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Comment

Interactive comment on “Delivery of anthropogenic bioavailable iron from mineral dust and combustion aerosols to the ocean” by A. Ito and Z. Shi

A. Ito and Z. Shi

akinorii@jamstec.go.jp

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We would like to thank the reviewer for his/her constructive comments for the improvement of our manuscript.

Specific Comments

Comment 1: p. 23052 line 8: Here, we, for the first time . . . - Please rephrase.

Response: This was completed (see also reply to comments by Reviewer 1).

Comment 2: p. 23053 line 15: ‘Anthropogenic’ secondary soluble Fe from dust. Please define whether you take also into account the Fe-dissolution due to natural acidity in

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the "anthropogenic" fraction of soluble Fe.

Response: The natural emissions of dimethylsulfide (DMS), sulfur dioxide (SO₂), nitrogen oxides (NO_x), volatile organic compounds (VOCs), and ammonia (NH₃) are not changed between current and pre-industrial periods in our simulations. Thus Fe-dissolution due to natural acidity is not included in the "anthropogenic" fraction of soluble Fe, as in Ito and Xu (2014). This is reflected in p.9, l.153-157.

"The same natural emissions of dimethylsulfide (DMS), sulfur dioxide (SO₂), nitrogen oxides (NO_x), volatile organic compounds (VOCs), and ammonia (NH₃) are used for both periods in our simulations, as we use the same meteorological data set. Thus Fe-dissolution due to natural acidity is not included in the "anthropogenic" fraction of soluble Fe, as in Ito and Xu (2014)."

Comment 3: p. 23056 lines 1-6: Please rephrase (preferably by avoiding the use of too short –telegraphic - sentences).

Response: To avoid the use of too short sentences, which were shorter from previous version of our paper, we moved all the details on the Tibesti dust, which were provided in Shi et al. (2011; 2015), to supplementary material 2 (as suggested by Reviewer 1).

Comment 4: p. 23057 line 7: Please define "each" chosen time point in the text.

Response: We rephrased the sentence and move it to supplementary material 2, as is shown in followings.

"Aliquots of the dust suspension were separated by filtering through a 0.2 μm filter directly into HCl (final concentration 0.2 N HCl), and the filtrates were stored for a maximum of one month at 4 °C until Fe analysis. The chosen time points to take samples were pre-set similar to Shi et al. (2011)."

Comment 5: Section 2: Please provide a Table with the characteristics of each experiment to help the readers to overview more easily the differences among the experiments.

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Response: We added a new Table 1. This is reflected in p.7, l.110-112.

“In order to determine the Fe dissolution kinetics in the dust aerosol water, which contains organic ligands, such as oxalate, and high concentration of inorganic ions, such as sulfate, four sets of time dependent dissolution experiments were performed, as is summarized in Table 1.”

Comment 6: Section 3, p.23057, line 25: Please refer to the highest pressure level in the vertical (in hPa).

Response: This is added in p.8, l.141-144.

“Simulations have been performed with a horizontal resolution of $2.0^\circ \times 2.5^\circ$ and 59 vertical layers with a top boundary at 0.01 hPa using meteorological fields for the year 2010 (and 2011 for the comparison with the field measurements).”

Comment 7: p. 23058, line 1: ‘. . . emissions of precursor gases’. Precursor gases of what? Please rephrase.

Response: This is revised in p.8, l.145-148:

“We run the model with emissions of primary aerosols and precursor gases of secondary aerosols such as sulfate, nitrate, ammonium, and oxalate for the preindustrial era and the present day to disentangle the naturally and anthropogenically-perturbed components (Table 2), as described in Ito et al. (2014).”

Comment 8: p. 23058, lines 21-24: It is not clear why Fe emissions in 1-3 bins are larger? Please explain how the mineral and Fe content are applied in each bin in your model.

