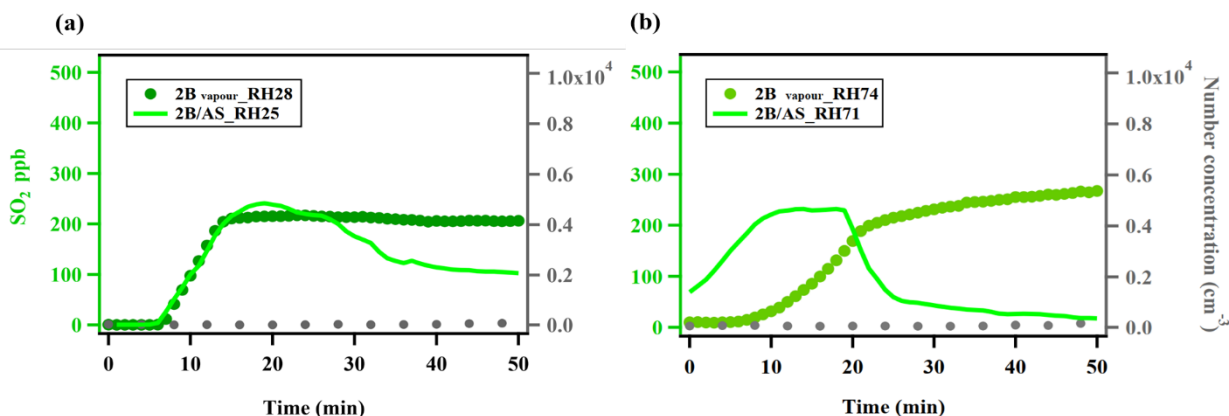
**Response:**

The custom-built SMPS in our lab uses the recirculated excess flow as the sheath flow during the measurements. We typically start SMPS at the very beginning of each experiment to measure the background aerosol concentration inside the chamber. After sampling from the chamber continuously for at least 30 minutes, we expect that the recirculation flow has a RH similar to what inside the chamber. As a result, we do not expect water evaporation inside the SMPS has a significant impact during our measurements.

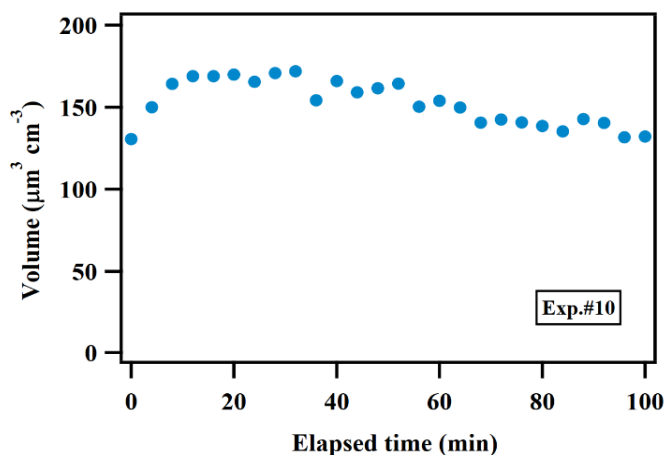
6. Could SO<sub>2</sub> interacts with peroxides on the wall during the experiments? This includes the peroxides in the particles deposited on the wall and the gas-phase peroxides that were deposited on the wall.

**Response:**

Thank you for the comments. There was no SO<sub>2</sub> decay when peroxide vapours were introduced into the chamber without particles under both low and high RH conditions, as shown in Figure S6a and S6b, respectively. This result indicates that there is no interaction between SO<sub>2</sub> and any gas-phase peroxides that immediately deposit on the chamber wall.



Another possibility is for peroxide/ammonium sulfate particles to deposit on the chamber wall, and for SO<sub>2</sub> to interact with deposited peroxides. However, most of the particles remain suspended (80-90%) during the  $\gamma_{SO_2}$  measurements (<10 minutes) as indicated by the following SMPS data for Exp.10.



Also, we did not observe any significant SO<sub>2</sub> loss at the beginning of each experiment before introducing aerosol into the chamber. Thus, SO<sub>2</sub> loss caused by deposited peroxides from the

previous experiments can also be excluded. The chamber was flushed overnight between each experiment with zero air to minimize carryover.