Response to reviewer comments:

Reviewer 1:

We would like to thank the reviewer for his/her constructive comments. Since comments by Reviewer 1 were based on the version (acp-2015-487-manuscript-version1) that has not been revised after initial submission, our responses and revisions to the manuscript will be slightly different when citing line numbers.

Specific Comments

__Comment 1__. Introduction: The aim of the study is provided both in the first and last paragraph of this section. Please reorganize, the aim should be mentioned in the same section, preferably in the last paragraph. Moreover, avoid redundancy, lines 122-126 are not required. The titles of each section should be enough for the reader to understand and of course from what it is already mentioned in this paragraph.

__Response:__ We deleted the last sentence in the first paragraph to avoid redundancy, and merged it to the sentence in the last paragraph of this section in the revised paper, p. 6, l. 102-106, as is shown in following. We also deleted the sentences in *lines 122-126*.

"The model estimates "anthropogenic" soluble Fe supply from both dust and combustion sources to the oceans in association with past changes in air quality (including direct emission of soluble Fe in primary anthropogenic aerosol as well as conversion of insoluble Fe in Fe-containing aerosols to soluble Fe due to increased aerosol acidity) based on the Intergovernmental Panel on Climate Change (IPCC) emission data set."

__Comment 2.__ Laboratory experiments: Details on the Tibesti dust are provided in Shi et al. (2011a; 2015). So I would suggest in order to keep the manuscript short and to the point to start this section with line 139 adding just the information that using the procedure in the above reference little impact has been seen on Fe speciation and dissolution at acidic pH. The last comment is essential, however if the reader needs additional information they can look into the citation. Moreover, the detection limit for the dissolved Fe through the spectrophhotometric method seems to be rather high compared to others in the literature.

35 ***Response:*** We moved the details on the Tibesti dust to supplementary material 2. The detection
36 limit for the dissolved Fe is 0.05 µmol/L, which is much lower than the measurements in our
37 experiments. This is reflected in the Supplement, as follows.

38

39 "The detection limit for dissolved Fe is 0.05 µM (Shi et al., 2015), which is much lower than the
40 measurements in our experiments."

41

42 ***Comment 3:*** *Development of a new Fe dissolution scheme based on new experimental results:*
43 *Focus on the new findings of your study i.e. Figure 3 comparison with literature not needed, it is*
44 *mentioned in the manuscript. Lines 283-291 are results from previous reference. Yet again too*
45 *much you should be concise as in Section 5.*

46

47 ***Response:*** We deleted the comparison with Ito and Xu (2014) (blue squares) in Figure 3. But
48 *Lines 283-291* represent the comparison of new results in this work with previous results in Shi
49 et al. (2011). We rephrase the sentences in the revised paper, p.13, l.261-268, as is shown in
50 followings.

51

52 "The calculated thermodynamic solubility of this Fe pool at pH 2 is -3.34 (mol L^{-1} on a log
53 scale). This is comparable to the previously measured thermodynamic solubility of nanogoethite,
54 which is -3.6 (mol L^{-1}) at pH = 2 (see Fig.7 in Shi et al. 2011). Thus this Fe pool likely includes
55 ferrihydrite and reactive nano-Fe oxides aggregated on the mineral surface. This is consistent
56 with higher Fe solubility of 1.2% as compared to that of the highly reactive Fe (0.63%) (Shi et al.,
57 2011). Only 3.3% of Fe was dissolved at a dust/liquid ratio of 10 g L^{-1} and pH 2, and Fe
58 dissolution stopped at 180 h. The calculated thermodynamic solubility of the second Fe pool is $-$
59 3.55 (mol L^{-1})."

60

Technical Corrections

62 ***Comment 4:*** *Page 2, line 15-17: I suggest you change the phrase "Here, we, for the first time,*
63 *interactively combined laboratory kinetic experiments with global aerosol modeling to more*
64 *accurately quantify anthropogenic soluble Fe due to air pollution." to "In this study, for the first*
65 *time, we interactively combined laboratory kinetic experiments with global aerosol modeling to*
66 *more accurately quantify anthropogenic soluble Fe due to air pollution.".*

67

68 ***Response:*** Thanks and this has now been changed.

69

70 ***Comment 5:*** *Page 2, line 17, 19: I would suggest replacing "We firstly examined..." with*
71 *"Firstly, we examined..." and "We then..." with "Then, we...", respectively for lines 17 and 19.*

72

73 ***Response:*** Thanks and this has now been changed to "Firstly, we determined..." and "Then,
74 we...".

75

76 ***Comment 6:*** *Page 4, line 41-43: Please re-write the sentence i.e. "Thus, improved quantification*
77 *of atmospheric delivery of bioavailable Fe is essential to estimate more accurately the long-term*
78 *carbon sink (Jickells et al. 2005).".*

79

80 ***Response:*** Now changed to *"*<u>Thus, improved quantification of atmospheric delivery of</u>
81 <u>bioavailable Fe is essential to quantify the long-term carbon sink (Jickells et al. 2005).</u>*"*

82

83 ***Comment 7:*** *Page 13, line 251: I believe the author meant "Almost identical slopes were found*
84 *at ....".*

85

86 ***Response:*** This is corrected.

87

References

88 **References**
89 Ito, A. and Xu, L.: Response of acid mobilization of iron-containing mineral dust to improvement of air
90 quality projected in the future, Atmos. Chem. Phys., 14, 3441–3459, doi:10.5194/acp-14-3441-
91 2014, 2014.
92 Jickells, T. D., An, Z. S., Andersen, K. K., Baker, A. R., Bergametti, G., Brooks, N., Cao, J. J., Boyd, P.
93 W., Duce, R. A., Hunter, K. A., Kawahata, H., Kubilay, N., LaRoche, J., Liss, P. S., Mahowald,
94 N., Prospero, J. M., Ridgwell, A. J., Tegen, I., and Torres, R.: Global iron connections between
95 desert dust, ocean biogeochemistry, and climate, Science, 308, 67–71,
96 doi:10.1126/science.1105959, 2005.
97 Shi, Z., Bonneville, S., Krom, M., Carslaw K., Jickells, T., Baker, A., and Benning, L.: Iron dissolution
98 kinetics of mineral dust at low pH during simulated atmospheric processing, Atmos. Chem. Phys.,
99 11, 995–1007, doi:10.5194/acp-11-995-2011, 2011.
100 Shi, Z., Krom, M. D., Bonneville, S., and Benning, L. G.: Atmospheric processing outside clouds
101 increases soluble iron in mineral dust, Environ. Sci. Technol., 49, 1472−1477,
102 doi:10/1021/es504623, 2015.
103

104 **Reviewer 2**

105

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

108

109 **Specific Comments**

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

111

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

113

114 *Comment 2:* *p. 23053 line 15: 'Anthropogenic' secondary soluble Fe from dust. Please define*
115 *whether you take also into account the Fe-dissolution due to natural acidity in the*
116 *"anthropogenic" fraction of soluble Fe.*

117

118 *Response:* The natural emissions of dimethylsulfide (DMS), sulfur dioxide (SO$_2$), nitrogen
119 oxides (NO$_x$), volatile organic compounds (VOCs), and ammonia (NH$_3$) are not changed
120 between current and pre-industrial periods in our simulations. Thus Fe-dissolution due to natural
121 acidity is not included in the "anthropogenic" fraction of soluble Fe, as in Ito and Xu (2014).
122 This is reflected in p.9, l.153-157.

123

124 "The same natural emissions of dimethylsulfide (DMS), sulfur dioxide (SO$_2$), nitrogen oxides
125 (NO$_x$), volatile organic compounds (VOCs), and ammonia (NH$_3$) are used for both periods in our
126 simulations, as we use the same meteorological data set. Thus Fe-dissolution due to natural
127 acidity is not included in the "anthropogenic" fraction of soluble Fe, as in Ito and Xu (2014)."

128

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

131

132 *Response:* To avoid the use of too short sentences, which were shorter from previous version of
133 our paper, we moved all the details on the Tibesti dust, which were provided in Shi et al. (2011;
134 2015), to supplementary material 2 (as suggested by Reviewer 1).

135

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

137

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

140

"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)."

145

__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.*

148

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

150

"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."

154

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

157

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

159

"Simulations have been performed with a horizontal resolution of 2.0° × 2.5° 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)."

163

__Comment 7:__ *p. 23058, line 1: '. . . emissions of precursor gases'. Precursor gases of what? Please rephrase.*

166

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

168

"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 (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."

209 ***Comment 9:*** *p. 23061: It is not clear what is the stoichiometric number of moles of Fe per mole*
210 *of mineral. Please define the chemical form in each pool of Fe-mineral.*

211

212 ***Response:*** Theoretically, 1 mol of Fe_2O_3 produces 2 moles of Fe. At the initial period, however,
213 elements are incongruently dissolved in solution from minerals (e.g., Malmström and Banwart,
214 1997; Brandt et al., 2003). Thus the stoichiometric number of moles of Fe per mole of mineral is
215 empirically determined for Fe dissolution rate as in the equation (1). This is reflected in p.13,
216 l.268-270:

217

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

221

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

223

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

226

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

230

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

235

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

239

240 ***Comment 11:*** *p.23064, lines 14-17: Please provide separately the strength (e.g. in Tg Fe yr-1) of*
241 *the calculated proton-, oxalate-promoted and quasi-photo-reductive Fe-dissolution, and discuss*
242 *in more details their relative contribution on dissolved Fe deposition flux.*

243 *What is the fractional contribution of each Fe-dissolution scheme on the calculated dissolved*
244 *iron fraction?*

245

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

268

269 "In previous studies, which implemented the proton-promoted Fe dissolution with no organic
270 ligand, the Fe dissolution was significantly suppressed due to the dust alkalinity, particularly in
271 the Southern Hemisphere (Meskhidze et al., 2005; Ito and Feng, 2010; Johnson et al., 2010; Ito
272 and Xu, 2014).

273

274 "This is reflected in higher contribution of oxalate-promoted ($i = 2$ and 3) dissolution to total
275 soluble Fe deposition in the sensitivity simulations for mineral aerosols, compared to that ($i = 2$)
276 in the base simulations (Fig. S5). We note that higher contribution of proton-promoted ($i = 1$)
277 dissolution near the source regions may include the effects of oxalate on Fe dissolution via the
278 suppression of mineral dissolution as well as the soluble Fe content at emission. As a result, the
279 proton-promoted dissolution scheme contributed the majority of soluble Fe deposition to the
280 ocean, 90% for the base case and 69% for the sensitivity case, respectively. Since this Fe
281 dissolution is not only due to the proton-promoted dissolution by definition, we demonstrate the
282 effect of different assumption on the initial period of enhanced Fe release. In an additional
283 sensitivity simulation, we use 0.1% for the initial Fe solubility of mineral dust (Hand et al., 2004;
284 Ito and Xu, 2014). The model results show that the contribution of dissolution scheme to total

285 soluble Fe deposition depends on the assumption on the initial Fe solubility at emission (Fig.
286 S6)."

287

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

292

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

294

295 "Fig. S5   Contribution of proton-promoted scheme and oxalate-promoted scheme to the
296 total soluble Fe deposition calculated in the base and sensitivity simulations for dust aerosols. **(a)**
297 Ratio (%) of the soluble Fe deposition from proton-promoted scheme ($i = 1$) to the total soluble
298 Fe deposition in the base simulations, **(b)** ratio (%) of the soluble Fe deposition from oxalate-
299 promoted scheme ($i = 2$) to the total soluble Fe deposition in the base simulations, **(c)** ratio (%)
300 of the soluble Fe deposition from proton-promoted scheme ($i = 1$) to the total soluble Fe
301 deposition in the sensitivity simulations, and **(d)** ratio (%) of the soluble Fe deposition from
302 oxalate-promoted scheme ($i = 2$ and 3) to the total soluble Fe deposition in the sensitivity
303 simulations. The formation of the amorphous $Fe(OH)_3(s)$ suppresses the oxalate-promoted
304 dissolution from mineral aerosols in the base simulations, while no such effect was considered
305 for quasi-light-induced reductive dissolution in the sensitivity simulation (i.e., $f_3 = 1$)."

306

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

308

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

319

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

321

"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)."

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 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

360 wet Fe-containing aerosols in four size bins to obtain good agreement regarding oxalate with the
361 observations over the ocean (see Figure S3 in Ito, 2015)."