Response: Our previous version used the mineralogical database compiled by Nickovic et al. (2012) and Fe content measured by Journet et al. (2008). As was described by Journet et al. (2014), “When we take the total iron oxide fraction, the cumulative abundance of hematite and goethite from our database amounts to a larger mass fraction

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(about 33% higher in average) than the hematite content from Nickovic et al. (2012)". The mineral fractions in clay-sized and silt-sized soils are listed in Table 1 by Journet et al. (2014). All Fe-containing minerals (i.e., hematite, goethite, illite, smectite, kaolinite, chlorite, vermiculite, and feldspars) are found in the clay-sized soils and only goethite, chlorite, and feldspars are in the silt-sized soils. The conversion of soil mineralogy to dust aerosol mineralogy for a given transport particle size is described by Scanza et al. (2015). We use the same equations as in Scanza et al. (2015) to calculate the contribution of the silt and clay soil fractions to each of the four dust aerosol size bins. We revised the sentences in p.9, l.158-164 and l.167-176:

"Previously, Ito and Xu (2014) used the mineralogical database compiled by Nickovic et al. (2012) and Fe content for hematite (69.9%), illite (4.0%), smectite (11%), kaolinite (0.24%), and feldspars (0.34%) (Journet et al., 2008). Here, the updated global database of mineral composition and Fe content for hematite (69.9%), goethite (62.8%), illite (4.3%), smectite (2.6%), kaolinite (0.23%), chlorite (12.3%), vermiculite (6.71%), and feldspars (0.34%) in clay-sized and silt-sized soils (CASE 1 in Journet et al., 2014) was used to estimate the emissions of Fe and calcite in dust aerosols."

"The mineral fractions in clay-sized and silt-sized soils are also distributed in the 4 size bins following the brittle fragmentation theory after Scanza et al. (2015). All the Fe-containing minerals are found in the clay-sized soils, while only three minerals (i.e., goethite, chlorite, and feldspars) are in the silt-sized soils. Thus Fe content averaged in the 1–3 size bins (3.6%) is higher than the largest one (2.3%), in contrast to constant Fe content (3.1%) with size in previous version. As a result, global Fe emission from dust (69 Tg yr⁻¹) is slightly smaller than that estimated in the previous version (79 Tg yr⁻¹) (Ito, 2015). The sum of Fe emission in the smaller size from bin 1 to bin 3 in this study (25 Tg yr⁻¹) is larger than that in the previous version (22 Tg yr⁻¹). Consequently, smaller dust particles may transport more Fe to remote regions relative to larger particles."

Comment 9: p. 23061: It is not clear what is the stoichiometric number of moles of Fe

per mole of mineral. Please define the chemical form in each pool of Fe-mineral.

Response: Theoretically, 1 mol of Fe_2O_3 produces 2 moles of Fe. At the initial period, however, elements are incongruently dissolved in solution from minerals (e.g., Malmström and Banwart, 1997; Brandt et al., 2003). Thus the stoichiometric number of moles of Fe per mole of mineral is empirically determined for Fe dissolution rate as in the equation (1). This is reflected in p.13, l.268-270:

“The above experimental dataset is used to determine the model parameters to predict the influence of solution saturation state on the Fe dissolution rates (see Table 3 and discussion below).”

We add following sentence to the footnote #5 in Table 3:

“The stoichiometric number of moles of Fe per mole of mineral is empirically determined for Fe dissolution rate as in the equation (1).”

Comment 10: p.23064, line 1: It is not clear if the function g is the same as in Ito (2015). In that paper it is mentioned that the parameters were fit to the experimental data for coal fly ash. Do you use the same approximation also for mineral dust?

Response: Yes, we use the same parameterization for mineral dust. The function considers competition for oxalate between surface Fe and dissolved Fe in our model. Thus excess oxalate is needed to induce significant Fe dissolution (Chen and Grassian, 2013). The following sentence is added in p.16, l.323-326.

“We apply the same equation for mineral dust, g_i , as in Ito (2015). Thus excess oxalate is needed to form mononuclear bidentate ligand with surface Fe and promote Fe dissolution significantly (Chen and Grassian, 2013).”

Comment 11: p.23064, lines 14-17: Please provide separately the strength (e.g. in Tg Fe yr^{-1}) of the calculated proton-, oxalate-promoted and quasi-photo-reductive Fe-dissolution, and discuss in more details their relative contribution on dissolved Fe deposition flux. What is the fractional contribution of each Fe-dissolution scheme on the

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calculated dissolved iron fraction?

