

Response to Reviewers' comments RC2 (Manuscript Ref. NO.: acp-2017-120)

We appreciate the referee for the time spent on our work and the constructive comments. The quality of our work has been improved greatly according to the thoughtful suggestions. The detailed responses to specific questions are presented in the following.

Reviewer #2:

Overall Comment

This manuscript represents a model for evaluating the importance of dust in sulfate formation, particularly in adding the kinetics and mechanism of heterogeneous photocatalytic reactions of SO₂ on mineral dust in the model. It is essential to consider the photooxidation of SO₂ in order to improve the accuracy of sulfate formation modeled in the atmosphere. Therefore, this study is of substantial interest. However, some major points should be carefully considered before it is published.

Comment 1: The indoor chamber data shows that, in the absence of ATD particles, [SO₄²⁻]_T at 55% RH is two times larger than that at 19% RH (Table 1 L1A, B and C), but when RH increases to 80%, the enhancement of [SO₄²⁻]_T is not distinct. Additionally, in the presence of ATD particles, [SO₄²⁻]_T is unexpectedly lower than that in the absence of ATD at 55% RH (Table 1 L3 and L1B), contrary to that at 80% RH (Table 1 L4 and L1C). However, these observations are not discussed in the manuscript and shown in the model.

Response: The data of Table 1 is obtained and reorganized from previous study (Park and Jang, 2016). In Table 1, [SO₄²⁻]_T is the observation of total sulfate concentration which is dependent of the initial SO₂, RH, dust concentration and the duration of the experiment. Figure 2 illustrates the impact of RH on uptake coefficient of SO₂ with and without UV light. The uptake coefficients which were determined using fitting the kinetic model to experimental data agree with those reported in the previous work by Park and Jang (2016). Exp. L1A, L1B and L1C in Table 1 were for SO₂ oxidation without dust particles and removed in the revised manuscript because they were not used for this paper.

Comment 2: In addition to react with SO₂ and NO₂, OH radicals produced on the surface of particles under UV conditions can undergo heterogeneous reaction with particles as well as self-reactions, resulting in the significant decrease of OH radicals participate in the oxidation of SO₂ and NO₂, and subsequently overestimating sulfate and nitrate formation in the model. Furthermore, in addition to compete OH radicals with SO₂, the presence of NO₂ can also react with SO₂ on the surface of particles to promote sulfate formation at high RHs as like in aqueous phase. However, these mechanisms were not considered in dust phase in the model (Table S1).

Response: In our model, the apparent rate constant of the formation of the dust-phase OH radicals is estimated using indoor chamber data. The synergistic effect of NO₂ on sulfate formation under

UV light is explained by the HONO production through the reaction of NO₂ with electrons or holes in dust phase (R16). HONO will then be decomposed via photolysis to form OH radicals (R17).

Comment 3: In Figure 3, it seems that modeled results are not in agreement with experimental observations at scenarios (a) without ATD particles and (b) low loadings of dust particles, especially for time-changing trends, meaning that the gas and aqueous phase reaction of SO₂ may be not well considered in the model. The authors should give explanations or speculations for this discrepancy in the manuscript.

Response: Please also fine the response to comment 5 from reviewer 1. We agree with the reviewer's comment. The estimation of aerosol water content was incorrect in the previous simulation due to the wrong input of aerosol acidity. By correcting this error, the model simulation of sulfate and nitrate has been greatly improved (Figs 3 and 4).

Comment 4: The authors estimated gas-particle partitioning constant of NO₂, K_{d,NO_2} , based on the relationship between the Henry's law constants of NO₂ and SO₂ (Eq. 15), but K_{d,O_3} is obtained from literature results (Eq. 14). Is it reasonable to estimate K_{d,NO_2} according to Eq. (15)? And why K_{d,NO_2} and K_{d,O_3} are set based on different method since previous studies have investigated the heterogeneous reaction of NO₂ on mineral dust as well? Moreover, in Section 3.2.1 the authors considered the influence of RH on K_{d,SO_2} , however, the expression of K_{d,NO_2} and K_{d,O_3} . The concentration otration of which is also closely related sulfate formation in the model, was not shown as a function of RH.

