Biogeosciences
Discussions

Interactive comment on "Changes in dissolved iron deposition to the oceans driven by human activity: a 3-D global modelling study" *by* S. Myriokefalitakis et al.

Anonymous Referee #1

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General comments

The response of dissolved iron deposition to human activity is not known well. The authors presented a comprehensive global 3-D modeling study for dissolved iron. The analysis of the changes in anthropogenic emissions results in significant changes in soluble iron deposition due to changes in atmospheric acidity. The work conducted in this paper may contribute to improve our understanding of iron cycle, although more works will be required to improve the oxalate-promoted dissolution in aerosols. I have some comments and questions to improve this paper.

Specific comments

Abstract

p. 3945, l.9: What do you mean by "up to" 50%?

1 Introduction

p.3947, l.19: 3% should be replaced with 5% of hematite in dust.

p.3948, l.17: inorganic should be replaced with inorganic acids. Please delete ammonium.

p.3948, l.26: More recent study developed an explicit scheme for iron dissolution of combustion aerosols due to photochemical reactions with inorganic and organic acids in solution (Ito, 2015).

p. 3949, l.3: Please correct the reference of Mahowald et al. (2009) to Luo et al (2008).

p. 3949, l.10: The sentence for the same study is repeated. Please correct or delete it (see above).

2.1 Emissions

p.3951, l. 13: How did you calculate the dust emissions of 1090 Tg/yr for the year 2008 from the AEROCOM emission of 1678 Tg/yr for the year 2000?

p.3951, l. 19: How did you calculate the emissions for the year 2008 from the ACCMIP database for the year 2000?

p. 3952, l.3: How did you apply the $1° \times 1°$ dataset to the dust emission in the $6° \times 4°$ model?

2.4.1 Proton-promoted iron dissolution

p.3954, l.16: It reads that the pH values do not depend on aerosol sizes and types. Do you assume the internal mixing of all the aerosols in calculating aerosol water pH? What is the definition of aerosol water pH in your model?

p. 3954, l.21: Why did you use the mean percent mass content of particles for dust, instead of the mineralogy map? How did you consider the dissolution (e.g., calcite and magnetite) and precipitation (e.g., gypsum) for these minerals?

p. 3955, l.3, Table 2: The values of KMIN for KAOLINITE and FELDSPARS are different from those in the reference, but are identical to that for HEMATITE. Please check the values.

2.4.2 Organic ligand-promoted iron dissolution

p. 3956, l.5: How did you set the cloud life time?

p.3956, l.19: The reaction rate for OXL-promoted Fe dissolution was determined in cloud water conditions, so that this was only applied to cloud droplets. I agree that this oxalate-promoted dissolution should not be applied to mineral aerosols under these low pH conditions (see below). However, if you want to argue that "under these low pH conditions, ligand-promoted Fe dissolution may be suppressed significantly", please show the results. It is more likely that ligand-promoted Fe dissolution is suppressed "under low oxalate concentration" (Ito 2015), because of no significant oxalic acid sources near the desert regions, as you also mentioned in this manuscript.

2.5 Aqueous-phase chemistry scheme

Lin et al. (2014) showed that the model with iron chemistry underestimated oxalate measurements. Please show the comparison of oxalate measurements with iron chemistry, as in Fig 6 (b) of Myriokefalitakis et al. (2011).

2.6 Iron dissolution scheme

Figure S9: This figure was requested in review of Johnson and Meskhidze (2013), but was not shown (Interactive comment on Geosci. Model Dev. Discuss., 6, 1901, 2013). It is extremely hard to accept higher iron solubility (10%) for mineral dust with oxalate at pH = 8.5 than that at pH = 1.5 after 10 days in reality. Laboratory studies for dust aerosols showed that dissolved Fe with oxalate is higher at lower pH (see Figure S2 in

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Chen and Grassian, 2013). This is mainly because the oxalate-promoted dissolution rate of minerals is dependent on the mineral surface concentration of oxalate. Please show the spatial distribution of SFe (%) for dust aerosols and pH in water (see below).

3.4 Model iron concentration evaluation

Did you use daily or monthly or annual mean concentration for the comparison with the daily measurements? Please clarify this. Could you show the comparison of iron solubility?

3.5 Iron deposition

Please show the spatial distribution of iron solubility for mineral dust. Could you also show the spatial distribution of iron solubility for the fast-released iron, intermediate-released iron, and slowly-released iron, respectively, in supplementary materials?

3.6 Model iron deposition evaluation

Could you show the comparison of iron solubility?

4.1 Past and future changes in iron dissolution

Figure S4: Could you show the distributions of aerosol pH and cloud pH?

p. 3965, l.27: How did you separate the proton Fe dissolution from ligand Fe dissolution? Please discuss iron speciation quantitatively, by showing figure or table.

p. 3966, l.6: Please show the comparison of iron speciation with the observation quantitatively. Figure 4c shows the ratio is less than 10% over the significant portions of the ocean. If the modeled ratio is higher in rainwater, please show the results.

4.2 Past and future changes in iron dissolution

Please rephrase it.

Figure 8 and Figure S8 are confusing. If Figure 8(e) and 8(f) represent mineral dust only, why the changes in DFe are so large in the Southern Hemisphere? If Figure 8(e)

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and 8(f) represent the total DFe, what is the difference from Figure S8(a) and S8(b)? Please explain more clearly.

4.3 Biogeochemical implications

p.3968, l. 6 and Figure 9: If "to a lesser extent" is true for the Southern Ocean, the large increase is due to the mineral Fe dissolution. This is not true in Figure 8 (a).

References

Chen, H., and Grassian, V. H.: Iron dissolution of dust source materials during simulated acidic processing: The effect of sulfuric, acetic, and oxalic acids, Environ. Sci. Technol., 47, 10312−10321, 2013.

Ito, A.: Atmospheric processing of combustion aerosols as a source of bioavailable iron, Environ. Sci. Technol. Lett., 2 (3), 70–75, 2015.

Johnson, M. S., and Meskhidze, N.: Atmospheric dissolved iron deposition to the global oceans: effects of oxalate-promoted Fe dissolution, photochemical redox cycling, and dust mineralogy, Geosci. Model Dev., 6, 1137–1155, 2013.

Lin, G., Sillman, S., Penner, J. E., and Ito, A.: Global modeling of SOA: the use of different mechanisms for aqueous phase formation, Atmos. Chem. Phys., 14, 5451−5475, 2014.

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