Response: We show the fractional contribution of proton-promoted scheme and oxalate-promoted scheme on the calculated soluble Fe deposition in Fig. S5. The differences between base case and sensitivity case demonstrate the effect of quasi-photo-reductive Fe-dissolution. As we cited in introduction, in previous studies, the proton-promoted Fe dissolution was treated with no oxalate, and thus the Fe dissolution was significantly suppressed due to the dust alkalinity, particularly in the Southern Hemisphere (Meskhidze et al., 2005; Ito and Feng, 2010; Johnson et al., 2010; Ito and Xu, 2014). However, our current model considered the interactions of the three different processes via the suppression of mineral dissolution (i.e., fi, gi, and the consumption of oxalate due to photolysis of the Fe-oxalate complex in aqueous chemistry). Moreover, we consider the initial period of enhanced Fe release rate, as shown in Fig. 3. For instance, the dissolution of ferrihydrite occurs within 1 hour at highly acidic condition. In this case, we assign this Fe dissolution to proton-promoted dissolution, but this Fe dissolution may include the effects of oxalate on Fe dissolution via the suppression of mineral dissolution in the global model as well as the soluble Fe content at emission. As a result, the proton-promoted dissolution scheme contributed the majority of soluble Fe deposition to the ocean, 90% for the base case and 69% for the sensitivity case, respectively. Since this Fe dissolution is not only due to the proton-promoted dissolution by definition, we demonstrate the effect of different assumption on the initial period of enhanced Fe release. In an additional sensitivity simulation, we use 0.1% for the initial Fe solubility of mineral dust (Hand et al., 2004; Ito and Xu, 2014). The assumption of initial Fe solubility also affects the relative contribution on anthropogenic soluble Fe input. Here, we added our discussion on the relative contribution in p.5, l.62-65, p.20, l.413-425, and p.23, l.472-475, as follows.

“In previous studies, which implemented the proton-promoted Fe dissolution with no organic ligand, the Fe dissolution was significantly suppressed due to the dust alkalinity, particularly in the Southern Hemisphere (Meskhidze et al., 2005; Ito and Feng, 2010;

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Johnson et al., 2010; Ito and Xu, 2014).

“This is reflected in higher contribution of oxalate-promoted ($i = 2$ and 3) dissolution to total soluble Fe deposition in the sensitivity simulations for mineral aerosols, compared to that ($i = 2$) in the base simulations (Fig. S5). We note that higher contribution of proton-promoted ($i = 1$) dissolution near the source regions may include the effects of oxalate on Fe dissolution via the suppression of mineral dissolution as well as the soluble Fe content at emission. As a result, the proton-promoted dissolution scheme contributed the majority of soluble Fe deposition to the ocean, 90% for the base case and 69% for the sensitivity case, respectively. Since this Fe dissolution is not only due to the proton-promoted dissolution by definition, we demonstrate the effect of different assumption on the initial period of enhanced Fe release. In an additional sensitivity simulation, we use 0.1% for the initial Fe solubility of mineral dust (Hand et al., 2004; Ito and Xu, 2014). The model results show that the contribution of dissolution scheme to total soluble Fe deposition depends on the assumption on the initial Fe solubility at emission (Fig. S6). The model results suggest that the initial soluble Fe content from dust source regions such as South America (Patagonia), Australia, and southern Africa may be important for the supply of soluble Fe to the Southern Ocean. The proton-promoted dissolution scheme contributed 77% for the additional sensitivity case, which is between our base and sensitivity simulations.”

“It should be noted that anthropogenic soluble Fe input is also sensitive to the soluble Fe content at emission. The additional sensitivity simulation with the initial Fe solubility (0.1%) for dust aerosols indicates smaller contribution of anthropogenic component near the source regions (Fig. S7).”

We add a new Fig. S5 with the following caption:

“Fig. S5 Contribution of proton-promoted scheme and oxalate-promoted scheme to the total soluble Fe deposition calculated in the base and sensitivity simulations for dust aerosols. (a) Ratio (%) of the soluble Fe deposition from proton-promoted scheme ($i =$

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1) to the total soluble Fe deposition in the base simulations, (b) ratio (%) of the soluble Fe deposition from oxalate-promoted scheme ($i = 2$) to the total soluble Fe deposition in the base simulations, (c) ratio (%) of the soluble Fe deposition from proton-promoted scheme ($i = 1$) to the total soluble Fe deposition in the sensitivity simulations, and (d) ratio (%) of the soluble Fe deposition from oxalate-promoted scheme ($i = 2$ and 3) to the total soluble Fe deposition in the sensitivity simulations. The formation of the amorphous $\text{Fe}(\text{OH})_3(\text{s})$ suppresses the oxalate-promoted dissolution from mineral aerosols in the base simulations, while no such effect was considered for quasi-light-induced reductive dissolution in the sensitivity simulation (i.e., $f_3 = 1$)."