362

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

365

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

368

369 "The averaged WSOC concentration in our model (330 ± 470 ng m^{-3}) is consistent with the
370 measurements (330 ± 290 ng m^{-3}). The higher Fe solubility measured in water (pH = 5.5) for the
371 excess WSOC with Fe-binding functionalities (e.g., –COOH, –NH$_2$) may suggest a potential role
372 of the organic compounds in aerosols for the delivery of Fe to the ocean in soluble form
373 (Wozniak et al., 2013, 2015). Here, similar plots can be obtained even with a constant WSOC
374 concentration at 330 (ng m^{-3}) (Fig. S4). The results indicate that the variability in Fe solubility is
375 nearly independent of the variability in WSOC concentration, possibly because of the excess
376 ligands to stabilize Fe in solution at low Fe loading."

377

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

379

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

386

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

392

393 ***Response:***

394 We do not expect a more acidic condition near dust source region except sub-micron particles
395 over North Africa, where buffering capacity of dust is exceeded (see Fig. S3). The effect of

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

406

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

409

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

415

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

417

418 "Fig. S3   Spatial distribution of vertically and annually averaged dust pH for **(a)** bin 1
419 (radius: <0.63 μm), **(b)** bin 2 (radius: 0.63–1.25 μm), **(c)** bin 3 (radius: 1.25–2.5 μm), and **(d)** bin
420 4 (radius: 2.5–10 μm) for the present day."

421

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

426

427 ***Response:*** This is shown in Figure 6 in Lin et al. (2014). Our model with Fe chemistry
428 significantly underpredicted oxalate measurements. As was shown for Arizona test dust in Figure
429 S4 by Chen and Grassian (2013), the oxalic acid concentration decreased rapidly with Fe
430 dissolution under irradiation within 4 hours. The consumption of oxalate due to photolysis of the
431 Fe-oxalate complex is included in aqueous chemistry, as in reaction number 44 in Table S6 of
432 Lin et al. (2014). Thus, the model underestimates are mainly due to the photodecomposition of
433 Fe(III) oxalate species. As was discussed in Lin et al. (2014), other factors, which might also

434   contribute to the model underestimation, include a lack of fast secondary production from local
435   sources, low cloud water content, and high deposition rates in the model. As was shown in
436   Figure S3 by Ito (2015), the comparison with the measurements over the ocean shows reasonable
437   agreement, but this is partly because we used an extra glyoxal source of 20 Tg yr^{-1} over the
438   oceans, following the work of Myriokefalitakis et al. (2011), as in Ito et al., (2015), and mostly
439   because we turned off the Fe chemistry in cloud water, as in Ito (2015). As was discussed in this
440   paper and in Ito (2015), Fe in atmospheric water might not be readily available for Fe-oxalate
441   complexes but often present in more stable forms. Clearly, more work is required for the role of
442   Fe in the net formation of oxalate. Because we focus on Fe dissolution in mineral aerosols, Fe
443   chemistry is disabled in cloud water to obtain a good agreement regarding oxalate with the
444   observations over the ocean.

445

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

447

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

450

451   ***Comment 16:*** *p. 23067, line 10: 'in good agreement with "the" measurements'*

452

453   ***Response:*** This is corrected.

454

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

457

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

460

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

463

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

466

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

469

470 **_Comment 19:_** *p. 23078 line 1: Please correct "Fe Tg yr-1 " with "Tg Fe yr-1 "*

471

472 **_Response:_** This is corrected.

473
474 **References**
475 Brandt, F., Bosbach, D., Krawczyk-Bärsch, E., Arnold, T., and Bernhard, G.: Chlorite dissolution in the
476   acid pH-range: A combined microscopic and macroscopic approach, Geochim. Cosmochim. Acta,
477   67, 1451–1461, doi:10.1016/S0016-7037(02)01293-0, 2003.
478 Chen, H. and Grassian, V. H.: Iron dissolution of dust source materials during simulated acidic
479   processing: The effect of sulfuric, acetic, and oxalic acids, Environ. Sci. Technol., 47,
480   10312−10321, doi:10.1021/es401285s, 2013.
481 Hand, J. L., Mahowald, N. M., Chen, Y., Siefert, R. L., Luo, C., Subramaniam, A., and Fung, I.:
482   Estimates of atmosphericprocessed soluble iron from observations and a global mineral aerosol
483   model: Biogeochemical implications, J. Geophys. Res., 109, D17205,
484   doi:10.1029/2004JD004574, 2004.
485 Ito, A.: Atmospheric processing of combustion aerosols as a source of bioavailable iron, Environ. Sci.
486   Technol. Lett., 2 (3), 70–75, doi: 10.1021/acs.estlett.5b00007, 2015.
487 Ito, A. and Feng, Y.: Role of dust alkalinity in acid mobilization of iron, Atmos. Chem. Phys., 10, 9237–
488   9250, doi:10.5194/acp-10-9237-2010, 2010.
489 Ito, A., Lin, G., Penner, J. E.: Reconciling modeled and observed atmospheric deposition of soluble
490   organic nitrogen at coastal locations, Global Biogeochem. Cy., 28, 617–630,
491   doi:10.1002/2013GB004721, 2014.
492 Ito, A., Lin, G., and Penner, J. E.: Global modeling study of soluble organic nitrogen from open biomass
493   burning, Atmos. Environ., 121, 103–112, 10.1016/j.atmosenv.2015.01.031, 2015.
494 Ito, A. and Xu, L.: Response of acid mobilization of iron-containing mineral dust to improvement of air
495   quality projected in the future, Atmos. Chem. Phys., 14, 3441–3459, doi:10.5194/acp-14-3441-
496   2014, 2014.
497 Johnson, M. S., Meskhidze, N., Solmon, F., Gassó, S., Chuang, P. Y., Gaiero, D. M., Yantosca, R. M.,
498   Wu, S., Wang, Y., and Carouge, C.: Modeling dust and soluble iron deposition to the South
499   Atlantic Ocean, J. Geophys. Res., 115, D15202, doi:10.1029/2009JD013311, 2010.
500 Journet, E., Desboeufs, K. V., Caquineau, S., and Colin, J.-L.: Mineralogy as a critical factor of dust iron
501   solubility, Geophys. Res. Lett., 35, L07805, doi:10.1029/2007GL031589, 2008.
502 Journet, E., Balkanski, Y., and Harrison, S. P.: A new data set of soil mineralogy for dust-cycle modeling,
503   Atmos. Chem. Phys., 14(8), 3801–3816, doi:10.5194/acp-14-3801-2014, 2014.
504 Kieber, R. J., Skrabal, S.A., Smith, B., and Willey, J. D.: Organic complexation of Fe(II) and its impact
505   on the redox cycling of iron in rain, Environ. Sci. Technol., 39, 1576−1583, 2005.
506 Lin, G., Sillman, S., Penner, J. E., and Ito, A.: Global modeling of SOA: the use of different mechanisms
507   for aqueous-phase formation, Atmos. Chem. Phys., 14, 5451–5475, doi:10.5194/acp-14-5451-
508   2014, 2014.
509 Malmström, M., and Banwart, S.: Biotite dissolution at 25°C: The pH dependence of dissolution rate and
510   stoichiometry, Geochim. Cosmochim. Acta, 61(14), 2779–2799, 1997.
511 Meskhidze, N., Chameides, W. L., and Nenes, A.: Dust and pollution: A recipe for enhanced ocean
512   fertilization?, J. Geophys. Res., 110, D03301, doi:10.1029/2004JD005082, 2005.

513 Myriokefalitakis, S., Tsigaridis, K., Mihalopoulos, N., Sciare, J., Nenes, A., Kawamura, K., Segers, A.,
514   and Kanakidou, M.: In-cloud oxalate formation in the global troposphere: a 3-D modeling study,
515   Atmos. Chem. Phys., 11, doi:10.5194/acp-11-5761-2011, 5761–5782, 2011.
516 Nickovic, S., Vukovic, A., Vujadinovic, M., Djurdjevic, V., and Pejanovic, G.: Technical Note: High-
517   resolution mineralogical database of dust-productive soils for atmospheric dust modeling, Atmos.
518   Chem. Phys., 12, 845–855, doi:10.5194/acp-12-845-2012, 2012.
519 Scanza, R. A., Mahowald, N., Ghan, S., Zender, C. S., Kok, J. F., Liu, X., Zhang, Y., and Albani, S.:
520   Modeling dust as component minerals in the Community Atmosphere Model: development of
521   framework and impact on radiative forcing, Atmos. Chem. Phys., 15, 537–561, doi:10.5194/acp-
522   15-537-2015, 2015.
523 Shi, Z., Bonneville, S., Krom, M., Carslaw K., Jickells, T., Baker, A., and Benning, L.: Iron dissolution
524   kinetics of mineral dust at low pH during simulated atmospheric processing, Atmos. Chem. Phys.,
525   11, 995–1007, doi:10.5194/acp-11-995-2011, 2011.
526 Shi, Z., Krom, M. D., Bonneville, S., and Benning, L. G.: Atmospheric processing outside clouds
527   increases soluble iron in mineral dust, Environ. Sci. Technol., 49, 1472−1477,
528   doi:10/1021/es504623, 2015.
529 Sorooshian, A., Wang, Z., Coggon, M. M., Jonsson, H. H., and Ervens, B.: Observations of sharp oxalate
530   reductions in stratocumulus clouds at variable altitudes: organic acid and metal measurements
531   during the 2011 E-PEACE campaign, Environ. Sci. Technol., 47, 7747−7756,
532   doi:10.1021/es4012383, 2013.
533 Wang, Z., Sorooshian, A., Prabhakar, G., Coggon, M. M., and Jonsson, H. H.: Impact of emissions from
534   shipping, land, and the ocean on stratocumulus cloud water elemental composition during the
535   2011 E-PEACE field campaign, Atmos. Environ., 89, 570–580,
536   doi:10.1016/j.atmosenv.2014.01.020, 2014.
537 Willey, J. D., Kieber, R. J., Humphreys, J. J., Rice, B. C., Hopwood, M. J., Avery, G. B. and Mead R. N.:
538   The role of fossil fuel combustion on the stability of dissolved iron in rainwater, Atmos. Environ.
539   107, 187−193, 2015.
540 Wozniak, A. S., Shelley, R. U., Sleighter, R. L., Abdulla, H. A. N., Morton, P. L., Landing, W. M., and
541   Hatcher, P. G.: Relationships among aerosol water soluble organic matter, iron and aluminum in
542   European, North African, and Marine air masses from the 2010 US GEOTRACES cruise, Mar.
543   Chem., 153, 24–33, doi:10.1016/j.marchem.2013.04.011, 2013.
544 Wozniak, A. S., Shelley, R. U., McElhenie, S. D., Landing, W. M., and Hatcher, P. G.: Aerosol water
545   soluble organic matter characteristics over the North Atlantic Ocean: Implications for iron-
546   binding ligands and iron solubility, Mar. Chem., 173, 162–172,
547   doi:10.1016/j.marchem.2014.11.002, 2015.
548

549 **Delivery of anthropogenic bioavailable iron from mineral dust and combustion aerosols to**
550 **the ocean**

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555 Running Title: **Anthropogenic bioavailable Fe deposition**

558 **Abstract.** Atmospheric deposition of anthropogenic soluble iron (Fe) to the ocean has been

559 suggested to modulate primary ocean productivity and thus indirectly affect the climate. A key

560 process contributing to anthropogenic sources of soluble Fe is associated with air pollution,

561 which acidifies Fe-containing mineral aerosols during their transport and leads to Fe

562 transformation from insoluble to soluble forms. However, there is large uncertainty in our

563 estimate of this anthropogenic soluble Fe. ~~Here, we~~In this study, for the first time, we

564 interactively combined laboratory kinetic experiments with global aerosol modeling to more

565 accurately quantify anthropogenic soluble Fe due to air pollution. ~~We firstly examined~~Firstly, we

566 determined Fe dissolution kinetics of African dust samples at acidic pH values with and without

567 ionic species commonly found in aerosol water (i.e., sulfate and oxalate). ~~We then~~Then, we

568 constructed a new empirical scheme for Fe release from mineral dust due to inorganic and

569 organic anions in aerosol water, by using acidity as a master variable. We implemented this new

570 scheme and applied an updated mineralogical emission database in a global atmospheric

571 chemistry transport model to estimate the atmospheric concentration and deposition flux of

572 soluble Fe under preindustrial and modern conditions. Our improved model successfully

573 captured the inverse relationship of Fe solubility and total Fe loading measured over the North

574 Atlantic Ocean (i.e., 1–2 orders of magnitude lower Fe solubility in North African- than

575 combustion-influenced aerosols). The model results show a positive relationship between Fe

576 solubility and water soluble organic carbon (WSOC)/Fe molar ratio, which is consistent with

577 previous field measurements. We estimated that deposition of soluble Fe to the ocean increased

578 from 0.05–0.07 Tg Fe yr^{-1} in preindustrial era to 0.11–0.12 Tg Fe yr^{-1} in present days, due to air

579 pollution. Over the High Nitrate Low Chlorophyll (HNLC) regions of the ocean, the modeled Fe

580 solubility remains low for mineral dust (<1%) in a base simulation but is substantially enhanced

581 in a sensitivity simulation, which permits the Fe dissolution for mineral aerosols in the presence

582 of excess oxalate under low acidity during daytime. Our model results suggest that human

583 activities contribute to about half of the soluble Fe supply to a significant portion of the oceans in

584 the Northern Hemisphere, while their contribution to oceans in high latitudes remains uncertain

585 due to limited understanding of ~~dust~~ Fe source and its dissolution under pristine conditions.

