Response to Editor's comments (Manuscript Ref. NO.: acp-2017-120)

We appreciate the editor for the thoughtful comments and guidance. The manuscript has been carefully checking for the errors and the consistency in model description. The responses to the comment are shown below.

1) Referee #1, Comment 1: The partitioning between the gas and condensed phase are treated in a similar way, despite being fundamentally different in nature. For a solid surface, the adsorption and desorption processes do follow a different formalism, typically through a Langmuir-Hinshelwood formalism which takes into account a given number of adsorption sites. The consequences is that adsorption decreases with time or increasing concentration, while here it is simulated in a constant way with time. how can you justify such an assumption? Also products such as sulfate are probably staying on the surface, thereby also using adsorption sites i.e., poisoning the surface. How would your model change if you implement such time/concentration dependence?

Previous Response: We assumed that the gas-particle partitioning onto dust is operated by an absorption process (Eq. 7) by several reasons (see section 3.2.1). First, unlike pure metal oxide which is governed by the adsorptive partitioning, the composition of authentic mineral dust such as Arizona Test Dust (ATD) is complex. The fresh ATD contains inorganic salts that are hygroscopic and form the water film above efflorescence relative humidity or deliquescence relative humidity. Second, the partitioning process is dynamic due to the formation of various hygroscopic salts of sulfate and nitrate due to the reaction of alkaline carbonates and metal oxides with inorganic acids (sulfuric acid and nitric acid). Third, the sulfate formation in our study increased as increasing humidity due to the dissolution of tracers into the water layer (see section 3.2.1). If partitioning is processed by the adsorptive mode, water molecules compete for the site with tracers and reduce partitioning of tracers (Cwiertny et al., 2008). The amount of the surface water on dust particles, which was measured using FTIR (submitted in the other journal), was multi-layered.

Editor: It seems to me that the only change in response to this comment was that you replaced all 'adsorption' by 'absorption' in the manuscript. However, this raises more questions than it adds to clarification. You argue that the hygroscopic fraction of the dust forms an aqueous phase where then the chemical processing in the 'dust phase' occurs. Thus, the extent of this processing will depend on the mass (volume) of the hygroscopic dust material. It is not clear to me why parameters such as the absorption rate constants (e.g. R5 and Equation 5) can be used that relate to a particle surface (m-2) and not to a (partial) particle volume. This should be clarified throughout the manuscript. The text should be carefully checked for consistency (e.g. p. 15, l. 10 'adsorption-desorption') and conclusions should be refined (e.g. why is BET surface area needed (p. 20, l. 26) if the hygroscopic material determines the reactions medium?)

Response to Editor: We agree with the Editor's view. In the revised manuscript, we use word "adsorption-desorption" for gas-dust partitioning of tracers (i.e., SO2 or NO2). Unlike partitioning on pure metal oxide, gas-dust partitioning is processed on the multilayer coated dust with water molecules. In order to clarify this, the sentence was added into the revised manuscript and reads now, “The partitioning processes between the gas phase and multilayer coted dust were treated by the adsorption–desorption kinetic mechanism.” (1st paragraph in Section 3). Please also see the 1st paragraph of Section 3.2.1 Gas–dust particle partitioning.

Editor, 2nd round of comments: I am more confused than before now. Initially, the reviewer had pointed out the fundamental differences between adsorption and absorption with different formalisms. The reviewer explained that

“The consequences is that adsorption decreases with time or increasing concentration, while here it is simulated in a constant way with time. how can you justify such an assumption? Also products such as sulfate are probably staying on the surface, thereby also using adsorption sites i.e., poisoning the surface.”

Instead of addressing this point and explaining possible consequences of surface effects (such as poisoning) you simply changed ‘adsorption’ to ‘absorption’ throughout the manuscript and argued that the description of an aqueous phase process is justified. Now, in the newly revised version, everything was changed back to ‘adsorption’ but the reviewer’s comment was not addressed at all. Please, justify clearly the formalism you use and use a constant description of the processes so that the equations that describe your experimental system make sense and can be applied by other researchers.

