

Response to Referee #1

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

Abstract

1) *The model simulations were carried out using three different minerals for a range of the uncertainty. Please present the range of dissolved Fe deposited to global ocean.*

We agree with the reviewer. The following text was added to the abstract of our updated manuscript: “Model sensitivity simulations suggest Fe_d fluxes to the oceans can range from ~50% reduction to ~150% increase associated with the uncertainty in Fe-containing minerals commonly found in dust particles.”

2) *When you set the Fe content to 3.5%, how did you treat the dissolution/precipitation reactions of hematite, goethite, and illite in the proton-promoted dissolution mechanism? For example, how did you estimate the Fe dissolution rate from the illite dissolution rate (mol m⁻² s⁻¹)? How did you calculate the reaction activity quotients for these reactions? For instance, when you used illite as the main Fe-containing mineral, how did you consider the backward reactions for illite and iron dissolutions?*

We thank the reviewer for pointing out the need for further explanation of this topic. The following discussion on the proton-promoted dissolution of each Fe-containing mineral has been added to the methods section of the updated manuscript: “The K_{p_i} values for hematite and illite dissolution rates are calculated from the temperature-dependent equations in Table 8 of Meskhidze et al. (2005) and K_{p_i} , the proton-promoted dissolution rate constant for goethite (mol m⁻² s⁻¹), is derived from Cornell (1976) as:

$$K_{p_i} = 1.4 \times 10^{-11} * \exp \left[1.1 \times 10^4 * \left(\frac{1}{298} - \frac{1}{T} \right) \right]$$

The K_i^r for each individual mineral is then applied to Eq. (24) in Meskhidze et al. (2005) in order to calculate the concentration of mineral Fe dissolved per time step in the model. The empirical parameter (m), specific surface area of the mineral (A), weight fraction of the mineral in dust (W), and equilibrium constants (K_{eq}) used in the proton-promoted dissolution of hematite and illite are listed in Meskhidze et al. (2005). For goethite we use the following values $m = 0.5$, $A = 38 \text{ m}^2 \text{ g}^{-1}$, $W = 5.7\%$, and $K_{eq} = 0.43 \text{ mol}^2 \text{ kg}^{-2}$ (Cornell, 1976; Cheah et al., 2003). Following the dissolution/precipitation method of Meskhidze et al. (2005), at every time step in the model, rate constants for mineral dissolution/precipitation are derived based on Fe_d , dissolved chemical species, solution pH, temperature, and ionic strength. For any particular mineral (i.e., hematite, goethite, or illite), if the solution remains under-saturated with respect to Fe(III), mineral dissolution proceeds. However, when the solution becomes super-saturated with respect to Fe(III), mineral dissolution stops and amorphous $Fe(OH)_3(s)$ precipitates. For all the simulations conducted during this study the solution remained under-saturated with respect to Fe(II).

3) Please list the values for m (empirical parameter), A (specific surface area of mineral), W (weight fraction of the mineral in dust), and K_{eq} (equilibrium constant) used for goethite dissolution.

See our response to comment #2.

4) How did you convert the units when you calculated the linear fit? How did you consider the Fe dissolution kinetics of oxalate-coated minerals and the pH effect on the solubility of oxalate-coated minerals?

The Kl_i rates ($\text{mol m}^{-2} \text{s}^{-1}$) were calculated using the amount of Fe_d measured ($\mu\text{g hr}^{-1}$) in each dissolution experiment (60 min) listed in Table 4 of Paris et al. (2011), the amount of mineral used in each dissolution experiment, and the Fe mass percentage of each mineral used in Paris et al. (2011) (3.38%, 57.48%, and 62.87% for illite, hematite, and goethite, respectively). Multiplying the total mineral mass used (15 mg) by the Fe mass percentages of each mineral results in the total amount of Fe present during each experiment. The unit conversion for the amount of Fe_d formed (from $\mu\text{g hr}^{-1}$ to $\mu\text{mol s}^{-1}$) was conducted using the molar mass of Fe (55.8 g mol^{-1}). Dividing this value by the total Fe present and the specific surface area of each mineral used in Paris et al. (2011) (9, 1, 33 $\text{m}^2 \text{g}^{-1}$ for hematite, goethite, and illite, respectively) results in the Fe_d production per unit area per second ($\mu\text{mol m}^{-2} \text{s}^{-1}$). This value can easily be converted to $\text{mol m}^{-2} \text{s}^{-1}$ which are the units of oxalate-promoted dissolution rates (Kl_i) used in our model. We have added the following text to the updated manuscript: “To calculate these Kl_i rates we applied the total mineral mass used in each dissolution experiment of Paris et al. (2011) (15 mg), Fe mass percentage of each mineral (3.38%, 57.48%, and 62.87% for illite, hematite, and goethite, respectively), and the individual mineral specific surface areas (9, 1, 33 $\text{m}^2 \text{g}^{-1}$ for hematite, goethite, and illite, respectively) used in Paris et al. (2011).”