1 Introduction

Changes in supply of nutrients such as bioavailable iron (Fe) from the atmosphere to the ocean have altered oceanic carbon uptake, but significant uncertainties remain on the magnitude of this effect (Ciais et al., 2013). Thus improved quantification of atmospheric delivery of bioavailable Fe is essential to ~~estimate~~quantify the long-term carbon sink ~~more accurately~~ (Jickells et al. 2005). The present study focuses on "potentially" bioavailable Fe, which includes colloidal materials and aqueous species (often operationally defined as soluble Fe). The response of the aerosol Fe solubility (i.e., soluble Fe / total Fe) to air pollution is a key uncertainty in our understanding of the biogeochemical cycle of Fe, marine ecosystem, and climate (Mahowald et al., 2009; Shi et al. 2012; Hajima et al., 2014). ~~We use the term "anthropogenic" soluble Fe here as primary soluble Fe from oil combustion aerosols and secondary soluble Fe from both dust and combustion aerosols, due to the changes in emissions of precursor gases and aerosols from fossil fuel use and biofuel combustion between the preindustrial era and the present day (Ito et al., 2014).~~

Atmospheric processing of mineral dust has been hypothesized to be an important source of soluble Fe to the oceans because of acidic condition in aerosol water (Zhuang et al. 1992; Meskhidze et al., 2003). Previous chemical transport models used mineral dissolution rates and stoichiometric numbers of Fe in minerals to estimate Fe release rates from mineral aerosols (Meskhidze et al., 2005; Solmon et al., 2009; Ito and Feng, 2010; Ito, 2012). Laboratory studies for mineral dust have demonstrated that the Fe release rates used in previous global models were much slower than the measurements during a typical aerosol lifetime of 2–7 days (Mackie et al., 2005; Shi et al., 2011). The initial period of enhanced concentration of elements, which are incongruently dissolved in solution from phyllosilicate minerals, is well known in laboratory

609   works (e.g., Malmström and Banwart, 1997; Brandt et al., 2003). Much slower quasi-steady state

610   dissolution rates after 10–14 days are typically observed for aluminosilicate minerals in acid

611   solutions (Amram and Ganor, 2005; Lowson et al., 2005; Golubev et al., 2006; Rozalén et al.,

612   2008; Bibi et al., 2011). Recent atmospheric chemical transport models have adopted the initial

613   period of enhanced Fe release rate for the proton-promoted dissolution (Ito and Xu, 2014;

614   Myriokefalitakis et al., 2015). ~~It needs to be mentioned that~~In previous studies, which

615   implemented the proton-promoted Fe dissolution ~~is~~with no organic ligand, the Fe dissolution was

616   significantly suppressed due to the dust alkalinity, particularly in the Southern Hemisphere

617   (Meskhidze et al., 2005; Ito and Feng, 2010; Johnson et al., 2010; Ito and Xu, 2014). Currently,

618   ferric sulfate is treated as water-soluble Fe in oil combustion aerosols at emission (Ito, 2013,

619   2015; Myriokefalitakis et al., 2015; Wang et al., 2015).

620   Previous laboratory studies suggest that different acid types and photochemical reactions

621   affect proton-promoted Fe dissolution rates of mineral dust, in addition to the types of Fe species

622   associated with mineral source materials (Cwiertny et al., 2008; Fu et al., 2010; Rubasinghege et

623   al., 2010). However, all previous laboratory experiments were conducted in absence of

624   ammonium salt, such as sulfate, which are ubiquitous in aerosol water. Some of anions in aerosol

625   water are known to be effective inorganic ligands, which form the complexes with Fe in solution

626   (Cornell and Schwertmann, 2003). In batch experiments, the mineral dissolution rate at high

627   dust/liquid ratio can be influenced by different ability of these anions to form soluble complexes

628   with metals (Hamer et al., 2003). Thus the effect of decrease of the activity of Fe^{3+} on the Fe

629   dissolution rates via the formation of aqueous complexes needs to be assessed in laboratory

630   experiments to constrain the degree of suppression used in models.

631   Recently, global atmospheric transport model studies have emphasized the role of oxalate

632   for promoting Fe dissolution from Fe-containing aerosols (Luo and Gao, 2010; Johnson and

633   Meskhidze, 2013; Ito, 2015; Myriokefalitakis et al., 2015) (see the Supplement). Moreover,

634   oxalate-promoted dissolution of Fe is suppressed at low concentrations of oxalate near strong Fe

635   sources (Ito, 2015), because excess oxalate is necessary to induce significant Fe dissolution

636   (Chen and Grassian, 2013). These modeling studies highlighted the importance of oxalate-

637   promoted Fe dissolution for mineral dust over the remote oceans. However, a constant oxalate-

638   promoted dissolution rate with time for mineral dust has been prescribed in previous models

639   regardless of different dissolution behaviors in different Fe types, due to a lack of experimental

640   data for oxalate-promoted Fe dissolution kinetics.

641   Here, we conducted a series of laboratory experiments to examine how inorganic and

642   organic ligands in solution (i.e., sulfate and oxalate) affect Fe dissolution rates in mineral dust.

643   The experimental data were then used to derive a new Fe release scheme, which is implemented

644   in a global chemical transport model to quantify the effect of atmospheric processing of mineral

645   aerosols on Fe mobilization. This study incorporates the proton- and oxalate-promoted Fe

646   dissolution schemes for the mineral aerosols in our model (Ito, 2015). We also examine quasi-

647   photo-reductive dissolution scheme for mineral aerosols in a sensitivity simulation.

648   Determination of Fe dissolution for different types of Fe requires three key parameters of Fe

649   release rate, degree of suppression, and Fe content. We implement three-stage kinetic process for

650   the Fe dissolution scheme to dust aerosols. We use the updated version of the mineralogical

651   database for Fe content in soils (Journet et al., 2014). To assess model assumptions for Fe

652   dissolution, the calculated Fe solubility is evaluated against field observations in relation to total

653   Fe loading and water soluble organic carbon (WSOC) over the North Atlantic Ocean (Wozniak

et al. 2013, 2015). The model ~~provides the~~estimates "anthropogenic" soluble Fe supply from both dust and combustion sources to the oceans in association with past changes in air quality (including direct emission of soluble Fe in primary anthropogenic aerosol as well as conversion of insoluble Fe in Fe-containing aerosols to soluble Fe due to increased aerosol acidity) based on the Intergovernmental Panel on Climate Change (IPCC) emission data set. ~~The experimental and model approaches are presented in Section 2 and 3, respectively. Section 4 describes the experimental results and the development of the new Fe release scheme. The response of soluble Fe deposition to changes in air pollution and the comparisons of the model with observations are described in the Section 5 followed by the summary of our findings in the Section 6.~~

2 Laboratory experiments

In this study, we used the same Tibesti dust sample as in Shi et al. (2011~~, 2015~~). We followed a similar methodology as in Shi et al. (2011). Please see supplementary materials for more details. ~~Highly reactive Fe on the mineral surface was 0.63% of the total Fe (Shi et al., 2011a). More crystalline Fe oxides on the mineral surface represent 37.7% of total Fe in the Tibesti dust. The rest of Fe is associated with aluminosilicates.~~

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 ~~following the same methodology~~, as is summarized in ~~Shi et al. (2011).~~Table 1. The experiments include the dissolution of Fe in the Tibesti dust:

(Experiment 1) at a dust/liquid ratio of 1 g L^{-1} in 0.05 and 0.005 mol L^{-1} sulfuric acid solution only (i.e., no $(NH_4)_2SO_4$) (pH = 1.3, ionic strength I = 0.15 M; and pH = 2.1, I = 0.015

676   M). The pH values in highly acidic solutions were estimated from molality and activity

677   coefficient, which were calculated using E-AIM III aqueous solution simulator (Wexler and

678   Clegg, 2002).

679   (Experiment 2) at a dust/liquid ratio of 1 g L^{-1} in 0.05 and 0.0005 mol L^{-1} sulfuric acid

680   solution with 1 mol L^{-1} (NH$_4$)$_2$SO$_4$ (pH = 2 and I = 3.15 M; and pH = 3.1 and I = 3.015 M) only

681   (i.e., no oxalate) and in 0.1 mol L^{-1} HCl solution with 3 mol L^{-1} NH$_4$Cl (ionic strength I = 3.2

682   mol L^{-1}) (pH = 0.9; note that activity coefficient for H$^+$ in this solution is higher than 1), and at a

683   dust/liquid ratio of 10 g L^{-1} in 0.05 mol L^{-1} sulfuric acid solution with 1 mol L^{-1} (NH$_4$)$_2$SO$_4$ (pH

684   = 2, I = 3.15 mol kg^{-1}). The pH values with high ionic strength (I > 3 mol L^{-1}) were estimated

685   using E-AIM III thermodynamic model (Wexler and Clegg, 2002).

686   (Experiment 3) at a dust/liquid ratio of 1 g L^{-1} in 0.05 and 0.0005 mol L^{-1} sulfuric acid

687   solution with both 1 mol L^{-1} (NH$_4$)$_2$SO$_4$ and 0.03 mol L^{-1} of oxalate (as sodium oxalate) (pH = 2,

688   I = 3.15 M; and pH = 3.1, I = 3.015 M). The chosen amount of oxalate is based on the molar

689   ratio of oxalate and sulfate in ambient PM$_{2.5}$ samples (Yu et al., 2005).

690   (Experiment 4) at a dust/liquid ratio of 60 mg L^{-1}, 10 g L^{-1} and 50 g L^{-1} in 0.005 mol L^{-1}

691   sulfuric acid solution (pH 2). The pH was continuously monitored during the experiments at four

692   different dust/liquid ratios (i.e., 60 mg L^{-1}, 1 g L^{-1}, 10 g L^{-1} and 50 g L^{-1}) and once the pH

693   change was more than 0.1 pH unit, acids were added to decrease the pH to 2. This aims to

694   determine how different dust/liquid ratios affect the Fe dissolution kinetics in comparison with

695   experiment (1) (1 g L^{-1}).

696   ~~At each chosen time point, an aliquot of the dust suspension was taken with a syringe and~~

697   ~~filtered through a 0.2 μm filter directly into HCl (final concentration 0.2 N HCl), and the filtrates~~

698 ~~were stored for a maximum of one month at 4 °C until Fe analysis. Filtration through 0.2 μm~~

699 ~~pore sized filters is commonly used for measurements of dissolved species from dust suspension,~~

700 ~~especially at near-neutral pH. Fe colloids tend to aggregate or adhere to mineral surface, which~~

701 ~~are efficiently retained by a 0.2 μm filter (Shi et al., 2009, 2015). Spectrophotometric ferrozine~~

702 ~~method was used to quantify the dissolved Fe concentration in this study. The solutions from the~~

703 ~~high ionic experiments ($I > 3$ mol L^{-1}) were diluted 100 times with acidified Milli-Q water (0.01~~

704 ~~mol L^{-1} HCl) before measurement to avoid interferences. The precision of Fe measurement is~~

705 ~~±1.2% (1 s, n = 6) and the detection limit for dissolved Fe is 0.05 μM (Shi et al., 2015).~~

3   Model description

707   This study uses the Integrated Massively Parallel Atmospheric Chemical Transport

708 (IMPACT) model (Rotman et al., 2004; Liu et al., 2005; Feng and Penner, 2007; Ito et al., 2007,

709 2012, 2014, 2015; Lin et al., 2014; Xu and Penner, 2012; Ito, 2015). The model is driven by

710 assimilated meteorological fields from the Goddard Earth Observation System (GEOS) of the

711 NASA Global Modeling and Assimilation Office (GMAO). Simulations have been performed

712 with a horizontal resolution of $2.0° \times 2.5°$ and 59 vertical layers <u>with a top boundary at 0.01 hPa</u>

713 using meteorological fields for the ~~years~~<u>year</u> 2010 (and 2011 for the comparison with the field

714 measurements).

