Response to Reviewers' comments RC2 (Manuscript Ref. NO.: acp-2018-68)

We would like to thank the referee for the thoughtful comments on our work. We have carefully studied these comments and modified the manuscript. The detailed responses to the specific questions were presented in the following.

Referee #2:

Overall Comment for Referee #2:

This is an interesting study where the SO_2 and NO_x oxidation on mineral dust was investigated by means of simulation chambers, and simulated using the Atmospheric Mineral Aerosol Reaction (AMAR) model. Different dust particles (Gobi desert GDD and Arizona test dust ATD) were considered and their differences in reactivity and buffer capacity are discussed. Overall this paper is well written and addresses an important topic (mineral dust is an important category of aerosols), I would therefore recommend its publication once the authors have had a chance to discuss the comments (some are major) raised below.

Comment 1: I have a conceptual problem with the AMAR model, which takes into account processes in three phases: the gas phase, inorganic salt-seeded aqueous phase, and dust phase, implying that uptake is treated as absorption (according to Henry's law). However, for many studies involving the uptake of traces gases on mineral dust, a Langmuir type behavior has been reported, showing an adsorption behavior that could typically contradict the assumption of absorption. Also, water and several gases have been showing to exhibit competitive adsorption properties, going against the absorption assumption. Could it not be that this two assumption would correspond to two completely different humidity regimes? Maybe the authors could comment on that, and strengthen their assumptions in the manuscript.

Response: The path for uptake of gaseous species onto dust particles changes depending on the environmental conditions. For the dry dust particles at very low humidity (less than 20% RH), the uptake of trace gases may follow the adsorption and desorption processes. Gustafsson et al. (2005) reported that ATD particles showed a considerably high affinity to water that the water content in ATD particles, which was measured by the thermogravimetric method, ranged 2-4 monolayers based on the BET surface area under the ambient humidity (20%-80%). Therefore, our model approach begins with the absorption mode. As dust particles ages by the reaction of dust components (e.g., $CaCO_3$ and $MgCO_3$) with nitric acid, dust particles become even more hygroscopic (2 times higher than fresh dust).

In order to respond to the reviewer, we add the explanation of our assumption with absorption mode in the 1st paragraph of Sect. 3.1 and reads now, "Under ambient conditions (RH higher than 20%), studies showed that the water content in dust particles ranged 2-4 monolayers based on the BET surface area (Gustafsson et al., 2005;Yu et al., 2017). Therefore, we assume that the gas–dust partitioning of trace gases is governed by the absorption process."

Comment 2: Concerning the determination of the photoactivation parameters, have you checked how much is simply due to bleaching of the dye? That is a commonly reported issue in photocatalytic degradation of dyes on TiO_2.

Response: Figure S3 showed the degradation of the dye with and without dust. In the absence of dust particles, the decay of the dye was negligible (Fig. S3(c)). The sentence is added to the Sect 2.3 and reads, "The degradation of dye was significant only in the presence of dust particles".

Comment 3: In addition, the organic compound may also directly react with the electron-hole pair changing the reaction mechanism given in (R2) to (R5). Do you have any indication that this is occurring with the selected dye?

Response: We agree with the reviewer that the dye compound on dust may react with electrons-hole pairs. However, the amount of dye that is coated on dust particles (<1 µg per 200 µg of dust) is much smaller than water content (~ 50% of dry dust mass at 50% RH) on dust particles. Additionally, dust contacts with abundant oxygen molecules at the interface between gas and dust surface**.** If the primary process of the degradation of the dye is the reaction with an electron-hole pair, the degradation of dye is independent of humidity. As shown in Fig. 3, the estimated photoactivation parameters of both GDD and ATD particles increase with increasing humidity suggesting the importance of the role of water molecules to oxidize dye molecules. This explanation was also added to the end of Sect. 3.3 and reads now, "Additionally, the estimated photoactivation parameters of both GDD and ATD particles increase with increasing humidity suggesting the importance of the role of water molecules to heterogeneous oxidation reactions."

Comment 4: did you performed any elemental analysis of the two samples, or just for the GDD as ATD has a known composition? This should then provide a basis for explaining the difference in the photoactivation parameters.

Response: Please also find the response to the comment 1 from referee #1. The fraction of elements in the GDD and ATD samples were previously analyzed by Park et al. (2017) using energy dispersive spectroscopy (EDS). The measured fractions of Fe and Ti in GDD is noticeably higher than that in ATD, which may explain GDD's higher photoactivation ability. The correlation of photoactivation ability and the dust metal composition needs to be parameterized in future.

Comment 5: Sulfate is very often considered as a poison for surfaces, as it passivates very rapidly reactive surfaces. However, the outcome of the AMAR does show that (probably due to the absorption assumption discussed above). Have you built in some capacity to have surface saturation or not at all?

Response: We have thought about this issue. We also think that sulfuric acid coating can damage photocatalytic ability of dust due to the reaction with conductive metal oxides (e.g., iron oxide and tritium oxide). However, the modification of photocatalytic ability of dust may needs great amounts of sulfuric acid and reaction time. In general, chamber experiments are conducted in high concentrations (~100 ppb SO_2, ~40 ppb NO_x and ~400 µg cm^{-3} GDD for 10 consecutive hours) compared to the typical ambient condition (20 ppb SO_2 even for highly polluted urban areas). We did not observe the reduction in photoactivation ability by coating dust with sulfuric acid during our chamber experiments. In order to estimate the length of time to yield the similar amount of sulfate with chamber-generated sulfate, we simulate sulfate formation using AMAR model under the polluted ambient condition (20 ppb of initial SO_2, 40 ppb NO_x and 400 µg cm^{-3} of GDD under environmental conditions at January 13, 2016). Our calculation shows that it takes 5-6 days. The reported average lifetime of airborne dust particles is ~4.3 days (S. et al., 2004;Scheuvens and Kandler, 2014), though their lifetime varies with particle size. Hence, the most dust particles possibly settle down before they are significantly damaged by sulfuric acid coating. We conclude that dust's photocatalytic ability may not significantly changed during atmospheric aging. This explanation is added to the end of the 1st paragraph of Sect.5 Atmospheric implications and reads now.

"It is known that Inorganic acids can corrode metal oxides, but they first react with alkaline carbonates on dust. Additionally, the excess amount of sulfuric acid beyond the dust buffering capacity can be titrated by ammonia, which is ubiquitous in ambient air. Thus, the acidity of dust particles may not be high enough to damage the photocatalytic ability of mineral dust particles under ambient conditions. Based on our simulation (Fig. S9), it takes 5-6 days under the ambient conditions to produce the similar amount of sulfate observed in chamber studies (Fig. 4) and it is even longer than the reported average lifetime of airborne dust particles (~4.3 days) (S. et al., 2004;Scheuvens and Kandler, 2014)**.** Therefore, most dust particles possibly would settle down before they are significantly corroded by sulfuric acid coating."

Comment 6: Figure 4 seems to show that the model does capture the nitrate formation at longer times. How do you explain this? Is there any renoxification process taking place in this system?

Response: In the AMAR model, the uptake of HNO_3 on dust is controlled by both gas-dust partitioning and heterogeneous reactions. In general, HNO_3 is abundant in urban areas due to high concentration of NO_x. The gaseous concentration of volatile HNO_3 (63.1 mmHg at 25 C°) is much higher than that needed for buffering dust. By this credential, nitrate salt is quickly regenerated even with the condition that nitrate is decomposed by renoxification. Thus, nitrate on the dust phase will be depleted only when alkaline cations react with other acids, which have the lower volatility than nitric acid.

Reference:

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