We add a new Fig. S6 with the following caption:

"Fig. S6 Contribution of proton-promoted scheme, oxalate-promoted scheme, and soluble Fe at emission to the total soluble Fe deposition calculated in additional sensitivity simulations for dust aerosols. To demonstrate the effect of different assumption on the initial period of enhanced Fe release for a comparison with Fig. S5, we use 0.1% for the initial Fe solubility of mineral dust in additional sensitivity simulations (Hand et al., 2004; Ito and Xu, 2014). (a) ratio (%) of the soluble Fe deposition from proton-promoted scheme ($i = 1$) to the total soluble Fe deposition in additional sensitivity simulations, (b) ratio (%) of the soluble Fe deposition from oxalate-promoted scheme ($i = 2$ and 3) to the total soluble Fe deposition in additional sensitivity simulations, and (c) ratio (%) of the soluble Fe deposition from the initial soluble Fe at emission to the total soluble Fe deposition in additional sensitivity simulations."

We add a new Fig. S7 with the following caption:

"Fig. S7 Ratio of anthropogenic to total soluble Fe deposition in the present day from additional sensitivity simulations. To demonstrate the effect of different assumption on the initial period of enhanced Fe release for a comparison with 0% for the initial Fe solubility of mineral dust in Fig. 7f, we assumed an initial Fe solubility of mineral dust of 0.1% in an additional sensitivity simulation (Hand et al., 2004; Ito and Xu, 2014)."

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We add following sentence to the footnote in Table 2:

“We also examined the initial Fe solubility of mineral dust (0.1%) in an additional sensitivity simulation (Hand et al., 2004; Ito and Xu, 2014).”

Comment 12: p.23065, line 24: Please show separately the calculated Fe(II) and Fe(III) surface distributions and also discuss their relative contribution to the total Fe-solubility.

Response: The fractional contribution of Fe(II) and Fe(III) surface distributions are the same as in Lin et al. (2014). Thus Fe(III)-oxalate complex is the major form of Fe in modeled solution. However, it is likely that a strong organic complexation of Fe(II) in rainwater helps to stabilize Fe in dissolved form (Kieber et al., 2005; Willey et al., 2015). In revised paper, we show similar plots of the variability of the total Fe solubility vs. the variability of Fe/WSOC molar ratio even with a constant WSOC concentration (see below our response to comment 13). The results indicate that the variability in the total Fe solubility is nearly independent of the variability in WSOC concentration, possibly because of the excess ligands to stabilize Fe in solution at low Fe loading, keeping in mind that soluble Fe may include colloidal materials. Because of a lack of knowledge of specific organic compounds and their formation rates in cloud and aerosol water, it is premature to draw conclusions regarding the nature of Fe-organic complexes and thus the fractional contribution of Fe(II) and Fe(III). The following sentences are added in p.11, l.181-192.

“The aqueous-phase chemical reactions for the formation of oxalate are the same as described by Lin et al. (2014), except for the treatment of the Fe chemistry in aerosol and cloud water as in Ito (2015). Thus Fe(III)-oxalate complex is the major form of Fe in modeled solution. The photolysis of Fe-oxalate complex can contribute to a significant oxalate sink in cloud water influenced by ship emissions (Sorooshian et al., 2013; Wang et al., 2014). On the other hand, complexation of Fe(II) with stronger organic ligands from fossil fuel combustion may be more important for the stability of Fe dissolved in rain water (Kieber et al., 2005; Willey et al., 2015). Here, we focus

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on the acid mobilization of relatively insoluble Fe in Fe-containing minerals to soluble Fe. Because of the lack of knowledge regarding the specific ligands and formation rates of Fe-organic complexes, Fe chemistry is disabled in cloud and rain water but implemented for Fe-containing wet aerosols in four size bins to obtain good agreement regarding oxalate with the observations over the ocean (see Figure S3 in Ito, 2015).”

Comment 13: Section 5: It is not clear why you use the Fe/WSOC ratio. Please also make a statement and show how good your model simulates the observed WSOC concentrations.

Response: The following sentences are added in p.19, l.388-398 to explain why we show Fe/WSOC ratio.