715   We run the model with emissions of <u>primary aerosols and </u>precursor gases ~~and aerosols~~<u>of</u>

716 <u>secondary aerosols such as sulfate, nitrate, ammonium, and oxalate</u> for the preindustrial era and

717 the present day to disentangle the naturally and anthropogenically-perturbed components (Table

718 ~~1~~<u>2</u>), as described in Ito et al. (2014). The emission data sets for anthropogenic activities such as

719 fossil fuel use and biofuel combustion are taken from the historical emissions for IPCC Fifth

Assessment (AR5) report for the preindustrial era and the present day (Lamarque et al., 2010). The present-day estimates for mineral aerosols from arid and semiarid regions as well as combustion aerosols from biomass burning are used together with anthropogenic emission changes (Ito and Xu, 2014; Ito et al., 2015; Ito, 2015). The same natural emissions of dimethylsulfide (DMS), sulfur dioxide (SO_2), nitrogen oxides (NO_x), volatile organic compounds (VOCs), and ammonia (NH_3) 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).

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). TheHere, 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 size distribution at emission follows the mass fractions of emitted soil particles in Kok (2011). The mass fluxes of mineral dust at emission are interpolated to represent four model size bins (radius: <0.63, 0.63–1.25, 1.25–2.5, and 2.5–10 μm) with the theoretical expression (Ito et al., 2012). The mineral fractions in clay-sized and silt-sized soils are also distributed in the 4 size bins following the brittle fragmentation theory (Scanza et al., 2015). 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), which used high Fe content for smectite (11after 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

(Journet et al., 2014). Thus~~%) (Journet et al., 2008). The sum of Fe emission in the smaller size from bin 1 to bin 3 (25 Tg yr^{-1}) is larger than the previous one (22 Tg yr^{-1}), because~~ 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.

Mineral dust aging process with the formation of soluble materials in aerosol and cloud water (e.g., sulfate, nitrate, ammonium, and oxalate) is explicitly simulated in the model (Ito and Xu, 2014; Ito, 2015). ~~We also~~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 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, a complexation of Fe(II) with stronger organic ligands from fossil fuel combustion may be important for the stability of Fe dissolved in rain water (Kieber et al., 2005; Willey et al., 2015). Here, we focus 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

766 observations over the ocean (see Figure S3 in Ito, 2015). The deposition velocities of soluble Fe

767 depend on the aerosol types and size bins, and follow the aging of the parent aerosols in the

768 atmosphere (Ito and Xu, 2014). Here, we developed a new Fe release scheme in mineral dust

769 (see section 4) to improve the previously used scheme (Ito and Xu, 2014). The new scheme is

770 implemented in the IMPACT model for simulations in section 5.

771 **4.   Development of a new Fe dissolution scheme based on new experimental results**

772   In our model, Fe release from aerosols due to chemical processing is calculated based on

773 an online simulation of aqueous-phase chemistry (Ito and Feng, 2010; Ito, 2012; Ito and Xu,

774 2014; Ito, 2015). Ito and Xu (2014) have developed a Fe dissolution scheme that considers the

775 types of Fe species associated with mineral source materials, mainly based on the measurements

776 by Shi et al. (2011). Following their studies, three Fe pools are characterized by ferrihydrite,

777 nano-sized Fe oxides, and heterogeneous inclusion of nano-Fe grains in aluminosilicates (e.g.,

778 illite, smectite, and chlorite). Here we developed a new Fe dissolution scheme, which considers

779 our laboratory experimental datasets regarding: (1) the formation of Fe inorganic and organic

780 complexes in solution and (2) the formation of surface complexes between oxalate and Fe oxides,

781 following Ito (2015) for combustion aerosols.

782   Fig.Figure 1 and Fig. S1 in the Supplement demonstrate the effects of inorganic anions to

783 form soluble complexes with Fe at different dust/liquid ratios on dissolution rates measured in

784 acidic solution. Fig.Figure 1 shows that the pH = 2 (0.05M H_2SO_4, 1M $(NH_4)_2SO_4$, red triangles)

785 and pH = 2.1 (0.005M H_2SO_4, green diamonds) cases at 1 g dust L^{-1} have significantly different

786 Fe dissolution rates. The one with high ionic strength (red triangles, Figure 1) has a much higher

787 dissolution rate than predicted by the small difference in the pH values. It is expected that one

788 pH unit can lead to 3–4 times difference in dissolution rates as shown here and by Shi et al.

789 (~~2011a). Higher ionic strength has a tendency to decrease the thermodynamic solubility but~~

790 ~~the~~2011). The presence of complexing ions such as sulfate in this case has the potential to

791 accelerate the dissolution rate by absorption or by complexation with Fe dissolved in solution

792 (Cornell and Schwertmann, 2003). We observed a good agreement of measurements between at

793 1 g L^{-1} dust in 0.05 mol L^{-1} sulfuric acid solution with 1 mol L^{-1} $(NH_4)_2SO_4$ (pH = 2.0, red

794 triangles) and at 60 mg L^{-1} dust in 0.005 mol L^{-1} sulfuric acid solution without $(NH_4)_2SO_4$ (pH =

795 2.11, black circles). Thus the solution remains under-saturated with respect to Fe(III), because

796 essentially all aqueous Fe(III) species (> 99%) is complexed with sulfate (i.e., $FeSO_4^+$) in 0.05

797 mol L^{-1} sulfuric acid solution with 1 mol L^{-1} $(NH_4)_2SO_4$ (pH = 2.0) (Meskhidze et al., 2005; Ito,

798 2015). The higher dust/liquid ratio at 10 g L^{-1} (blue squares) exhibits lower Fe dissolution rate

799 after the initial period of enhanced Fe release rate, possibly due to the re-adsorption of solution

800 phase Fe onto the particulate phase, as the solution with $(NH_4)_2SO_4$ is under-saturated with

801 respect to Fe(III) (Spokes and Jickells, 1996; Bibi et al., 2011).

802   Our data indicate that addition of complexing agents (i.e., sulfate in Fig. 1 and chlorite in

803 Fig. ~~S1 in the Supplement~~S1) accelerated dissolution of Fe minerals by binding Fe released from

804 the surface in solution (Zhang et al., 1985; Xu and Gao, 2008). Almost identical slopes were

805 found <u>at</u> between ~~at~~ 1 g L^{-1} dust in 0.05 mol L^{-1} sulfuric acid solution with 1 mol L^{-1} $(NH_4)_2SO_4$

806 (pH = 2.0, red triangles) and ~~at~~ 60 mg L^{-1} dust in 0.005 mol L^{-1} sulfuric acid solution without

807 $(NH_4)_2SO_4$ (pH = 2.0, black circles) during a typical aerosol lifetime (Fig. 1). Thus we chose

808 dust/liquid ratios of 1 g L^{-1} in sulfuric acid solution with 1M ammonium sulfate to represent

809 proton-promoted Fe dissolution scheme for mineral dust.

810   ~~Fig.~~Figure 2 demonstrates the impact of oxalate on Fe dissolution rate (black circles). The

811   addition of 0.03 M $Na_2C_2O_4$ accelerated the dissolution of Fe in dust (1 g dust L^{-1} solution, 0.05

812   M H_2SO_4 or 0.005 M H_2SO_4, with 1 M $(NH_4)_2SO_4$). Dissolved Fe concentration was 60% higher

813   at 72 h in the 0.05 M H_2SO_4 and 1 M $(NH_4)_2SO_4$) dust suspensions with oxalate. It was over

814   100% higher at 72 h in the 0.005 M H_2SO_4 and 1 M $(NH_4)_2SO_4$) dust suspensions when added

815   oxalate. The higher activity of protons can facilitate the oxalate-promoted dissolution process by

816   protonating the hydroxyl (OH) groups at the surface of hydrous Fe oxides, thereby contributing

817   to increasing the number of positively charged surface sites. This increase promotes ligand

818   adsorption, and weakening of the Fe-O bond, which permits the reaction between oxalate and Fe

819   sites by ligand exchange (Cornell and Schwertman, 2003; Ramos et al., 2014). Although the

820   protonation of the ligands in solution increases at higher activity of protons, the adsorption

821   mechanism of $HC_2O_4^-$ involves the loss of a proton during the ligand-exchange adsorption

822   reaction or during the transfer process from bulk solution to the mineral surface (Yoon et al.,

823   2004). Consequently, the amount of absorbed complex on the mineral surface is higher in

824   solutions at pH < 7 when the overall charge at the reactive surface sites is positive, compared to

825   that at lower activity of protons (Zhang et al., 1985; Xu and Gao, 2008; Lanzl et al., 2012;

826   Ramos et al., 2014). The surface biding sites for adsorbed oxalate become saturated at high

827   proton and high oxalate concentrations, and thus oxalate-promoted dissolution rates are almost

828   independent of pH for mineral dust (Yoon et al., 2004; Cama and Ganor, 2006; Lanzl et al.,

829   2012).

830   Experimental data in Fig. 3 demonstrate that the Fe release under higher dust/solution

831   ratios is suppressed when the solution becomes super-saturated with respect to Fe(III), as

832   observed by the decrease in the rate (black circles). At low dust/liquid ratio of 60 mg L^{-1} at pH

833   2.1 (H^+ concentration of 0.01 mol L^{-1}), Fe dissolution continued even after 800 hours. The rate

834   of Fe dissolution decreased substantially with increasing dust/liquid ratio. At a dust/liquid ratio

835   of 50 g L^{-1}, Fe dissolution stopped at 180 h and only 1.2% (10 µmol g^{-1}) of the total Fe was

836   dissolved, half of which released in the first hour. ~~According to Shi et al. (2011), this~~

837   ~~corresponds to the first Fe pool of Tibesti PM~~$_{20}$~~at pH = 2.~~ The calculated thermodynamic

838   solubility of this Fe pool at pH 2 is −3.34 (mol L^{-1} on a log scale). This is ~~slightly larger~~

839   ~~than~~comparable to the <u>previously</u> measured ~~thermodynamic~~ solubility of nanogoethite, which is

840   −3.6 (mol L^{-1}) at pH = 2 (see Fig.7 in Shi et al. 2011). ~~This~~<u>Thus this</u> Fe pool ~~can include~~<u>likely</u>

841   <u>includes</u> ferrihydrite and reactive nano-Fe oxides aggregated on the mineral surface. This is ~~also~~

842   consistent with higher Fe solubility of 1.2% ~~than~~<u>as compared to that of the</u> highly reactive Fe

843   (0.63%) (Shi et al., 2011). Only 3.3% of Fe was dissolved at a dust/liquid ratio of 10 g L^{-1} and

844   pH 2, and Fe dissolution stopped at 180 h. ~~According to Shi et al. (2011), this represents the total~~

845   ~~of first and second Fe pools of Tibesti PM~~$_{20}$~~at pH = 2. The calculated thermodynamic~~<u>The</u>

846   <u>calculated</u> solubility of the second Fe pool is −3.55 (mol L^{-1}). The above experimental dataset is

847   used to determine the model parameters to predict the influence of solution saturation state on

848   the Fe dissolution rates (see <u>Table 3 and</u> discussion ~~on Fig. 3~~ below).

