

Interactive comment on “Atmospheric Processing of Iron in Mineral and Combustion Aerosols: Development of an Intermediate-Complexity Mechanism Suitable for Earth System Models” by Rachel A. Scanza et al.

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Received and published: 30 June 2018

Referee comments are in black and the authors responses are in red. When text from the manuscript is quoted, new text is in bold face.

Referee 1: Interactive comment on “Atmospheric Processing of Iron in Mineral and Combustion Aerosols: Development of an Intermediate-Complexity Mechanism Suitable for Earth System Models” by Rachel A. Scanza et al.

General comments:

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Parameterizations and simplifications in atmospheric processing of iron in aerosols are required for multi-decadal and centennial simulations. The authors presented a comprehensive modeling study of labile iron, assuming fast iron dissolution rates in cloudy grid boxes by applying “in-cloud” iron dissolution rates. The work conducted in this paper may contribute to improve our understanding of iron cycle, although more works will be required to improve the atmospheric processing of iron in aerosols. I have some comments and questions to improve this paper. In particular, there are many tuning parameters which should be clarified for future studies, although the paper is well written.

We thank the referee for the careful evaluation and helpful comments to improve the quality of the manuscript. We revise the text to clarify and address the referee’s comments.

Specific comments: Abstract p.1., l.19, p.9, l.27, and p.16, l.25: Please rephrase “within range of the observational mean”, as you explained “less than 1 signifies an underestimation” in p.11, l.32. We modify the text on page 1, lines 18-19: “We define a semi-quantitative metric as the model mean at points with observations divided by the observational mean (MMO). The model is in reasonable agreement with observations of fractional iron solubility with an MMO of 0.86.”

We modify the text on page 9, line 24: “The MMO does not intend to evaluate the model’s ability to capture observational variability but simply to assess if the model can reasonably estimate the observational mean.”

We modify the text on page 16, line 25: “. . .fractional iron solubility MMO is 0.86, indicating that while the model is not capturing all of the observational variability, it is in reasonable agreement with the observational mean.”

p.1.,l.25, p.10, l.13, and Table 5a: This contradicts to the main conclusion from previous version (Luo et al., 2008). Figure S1 indicated the underestimates of iron below 15S, suggesting the omission of optimization of dust emissions. Since the total iron

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in combustion aerosols are emitted following Luo et al. (2008), you must predict lower dust emissions in the Southern Hemisphere. After you switched the coupled simulation to the off-line simulation, how did you scale the dust emissions? Since the dust emissions strongly depend on the meteorology, you needed to optimize dust emissions. If you did not, please clarify the omission of optimization of dust emissions and the underestimates of iron below 15S.

All model simulations in this study were conducted with optimized dust emissions following Albani et al., 2014 and forced with MERRA reanalysis meteorology. In Albani et al, 2014, the dust is optimized to best match AOD in the source regions, deposition and concentration. As in other models (Hunees et al., 2011), we cannot match both deposition and surface concentrations at the same time. Here we only compare to surface concentrations and add the following test on page 4 to make this more clear: “The dust module was tuned to best match aerosol optical depth (AOD), deposition and surface concentration data (Albani et al., 2014). Similar to other models (Hunees et al., 2011), our model is unable to simultaneously match the surface concentration and deposition data in remote regions, and since here we only show concentration data, it will appear that the model overpredicts surface concentrations of dust.”

TableS2d lists emissions of total iron in dust and combustion aerosols at 56.9 and 1.9 Tg/year respectively, and is very close to the total iron emissions reported in Luo et al., 2008 (55 and 1.7 Tg/year). The main conclusion in Luo et al., 2008 is “we obtain the result that deposition of soluble iron from combustion contributes 20 – 100% of the soluble iron deposition over many ocean regions.” Therefore, our conclusions support those of that study and are within their range. The model we use in this study is structurally different to the MATCH model used in Luo et al., 2008 and the reanalysis meteorology used to drive MATCH is NCEP, compared to MERRA reanalysis meteorology used here; therefore, a like-for-like comparison of results with those in Luo et al., 2008 cannot be done as the Reviewer suggests and differences are instead a reflection of the different model structures and meteorology data sets used.

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We also add the following text on page 10, lines 16-17: “. . .surface concentrations of dust are generally over-predicted with the exception of remote SH ocean regions. In addition, most dust models exhibit a low bias in SH dust deposition (e.g., Hunees et al., 2010;Hunees et al., 2011;Albani et al., 2014).”