“The averaged WSOC concentration in our model (330 ± 470 ng m⁻³) is consistent with the measurements (330 ± 290 ng m⁻³). The higher Fe solubility measured in water (pH = 5.5) for the excess WSOC with Fe-binding functionalities (e.g., –COOH, –NH₂) may suggest a potential role of the organic compounds in aerosols for the delivery of Fe to the ocean in soluble form (Wozniak et al., 2013, 2015). Here, similar plots can be obtained even with a constant WSOC concentration at 330 (ng m⁻³) (Fig. S4). The results indicate that the variability in Fe solubility is nearly independent of the variability in WSOC concentration, possibly because of the excess ligands to stabilize Fe in solution at low Fe loading.”

We add a new Fig. S4 with the following caption:

“Fig. S4 The Fe/WSOC molar ratio versus Fe solubility for model estimates (red squares) and measurements (black circles) over the cruise tracks. The measurements are obtained from Wozniak et al., (2013, 2015). The number of modeled data points (84) is larger than the measurements (37), because each daily average is calculated for each sampling date at each center of cruise location. A constant WSOC concentration at 330 (ng m⁻³) is used for both the model estimates and measurements in this figure for a comparison with Fig. 5b.”

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Comment 14: p. 23066 lines 4-7: Please explain why do you make this statement? Did you expect a different model behavior (more acidic) near dust source regions? If yes why? Do you take into account the effect of buffering capacity of dust in each bin? Please show in the supplement global figures of the pH values i) for aerosol (in each bin) and ii) for cloud water, that your model takes into account.

Response: We do not expect a more acidic condition near dust source region except sub-micron particles over North Africa, where buffering capacity of dust is exceeded (see Fig. S3). The effect of buffering capacity of dust in each bin is taken into account as in Ito and Xu (2014). If the calcite is externally mixed with Fe-containing minerals, more acidic condition would be expected (Ito and Feng, 2010). In this case, the suppression of Fe dissolution would not work near the source region of dust aerosols, and thus higher Fe solubility would be predicted. Please also see response to comment 11 above. The pH values for aerosol water are shown in a new Fig. S3. The aqueous Fe chemistry is turned off in cloud water. Thus the pH values for cloud water are not changed significantly from that shown in Fig. S1 by Lin et al. (2014) (see also above). Furthermore, there is no Fe-dissolution for cloud water in our model. Therefore, the figures of the pH values for cloud water were not shown in this paper. The sentences are added in p.10, l.179-180 and p.18, l.377-382, as follows.

“The values of the pH of the aerosol water used in the calculations of the dissolution rates are estimated for all of the wet aerosols in each size bin, as in Ito and Xu (2014).

“The internal mixing of alkaline minerals with Fe-containing minerals in aqueous chemistry for mineral dust can lead to higher pH and thus suppress the Fe dissolution near the source regions, compared to the external mixing (Ito and Feng, 2010). The model predicts relatively higher pH values for dust aerosols except submicron particles near the source regions, because the dust alkalinity reservoir (i.e., calcite) is able to buffer the acidification (Fig. S3).”

We add a new Fig. S3 with the following caption:

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“Fig. S3 Spatial distribution of vertically and annually averaged dust pH for (a) bin 1 (radius: $<0.63 \mu\text{m}$), (b) bin 2 (radius: $0.63\text{--}1.25 \mu\text{m}$), (c) bin 3 (radius: $1.25\text{--}2.5 \mu\text{m}$), and (d) bin 4 (radius: $2.5\text{--}10 \mu\text{m}$) for the present day.”

Comment 15: Please show the oxalate concentrations that your model simulates for the current Fe-dissolution scheme. What is the effect of the new Fe-dissolution scheme on the simulated oxalate concentrations compared to previous model status and how good the new oxalate concentrations are compared to measurements?

Response: This is shown in Figure 6 in Lin et al. (2014). Our model with Fe chemistry significantly underpredicted oxalate measurements. As was shown for Arizona test dust in Figure S4 by Chen and Grassian (2013), the oxalic acid concentration decreased rapidly with Fe dissolution under irradiation within 4 hours. The consumption of oxalate due to photolysis of the Fe-oxalate complex is included in aqueous chemistry, as in reaction number 44 in Table S6 of Lin et al. (2014). Thus, the model underestimates are mainly due to the photodecomposition of Fe(III) oxalate species. As was discussed in Lin et al. (2014), other factors, which might also contribute to the model underestimation, include a lack of fast secondary production from local sources, low cloud water content, and high deposition rates in the model. As was shown in Figure S3 by Ito (2015), the comparison with the measurements over the ocean shows reasonable agreement, but this is partly because we used an extra glyoxal source of 20 Tg yr^{-1} over the oceans, following the work of Myriokefalitakis et al. (2011), as in Ito et al., (2015), and mostly because we turned off the Fe chemistry in cloud water, as in Ito (2015). As was discussed in this paper and in Ito (2015), Fe in atmospheric water might not be readily available for Fe-oxalate complexes but often present in more stable forms. Clearly, more work is required for the role of Fe in the net formation of oxalate. Because we focus on Fe dissolution in mineral aerosols, Fe chemistry is disabled in cloud water to obtain a good agreement regarding oxalate with the observations over the ocean.