849   Based on above laboratory results (Figs. 2 and 3), Fe dissolution from mineral dust

850   aerosols is treated explicitly as a kinetic process that depends on the pH, ambient temperature,

851   the degree of solution saturation, and competition for oxalate between surface Fe and dissolved

852   Fe in our model (Table ~~2~~<u>3</u>). The net Fe dissolution rates (ΣRFe_i in units of moles of dissolved Fe

853   per Fe gram of Fe-containing mineral particle per second) for the proton-promoted ($i = 1$),

854   oxalate-promoted ($i = 2$), and quasi-photo-reductive ($i = 3$) Fe dissolution schemes can be

855   empirically described using the following equation, which is similar to the formulation applied

856   for Fe-containing minerals (Zhang et al., 1985; Lasaga et al., 1994; Hamer et al., 2003;

857   Meskhidze et al., 2005; Lanzl et al., 2012; Ito and Xu, 2014; Ito, 2015):

858    $RFe_i = k_i(\text{pH, T}) \times a(H^+)^{mi} \times f_i \times g_i$ (1)

859   where k_i is the 'far-from-equilibrium' (i.e., $f_i = 1$ and $g_i = 1$) Fe release rate (moles Fe g^{-1} s^{-1}),

860    $a(H^+)$ is the H^+ activity, m_i represents the empirical reaction order for protons, and f_i and g_i

861   account for the suppression.

862   The Fe release rate, k_i, is estimated for the proton- and oxalate-promoted dissolution

863   schemes by fitting the parameters to our measurements in sulfuric acid and ammonium sulfate

864   (experiment (2) and (3)) with and without oxalate (Fig. 2). Fe release from mineral dust under

865   acidic conditions is characterized by initial rapid Fe release and subsequent slow Fe release

866   (Desboeufs et al., 1999; Mackie et al., 2005; Cwiertny et al., 2008; Shi et al. 2011). Since the

867   typical lifetime of mineral dust is about a week, the initial rapid Fe release rates are important for

868   the atmospheric processing of mineral dust. ~~The~~A three-stage kinetic model is used to describe

869   the Fe release behavior of mineral dust: 1st stage is characterized by a rapid dissolution of

870   hydrous ferric oxide (HFO) on the surface of minerals, 2nd stage is an intermediate stage of nano-

871   sized Fe oxides dissolution from the surface of minerals, and 3rd stage is the Fe release from fine-

872   grained materials, which are internally mixed with aluminosilicate particles, as the mineral

873   surface is slowly dissolved. Here, we prescribe the content of HFO (0.65%) and nano-sized Fe

874   oxides (1.3%) on the surface of minerals. The content of HFO is ~~consistent with~~similar to that of

875   the highly reactive Fe measured on the mineral surface and within the range of the first Fe pool

876   from 0.5% to 2.9% (Shi et al., 2011). The content of nano-sized Fe oxides is also within the

877   range of the second Fe pool from 1.0% to 3.5%. The proton-promoted dissolution rates for stage

878   I and II are strongly dependent on pH. A comparable strong dependence on pH was also reported

879   for nano-sized hematite (Lanzl et al., 2012). The similarity in our Fe release rates to those of

880   illite suggests that Fe is mainly released from the reactive surface on Fe-containing minerals by

881   similar mechanisms to alminosilicates (Fig. ~~S2 in the Supplement~~S2), which involve inward

882   movement of dissolution from the grain edges (Brandt et al., 2003; Rozalén et al., 2008).

883   Consequently, we can avoid the need to explicitly treat individual Fe-containing minerals to

884   represent dissolution processes that occur on the timescale of aerosol lifetime by using equation

885   (1), which is similar to the treatment applied for combustion aerosols (Ito, 2015).

886   The enhanced mineral dissolution in the presence of chelating ligands such as oxalate has

887   been attributed to both the ligand adsorption at the surface of mineral and complex formation in

888   solution (Drever and Stillings, 1997). The differences between with (i.e., measured overall rate)

889   and with no oxalate (i.e., proton-promoted dissolution rate) can be attributed to the surface

890   complexation (i.e., oxalate-promoted dissolution rate). We observed rates of oxalate-promoted

891   dissolution to be almost independent of pH for stage I and III~~,~~ (Table 3), but could not calculate

892   the empirical reaction order for stage II from the measurements. Lanzl et al. (2012) found that

893   this value was nearly independent of pH (< 4.0) and particle size between 8 nm and 90 nm

894   hematite (Zhang et al., 1985). Thus we apply the same value to stage II as in stage I. The

895   calculations (red squares) reproduce the initial rapid Fe release and subsequent slow Fe release

896   due to the proton- and oxalate-promoted Fe dissolution. The calculations also reproduce the

897   enhancement in the Fe solubility due to the effects of oxalate under acidic conditions, compared

898   with proton-promoted dissolution, as was observed for Arizona test dust in previous study (Chen

899   and Grassian, 2013). The activation energy for k_i is described by a function of pH and

900   temperature for soils (Bibi et al., 2014). The Fe release is suppressed by the degree of saturation,

901   f_i, and competition for oxalate between surface Fe and dissolved Fe, g_i, (Ito, 2015). We apply the

902   same equation for mineral dust, g_i, as in Ito (2015). Thus excess oxalate is needed to form

903   mononuclear bidentate ligand with surface Fe and promote Fe dissolution significantly (Chen

904   and Grassian, 2013). The function f_i ($0 \leq f_i \leq 1$) is given by

905         $$f_i = 1 - (a_{Fe} \times a_H^{-ni}) / Keq_i \qquad\qquad (2)$$

906   in which a_{Fe} is the concentration of Fe^{3+} in aerosol water (mol L^{-1}), n_i is the stoichiometric ratio,

907   and Keq_i is the equilibrium constant measured.

908   ~~Fig. 3 suggests that the parameters used in this work (equation (2), red squares) are better~~

909   ~~constrained by the experimental data (black circles), compared to Ito and Xu (2014) (blue~~

910   ~~squares).~~ Results of previous laboratory experiments in batch experiments showed that oxalate

911   had negligible effect on the Fe dissolution of hematite at higher pH values ($\geq$ pH = 5) under dark

912   conditions (Zhang et al., 1985; Xu and Gao, 2008; Lanzl et al., 2012). The decrease in proton

913   concentration (e.g., during activation into cloud droplets or neutralization by carbonate) could

914   lead to formation of the amorphous $Fe(OH)_3(s)$ that coats on the mineral surfaces (Shi et al.,

915   2009, 2015) and inhibits both the adsorption of oxalate and the detachment of surface Fe-oxalate

916   (Zhang et al., 1985; Jang et al., 2007; Rozalén et al., 2014). This effect was not considered in

917   previous modeling studies for mineral dust, which could calculate enhanced Fe solubility at

918   higher pH ($\geq$ 3) due to oxalate-promoted dissolution (Luo and Gao, 2010; Johnson and

919   Meskhidze, 2013; Myriokefalitakis et al., 2015).

920   Paris et al. (2011) concluded that the light-induced reductive dissolution was not the

921   principal process to explain the increase in Fe solubility under low dissolved Fe and low oxalate

922   concentrations. However, the Fe release from the reactive surface on Fe-containing minerals was

923   observed at higher pH values (≥ 5) under high dissolved Fe and high oxalate concentrations and

924   irradiation conditions (Lanzl et al., 2012; Chen and Grassian, 2013). Two rate-limiting steps are

925   possibly involved in apparent contradictions at higher pH: the adsorption of oxalate on the oxide

926   surfaces at low dissolved Fe concentration (i.e., far from dissolution equilibrium) and the

927   detachment of surface Fe-oxalate via photo-induced ligand-to-metal charge transfer as

928   dissolution equilibrium is approached (Kraemer and Hering, 1997). To examine the uncertainty

929   in Fe release at higher pH values, no pH effect on the suppression of quasi-photo-induced Fe

930   dissolution for mineral aerosols was performed in the sensitivity simulation. In analogy to the

931   combustion aerosols (Chen and Grassian, 2013; Ito, 2015), we apply the same rate constant to

932   quasi-photo-induced dissolution as in oxalate-promoted dissolution and we set $f_3 = 1$ in equation

933   (1). The quasi-photo-induced dissolution rate is calculated by scaling the photolysis rate of H_2O_2

934   estimated in the model, following Ito (2015). The photo-degradation of oxalate due to photolysis

935   of Fe-oxalate complexes is simulated for Fe-containing aerosols in aqueous chemistry (Lin et al.,

936   2014; Ito, 2015).

937 **5.**   **Modeling results and discussion**

938   The model-calculated concentrations of total and soluble Fe in aerosols have been

939   extensively compared with field observations (Ito and Feng, 2010; Ito, 2012, 2013, 2015; Ito and

940   Xu, 2014). Here, model-calculated daily average surface concentrations of soluble Fe (red

941   squares) were compared with the measurements (black circles) during the 2010 and 2011 U.S.

942   GEOTRACES ~~cruise~~cruises over the North Atlantic (Fig. 4) (Wozniak et al., 2013, 2015). The

943   model-calculated variability at each latitude and longitude represents the daily variability during

944   the sampling dates. The modeled soluble Fe concentration exhibits a latitudinal variability, which

945   is similar to that of the measurements, with low values over the remote ocean (<0.5 ng m^{-3}),

946   intermediate values near European continents, and high values near North African continents (>5

947   ng m^{-3}) (Fig. 4a). The modeled soluble Fe concentration shows a longitudinal variability, which

948   is also similar to that of the measurements, with low values over the remote ocean (<0.5 ng m^{-3}),

949   intermediate values near North American continents, and high values near North African

950   continents (>2 ng m^{-3}) (Fig. 4b).

951   ~~Fig.~~Figure 5 displayed the daily averaged, model-calculated surface total aerosol Fe

952   loading, Fe solubility, Fe/WSOC molar ratio, and dust/combustion ratio for soluble Fe (red

953   squares) over the 2010 and 2011 US GEOTRACES cruise tracks in comparison with the

954   measurements (black circles) by Wozniak et al. (2013, 2015). As previously reported in Ito

955   (2013), the oil combustion from shipping mainly contributes to high Fe solubility at low Fe

956   loading observed over the high latitude North Atlantic Ocean (Fig. 5a). In this study, low Fe

957   solubility near North African continent was successfully simulated. The internal mixing of

958   alkaline minerals with Fe-containing minerals in aqueous chemistry for mineral dust can lead to

959   higher pH and thus suppress the Fe dissolution near the source regions, compared to the external

960   mixing (Ito and Feng, 2010). The model predicts relatively higher pH values for dust aerosols

961   except submicron particles near the source regions, because the dust alkalinity reservoir (i.e.,

962   calcite) is able to buffer the acidification (Fig. S3). While our model has incorporated the initial

963   rapid Fe release rate in acid solutions with oxalate explicitly, the comparisons with observations

964   support the suppression of Fe dissolution under low acidity and low oxalate concentration near

965   the source region of dust aerosols. ~~Furthermore, the~~

966   The Fe/WSOC molar ratios in aerosols influenced by combustion aerosols are 2–3 orders

967   of magnitude lower than those near North African continent, which are also consistent with the

968   observations (Wozniak et al., 2013, 2015) (Fig. 5b). The averaged WSOC concentration in our

969 model (330 ± 470 ng m^{-3}) is consistent with the measurements (330 ± 290 ng m^{-3}). The higher Fe

970 solubility measured in water (pH = 5.5) for the excess WSOC with Fe-binding functionalities

971 (e.g., $-COOH$, $-NH_2$) may suggest a potential role of the organic compounds in aerosols for the

972 delivery of Fe to the ocean in soluble form (Wozniak et al., 2013, 2015). Here, similar plots can

973 be obtained even with a constant WSOC concentration at 330 (ng m^{-3}) (Fig. S4). The results

974 indicate that the variability in Fe solubility is nearly independent of the variability in WSOC

975 concentration, possibly because of the excess ligands to stabilize Fe in solution at low Fe loading.

976 The use of our process-based model demonstrates that chemical reactions and mixing with

977 combustion aerosols are the main mechanisms to cause the high Fe solubility at low Fe loading

978 in the North Atlantic (Fig. 5c). As previously discussed in Ito (2013), this is consistent with the

979 observations (e.g., Sedwick et al., 2007; Séguret -et al., 2011).

980   The suppression of Fe dissolution under low proton and low oxalate concentrations leads to

981 the lower Fe solubility of mineral dust deposited to the ocean (0.64%–0.71%) on a global mean

982 in present days (Table 4). The Fe solubility for mineral dust varies spatially over the remote

983 oceans, due to the proton-, oxalate-promoted, and quasi-photo-reductive Fe dissolution (Fig. 6).