Introduction p.2, l.5: typo, HNLC.

fixed.

p.3, l.13 and p.5, 1.8: More recent study developed an iron dissolution scheme that reduced the number of mineral tracers for implementation in Earth system models (Ito and Shi, 2016).

We modify the text by adding the following sentence on page 3, lines 9-10: “A more recent study developed an iron dissolution scheme with fewer mineral tracers to allow for simulations using Earth system models (Ito and Shi, 2016).”

Methods p.4, l.15: Please clarify the link between three source modes and the size distribution across dust bins in p.4, l.18 The particle size distributions for each dust bin are calculated from the mass fraction from the source trimodal PDF to the transport bins following (Eq. 12, Zender et al., 2003). The dust bins are bounded at 0.1, 1.0, 2.5, 5.0 and 10.0um with prescribed mass median diameter and standard deviation of 3.5um and 2.0, respectively. Three source modes described in Schulz et al., 1998, D’Almeida, 1987 and Zender et al., 2003 are defined by observed mass median diameter and geometric standard deviation (see Table 1, Zender et al., 2003). The portion of the mass fraction from each source mode to each of the 4 dust bins is described in (Table 2, Zender et al., 2003), and the bin fractions are modified following brittle fragmentation theory (Kok, 2011).

We modify the text by adding the following on page 4, lines 16-20:

“The three source modes are defined by observed mass median diameter and geometric standard deviation (d’Almeida, 1987;Schulz et al., 1998;Table 1, Zender et al.,

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2003). Bin widths are prescribed at 0.1-1.0, 1.0-2.5, 2.5-5.0, and 5.0-10.0 μm (Mahowald et al., 2006; Zender et al., 2003) and have fixed lognormal sub-bin distributions (mass median diameter = $3.5\mu\text{m}$, $\sigma = 2.0$) (Zender et al., 2003). The size distribution across dust bins was modified from the release version of the model to follow the brittle fragmentation theory of vertical dust flux . . .”

p.4, l.24: Please specify the sub-time step for multiple in-cloud cycles for aerosols and clarify the contact time of aerosols with cloud droplets. CAM4 aerosols do not interact with clouds with the exception of modeled iron and sulfate particles, the chemistry of which is explicitly simulated within clouds using the simple approximations developed here. In this study, with the CAM4 aerosol configuration, we are not actually simulating dissolution and evaporation of dust and oxalate particles within a cloud droplet but rather estimating it via simplified dissolution rates (Eq. 1-3).

We modify the text on page 4, lines 25-28: “CAM4 allows for multiple cycles of condensation and evaporation (Gent et al., 2011; Hurrell et al., 2013; Neale et al., 2013) in order to match observational estimate of approximately three in-cloud cycles for aerosols (Lelieveld et al., 1998; Crutzen and Zimmerman, 1991); the model time step is 30 minutes with 20 sub-time steps for in-cloud chemistry.”

p.6, l.25: Please show the results of pH from REF and SS5. Added a new figure for Supplement (Figure S3).

p.6, l.29 and Figure 1: Please correct the unit in Figure 1. The iron dissolution rates from Eq. (3) at oxalate concentration = 0 are higher than those from Eq. (1). However, the iron dissolved at oxalate concentration = 0 is already considered in FeRR. Please show the comparison of Fe solubility estimated using equations (1) and (3) from illite at oxalate concentration = 0 with Fig. S2 in Ito and Shi (2016). If you assume fast iron dissolution rates in cloudy grid boxes, please clarify it.

Units in figure one RFe vs. pH:

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$R_{\text{Fe}} = K(T) \times a(\text{H})^m \times f(\text{oxalate}) \times A \times \text{MW}$ where,

$K(T)$ has units of $(\text{mol m}^{-2} \text{s}^{-1})$ $a(\text{H})^m$ is unitless $f(\text{oxalate})$ is unitless A has units of $(\text{m}^2 \text{g}^{-1})$ MW has units of (g mol^{-1}) $\hat{\text{a}}\hat{\text{L}}\hat{\text{t}}^{-1} \text{mol} / (\text{m}^2 \text{s}^{-1}) \times \text{m}^2 \text{g}^{-1} \times \text{g} / \text{mol} = \text{s}^{-1}$

The iron dissolution rate at $[\text{C}_2\text{O}_4^{2-}] = 0$ utilizes Table 4 in Paris et al., with our method for best fit which was a result of multiple different simulations where the intercept was examined to find the best match observations of %Fes. Regardless of the presence of $\text{C}_2\text{O}_4^{2-}$, the non-zero intercept with units of (s^{-1}) for $K_{\text{i,oxalate}}$ accounts for (non-oxalate) in-cloud organic ligand processing which is always present.