Total Fe dissolution rates are calculated in the model as the sum of proton- and oxalate-promoted dissolution. This was shown in Eq. (2) and both individual Fe dissolution processes are described in section 2.2.3 in the original manuscript.

5) My major concern is the extrapolation method of oxalate-promoted Fe dissolution based on the laboratory experiments with only 1 hour of contact time (Paris et al., 2011). The oxalate-promoted Fe dissolution rate in your model is constant with time and pH, which is apparently contradicted to the laboratory measurements (e.g., Xu and Gao, 2008). Please show the comparison of the Fe dissolution rates for higher pH values with time.

We believe there is no clear contradiction between the results of Xu and Gao (2008) and that of Paris et al. (2011). The reason for the differences could be the amount of total Fe used in each experiment. In the study by Xu and Gao (2008) hematite concentrations of 5 g L^{-1} ($\sim 0.1 \text{ M}$) were used during Fe dissolution experiments at $\text{pH} = 2.4$. Using a range of equilibrium constants for dissolved Fe(III) with amorphous Fe (between 1.5×10^3 - $9.1 \times 10^3 \text{ mol L}^{-1}$) ($\log K_{eq} = 3.19$ - 3.95) reported in past literature (Lindsay, 1979; Stumm and Morgan, 1981; Jang et al., 2007) it can be calculated ($\log[\text{Fe}^{3+}]_{\text{max}} = \log K_{eq} - 3 \cdot \text{pH}$) that very small fractions ($\ll 1\%$) of Fe can be

dissolved before reaching the thermodynamic equilibrium. The decrease in dissolved Fe dissolution with the increase in total amount of Fe has been well documented in past studies and is summarized in a synthesis of globally-distributed measurements presented in Sholkovitz et al. (2012).

On the other hand, Paris et al. (2011) used much smaller amounts of total Fe ($< 15 \text{ mg L}^{-1}$) with oxalate concentrations that are representative of natural atmospheric conditions and are much smaller than the oxalate concentrations used in Xu and Gao (2008).

Overall, our model explicitly considers the equilibrium between Fe containing minerals and dissolved forms in a solution (i.e., Fe(II) and Fe(III)); therefore, no additional tuning is required to reproduce the reduction of Fe dissolution rates with the increase of Fe_d .

6) Please separate paragraphs for SMVGEAR II and ISORROPIA from the introduction of past studies. Please explain the role of each module at first in each paragraph, and then explain what you modified.

The methods section has been changed in the updated manuscript to address the reviewer's comment. The text now reads: "The standard GEOS-Chem tropospheric chemical mechanism consists of over 100 species and 300 reactions integrated using the stiff-ordinary first order differential equation solver Sparse Matrix Vectorized GEAR II (SMVGEAR II) (Jacobson and Turco, 1994; Jacobson, 1995, 1998). The methods used in SMVGEAR II allow the solver to resolve equations quickly and accurately in global 3-D models. During this study, in order to simulate the photochemical/chemical cycle of Fe(III) and Fe(II) complexes, oxalate, H_2O_2 , and radical species OH^\cdot , HO_2^\cdot , $\text{O}_2^{\cdot-}$, additional kinetic, photochemical, and aqueous-phase equilibrium reactions listed in Tables 3 and 4 (apart from those described in Meskhidze et al., (2005)) were added into SMVGEAR II. Aqueous concentrations of oxidant species were calculated using temperature dependent Henry's Law. To account for species that do not achieve equilibrium due to mass transfer kinetic limitations between phases (e.g., OH and HO_2) we calculate the transfer coefficient following the methods of Myriokefalitakis et al. (2011). The GEOS-Chem model calculates photolysis frequencies using the Fast-J radiative transfer algorithm of Wild et al. (2000), with a seven-wavelength quadrature scheme that calculates photolysis rates throughout the troposphere in the presence of an arbitrary mix of cloud and aerosol layers (Olsen et al., 1997; Wild et al., 2000). In order to simulate the diurnal variations of photochemical processes, photolysis calculations are performed every hour in the model.

