

Response to Referee #2

We would like to thank the reviewer for his/her thorough evaluation and comments which have led to the improvement of our manuscript. Reviewer comments are in italics and authors responses are in standard font.

1) Oxalate/aerosol/cloud. The oxalate concentration in the dust coating is linearly linked to dust-sulfate concentration so is ultimately driven by gas phase sulfuric acid uptake by dust. However oxalate might be well correlated to sulfate in measurements because of common in cloud path of formation, which are different from dust sulfate formation via gas phase uptake. Is this a limit in the estimation of dust-oxalate? Are there any interaction between aerosol and in-cloud oxalate/sulfate taken into account?

We thank the reviewer for this important clarification. In the model only sulfate formed on mineral dust particles is used as a proxy to calculate dust-oxalate concentrations. The amount of model-predicted dust-sulfate formed is driven by sulfur dioxide (SO₂) and sulfuric acid (H₂SO₄) uptake onto mineral dust particles from the gas phase, as well as aqueous (in-cloud sulfate formation) phase. Therefore, this assumption will take into account the in-cloud formation of oxalate. To clarify this point the following text has been added to methods section of the updated manuscript: “Model-predicted dust-sulfate concentrations are primarily driven by the uptake of sulfur dioxide (SO₂) and sulfuric acid (H₂SO₄) from the gas and aqueous phase (in-cloud sulfate formation).”

2) Oxalate promoted dissolution rate does not depends on pH and is estimated from experiment conducted at pH = 4.7, so rather acidic conditions. Since dust-coating is likely to be alkaline due to calcite buffering, could this approach be a source of overestimation for oxalate promoted dissolution?

We thank the reviewer for this astute observation. However, as stated in the original manuscript, oxalate-promoted mineral Fe dissolution rates are calculated with the linear fits derived from Paris et al. (2011) after “subtracting out the amount of dissolved Fe (Fe_d) produced in the absence of oxalate”. Therefore, the amount of Fe_d produced when no oxalate is present, due to the acidic condition of the solution (pH = 4.7), is removed and only Fe_d formed due to the addition of oxalate is considered in our oxalate-promoted mineral dissolution rates.

3) Kinetic of cycling. You mention that some kinetic reactions were added to the chemical solver to account for photochemical processes in the aqueous phase. Does ‘aqueous phase’ relate here to the aerosol coating solution only, or is there also any extension to cloud water chemistry?

The aqueous phase chemical equations presented in this work are applied for both aerosol and cloud water environments. For aerosol solution, the amount of water is calculated using the thermodynamic module ISORROPIA. When the model-predicted dust particle is within a cloud, the liquid water content is set to the temperature-dependent cloud water concentration calculated in GEOS-Chem. While the chemical species present and reactions used in the model are the same for both aerosol and cloud water conditions the pH and ionic strength of the solution will

differ. These variables help determine mineral dissolution/precipitation kinetics and are controlling factors of Fe_d concentration. To clarify, the following text has been added to the methods section of the updated manuscript: “These reactions are calculated for both aerosol solution and cloud water environments. Aerosol liquid water content is calculated by the thermodynamic module ISORROPIA (Nenes et al., 1998). When dust aerosols are predicted to be within a cloud, the liquid water content is set to the temperature-dependent cloud water concentration predicted by GEOS-Chem.”

4) Fed-deposition. *A couple of word/references on the quality of the dust modeling could be added here. Is the dust simulation considered as realistic? There is usually a large variability in term of global dust deposition flux estimation (e.g cf AEROCOM model inter-comparisons). Where does GEOS-CHEM stand in this regard?*

GEOS-Chem predictions of mineral dust emission, transport, and deposition have been shown to compare well to past modeling studies, in situ measurements, and remote sensing data (e.g., Solmon et al., 2009; Johnson et al., 2010, 2011, 2012). Overall, there is large variability in different model predictions of total global mineral dust deposition (ranging from ~700 to 4400 Tg yr⁻¹ in AEROCOM phase 1) (Huneeus et al., 2011). During the time period of the current publication we calculate that GEOS-Chem predicted a total annual dust deposition of ~1600 Tg yr⁻¹ which is generally consistent with the average value of ~1900 Tg yr⁻¹ determined from all the models used in AEROCOM phase 1. The following discussion has been added to the methods section of the revised manuscript: “GEOS-Chem emits and deposits, on average, ~1500 Tg yr⁻¹ of mineral dust globally (~1600 Tg yr⁻¹ was predicted during the simulated time period of this study). This model-predicted flux is consistent with the average global dust deposition value of ~1900 Tg yr⁻¹ (ranging between ~700 to 4400 Tg yr⁻¹) determined from all models used during the AEROCOM phase 1 project (Huneeus et al., 2011).”