We add the following text on page 7: “The iron dissolution rate at $[\text{C}_2\text{O}_4^{2-}] = 0$ utilizes (Table 4, Paris et al., 2011) with our method for best fit which was a result of multiple different simulations where the intercept was examined to find the best match to observations of %Fes. The non-zero intercept for $K_{\text{i,oxalate}}$ accounts for (non-oxalate) in-cloud organic ligand processing.”

We assume iron dissolution rate in cloudy grid boxes following the higher solubility for Femed, which can be found in the text on page 6, line 33 “. . .we use the Femed dissolution rate for the remaining combustion iron.

We also add a figure in the supplement, Figure S4 showing the Fe solubility from illite with time.

p.7, Eq. (2) and p.8, Eq. (4): How did you determine the scaling factor of 15? Multiple simulations were performed to choose our reference case and the factor of 15 produced the best match to previous modeling studies with more explicitly simulated oxalate. Since CAM4 aerosols do not interact with clouds, it was necessary to parameterize this interaction and to select an appropriate scaling factor to best match the oxalate distribution (Fig. 2, Myriokefalitakes et al., 2011) and observations of fractional iron solubility.

We added the following text on page 7, lines 10-13: “In choosing our reference case,

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multiple simulations were conducted to best match observations of fractional iron solubility and the surface distribution of oxalate (Figure 2a,c, Myriokefalitakis et al., 2011); the factor of 15 in Eq. (2) yielded the best results.”

p.7, l.8: Please show the comparison of oxalate from REF and SS2 with observations, assuming that oxalate remains in the particulate phase upon cloud evaporation. Please clarify if you assume high oxalate concentration in the aerosols in cloudy grid boxes. The oxalate concentration in cloudy gridboxes is calculated with Equation 2. Regions with both clouds and oxalate concentrations shown in Figure 2 will have high oxalate concentrations and thus faster dissolution. We are unable to show a direct comparison of REF and SS2 particulate phase oxalate given that CAM4 aerosols (except sulfate) do not interact with clouds and were only parameterized using proxy species. However, we refer the Reviewer to Figure 2 in this study and Figure 2 (a,c) in Myriokefalitakis et al., 2011, which shows good agreement when using organic carbon as the proxy for oxalate in CAM4. This has been stated in the manuscript already so no additional text is required.

p.8, l.14: Since these values strongly depend on the meteorology, you needed to optimize the tuning parameters (see comments on p.8, l.18 and p.11, l.24). If you did not, please clarify the omissions of optimization. Tuning parameters for dust emission were optimized following Albani et al., 2014. Page 8, lines 14-16 describe the very simple iron dissolution parameterization for SS3 from Hand et al., 2004. Please see our response to the second specific comment.

p.8, l.18: How did you determine the scaling factor of 5? Simulations in Hand et al., 2004 did not take into account any combustion iron. Combustion iron vs dust iron solubility is not well understood. Particularly, a wide range of initial dust solubility (0.1 – 1+% (Luo et al., 2008;Jickells et al. 2005;Shi et al., 2012;Johnson and Meskhidze, 2013;Ito and Xu, 2014). Using our reference case, the annually-average global Fes emissions (0.5069 Tg/year) divided by total dust Fe emissions (56.9 Tg/year) yields an initial dust %Fes of 0.89%. Assuming combustion %Fes of 4%, this corresponds to an

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enhancement of 4.5 times (although this could potentially range from 40 to less than 4 times).

We add the following text on page 8, lines 19-24: “Hand et al., 2004 did not take into account iron from combustion aerosols and there are a wide range of reported dust Fe solubilities at emission, 0.1-1+% (Luo et al., 2008;Jickells et al. 2005;Shi et al., 2012;Johnson and Meskhidze, 2013;Ito and Xu, 2014). To account for the typically higher solubilities associated with combustion iron, and using Fes/Fet for dust iron (Table S2d), we assume an initial solubility for combustion and dust Fe of 4% and 0.89%, respectively; this corresponds to an enhancement of 4.5 times and hence chose, somewhat arbitrarily, to increase the dissolution rate by a factor of 5.”