The following sentence is added in p.22, l.452-453.

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“Thus the consumption of oxalate due to photolysis of the Fe-oxalate complex may be limited due to complexation with stronger ligands in atmospheric water.”

Comment 16: p. 23067, line 10: ‘in good agreement with “the” measurements’

Response: This is corrected.

Comment 17: p. 23067, line 12: Does your model apply aqueous-phase chemistry in rain droplets? How do you treat dissolved Fe wet deposition in the model?

Response: No, aqueous-phase chemistry is not applied in rain water. The following sentence is added in p.10, l.192-194.

“The deposition velocities of soluble Fe depend on the aerosol types and size bins, and follow the aging of the parent aerosols in the atmosphere (Ito and Xu, 2014).”

Comment 18: p. 23068: Please provide the amount (in Tg Fe yr⁻¹) and the spatial distribution of Fe-dissolution for aerosol and cloud water separately.

Response: There is no Fe-dissolution for cloud water in our model (based on Shi et al., 2015), please see above.

Comment 19: p. 23078 line 1: Please correct “Fe Tg yr⁻¹ “ with “Tg Fe yr⁻¹ ”

Response: This is corrected.

References

Brandt, F., Bosbach, D., Krawczyk-Bärsch, E., Arnold, T., and Bernhard, G.: Chlorite dissolution in the acid pH-range: A combined microscopic and macroscopic approach, *Geochim. Cosmochim. Acta*, 67, 1451–1461, doi:10.1016/S0016-7037(02)01293-0, 2003.

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, doi:10.1021/es401285s, 2013.

Hand, J. L., Mahowald, N. M., Chen, Y., Siefert, R. L., Luo, C., Subramaniam, A., and Fung, I.: Estimates of atmospheric processed soluble iron from observations and a global mineral aerosol model: Biogeochemical implications, *J. Geophys. Res.*, 109, D17205, doi:10.1029/2004JD004574, 2004.

Ito, A.: Atmospheric processing of combustion aerosols as a source of bioavailable iron, *Environ. Sci. Technol. Lett.*, 2 (3), 70–75, doi: 10.1021/acs.estlett.5b00007, 2015.

Ito, A. and Feng, Y.: Role of dust alkalinity in acid mobilization of iron, *Atmos. Chem. Phys.*, 10, 9237–9250, doi:10.5194/acp-10-9237-2010, 2010.

Ito, A., Lin, G., Penner, J. E.: Reconciling modeled and observed atmospheric deposition of soluble organic nitrogen at coastal locations, *Global Biogeochem. Cy.*, 28, 617–630, doi:10.1002/2013GB004721, 2014.

Ito, A., Lin, G., and Penner, J. E.: Global modeling study of soluble organic nitrogen from open biomass burning, *Atmos. Environ.*, 121, 103–112, doi:10.1016/j.atmosenv.2015.01.031, 2015.

Ito, A. and Xu, L.: Response of acid mobilization of iron-containing mineral dust to improvement of air quality projected in the future, *Atmos. Chem. Phys.*, 14, 3441–3459, doi:10.5194/acp-14-3441-2014, 2014.

Johnson, M. S., Meskhidze, N., Solmon, F., Gassó, S., Chuang, P. Y., Gaiero, D. M., Yantosca, R. M., Wu, S., Wang, Y., and Carouge, C.: Modeling dust and soluble iron deposition to the South Atlantic Ocean, *J. Geophys. Res.*, 115, D15202, doi:10.1029/2009JD013311, 2010.

Journet, E., Desboeufs, K. V., Caquineau, S., and Colin, J.-L.: Mineralogy as a critical factor of dust iron solubility, *Geophys. Res. Lett.*, 35, L07805, doi:10.1029/2007GL031589, 2008.