5) A remark: *You state that the model compares well with previous model estimations. Given the amount of new processes you added, obtaining a very different result would not be shocking however? How do the other models compare in term of complexity and what is the added value of the new detailed approach?*

We agree with the reviewer that this point needs further clarification. We believe this study presents the most comprehensive method to predict Fe_d production in mineral dust currently available. The added value for using such a complex approach is that our calculations capture the large spatiotemporal variability in fluxes of Fe_d , dissolved Fe fractions (DIF), and Fe(II)/Fe(III) partitioning, measurements that only recently have become available. Furthermore, this approach provides the unique opportunity for coupling with other atmospheric and oceanic models to study variable interdisciplinary processes. To further emphasize this point the following text has been added to the conclusion section of the manuscript: “This complex approach to calculating Fe_d production in mineral dust is an improvement from past modeling studies as it more comprehensively captures the processes known to affect Fe dissolution rates and Fe_d concentrations in mineral dust (i.e., proton- and organic ligand-promoted Fe dissolution,

Fe(II)/Fe(III) redox cycling, dissolution rates of differing Fe-containing minerals, and accurate dust particle mineralogy). This allows our model to capture the existing large spatial and temporal variability of Fe_d deposition rates, DIF values, and Fe(II)/Fe(III) speciation. Additionally, the current model allows for the calculation of the impact of transition metal ions on atmospheric oxidant (e.g., HO_2 , OH) levels (e.g., Mao et al., 2012).

6) Perhaps in line with my previous remark: You propose some interesting sensitivity tests and show the influence of different assumptions on the Fe_d production, as well as the huge 75% difference brought by the oxalate-promoted mechanisms vs proton promoted. However there is another important parameter for the estimation of Fe_d flux which is the initial condition on DIF (at the emission), which is fixed to 0.45 % if I understood correctly. This might be a very sensitive factor for the estimation of Fe_d deposition flux (and explain the high value close to large pristine sources I). Perhaps the weight of this condition should be more emphasized in the paper (e.g. Do you have idea of how much the initial Fe_d contribute to the total deposited flux?): Some studies (Journet et al., Paris et al.) suggest that most of the dust-DIF variability is determined by the initial composition (clay content) vs atmospheric processing.

The reviewer is correct in that initial DIF values in mineral dust can play a key role in Fe_d deposition fluxes. In our past work of Johnson et al. (2010) we have shown that the initial DIF value may be the controlling factor on Fe_d deposition fluxes in pristine regions (e.g., South Atlantic Ocean). In Table 2 of Johnson et al. (2010) it is shown that by reducing the initial DIF value at the source region from 0.45% to 0.1% resulted in a ~80% decrease in total Fe_d deposition to the South Atlantic Ocean. The effect of the prescribed initial DIF is somewhat smaller (but still considerable) in regions strongly impacted by large quantities of anthropogenic pollutants. In order to emphasize the importance of prescribed initial DIF values, the following text was added to the results sections of the updated manuscript: “Our model-predicted Fe_d deposition fluxes and DIF values are highly dependent on the initially prescribed solubility of mineral Fe at the source region. This value is particularly important in pristine regions where atmospheric processing is less efficient in initiating Fe dissolution in mineral dust particles. While DIF values may vary between dust source regions we prescribe our initial DIF value according to the data of Fe_d from the reactive and poorly crystalline pool of Fe in dust precursor samples from the Sahara and Sahel regions of North Africa (Shi et al., 2012). Due to the importance of prescribed DIFs on Fe_d deposition fluxes, and the potential variability of this value between different dust source regions, it is suggested that future studies should be conducted to further refine this value for the global dust source regions.

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