p.8, l.23: Guo et al., 2016 and Weber et al., 2016 excluded dust events and reported high acidity for fine particles. Please see Extended Data Figure 1 in Weber et al., 2016. The pH estimate is higher than 3 even though SO4 concentration is higher than Na concentration. I strongly recommend simulations with lower pH for combustion aerosols but higher pH for dust than REF in future studies. This is an excellent suggestion and will be implemented in our current model development using this iron dissolution scheme within the modal aerosol module (MAM) in the CESM (Hamilton et al., in prep).

p.8, l.28: How did you estimate preindustrial chemistry and dust sources assuming present day climate conditions? Preindustrial chemistry is estimated from historical emission from CMIP5 and include reduced emissions of sulfate, OC and BC. (Lamarque et al., 2010). Preindustrial dust sources from 1850 are estimated based on those used in Mahowald et al., 2006 for late 19th century. Present day climate conditions indicate that we use the current MERRA reanalysis meteorology (e.g., temperature, wind speed, etc.), but should not be confused with chemistry which refers only to the atmospheric compositional state (in this case CO2 and oxidant concentrations. We add the following text on page 9: “Here we refer to “preindustrial chemistry” as historical emissions for CMIP5 (Lamarque et al., 2010) and includes reduced emissions for

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sulphate, OC, and BC. “

3 Results p.10, l.7: This is not the reason of the overestimates and underestimates (see the comments on p.1., l.25, p.10, l.13 and Table 5a). Dust emissions are optimized in all simulations; please see our previous response.

p.11, l.5 and p.13, l.1: Why did you estimate higher iron solubility (i.e., overestimate) in the finest particle size bin off the coast of North Africa? The value is higher than the initial iron solubility for dust aerosols in Table S2d. However, the initial iron solubility for the finest particle size bin should be higher than that. Please show the emissions in the finest particle size bin as in Table S2d.

The initial iron solubility for dust aerosols from Table S2d is 0.89% and when we include combustion aerosols the combined initial iron solubility for all bins is 0.99% (4% Fecomb). Fine mode emissions in units of kg m⁻² s⁻¹ for dust, Fetdust, Fetcomb, Fesdust, Fescomb are 1.93E+10, 1.02E+09, 2.4E+08, 3.6E+07 and 9.7E+06 respectively. The readily released iron from Ito and Xu, 2014 is presumed already soluble in bin1 and for bins 2-4, FeRR from kaolinite and feldspar is prescribed as soluble while 25% of FeRR from illite and smectite is prescribed, as stated in Section 2.3, lines 24-33. This corresponds to a higher initial solubility of dust iron in the finest size bin (3.6%); including combustion yields 3.7%.

We modify the Supplementary Material by adding a column in Table S2d for the fine mode emissions.

p.11, l.21, Tables 3 and 7: What is tau? In tables 3 and 7, tau is the annually-averaged global mean of insoluble iron turnover time (days). It is defined as the total insoluble iron from dust and combustion aerosols divided by the production of soluble iron from insoluble iron.

We add the following text to the table caption for Table 3 (page : “In the last two rows, tau is the annually-averaged global mean insoluble iron turnover time (days) and is

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defined as the total insoluble iron from dust and combustion aerosols divided by the production of soluble iron from insoluble iron. Mean %fesdep is the average fractional iron solubility at deposition to global ocean basins.”

We add the following text to the caption for Table 7: “. . .percent difference for the average production lifetime of Fes (days) labeled here as “tau” and the. . .”

p.11, l.24: Please indicate the values for “larger errors.” The underestimates suggest the omission of optimization (see the comment on p.8, l.14). Dust emissions are optimized in all simulations; please see our previous response.

p.13, l.30, Figure 8: Figures 8 (a) and (c) indicate the ratios of 2 over most regions. Did you set up the maximum ratios in your plots? Please correct it.

Yes we did and have modified the figure to account for this.

p.14: Please rephrase preindustrial “chemistry”. This is confusing, because the chemistry depends on the meteorology.

Preindustrial chemistry is estimated from CMIP5 historical emissions (Lamarque et al. , 2010), which should not be confused with the MERRA reanalysis meteorology used to drive all simulations in this study.

Acknowledgments p.17, l.16: D. H. is co-author fixed.

Tables p.21, Table 1: Please revise it to clarify the differences between REF and SS4.

SS4 is REF with spatial dependence of iron on mineralogy removed and the global average iron and calcite concentrations from the reference case are prescribed at emission. We add the following text in caption for Table 1a to clarify this difference: “SS4 tracers have no spatial dependence on mineralogy and have prescribed global average fractions from REF at emission.”

