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Interactive comment on “Response of acid mobilization of iron-containing mineral dust to improvement of air quality projected in the future” by A. Ito and L. Xu

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We would like to thank the reviewers for his/her constructive comments for the improvement of our manuscript. Our responses to the comments from Reviewer 2 are included in the followings.

Major Comments

Comment: 1. From the statement of page 28180, lines 23-25, it seems that only mineral dust and sea salt aerosol are separated into four different size bins. This is in contradiction to the statement of page 28181, lines 14-17. In addition, did the authors

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[Interactive Discussion](#)

[Discussion Paper](#)



assume that different size bins of mineral dust have the same mineral compositions as well as the same dissolution rates? The authors should have described how the 4 size bins of aerosol are treated differently in the model in more details.

Reply: The statement of page 28181, lines 14-17 is corrected in the revised paper, p.12, l.222.

Here, five types of aerosols (i.e., dust, sulfate, carbonaceous aerosols from fossil fuel combustion, carbonaceous aerosols from biomass burning, and sea salt) were assumed to be externally mixed in each size bin for the computation of aerosol chemistry while nitrate and ammonium were internally mixed within each aerosol type (Xu and Penner, 2012).

We assume that different size bins of mineral dust have the same mineral compositions but the dissolution rates are different because the dust pH is separately calculated for each size bin. This is stated in the revised paper, p.15, l.281.

We use the same effective mineral fractions for all sizes of aerosol particles, but these species (e.g., illite, smectite, calcite, hematite, and gypsum) are represented by specific tracers for each size bin. Since the dust pH is calculated for each bin separately, the dissolution rates are different among different size bins of mineral dust.

Comment: 2. While comparing the modeled Fe dissolution curves with experimentally measured Fe dissolution from African and Asian dust (page 28189, second paragraph), the author only adopted one experimental result from Shi et al. But the mineralogy of mineral dust can be quite varied, and experimental conditions to study iron solubility are quite different between different studies (researchers). The authors should have included more experimental data, rather than just relying on one single experiment.

Reply: We include the comparison with Australian dust measured by Mackie et al. (2005) in a new Fig 2. The mineral composition of the dust aerosol near Buronga, in the Mallee Region of southwest New South Wales and northwest Victoria, Australia, on

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March is taken from the model estimates using the mineralogical map. Inter-calibration studies from different experimental researchers would be desirable for the issue of different experimental conditions, as was done for field observations in GEOTRACES (Morton et al., 2013). The followings are added in the revised paper, in p. 24, l.451.

In Fig. 2, we compare the modeled Fe dissolution rate from Australian dust under acidic condition ($\text{pH} = 2.15$) with the measurement by Mackie et al. (2005). Overall, the Fe dissolution rate is in good agreement with that for Australian dust at diluted conditions ($< 20 \text{ mg L}^{-1}$) where amount of Fe release was related only to the time of extraction (Mackie et al., 2005). The overestimate in iron solubility after 3 hours may result from the lack of spatial variability of the mineral speciation of specific iron compounds in the iron map.

Comment: 3. Atmospheric processing and material composition can effect iron solubility of mineral dust and other iron containing aerosols (i.e. oil fly ash and coal fly ash). Have atmospheric processing and composition of combustion aerosols also been taken into account in the model? If not, the authors should have stated the assumptions and explained why the assumptions have been made in the manuscript.

Reply: Iron solubility for combustion aerosols depends on the source composition only, as described in Ito (2012, 2013). Soluble iron in oil fly ash might be formed via high-temperature combustion followed by a sulfuric acid condensation before filtration (Sippula et al., 2009). This sentence with the reference is added to p.7, l.128.

These species might be formed via high-temperature combustion followed by a sulfuric acid condensation before filtration (Sippula et al., 2009).

To make it clearer, the following has been added to the sentence, p.8, l.131.

Since the plume chemistry for the co-emitted species is a sub-grid scale phenomenon in our coarse-scale model, we simply prescribed the Fe solubility for each combustion aerosol (i.e., oil fly ash, coal fly ash, and biomass burning aerosols) when it is emitted

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(Ito and Feng, 2010; Ito, 2012, 2013).

