

## **Response to Reviewers' comments RC1 (Manuscript Ref. NO.: acp-2018-68)**

We appreciate the referees for the thoughtful and constructive comments on this manuscript. We believe that the quality of the manuscript has been greatly improved due to their valuable comments. The detailed responses to the specific questions from the reviewers were presented in the following.

### **Referee #1:**

#### **Overall Comment for Referee #1:**

Heterogeneous reactions of SO<sub>2</sub> and NO<sub>2</sub> with mineral dust affects the formation of nitrate and sulfate, and also impacts physicochemical properties of aerosol particles. Despite a number of studies carried out in the last 20 years, kinetics parameters have not been well constrained yet, especially under illuminated conditions. Yu and Jang carried out systematical laboratory work using an outdoor chamber, and developed a numerical model to describe these processes. The laboratory and modeling work is well done, and the manuscript is well written. I would like to recommend it for final publication after the following comments are adequately addressed.

**Comment 1:** Page 11, line1-2: why does GDD show higher photo-activation ability than ATD? Can this be explained by measured mineralogical components for these two types of dust?

**Response:** In order to respond to the reviewer's comment, we added some explanation to the end of section 3.3. "This difference in dust's photoactivation ability can be explained by the dissimilarity in their elemental compositions. As seen in the previous study by (Park et al., 2017), the elemental fraction of conductive metals such as iron and tritium appeared to be higher with the GDD of this study than reference ATD. The correlation between the metal compositions and photoactivation ability of dust particles needs to be explored in future."

**Comment 2:** Page 11, line 21-22: Why does GDD have higher buffering capacity than ATD? Is it related their carbonate contents? I would suggest the authors measure the carbonate (and iron oxides) contents for these two types of mineral dust.

**Response:** We added the explanation that why GDD has the higher buffering capacity than ATD (at the end of Sect. 3.4: Impact of the dust buffering capacity). This explanation reads now, “The difference in buffering capacity between GDD and ATD originates from the content of alkaline carbonates and partially metal oxides. The element analysis measured by (Park et al., 2017) showed that GDD contained the greater amount of alkaline metals (e.g., K, Ca, Na and Mg) and transition metals (e.g., Fe and Ti) than ATD. However, the reaction generally occurs on the surface of dust rather than the whole body of dust due to its solidity and tortuosity. Thus, the actual buffering capacity of dust is much smaller than the total amount of alkaline carbonates and metal oxides in bulk dust.”

**Comment 3:** Uptake coefficients have been widely used to describe the rates of heterogeneous reactions of mineral dust. Can the author derive uptake coefficients for their experiments under different conditions and then compared these values with those reported in previous studies?

**Response:** In order to respond to the reviewer, Sect. S2 was newly added into the revised supporting information and reads now.

The reactions of trace gases on the dust particles are traditionally expressed based on the first order reaction using the reactive uptake coefficient ( $\gamma$ ). In AMAR model, the oxidation of trace gases in dust phase includes the 1<sup>st</sup> order and the 2<sup>nd</sup> order reactions (Table S2). Furthermore, the rate constants of heterogeneous reactions are photocatalytically and dynamically changing through day and night. For convenience, we calculate  $\gamma$  of SO<sub>2</sub> and NO<sub>2</sub> using the gas-dust partitioning coefficients and the rate constants as follows (Yu et al., 2017),

$$\gamma_{dark,SO_2} = \frac{4K_{d,SO_2}k_{auto,SO_2}}{\omega_{SO_2}} \quad \text{for SO}_2 \text{ autooxidation} \quad (S1)$$

$$\gamma_{light,SO_2} = \frac{4K_{d,SO_2}(k_{photo,SO_2}[\text{OH}(d)]+k_{auto,SO_2})}{\omega_{SO_2}} \quad \text{for SO}_2 \text{ photooxidation} \quad (S2)$$

$$\gamma_{dark,NO_2} = \frac{4K_{d,NO_2}k_{auto,NO_2}}{\omega_{NO_2}} \quad \text{for NO}_2 \text{ autooxidation} \quad (S3)$$

$$\gamma_{light,NO_2} = \frac{4K_{d,NO_2}(k_{photo,NO_2}[\text{OH}(d)]+k_{auto,NO_2})}{\omega_{NO_2}} \quad \text{for NO}_2 \text{ photooxidation} \quad (S4)$$