Please also note the supplement to this comment:

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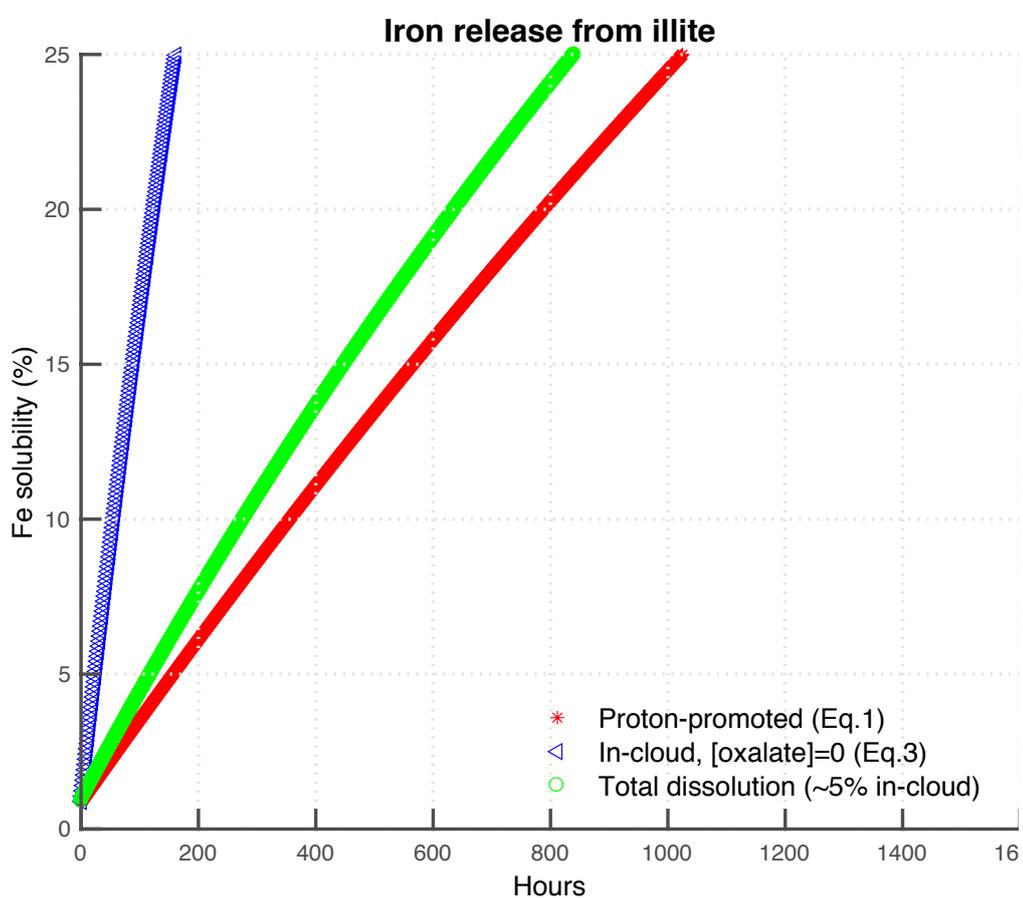
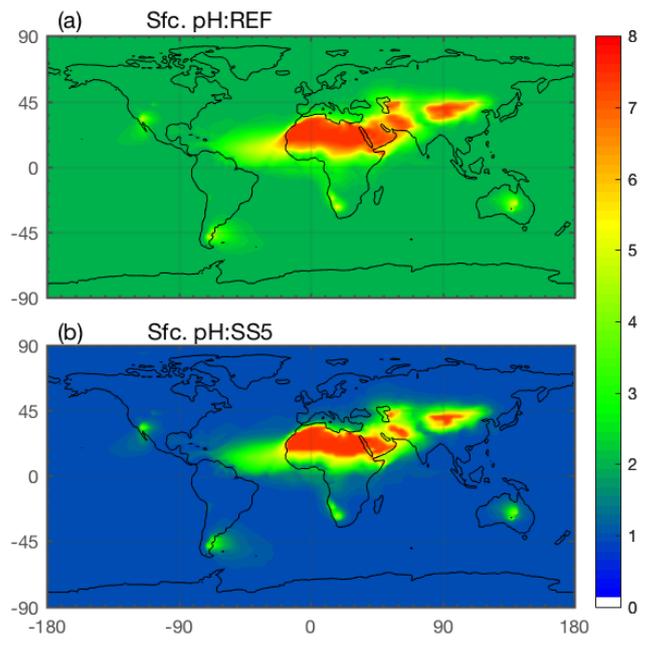


Fig. 1.

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C13