984 The Fe solubility ranges from 0.75 to 2% over the North Atlantic and Pacific in present days (Fig.

985 6a and 6c), which is relatively consistent with that (1%–2%) used in conventional ocean

986 biogeochemical models (Jickells et al. 2005). The base simulations result in low Fe solubility

987 (<1%) over the Southern Ocean in present days and significant portions of the ocean in

988 preindustrial era, due to the suppression of Fe dissolution under low proton concentrations (Fig.

989 6a and 6b). In contrast, the sensitivity simulations for mineral aerosols (i.e., $f_3 = 1$) lead to higher

990 Fe solubility (>1%) deposited to the remote oceans of high nitrate, low chlorophyll (HNLC)

991 regions such as the subarctic north Pacific, the east equatorial Pacific, and the Southern Ocean,

992   when quasi-photo-reductive dissolution was considered at higher pH values (Fig. 6c and 6d).

993   This is reflected in higher contribution of oxalate-promoted ($i = 2$ and 3) dissolution to total

994   soluble Fe deposition in the sensitivity simulations for mineral aerosols, compared to that ($i = 2$)

995   in the base simulations (Fig. S5). We note that higher contribution of proton-promoted ($i = 1$)

996   dissolution near the source regions may include the effect of oxalate on Fe dissolution via the

997   suppression of mineral dissolution as well as the soluble Fe content at emission. As a result, the

998   proton-promoted dissolution scheme contributed the majority of soluble Fe deposition to the

999   ocean, 90% for the base case and 69% for the sensitivity case, respectively. Since this Fe

1000 dissolution is not only due to the proton-promoted dissolution by definition, we also examined

1001 the effect of different assumption on the initial period of enhanced Fe release in an additional

1002 sensitivity simulation, in which we use 0.1% for the initial Fe solubility of mineral dust (Hand et

1003 al., 2004; Ito and Xu, 2014). The model results show that the contribution of dissolution scheme

1004 to total soluble Fe deposition depends on the assumption on the initial Fe solubility at emission

1005 (Fig. S6). The model results suggest that the initial soluble Fe content form dust source regions

1006 such as South America (Patagonia), Australia, and southern Africa may be important for the

1007 supply of soluble Fe to the Southern Ocean. The proton-promoted dissolution scheme

1008 contributed 77% for the additional sensitivity case, which is between our base and sensitivity

1009 simulations.

1010   The annually averaged rate of deposition of soluble Fe from dust and combustion sources

1011 to the oceans is presented in Fig. 7a and 7d for the base and sensitivity simulations, respectively.

1012 The total Fe solubility (Fig. 7b and 7e) is higher than that calculated from dust only over

1013 significant portions of the open ocean. However, our modeled Fe solubility (0.1%–0.5% and

1014 0.2%–0.7% for the base and sensitivity simulations, respectively) is still low over the South

1015 Atlantic east downwind from the Patagonian dust source regions where previous modeled Fe

1016 solubility deposited to the ocean (1.4%−2.0% by Mahowald et al., 2009; 0.5%−0.6% by Johnson

1017 et al., 2010) was significantly lower than that deduced from observations (7.5%−20% by Baker

1018 et al., 2013). Our modeled Fe solubility for dry deposition over the Atlantic (1.1%±1.9% and

1019 1.2%±2.0%) is in good agreement with the measurement (2.1%±2.2%), while that for wet

1020 deposition (3.4%±3.2% and 3.6%±3.3%) is significantly lower than the measurement

1021 (10.4%±4.6%) (Baker et al., 2013). Moreover, our monthly averaged Fe solubility (1%−4%) in

1022 wet deposition is an order of magnitude lower than that observed on the Kerguelen Islands in

1023 South Indian Ocean (82%±18% by Heimburger et al., 2013). This enhanced solubility may be

1024 due to unidentified reactive organic species in cloud and rain water, which contain Fe-binding

1025 functionalities (e.g., −COOH, −NH$_2$) such as humic-like substances from biomass burning and

1026 biologically derived materials from the ocean (Parazols et al. 2006; Deguillaume et al., 2014; Ito

1027 et al., 2014, 2015). The role of humic-like substances in the complexation and dissolution of Fe

1028 oxides over a wide pH range has received considerable attention in recent literatures (Al-

1029 Abadleh, 2015). The multiple ligands with high affinity for Fe binding can wrest aqueous Fe

1030 from any Fe–-oxalate complexes, allow the oxalate ligand to react with the surface Fe oxides,

1031 and assist the Fe–-oxalate detachment from the surface Fe oxides at intermediate pH (e.g., pH =

1032 5) (Cheah et al., 2003). Thus the consumption of oxalate due to photolysis of the Fe-oxalate

1033 complex may be limited due to complexation with stronger ligands in atmospheric water. On the

1034 other hand, functional groups on the humic molecule are less protonated at pH > 4, increase the

1035 probability of coating of organic matters on the reactive mineral surfaces, and thus inhibit the

1036 oxalate-promoted dissolution (Drever and Stillings, 1997). Clearly, more work is required to

elucidate the underlying mechanisms that promote Fe dissolution in cloud and rain water over the Southern Ocean in future studies.

The contributions of anthropogenic soluble Fe deposition to the present-days are examined in Fig. 7c and 7f for the base and sensitivity simulations, respectively. The soluble Fe deposition from both mineral dust and fossil fuel combustion sources due to changes in atmospheric pollution contributes more than half of the total soluble Fe deposition over significant portions of the open ocean in the Northern Hemisphere for the base simulations. The sensitivity simulations for mineral aerosols (i.e., $f_3 = 1$) lead to higher soluble Fe deposition in both present days and preindustrial era (Table 4) and result in lower anthropogenic soluble Fe deposition to the HNLC regions, due to almost no pH dependency of the quasi-photo-reductive dissolution. Of the total soluble Fe deposition from anthropogenic sources (excluding biomass burning) to the ocean (0.05–0.06 Tg Fe yr^{-1}), 67%−72% is from dust sources, 28%−33% is from fossil fuel combustion (Table 4). In contrast, our model indicated higher contribution of biomass burning aerosols in preindustrial era (42%−55% in total soluble Fe deposition to the ocean). It should be noted, howeverHowever, significant uncertainties remain on the magnitude of this source strength (Luo et al., 2008; Ito, 2011, 2012, 2015; Wang et al., 20152015). 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).

Our estimate of total Fe deposition to the ocean (10 Tg Fe yr^{-1}) is within the range of other models (Table 5). Our estimates of soluble Fe deposition to the oceans (0.05 and 0.07 Tg Fe yr^{-1} from the base and sensitivity simulations, respectively) in preindustrial era are in good agreement with that of Myriokefalitakis et al. (2015) (Table 5). The ratio of present-day soluble

1060 Fe deposition to the preindustrial era from the base simulation (47%) is in good agreement with

1061 that estimated by Luo et al. (2008) (46%), despite the use of various dissolution schemes,

1062 emission data sets, and atmospheric transport models. The sensitivity simulations, which include

1063 the quasi-photo-reductive dissolution for mineral aerosols (i.e., $f_3 = 1$), results in relatively small

1064 increases in the soluble Fe deposition in the global ocean (0.077 and 0.122 Tg Fe yr^{-1} on a global

1065 mean in preindustrial and present days, respectively). The global deposition is similar between

1066 our ~~two~~base and sensitivity simulations, mainly because of the suppression of proton-promoted

1067 (i.e., f_1) and oxalate-promoted (i.e., g_2) dissolution near the strong source regions of mineral dust.

1068 This is reflected in lower Fe solubility (1.1%−1.2% on a global mean), compared to those

1069 estimated by previous modeling studies (1.4%−15%, see Table 5 in Hajima et al., 2014).

1070 **6   Conclusions**

1071   We have developed a new scheme of Fe dissolution, which reproduced the proton- and

1072 oxalate-promoted dissolution behaviors of our experimental results for mineral dust. The batch

1073 dissolution experiments provided the Fe dissolution rates under far from equilibrium conditions

1074 and the parameters for degree of suppression as the saturation state approached equilibrium. Our

1075 model reproduced the slope of Fe solubility vs. total Fe loading measured over the North Atlantic

1076 Ocean. To investigate the uncertainty in the Fe dissolution associated with organic compounds,

1077 negligible pH effect on the quasi-photo-induced Fe dissolution for mineral aerosols was

1078 performed in the sensitivity simulations. The Fe release scheme allows us to reduce the number

1079 of mineral tracers for implementation in the Earth system models. At lower proton activity and

1080 lower oxalate concentration in aerosol water on dust particles near major dust sources, both

1081 proton and oxalate had no significant effect on the Fe dissolution in our model. and thus resulted

1082 in the lower Fe solubility of mineral dust deposited to the ocean (0.64%−0.71%) on a global

mean in present days. Fe release under more acidic condition in aerosol water due to air pollution

resulted in significant increases in soluble Fe deposition over large portions of the open ocean in

the Northern Hemisphere. In our model, low Fe solubility is estimated for mineral dust (< 1%)

over the Southern Ocean downwind from the dust source regions. The differences between our

base and sensitivity simulations for mineral aerosols are notable for low Fe loading over the

remote HNLC regions such as the subarctic north Pacific, the east equatorial Pacific, and the

Southern Ocean. However, the differences in Fe solubility between different simulations are

generally smaller than the differences between different model estimates and measurements. A

comprehensive comparison of model predicted Fe and its related species with observations is

therefore needed to elucidate the high Fe solubility observed under pristine conditions.

References

1103 Al-Abadleh, H. A.: Review of the bulk and surface chemistry of iron in atmospherically relevant

1104 systems containing humic-like substances (HULIS), RSC Adv., 5, 45785–45811,

1105 doi:10.1039/c5ra03132j, 2015.

1106 Amram, K. and Ganor, J.: The combined effect of pH and temperature on smectite dissolution

1107 rate under acidic conditions, Geochim. Cosmochim. Acta, 69, 2535–2546,

1108 doi:10.1016/j.gca.2004.10.001, 2005.

1109 Baker, A. R., Adams, C., Bell, T. G, Jickells, T. D., and Ganzeveld, L.: Estimation of

1110 atmospheric nutrient inputs to the Atlantic Ocean from 50°N to 50°S based on large-scale

1111 field sampling: Iron and other dust-associated elements, Global Biogeochem. Cy., 27,

1112 755–767, doi: 10.1002/gbc.20062, 2013.

1113 Bibi, I., Singh, B., and Silvester, E.: Dissolution of illite in saline–acidic solutions at 25°C,

1114 Geochim. Cosmochim. Acta, 75, 3237–3249, doi:10.1016/j.gca.2011.03.022, 2011.

1115 Bibi, I., Singh, B., and Silvester, E.: Dissolution kinetics of soil clays in sulfuric acid solutions:

1116 Ionic strength and temperature effects, Appl. Geochem., 51, 170–183,

1117 doi:10.1016/j.apgeochem.2014.10.004, 2014.

1118 Bonneville, S., Van Cappellen, P., and Behrends, T.: Microbial reduction of iron(III)

1119 oxyhydroxides: effects of mineral solubility and availability, Chem. Geol., 212, 255–268,

1120 doi:10.1016/j.chemgeo.2004.08.015, 2004.

1121 Brandt, F., Bosbach, D., Krawczyk-Bärsch, E., Arnold, T., and Bernhard, G.: Chlorite

1122 dissolution in the acid pH-range: A combined microscopic and macroscopic approach,

1123 Geochim. Cosmochim. Acta, 67, 1451–1461, doi:10.1016/S0016-7037(02)01293-0, 2003.

1124   Cama, J. and Ganor, J.: The effects of organic acids on the dissolution of silicate minerals: A

1125   case study of oxalate catalysis of kaolinite dissolution, Geochim. Cosmochim. Acta,

1126   70(9), 2191–2209, doi:10.1016/j.gca.2006.01.028, 2006.

1127   Ciais, P., Sabine, C., Govindasamy, B., Bopp, L., Brovkin, V., Canadell, J., Chhabra, A., DeFries,

1128   R., Galloway, J., Heimann, M., Jones, C., Le Quéré, C., Myneni, R., Piao, S., and

1129   Thornton, P.: Chapter 6: Carbon and Other Biogeochemical Cycles, in: Climate Change

1130   2013 The Physical Science Basis, edited by: Stocker, T., Qin, D., and Platner, G.-K.,

1131   Cambridge University Press, Cambridge, 2013.

1132   Cheah, S. F., Kraemer, S. M., Cervini-Silva, J., & Sposito, G.: Steady-state dissolution kinetics

1133   of goethite in the presence of desferrioxamine B and oxalate ligands: implications for the

1134   microbial acquisition of iron. Chem. Geol., 198(1), 63-75 doi:10.1016/S0009-

1135   2541(02)00421-7, 2003.