Comment: 4. Although the model has taken into account source material, mineralogy, surface acidity, and atmospheric processing effecting iron solubility, many recent studies have been suggested that organic acids, such as oxalic acid, might be very important in promoting atmospheric iron by providing protons for acid mobilization and by forming iron-organics complexes. The missing of the effect of organic acids in the model probably misled the model prediction.

Reply: Paris et al. (2011) examined the impact of oxalate on dissolution of Fe from dust during cloud processes. Their results showed that the iron solubility increased from 0.0025% to 0.26% when oxalate concentration was increased from 0 to 8 μM . The value of 0.26% due to oxalate-promoted Fe dissolution during cloud processes is generally smaller than the model-predicted values due to proton-promoted Fe dissolution in aerosol water, particularly in the Northern Hemisphere. This effect is potentially important in pristine regions where inorganic acids concentrations are too low to promote Fe dissolution in mineral dust particles but the oxalate concentration is high enough. Acknowledging that our model prediction is not a complete picture, we emphasize the importance for further investigation on the interactions between organic acids and iron in p.31, l.5598.

Paris et al. (2011) examined the effect of oxalate on iron dissolution from dust surrogate samples collected from the Sahara. Their results after 1 hour at pH = 4.7 showed that the iron solubility increased from 0.0025% to 0.26% when oxalate concentration was increased from 0 to 8 μM . The value of 0.26% due to oxalate-promoted Fe dissolution during cloud processes is generally smaller than the model-predicted values in deposited mineral dust due to proton-promoted Fe dissolution in aerosol water (global average to the ocean is 2.8% in Figure 7(d)), particularly in the Northern Hemisphere. However, the value of 0.26% at pH = 4.7 is larger than the water-soluble Fe content at emission in our model (global average at emission is 0.08%), which is consistent with iron solubility in agricultural soils (less than 0.1% at an extraction pH of 4.65) (Sillanpää,

Full Screen / Esc

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1982). Thus the effect of organic acid is potentially important in pristine regions where inorganic acids concentrations are too low to promote Fe dissolution from mineral dust particles but the organic acids concentrations are high enough. Acknowledging that our model prediction is not a complete picture, the chemical form of iron in aerosol and cloud water for investigations of photochemical reduction and ligand-promoted iron dissolution will be explored by using a multiphase process model that predicts aqueous oxalate formation in a future version of our model.

Our modeling approach (and thus the model output) is conceptually different from the modeling approach developed by Meskhidze et al. (2005). We estimate the filterable iron, while previous models estimate the dissolved iron (Luo et al., 2005; Luo and Gao, 2010; Johnson and Meskhidze, 2013). Since filterable iron does not only include the dissolved iron but also includes colloids and nanoparticles Fe in our model, whether these forms of iron have organic complexation or not in cloud water will not affect the calculated filterable iron deposition, if the readily released Fe at emissions is minor component in mineral dust. To clarify the differences in the operational definitions between filterable iron (solubility) and dissolved iron (fraction), we add the following in p.3, l.47 and p.31, l.598.

Studies using “ultrafiltration” in addition to a membrane pore diameter of $\approx 0.025 \mu\text{m}$ are assumed to measure dissolved iron only (Deguillaume et al., 2005). With decreasing crystal sizes, the dissolved iron fraction (i.e., the fraction of total aerosol iron that passes through $0.025 \mu\text{m}$ filters) of iron oxides increases and can approach the dissolved iron fraction of ferrihydrite (Kraemer, 2004). In this manuscript we use the terms iron solubility for the filterable iron case and dissolved iron fraction for the dissolved iron case.

Since filterable iron includes iron in aqueous phase, colloids, and nanoparticles in our model, whether iron in the forms of colloids and nanoparticles is transformed to iron-organics complexes (and thus dissolved iron) or not in cloud water will not affect the calculated filterable iron deposition, if the readily released Fe at emissions is minor

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component in mineral dust.

Minor Comments

Comment: 1. Page 28176, line 19. Missing period in “(Kraemer, 2004) Since”

Reply: This is correct in our uploading file. We will check it when printed.

Comment: 2. Page 28181, line 1. Spell out “DMS”

Reply: This is corrected as dimethylsulfide (DMS).

Comment: 3. Page 28184, line 27. Missing period in “(Table 1) Most iron is”

Reply: This is correct in our uploading file. We will check it when printed.

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