We thank the reviewer for the careful reading and the useful comments that helped improving our manuscript. All comments have been considered for the revision of our manuscript. Discussion has been improved to highlight also the importance of primary dissolved Fe emissions in the computed atmospheric deposition changes.

Reply to specific comments:

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

- For clarity, the sentence in the abstract has been rephrased as follows: 'Proton- and organic ligand-promoted Fe-dissolution in present-day TM4-ECPL simulations is calculated to be ~0.175 Tg-Fe yr^{-1}, approximately half of the calculated total primary DFe emissions from mineral and combustion sources in the model (~0.322 Tg-Fe yr^{-1}).*'*

2) p. 3947, l19: *3% should be replaced with 5% of hematite in dust.*

- The typo has been corrected.

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

- Corrected

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

- This manuscript has been submitted prior the publication of Ito (2015). We now make reference to that study as follows: "*A recent modelling study by Ito (2015), published after the submission of the present work, focusing on the atmospheric processing of Fe-containing combustion aerosols by photochemical reactions with inorganic and organic acids indicates that ligand (OXL)-promoted Fe dissolution more than doubles the calculated DFe deposition from combustion sources over certain regions of the global ocean.*"

4) *p. 3949, l.3: Please correct the reference of Mahowald et al. (2009) to Luo et al (2008) & p. 3949, l.10: The sentence for the same study is repeated. Please correct or delete it*

- We have rephrased this part to avoid repetition and to point to the original study by Luo et al (2008) as:
  "*Mineral-Fe represents ~95% of the global atmospheric TFe source, with combustion Fe sources responsible for the remaining ~5% (Luo et al., 2008; Mahowald et al., 2009). Luo et al. (2008) accounted for both soluble and insoluble forms of Fe emissions from biomass burning and anthropogenic combustion processes in relation to Black Carbon (BC) emissions and they estimated (based on observed Fe/BC ratios) that ~1.7 Tg-Fe·yr^{-1} are emitted to the atmosphere via combustion processes. Mahowald et al. (2009) also indicates that humans may significantly impact DFe deposition over oceans by increasing*

both the acidity of atmospheric aerosol, as well as the DFe emissions from combustion processes."

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

- Dust emission fields are specific for the year 2008 and provided by E. Vignati. They have been prepared using an application of the Tegen model (Tegen et al., JGR 107, D21, 2002), extended by B. Heinhold (JGR, 112, 2007) and adapted by E. Vignati using the ECMWF fields as input to be coherent with the TM4/TM5 input.

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

- ACCMIP emissions for the year 2008 are available on-line through the ECCAD database (http://eccad.sedoo.fr/eccad_extract_interface/JSF/page_meta.jsf). Appropriate information has been added in the revised manuscript in section 2.1.

7) *p 3952, l3: How did you apply the $1^\circ \times 1^\circ$ dataset to the dust emission in the $6^\circ \times 4^\circ$ model?*

- All inputs to the model are in 1^ox1^o resolution. The mineralogy datasets were first re-gridded (average) from the original 30s resolution to the 1◦ × 1◦ grid resolution and then applied to the daily dust emissions used by the model. Then the model re-grids the fields (sum or average) to the desired resolution. To clarify this, we added the following sentences in the manuscript:
  "In the present study, the global soil mineralogy dataset developed by Nickovic et al. (2012) at 30" resolution (~1 km) has been initially re-gridded to 1^ox1^o global resolution and applied to the 1^ox1^o daily dust emissions taken into account by TM4-ECPL."

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

- Aerosol pH values do depend on aerosol size and types. We add the following test in the manuscript: *"Aerosol pH and water are here calculated for each aerosol mode (Fig. S2a for the fine mode and Fig. S2b for the coarse mode). The pH values for each aerosol mode are calculated by the thermodynamic equilibrium model ISORROPIA II assuming internal mixing of the aerosols (Fountoukis and Nenes, 2007). Briefly, for each mode (fine and coarse) sulphate, nitrate, ammonium and sea-salt (i.e. K^+; Ca^{2+}; Mg^{2+}; Na^+; SO_4^{2-}; Cl^-) aerosols are assumed to be internally mixed. Carbonates ($CaCO_3$, $MgCO_3$) and gypsum ($CaSO_4$) are considered to be present in the silt soil particles (Meskhidze et al., 2005), with their impact on the coarse particulate H^+ and H_2O, to be calculated interactively by the ISORROPIA II. The dissolved Ca^{+2} and Mg^{+2} is distributed by the thermodynamic model among all possible solids."*

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

- The mean percent content had been used to limit the computing time. We have now repeated the simulations using the mineralogy map for the fraction of Ca^{+2} on dust by Nickovic et al. (2012). However, since that database does not provide mineralogy map for magnesite, the 5.5% fraction on dust as mentioned in Ito and Feng (2010) is used as in the discussion paper. The following sentence has been added in the text:
  "The global soil mineralogy dataset (Nickovic et al., 2012) has been applied on dust emissions to calculate the concentrations of Ca^{+2} on dust particles (calcite ($CaCO_3$) and gypsum ($CaSO_4$))."