Response: The estimation of the gas-dust partitioning coefficient of ozone is scaled using the gas-dust partitioning of SO₂ reported in literature and the ratio of Henry' constant of SO₂ to ozone, similar to NO₂ (the first sentence of Sect. 3.3.1). The partitioning process of tracers on the dust phase is treated as absorption and desorption process (please also see the response to the Comment 1 of Referee 1). The absorption process is influenced by the aerosol water content. Thus, we assume that relative ratio of the Henry's law constants normalized by constant of SO₂, is applicable to estimate the gas-dust partitioning coefficient of tracers. For example, the Henry's law constants of both NO₂ and ozone are $1.2 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$ at 298K (Chameides, 1984) and they are 100 times smaller than that of SO₂ ($1.2 \text{ mol L}^{-1} \text{ atm}^{-1}$)(Chameides, 1984). All gas-dust partitioning coefficients are dependent of humidity (see Eq. 7, 14, and 15).

Minor Comments:

Comment 5: Page 4 Line 27 "The detail description" should be "The detailed description"

Response: It was corrected.

Comment 6: Page 4 Line 21 The indoor chamber data of this study was obtained from our recent laboratory study (Park and Jang, 2016), however, $[SO_4^{2-}]_T$ values shown in Table 1 is different

with Park and Jang (2016) reported. For example, Table 1 D1, L1 B and L8 in the manuscript corresponding to Table 1 D1, L1D and L8 in Park and Jang (2016), respectively.

Response: The model simulation was performed against the data points over the course of the chamber experiment. The $[\text{SO}_4^{2-}]_T$ values in Table 1 are sourced from the last data point in time for each chamber experiment that previously reported by Park and Jang (2016). In order to drive the model parameters, the outliers were removed for some data sets. When data was available, different simulation time were used for some data sets. Data sets L1A, L1B, and L1C for SO_2 oxidation without dust particles were not used in this study. Thus, they were removed from Table 1. For the heterogeneous autoxidation of SO_2 in the presence of ozone, the newly produced indoor chamber data (Data D4 in Table 1) was used to drive the AMAR model. As described in the response to comment 5 of reviewer 1, we found the contamination of the NO_2 tank by nitric acid. Thus, we removed data sets L6 and L7 from Table 1. To insure the quality of the data used for the model, the new outdoor chamber data sets were produced for heterogeneous oxidation of SO_2 in the presence of NO_x and they were applied to model development: data on 04/14/2017 in Table 2 for driving model parameters and two data sets on 04/25/2017 for model evaluation.

Comment 7: Page 7 Line 19 and 21 “ $\text{SO}_4^{2-}\text{-NH}_4^+\text{-H}_2\text{O}$ ” should be “ $\text{SO}_4^{2-}\text{-NH}_4^+\text{-H}_2\text{O}$ ”.

Response: This has been done.

Comment 8: Page 11 Line 17 Give more detailed description about k_{autoo} and k_{OH,O_2} derived from the indoor chamber data.

Response: In the dark condition, the formation of sulfate is mainly from the autoxidation of SO_2 . By fitting the predicted sulfate concentration to the experimental observation (D1- D3 in Table 1), the SO_2 autoxidation reaction rate constant ($k_{\text{auto}}, \text{s}^{-1}$) is semiempirically determined. Also see the last third sentence of Sect. 3.2.2. Using same approach, k_{OH,O_2} is first estimated using indoor chamber data (L1-L3 in Table 1) at RH 20%, 55% and 80% and then regressed against RH. Also see the last sentence of the second paragraph of Sect. 3.2.3.

Comment 9: Page 14 Line 21 “L7 and L8 in Table 1” should be “L6 and L7 in Table 1”.

Response: It was corrected. Thank you very much for your comments.