1136   Chen, H. and Grassian, V. H.: Iron dissolution of dust source materials during simulated acidic

1137   processing: The effect of sulfuric, acetic, and oxalic acids, Environ. Sci. Technol., 47,

1138   10312−10321, doi:10.1021/es401285s, 2013.

1139   Cornell, R. M. and Schwertmann, U.: The iron oxides: Structure, properties, reactions,

1140   occurrence and uses, Wiley-VCH publishers, New York, 2003.

1141   Cwiertny, D. M., Baltrusaitis, J., Hunter, G. J., Laskin, A., Scherer, M. M., and Grassian, V. H.:

1142   Characterization and acid-mobilization study of iron-containing mineral dust source

1143   materials, J. Geophys. Res., 113, D05202, doi:10.1029/2007jd009332, 2008.

1144   Deguillaume, L., Desboeufs, K. V., Leriche, M., Long, Y., and Chaumerliac, N.: Effect of iron

1145   dissolution on cloud chemistry: from laboratory measurements to model results, Atmos.

1146   Pollut. Res, 1(4), 220–228, doi:10.5094/APR.2010.029, 2010.

Deguillaume, L., Charbouillot, T., Joly, M., Vaïtilingom, M., Parazols, M., Marinoni, A., Amato, P., Delort, A.-M., Vinatier, V., Flossmann, A., Chaumerliac, N., Pichon, J. M., Houdier, S., Laj, P., Sellegri, K., Colomb, A., Brigante, M. , and Mailhot, G.: Classification of clouds sampled at the puy de Dôme (France) based on 10 yr of monitoring of their physicochemical properties, Atmos. Chem. Phys., 14, 1485–1506, doi:10.5194/acp-14-1485-2014, 2014.

Desboeufs, K., Losno, R., Vimeux, F., and Cholbi, S.: pH dependent dissolution of wind transported Saharan dust, J. Geophys. Res., 104, 21287–21299, 1999.

Drever, J. I. and Stillings, L. L.: The role of organic acids in mineral weathering, Colloids Surfaces A, 120, 167–181, 1997.

Feng, Y. and Penner, J. E.: Global modeling of nitrate and ammonium: Interaction of aerosols and tropospheric chemistry, J. Geophys. Res., 112, D01304, doi:10.1029/2005JD006404, 2007.

Golubev, S. V., Bauer, A., and Pokrovsky, O. S.: Effect of pH and organic ligands on the kinetics of smectite dissolution at 25°C, Geochim. Cosmochim. Acta, 70(17), 4436–4451, doi:10.1016/j.gca.2006.06.1557, 2006.

Hajima, T., Kawamiya, M., Watanabe, M., Kato, E., Tachiiri, K., Sugiyama, M., Watanabe, S., Okajima, H., and Ito, A.: Modeling in Earth system science up to and beyond IPCC AR5, Progress in Earth and Planetary Science, 1:29, 1–25, doi:10.1186/s40645-014-0029-y, 2014.

Hamer, M., Graham, R., Amrhein, C., and Bozhilov, K.: Dissolution of ripidolite (Mg, Fe-chlorite) in organic and inorganic acid solutions, Soil Sci. Soc. Am. J., 67 (2), 654−661, 2003.

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

Heimburger, A., Losno, R., and Triquet, S.: Solubility of iron and other trace elements in rainwater collected on the Kerguelen Islands (South Indian Ocean), Biogeosciences, 10, 6617-6628, doi:10.5194/bg-10-6617-2013, 2013.

Ito, A.: Mega fire emissions in Siberia: potential supply of bioavailable iron from forests to the ocean, Biogeosciences, 8, 1679–1697, doi:10.5194/bg-8-1679-2011, 2011.

Ito, A.: Contrasting the effect of iron mobilization on soluble iron deposition to the ocean in the Northern and Southern Hemispheres, J. Meteorol. Soc. Japan, 90A, 167–188, DOI:10.2151/jmsj.2012-A09, 2012.

Ito, A.; Global modeling study of potentially bioavailable iron input from shipboard aerosol sources to the ocean, Global Biogeochem. Cy., 27, 1–10, doi: 10.1029/2012GB004378, 2013.

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., Kok, J., Feng, Y., and Penner, J.: Does a theoretical estimation of the dust size distribution at emission suggest more bioavailable iron deposition?, Geophys. Res. Lett., 39, L05807, doi:10.1029/2011GL050455, 2012.

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, 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.

Jang, J. H., Dempsey, B. A., and Burgos, W. D.: Solubility of hematite revisited: Effects of hydration, Environ. Sci. Technol., 41(21), 7303–7308, doi:10.1021/es8010139, 2007.

Jickells, T. D., An, Z. S., Andersen, K. K., Baker, A. R., Bergametti, G., Brooks, N., Cao, J. J., Boyd, P. W., Duce, R. A., Hunter, K. A., Kawahata, H., Kubilay, N., LaRoche, J., Liss, P. S., Mahowald, N., Prospero, J. M., Ridgwell, A. J., Tegen, I., and Torres, R.: Global iron connections between desert dust, ocean biogeochemistry, and climate, Science, 308, 67–71, doi:10.1126/science.1105959, 2005.

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.

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, doi:10.5194/gmd-6-1137-2013, 2013.

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 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.

Kok, J. F.: A scaling theory for the size distribution of emitted dust aerosols suggests climate models underestimate the size of the global dust cycle, P. Natl. Acad. Sci. USA, 108, 1016–1021, doi:10.1073/pnas.1014798108, 2011.

Kraemer, S. M. and Hering, J. G.: Influence of solution saturation state on the kinetics of ligand-controlled dissolution of oxide phases, Geochim. Cosmochim. Acta, 61(14), 2855–2866, 1997.

Lamarque, J.-F., Bond, T. C., Eyring, V., Granier, C., Heil, A., Klimont, Z., Lee, D., Liousse, C., Mieville, A., Owen, B., Schultz, M. G., Shindell, D., Smith, S. J., Stehfest, E., Van Aardenne, J., Cooper, O. R., Kainuma, M., Mahowald, N., McConnell, J. R., Naik, V., Riahi, K., and van Vuuren, D. P.: Historical (1850–2000) gridded anthropogenic and biomass burning emissions of reactive gases and aerosols: methodology and application, Atmos. Chem. Phys., 10, 7017–7039, doi:10.5194/acp-10-7017-2010, 2010.

Lanzl, C. A., Baltrusaitis, J., and Cwienty, D. M.: Dissolution of hematite nanoparticle aggregates: Influence of primary particle size, dissolution mechanism, and solution pH, Langmuir, 28, 15797–15808, doi:10.1021/la3022497, 2012.

1235   Lasaga, A. C., Soler, J. M., Ganor, J., Burch, T. E., and Nagy, K. L.: Chemical-weathering rate

1236   laws and global geochemical cycles, Geochim. Cosmochim. Acta, 58(10), 2361–2386,

1237   1994.

1238   Lin, G., Sillman, S., Penner, J. E., and Ito, A.: Global modeling of SOA: the use of different

1239   mechanisms for aqueous-phase formation, Atmos. Chem. Phys., 14, 5451–5475,

1240   doi:10.5194/acp-14-5451-2014, 2014.

1241   Lowson, R. T., Comarmond, M. C. J., Rajaratnam, G., and Brown, P. L.: The kinetics of the

1242   dissolution of chlorite as a function of pH and at 25°C, Geochim. Cosmochim. Acta,

1243   69(7), 1687–1699, doi:10.1016/j.gca.2004.09.028, 2005.

1244   Liu, X., Penner, J. E., and Herzog, M.: Global modeling of aerosol dynamics: Model description,

1245   evaluation and interactions between sulfate and non-sulfate aerosols, J. Geophys. Res.,

1246   110, D18206, doi:10.1029/2004JD005674, 2005.

1247   Luo, C. and Gao, Y.: Aeolian iron mobilisation by dust-acid interactions and their implications

1248   for soluble iron deposition to the ocean: a test involving potential anthropogenic organic

1249   acidic species, Environ. Chem., 7, 153–161, doi:10.1071/EN09116, 2010.

1250   Luo, C., Mahowald, N., Bond, T., Chuang, P. Y., Artaxo, P., Siefert, R., Chen, Y., and Schauer,

1251   J.: Combustion iron distribution and deposition, Global Biogeochem. Cy., 22, GB1012,

1252   doi:10.1029/2007GB002964, 2008.

1253   Mackie, D. S., Boyd, P. W., Hunter, K. A., and McTainsh, G. H.: Simulating the cloud

1254   processing of iron in Australian dust: pH and dust concentration, Geophys. Res. Lett., 32,

1255   L06809, doi:10.1029/2004GL022122, 2005.

1256   Mahowald, N. M., Engelstaedter, S., Luo, C., Sealy, A., Artaxo, P., Benitez-Nelson, C., Bonnet,

1257   S., Chen, Y., Chuang, P. Y., Cohen, D. D., Dulac, F., Herut, B., Johansen, A. M., Kubilay,

1258   N., Losno, R., Maenhaut, W., Paytan, A., Prospero, J. A., Shank, L. M., and Siefert, R.

1259   L.: Atmospheric iron deposition: Global distribution, variability, and human perturbations,

1260   Annu. Rev. Mar. Sci., 1, 245–278, doi:10.1146/annurev.marine.010908.163727, 2009.

1261   Malmström, M., and Banwart, S.: Biotite dissolution at 25°C: The pH dependence of dissolution

1262   rate and stoichiometry, Geochim. Cosmochim. Acta, 61(14), 2779–2799, 1997.

1263   Meskhidze, N., Chameides, W. L., Nenes, A., and Chen, G.: Iron mobilization in mineral dust:

1264   Can anthropogenic SO2 emissions affect ocean productivity?, Geophys. Res. Lett., 30,

1265   2085, doi:10.1029/2003GL018035, 2003.

1266   Meskhidze, N., Chameides, W. L., and Nenes, A.: Dust and pollution: A recipe for enhanced

1267   ocean fertilization?, J. Geophys. Res., 110, D03301, doi:10.1029/2004JD005082, 2005.

1268   Myriokefalitakis, S., Daskalakis, N., Mihalopoulos, N., Baker, A. R., Nenes, A., and Kanakidou,

1269   M.: Changes in dissolved iron deposition to the oceans driven by human activity: a 3-D

1270   global modelling study, Biogeosciences, 12, 3973–3992, doi:10.5194/bg-12-3973-2015,

1271   2015.

1272   Nickovic, S., Vukovic, A., Vujadinovic, M., Djurdjevic, V., and Pejanovic, G.: Technical Note:

1273   High-resolution mineralogical database of dust-productive soils for atmospheric dust

1274   modeling, Atmos. Chem. Phys., 12, 845–855, doi:10.5194/acp-12-845-2012, 2012.

1275   Paris, R., Desboeufs, K. V., and Journet, E.: Variability of dust iron solubility in atmospheric

1276   waters: Investigation of the role of oxalate organic complexation, Atmos. Environ., 45,

1277   6510–6517, doi:10.1016/j.atmosenv.2011.08.068, 2011.

1278   Parazols, M., Marinoni, A., Amato, P., Abida, O., Laj, P., and Mailhot, G.: Speciation and role of

1279   iron in cloud droplets at the puy de Dôme station, J. Atmos. Chem., 54(3), 267–281,

1280   doi:10.1007/s10874-006-9026-x, 2006.

Ramos, M. E., García-Palma, S., Rozalén, M., Johnston, C. T., and Huertas, F. J.: Kinetics of montmorillonite dissolution: An experimental study of the effect of oxalate, Chem. Geol., 363, 283–292, doi:10.1016/j.chemgeo.2013.11.014, 2014.

Rotman, D. A., Atherton, C. S., Bergmann, D. J., Cameron-Smith, P. J., Chuang, C. C., Connell, P. S., Dignon, J. E., Franz, A., Grant, K. E., Kinnison, D. E., Molenkamp, C. R., Proctor, D. D., and Tannahill, J. R.: IMPACT, the LLNL 3-D global atmospheric chemical transport model for the combined troposphere and stratosphere: Model description and analysis of ozone and other trace gases, J. Geophys. Res., 109, D04303, doi:10.1029/2002JD003155, 2004.