Journet, E., Balkanski, Y., and Harrison, S. P.: A new data set of soil mineralogy for

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dust-cycle modeling, *Atmos. Chem. Phys.*, 14(8), 3801–3816, doi:10.5194/acp-14-3801-2014, 2014.

Kieber, R. J., Skrabal, S.A., Smith, B., and Willey, J. D.: Organic complexation of Fe(II) and its impact on the redox cycling of iron in rain, *Environ. Sci. Technol.*, 39, 1576–1583, 2005.

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, doi:10.5194/acp-14-5451-2014, 2014.

Malmström, M., and Banwart, S.: Biotite dissolution at 25°C: The pH dependence of dissolution rate and stoichiometry, *Geochim. Cosmochim. Acta*, 61(14), 2779–2799, 1997.

Meskhidze, N., Chameides, W. L., and Nenes, A.: Dust and pollution: A recipe for enhanced ocean fertilization?, *J. Geophys. Res.*, 110, D03301, doi:10.1029/2004JD005082, 2005.

Myriokefalitakis, S., Tsigaridis, K., Mihalopoulos, N., Sciare, J., Nenes, A., Kawamura, K., Segers, A., and Kanakidou, M.: In-cloud oxalate formation in the global troposphere: a 3-D modeling study, *Atmos. Chem. Phys.*, 11, doi:10.5194/acp-11-5761-2011, 5761–5782, 2011.

Nickovic, S., Vukovic, A., Vujadinovic, M., Djurdjevic, V., and Pejanovic, G.: Technical Note: High-resolution mineralogical database of dust-productive soils for atmospheric dust modeling, *Atmos. Chem. Phys.*, 12, 845–855, doi:10.5194/acp-12-845-2012, 2012.

Scanza, R. A., Mahowald, N., Ghan, S., Zender, C. S., Kok, J. F., Liu, X., Zhang, Y., and Albani, S.: Modeling dust as component minerals in the Community Atmosphere Model: development of framework and impact on radiative forcing, *Atmos. Chem. Phys.*, 15, 537–561, doi:10.5194/acp-15-537-2015, 2015.

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Shi, Z., Bonneville, S., Krom, M., Carslaw K., Jickells, T., Baker, A., and Benning, L.: Iron dissolution kinetics of mineral dust at low pH during simulated atmospheric processing, *Atmos. Chem. Phys.*, 11, 995–1007, doi:10.5194/acp-11-995-2011, 2011.

Shi, Z., Krom, M. D., Bonneville, S., and Benning, L. G.: Atmospheric processing outside clouds increases soluble iron in mineral dust, *Environ. Sci. Technol.*, 49, 1472–1477, doi:10.1021/es504623, 2015.

Sorooshian, A., Wang, Z., Coggon, M. M., Jonsson, H. H., and Ervens, B.: Observations of sharp oxalate reductions in stratocumulus clouds at variable altitudes: organic acid and metal measurements during the 2011 E-PEACE campaign, *Environ. Sci. Technol.*, 47, 7747–7756, doi:10.1021/es4012383, 2013.

Wang, Z., Sorooshian, A., Prabhakar, G., Coggon, M. M., and Jonsson, H. H.: Impact of emissions from shipping, land, and the ocean on stratocumulus cloud water elemental composition during the 2011 E-PEACE field campaign, *Atmos. Environ.*, 89, 570–580, doi:10.1016/j.atmosenv.2014.01.020, 2014.

Wiley, J. D., Kieber, R. J., Humphreys, J. J., Rice, B. C., Hopwood, M. J., Avery, G. B. and Mead R. N.: The role of fossil fuel combustion on the stability of dissolved iron in rainwater, *Atmos. Environ.* 107, 187–193, 2015.

Wozniak, A. S., Shelley, R. U., Sleighter, R. L., Abdulla, H. A. N., Morton, P. L., Landing, W. M., and Hatcher, P. G.: Relationships among aerosol water soluble organic matter, iron and aluminum in European, North African, and Marine air masses from the 2010 US GEOTRACES cruise, *Mar. Chem.*, 153, 24–33, doi:10.1016/j.marchem.2013.04.011, 2013.

Wozniak, A. S., Shelley, R. U., McElhenie, S. D., Landing, W. M., and Hatcher, P. G.: Aerosol water soluble organic matter characteristics over the North Atlantic Ocean: Implications for iron-binding ligands and iron solubility, *Mar. Chem.*, 173, 162–172, doi:10.1016/j.marchem.2014.11.002, 2015.

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