Throughout the revised manuscript, you are using both ‘abs’ (e.g., p. 7) and ‘ads’ (e.g., p. 10) as indices for constants.

Please make sure that your discussion is consistent and address the reviewer’s comments.

4) Difference between dust chemistry and aqueous phase chemistry

Editor: Related to the comment above, I do not understand the fundamental difference between the aqueous phase chemistry (Section 3.1.3) and dust chemistry (Section 3.2). Both are reactions that occur in a bulk aqueous phase and thus mechanistically they should be treated equally (even though different chemical reactions occur). Please justify the differentiation into two types of processes. It should be stated throughout the manuscript that the ‘dust phase’ is also technically an aqueous phase

Response to Editor: Please also find the response to editor’s comment 1. The aqueous phase reaction is processed in a bulk phase while dust chemistry occurs in the multilayer comprising electrolytes and water on dust surfaces. Hence, the estimation of the water content on dust surfaces, which is influenced by hygroscopic properties of dust surfaces, temperature, and acidity, is essential as discussed in Section 3.2.1. The water content on dust surfaces is also dependent of the amount of dust (relevant to the surface area) and dust compositions.

Editor, 2nd round of comments: Here you argue again that the amount of water is dependent on the amount of dust – which is contradictory to the assumption of adsorption processes but rather points to an absorption process.

Please clarify and discuss consistently throughout the manuscript what kind of processes you are considering, what type of parameters are used and how they can be extrapolated and applied to other conditions so that your claim in the abstract

"The AMAR model, derived in this study with ATD particles, will provide a platform for predicting sulfate formation in the presence of authentic dust particles (e.g. Gobi and 30 Saharan dust)."

is justified.

5) Use of Henry's law constants

a) What is the ionic strength and/or acidity of the aqueous phases? Is the application of Henry's law constants (for ideal solutions) justified? If not, how does this affect the results and the possibility of extrapolation of the derived rate constants to other conditions?

Response to Editor: In AMAR, aerosol acidity ([H+], mol L-1) is estimated at each time step by E-AIM II (Clegg et al., 1998;Wexler and Clegg, 2002;Clegg and Wexler, 2011) corrected for the ammonia rich condition (Li and Jang, 2012; Li et al., 2015;Beardsley and Jang, 2016) as a function of inorganic composition measured by PILS-IC (Section 3.1.3).

For the highly concentrated electrolyte aerosol, the deviation of the compound's solubility predicted using Henry's constants from the actual solubility would be varied depending upon the chemical structure. In the current knowledge, we do not know the actual Henry's constant of each species in the highly concentrated electrolyte solution. For aqueous phase reactions (no dust), Henry's constants that are reported in the modeling paper by Liang and Jocobson (1999) were applied to the AMAR model. Although this implementation can be potentially problematic to predict sulfate production, our model simulation reasonably predicted outdoor chamber data (Figure 3(a) in Section 4.1)

For dust heterogeneous chemistry, Henry's constants of various tracers were used to scale their gas-dust partitioning coefficient based on the known value for SO2 on ATD dust particles (Section 3.2.1). For example, the literature value for the gas-ATD partitioning coefficient of SO2 was 1.3 m3 m-2 at 20% RH. The gas-ATD partitioning coefficient of SO2 is much greater than Henry's constant by several orders (105) when the same unit is applied to both constants (m3/µg). The scaling of the gas-ATD partitioning coefficients of the tracers of this study using Henry's constants may cause some inaccuracy in the estimation of the concentration of adsorbed tracers due to the difference in the activity coefficient of each compound in different media (dust surface vs. dilute aqueous phase). As shown in Figure 3 (Section 4.1), the sulfate production in the presence of ATD particles reasonably accorded with chamber data.

Editor, 2nd round of comments: The fact that your model can predict sulfate production reasonably well is not a proof that assuming that the Henry's law constant is correct. There could be cancelling effects that lead to the correct result for the wrong reason. Given the fact that you estimated several rate constants, the whole set of constants (partitioning, rate constants, Henry's law constants) might reproduce the observations; however, they might not properly represent the individual processes. If someone will use your model and apply it to other conditions, this will lead to biases in predicted sulfate formation.