Rozalén, M. L., Huertas, F. J., Brady, P. V., Cama, J., García-Palma, S., and Linares, J.: Experimental study of the effect of pH on the kinetics of montmorillonite dissolution at 25°C, Geochim. Cosmochim. Acta, 72(17), 4224–4253, doi:10.1016/j.gca.2008.05.065, 2008.

Rozalén, M., Ramos, M. E., Fiore, S., Gervilla, F., and Huertas, F. J.: Effect of oxalate and pH on chrysotile dissolution at 25°C: An experimental study, Am. Mineral., 99(4), 589–600, doi:10.2138/am.2014.4636, 2014.

Rubasinghege, G., Lentz, R. W., Scherer, M. M., and Grassian, V. H.: Simulated atmospheric processing of iron oxyhydroxide minerals at low pH: roles of particle size and acid anion in iron dissolution, Proc. Natl. Acad. Sci. U. S. A., 107, 6628–6633, doi:10.1073/pnas.0910809107, 2010.

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.

Sedwick, P. N., Sholkovitz, E. R., and Church, T. M.: Impact of anthropogenic combustion emissions on the fractional solubility of aerosol iron: Evidence from the Sargasso Sea, Geochem. Geophys. Geosyst., 8, Q10Q06 doi:10.1029/2007GC001586, 2007.

Séguret, M. J. M., Koçak, M., Theodosi, C., Ussher, S. J., Worsfold, P. J., Herut, B., .Mihalopoulos, N., Kubilay, N., and Nimmo, M.: Iron solubility in crustal and anthropogenic aerosols: The Eastern Mediterranean as a case study. Mar. Chem., 126, 229–238, doi:10.1016/j.marchem.2011.05.007, 2011.

Shi, Z., Krom, M. D., Bonneville. S., Baker, A. R., Jickells, T. D., and Benning, L. G.: Formation of iron nanoparticles and increase in iron reactivity in the mineral dust during simulated cloud processing, Environ. Sci. Technol., 43, 6592–6596, doi:10.1021/es901294g, 2009.

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., Jickells, T. D., Bonneville, S., Carslaw, K. S., Mihalopoulos, N., Baker, A. R., and Benning, L. G.: Impacts on iron solubility in the mineral dust by processes in the source region and the atmosphere: A review, Aeolian Res., 5, 21–42, doi:10.1016/j.aeolia.2012.03.001, 2012.

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.

1326 Solmon, F., Chuang, P. Y., Meskhidze, N., and Chen, Y.: Acidic processing of mineral dust iron

1327   by anthropogenic compounds over the north Pacific Ocean, J. Geophys. Res., 114,

1328   D02305, doi:10.1029/2008JD010417, 2009.

1329 Sorooshian, A., Wang, Z., Coggon, M. M., Jonsson, H. H., and Ervens, B.: Observations of sharp

1330   oxalate reductions in stratocumulus clouds at variable altitudes: organic acid and metal

1331   measurements during the 2011 E-PEACE campaign, Environ. Sci. Technol., 47,

1332   7747−7756, doi:10.1021/es4012383, 2013.

1333 Spokes, J. L. and Jickells, T. D: Factors controlling the solubility of aerosol trace metals in the

1334   atmosphere and on mixing into seawater, Aqua. Geochem., 1, 355−374, 1996.

1335 Wang, R., Balkanski, Y., Boucher, O., Bopp, L., Chappell, A., Ciais, P., Hauglustaine, D.,

1336   Peñuelas, J., and Tao, S.: Sources, transport and deposition of iron in the global

1337   atmosphere, Atmos. Chem. Phys., 15, 6247–6270, doi:10.5194/acp-15-6247-2015, 2015.

1338 Wang, Z., Sorooshian, A., Prabhakar, G., Coggon, M. M., and Jonsson, H. H.: Impact of

1339   emissions from shipping, land, and the ocean on stratocumulus cloud water elemental

1340   composition during the 2011 E-PEACE field campaign, Atmos. Environ., 89, 570–580,

1341   doi:10.1016/j.atmosenv.2014.01.020, 2014.

1342 Wexler, A. S. and Clegg, S. L.: Atmospheric aerosol models for systems including the ions H^+,

1343 NH_4^+, Na^+, SO_4^{2-}, NO_3^-, Cl^-, Br^-, and H_2O, J. Geophys. Res. 107, 4207,

1344   doi:10.1029/2001jd000451, 2002.

1345 Willey, J. D., Kieber, R. J., Humphreys, J. J., Rice, B. C., Hopwood, M. J., Avery, G. B. and

1346   Mead R. N.: The role of fossil fuel combustion on the stability of dissolved iron in

1347   rainwater, Atmos. Environ. 107, 187−193, 2015.

1348 Wozniak, A. S., Shelley, R. U., Sleighter, R. L., Abdulla, H. A. N., Morton, P. L., Landing, W.

1349 M., and Hatcher, P. G.: Relationships among aerosol water soluble organic matter, iron

1350 and aluminum in European, North African, and Marine air masses from the 2010 US

1351 GEOTRACES cruise, Mar. Chem., 153, 24–33, doi:10.1016/j.marchem.2013.04.011,

1352 2013.

1353 Wozniak, A. S., Shelley, R. U., McElhenie, S. D., Landing, W. M., and Hatcher, P. G.: Aerosol

1354 water soluble organic matter characteristics over the North Atlantic Ocean: Implications

1355 for iron-binding ligands and iron solubility, Mar. Chem., 173, 162–172,

1356 doi:10.1016/j.marchem.2014.11.002, 2015.

1357 Xu, N. and Gao, Y.: Characterization of hematite dissolution affected by oxalate coating, kinetics

1358 and pH, Appl. Geochem., 23, 783–793, doi:10.1016/j.apgeochem.2007.12.026, 2008.

1359 Xu, L. and Penner, J. E.: Global simulations of nitrate and ammonium aerosols and their

1360 radiative effects, Atmos. Chem. Phys., 12, 9479–9504, doi:10.5194/acp-12-9479-2012,

1361 2012.

1362 Yoon, T. H., Johnson, S. B., Musgrave, C. B., and Brown, G. E.: Adsorption of organic matter at

1363 mineral/water interfaces: I. ATR-FTIR spectroscopic and quantum chemical study of

1364 oxalate adsorbed at boehmite/water and corundum/water interfaces, Geochim.

1365 Cosmochim. Acta, 68(22), 4505–4518, doi:10.1016/j.gca.2004.04.025, 2004.

1366 Yu, J. Z., Huang, X.-F., Xu, J., and Hu, M.: When aerosol sulfate goes up, so does oxalate:

1367 Implication for the formation mechanisms of oxalate, Environ. Sci. Technol., 39, 128–

1368 133, doi:10.1021/es049559f, 2005.

1369 Zhang, Y., Kallay, N., and Matijević, E.: Interactions of metal hydrous oxides with chelating

1370 agents. 7. Hematite-oxalic acid and -citric acid systems, Langmuir, 1, 201–206, 1985.

1371   Zhuang, G., Yi, Z., Duce, R. A., and Brown, P. R.: Link between iron and sulphur cycles

1372   suggested by detection of Fe(II) in remote marine aerosols, Nature, 355, 537–539, 1992.

1373

Figures Captions

Fig. 1   Comparison of Fe solubility in solution (%) measured at two different dust/liquid ratios of 1 g L^{-1} (red triangles) and 10 g L^{-1} (blue squares) in 0.05 mol L^{-1} sulfuric acid solution with 1 mol L^{-1} (NH$_4$)$_2$SO$_4$ ($I = 3.15$ mol kg^{-1}), and dust/liquid ratios of 60 mg L^{-1} (black circles) and 1 g L^{-1} (green diamonds) in 0.005 mol L^{-1} sulfuric acid solution without (NH$_4$)$_2$SO$_4$ (pH = 2.0).

Fig. 2   Comparison of Fe solubility in solution (%) predicted using equation (1) with our measured Fe dissolution rates **(a)** with no oxalate at pH = 2, 0.05M H$_2$SO$_4$, 1M (NH$_4$)$_2$SO$_4$, **(b)** with no oxalate at pH = 3, 0.005M H$_2$SO$_4$, 1M (NH$_4$)$_2$SO$_4$, **(c)** with oxalate at pH = 2.1, 0.05M H$_2$SO$_4$, 1M (NH$_4$)$_2$SO$_4$, and 0.03 M Na$_2$C$_2$O$_4$, **(d)** with oxalate at pH = 3, 0.005M H$_2$SO$_4$, 1M (NH$_4$)$_2$SO$_4$, and 0.03 M Na$_2$C$_2$O$_4$. The red squares are calculated using equation (1) from the rate constants used in this study at each hour. The black circles are our measured data. The values of pH in solution are calculated using E-AIM (Wexler and Clegg, 2002, http://www.aim.env.uea.ac.uk/aim/aim.php).

Fig. 3   Comparison of Fe solubility in solution (%) predicted using equation (1) with the measured Fe dissolution rates at pH = 2, 0.005M H$_2$SO$_4$, and dust/solution of **(a)** 60 mg L^{-1}, **(b)** 1 g L^{-1}, **(c)** 10 g L^{-1}, and **(d)** 50 g L^{-1}. The red squares are calculated using equation (1) from the equilibrium constant (mol^2 kg^{-2}) used in this study at each hour. ~~The blue squares are calculated using equation (1) from the equilibrium constant (mol^2 kg^{-2}) used in Ito and Xu (2014).~~ The black circles are our measured data. The fraction of total dissolved Fe present as Fe(III) is prescribed at pH = 2 (0.2)

1396   in this calculation to emulate the experimental conditions, while the photochemical

1397   redox cycling between Fe(III) and Fe(II) in solution is explicitly simulated in our

1398   global model (Lin et al., 2014). The large fraction of Fe(II) in solution under the dark

1399   conditions is likely associated with the Fe dissolution of Fe(II)-containing solids

1400   (Cwienty et al., 2008). The initial fraction of Fe speciation is not critical in

1401   estimating the Fe redox speciation in aerosol water, because Fe(II) is quickly

1402   oxidized to Fe(III) in oxygenated water (Deguillaume et al., 2010).

1403   Fig. 4   Comparison of simulated (red squares) and observed (black circles) soluble Fe

1404   concentration (ng m^{-3}) during **(a)** 2010 and **(b)** 2011 U.S. GEOTRACES cruise over

1405   the North Atlantic (Wozniak et al., 2013, 2015). The number of modeled data points

1406   (84) is larger than the measurements (37), because each daily average is calculated

1407   for each sampling date at each center of cruise location.

1408   Fig. 5   **(a)** Atmospheric loading of total aerosol Fe (ng m^{-3}) versus Fe solubility for model

1409   estimates (red squares) and measurements (black circles) over the cruise tracks. **(b)**

1410   The Fe/WSOC molar ratio versus percent of soluble Fe in total Fe for model

1411   estimates (red squares) and measurements (black circles) over the cruise tracks. **(c)**

1412   The dust/combustion ratio for soluble Fe versus Fe solubility for model results over

1413   the cruise tracks. The measurements are obtained from Wozniak et al., (2013, 2015).

1414   The number of modeled data points (84) is larger than the measurements (37),

1415   because each daily average is calculated for each sampling date at each center of

1416   cruise location.

1417   Fig. 6   Ratio (%) of the soluble to total Fe deposition for mineral dust in **(a)** present days

1418   from base simulations, **(b)** preindustrial era from base simulations, **(c)** present days

1419   from sensitivity simulations, and **(d)** preindustrial era from sensitivity simulations.

1420   The formation of the amorphous $Fe(OH)_3(s)$ suppresses the oxalate-promoted

1421   dissolution from mineral aerosols in the base simulations, while no such effect was

1422   considered for quasi-light-induced reductive dissolution in the sensitivity simulation

1423   (i.e., $f_3 = 1$).

1424   Fig. 7   Deposition of soluble Fe (ng Fe m^{-2} s^{-1}) from dust and combustion sources to the

1425   oceans in present days, Fe solubility in present days, and ratio of increase from

1426   preindustrial to present to soluble Fe deposition in present days. The formation of the

1427   amorphous $Fe(OH)_3(s)$ suppresses the oxalate-promoted dissolution from mineral

1428   aerosols in the base simulations, while no such effect was considered for quasi-light-

1429   induced reductive dissolution in the sensitivity simulation (i.e., $f_3 = 1$).