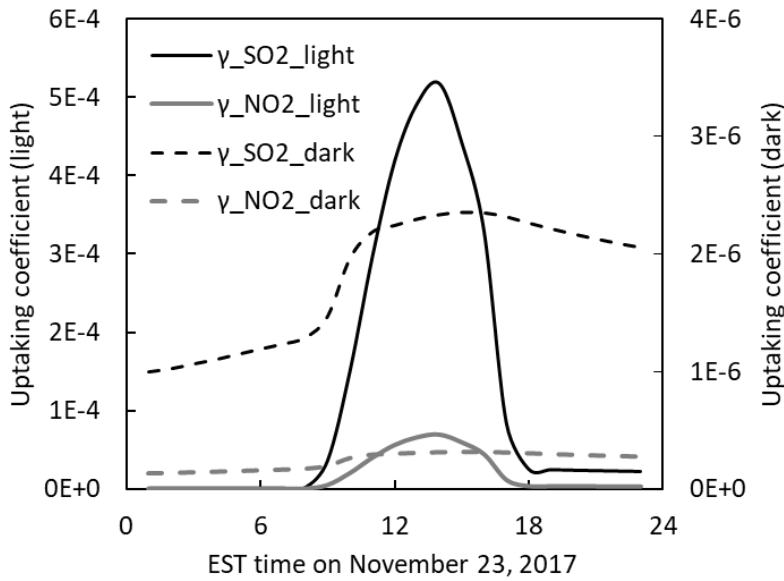
$\omega$  ( $\text{m s}^{-1}$ ) is the mean molecular velocity of gas species.  $k_{\text{auto}}$  ( $\text{s}^{-1}$ ) is the first order rate constant for autoxidation of  $\text{SO}_2$  or  $\text{NO}_2$  and  $k_{\text{photo}}$  ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) is the second order rate constant for photooxidation of  $\text{SO}_2$  or  $\text{NO}_2$  by OH radicals on dust particles.  $[\text{OH}(\text{d})]$  (molecule per cc of air) is the concentration of OH radicals on dust.  $K_d$  ( $\text{m}^3 \text{ m}^{-2}$ ) is the gas-dust partitioning coefficient and is calculated using the geometric surface concentration of airborne dust particles ( $A_{\text{dust}}$ ,  $\text{m}^2 \text{ m}^{-3}$ ).  $K_d$  can be calculated as,

$$K_d = \frac{[\text{gas}(\text{d})]}{[\text{gas}(\text{g})]A_{\text{dust}}} \text{ and} \quad (\text{S5})$$

$$K_d = \frac{k_{\text{up}}}{k_{\text{off}}}, \quad (\text{S6})$$

where  $[\text{gas}(\text{d})]$  and  $[\text{gas}(\text{g})]$  are the concentration of gas species in dust and gas phase, respectively.  $k_{\text{up}}$  and  $k_{\text{off}}$  is first calculated for  $\text{SO}_2$  and then scaled using Henry's law constant for other gaseous compounds (Yu et al., 2017). Figure S4 illustrates the time profile of  $\gamma$  under the ambient environmental conditions on November 23, 2017.

(a)



(b)

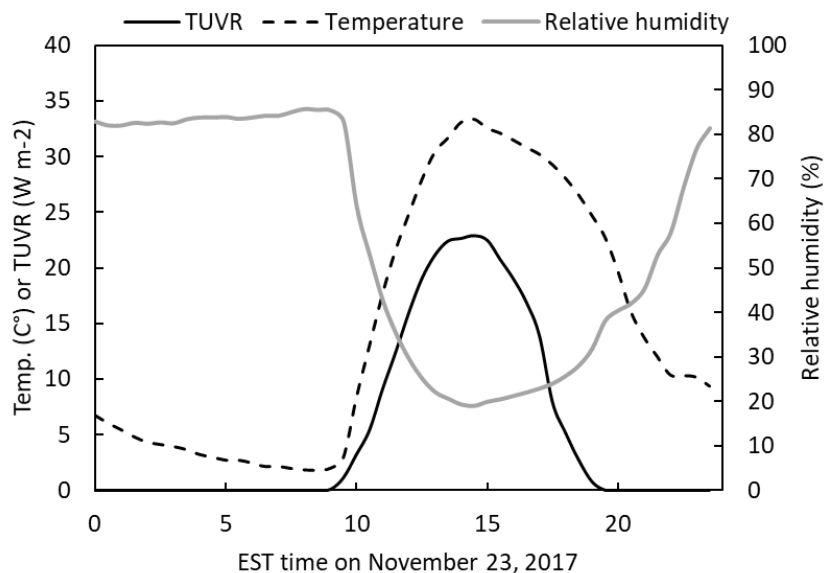


Figure S4. (a) Time profile of reactive uptake coefficient ( $\gamma$ ) of  $\text{SO}_2$  and  $\text{NO}_2$  on Gobi Desert Dust particles under ambient sunlight.  $\gamma$  is calculated using simulation results that are conducted with  $200 \mu\text{g m}^{-3}$  GDD particles, 40 ppb  $\text{SO}_2$  and 20 ppb  $\text{NO}_2$  under ambient conditions on 23 November 2017. The particle loss is not considered in the simulation. (b) Time profile of temperature ( $^\circ\text{C}$ ), relative humidity (%) and Total UV radiation (TUV,  $\text{W m}^{-2}$ ) on November 23, 2017 at Gainesville, Florida (latitude/longitude:  $29.64185^\circ/-82.347883^\circ$ ).

**Comment 4:** Page 2, line 11: Two important review papers on heterogeneous chemistry of mineral dust (Crowley et al., 2010; Tang et al., 2017) should be cited here.

**Response:** These two review papers have been cited in the revised manuscript.

**Comment 5:** Page 3, line 1 and line 8 (as well as a few other places in the manuscript): please change “tracers” to “trace gases”.

**Response:** Word “tracers” has been changed to “trace gases” in the revised manuscript.

**Reference:**

- Park, J., Jang, M., and Yu, Z.: Heterogeneous Photo-oxidation of SO<sub>2</sub> in the Presence of Two Different Mineral Dust Particles: Gobi and Arizona Dust, *Environ Sci Technol*, 51, 9605-9613, 10.1021/acs.est.7b00588, 2017.
- Yu, Z., Jang, M., and Park, J.: Modeling atmospheric mineral aerosol chemistry to predict heterogeneous photooxidation of SO<sub>2</sub>, *Atmos Chem Phys*, 17, 10001-10017, 2017.