ISORROPIA is an aerosol thermodynamics module used in GEOS-Chem to calculate the equilibrium solid-, aqueous- and gas-phase concentrations of the sodium - ammonium - chloride - sulfate - nitrate - liquid-water content system of an internally mixed aerosol (Nenes et al., 1998). Previously, ISORROPIA was modified to include reactions involving gas-phase CO_2 , aqueous-phase carbonates, and Fe-species (Meskhidze et al., 2005). This modified version of ISORROPIA is applied within GEOS-Chem/ Fe_d . Multicomponent activity coefficients for the major inorganic species were determined using the methods of Bromley (1973). Binary activity coefficients were calculated for each new ion pair using the formulation of Kusik and Meissner

(1978) and the q-parameters for each relevant salt listed in Table 9 of Meskhidze et al. (2005). Ionic strength and pH of the solution are calculated using the modified form of ISORROPIA. Activity coefficients for the following ions $\text{C}_2\text{O}_4^{2-}$, C_2O_4^- , FeO^{2+} , O_2^- have been neglected. To consider a potential salting out effect for electrically neutral species (H_2O_2 , HO_2 , OH , O_3 , O_2) activity coefficients were calculated as $10^{0.1*I}$ (Fischer and Peters, 1970), where I stands for the ionic strength of the solution. Additionally, the reactions listed in Tables 3 and 4 are calculated for both deliquesced aerosol solution and cloud water environments. Aerosol liquid water content is calculated in ISORROPIA and 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.”

7) *How did you treat the hydroperoxyl radical uptake from the gas phase in aerosol and cloud water? Did you use the same scheme as in Mao et al. (2013)?*

To account for species that do not achieve equilibrium due to mass transfer kinetic limitations between phases (i.e., hydroperoxyl radical (HO_2)) we calculate the transfer coefficient (k_t) using methods presented in Myriokefalitakis et al. (2011).

8) *Please list the temperature-dependent cross sections for each spectral intervals used in the Fast-J.*

The wavelength dependent absorption cross-sections of Fe species were calculated using the measured molar extinction coefficients of Zuo and Holgne (1992). In the study of Zuo and Holgne (1992) all irradiation procedures were conducted at 20°C (293°K). Due to the overall lack of information on the temperature-dependence of the absorption cross-sections of aqueous Fe species, absorption cross-sections measured at 20°C are prescribed for all the temperatures in our model. The absorption cross-sections of Fe species are referenced in the methods section and listed in a supplementary table of the updated manuscript.

9) *It would be beneficial to discuss oxalate concentrations in dust aerosols, since the focus of this study is on the dust. You mention that oxalate concentrations below 100 ng m⁻³ have a negligible impact. It may be helpful to show the global surface level concentration for oxalate in dust and total.*

We thank the reviewer for the suggestion of adding figures of total oxalate and dust oxalate surface level concentrations. These figures and the following text have been added to the results section of the updated manuscript: “Furthermore, Fig. S1 and S2 show the model-predicted seasonally-averaged surface level total oxalate concentrations and oxalate concentrations associated with mineral dust. When comparing Fig. S1 and S2 it can be seen that near the dust source regions much of the total oxalate is associated with dust. However, away from the dust sources the concentration of total oxalate is considerably higher compared to the amount of oxalate adsorbed on dust particles.

10) *Figure 6 and Table 5: Please show the results with illite and goethite for a range of the uncertainty.*

The comparison of the model-predicted Fe_d values to ambient data for illite and goethite has been included in the updated manuscript.

11) *Two effects of oxalate-promoted Fe dissolution and photochemical redox cycling are involved in this comparison. First, organic ligands promote Fe dissolution. Second, redox cycling between Fe(III) and Fe(II) changes the aqueous-solid saturation state with respect to Fe(III). Please clearly separate these two effects when you discuss the results.*

We thank the reviewer for pointing out the need for the clarification of these two separate processes influencing overall Fe dissolution. The text has been modified in the updated manuscript to read: “Our calculations suggest that globally, the implementation of oxalate-promoted Fe dissolution and the redox cycling between Fe(II) and Fe(III) led to ~75% increase in the Fe_d deposition to the oceans with complex spatiotemporal patterns.”

Technical corrections

Correct the citation of Heald et al. (2004) to Heald et al. (2006).

This has been changed.

Figures 3, 4, 7 and 9: Correct April to May.

Figures 3, 4, 5, 7, and 9 were changed in the updated manuscript accordingly.

Tables 2 and 5: Present the units.

The units for Tables 2 and 5 have been added in the updated manuscript.

Table S1: Add [between j] and Fe.

This has been changed in the updated manuscript.

References

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