- The dissolution and precipitation of Mg^{+2} and Ca^{+2} (carbonates and gypsum) are calculated by the thermodynamic equilibrium model. ISORROPIA II takes into account the sum of the aforementioned crustal species and based on thermodynamic equilibrium distributes them to various salts e.g. $CaCO_3$, $CaSO_4$, $Ca(NO_3)_2$, $CaCl_2$ etc. Moreover, ISORROPIA II assumes $MgSO_4(s)$ to be always deliquesced when an aqueous phase is present as well as that $CaSO_4$ is completely insoluble.

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

- We thank the reviewer for pointing these typos in the Table. It is now corrected.

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

TM4-ECPL is an offline CTM and does not explicitly calculate clouds and precipitation. These are input to the model taken from the ERA-interim ECMWF dataset.

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

- According to the Fe-dissolution scheme used in the present study, OXL (i.e. $(COO^-)_2$) and not the total oxalic acid (i.e. TOXL = $(COOH)_2$ + $HOOC\text{-}COO^-$ + $(COO^-)_2$) is considered to promote the Fe-dissolution (as also in the Johnson and Meskidze, 2013). Oxalic acid has pKa1 = 1.27 and pKa2 = 4.27 and since the mole fraction of $(COO^-)_2$ is suppressed significantly in acidic environments, the OXL-promoted Fe-dissolution is expected also to be suppressed. This is discussed in section 2.6, second paragraph and supported by the shown box model calculations.

- However, we agree with the reviewer that this sentence at the end of section 2.4.2 might be confusing thus it has been rephrased as:
  "Thus, under such conditions of low aqueous-phase OXL concentrations, the ligand-promoted Fe dissolution may be suppressed significantly"

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

- Indeed in our calculation, as well, Fe-chemistry suppresses OXL atmospheric production through the aqueous-phase Fe-oxalato complexes photo-dissociation to CO_2 via: $[Fe(C_2O_4)_2]^- + h\nu + (+ O_2) \rightarrow Fe^{2+} + C_2O_4^{2-} + 2CO_2 + O_2^-$
  The requested figure is now added in Fig. S3 in the supplement.

14) *Figure S9: This figure was requested in review of Johnson and Meskhidze (2013), but was not shown (Interactive comment on Geosci. Model Dev. Discuss., 6, 1901, 2013). It is extremely hard to accept higher iron solubility (10%) for mineral dust with oxalate at pH = 8.5 than that at pH = 1.5 after 10 days in reality. Laboratory studies for dust aerosols showed that dissolved Fe with oxalate is higher at lower pH (see Figure S2 in Chen and Grassian, 2013). This is mainly because the oxalate-promoted dissolution rate of minerals is dependent on the mineral surface concentration of oxalate. Please show the spatial distribution of SFe (%) for dust aerosols and pH in water (see below).*

- In the discussion paper we have performed 10 days dissolution 'box-model' simulations considering both pH and OXL concentrations constant in order to estimate the relative contribution of protons and oxalate concentrations (i.e. an Open System (see Seinfeld and Pandis, 2006, p. 318) where OXL and pH are maintained at constant values; presumably by continuous infusion of new OXL and acidic compounds (however not realistic)).
- In order to avoid any confusion we performed new simulations with pH values constant but with oxalate concentrations allowed to change during the simulation time. Initial oxalic acid concentrations are provided and oxalate is calculated by considering the transformation of oxalic acid among $(COOH)_2$, $HOOC\text{-}COO^-$, $(COO^-)_2$ and Ferrus/Ferric-Oxalato complexes in the aqueous phase as well as losses by photodissociation to CO_2 as shown in Table S2. These results are shown in the new figure S4.
- To satisfy the reviewer, we have now calculated separately the spatial distribution of SFe for mineral dust, as well as for fossil fuel and for biomass burning aerosol. These are now shown in the supplementary figures S6b,c,d respectively together with the total SFe in Figure S6a. The spatial distributions of pH in aerosol water and in clouds are shown as requested in the supplementary figures S2a-d.

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

- For comparison with the data compiled by Sholkovitz et al. (2013) for the Atlantic Ocean (Baker et al., 2013) and the Indian Ocean (Witt et al., 2006) we use daily mean model concentrations. We rephrased the text appropriately *"TM4-ECPL daily mean results are here validated against daily observations of total (Fig. 5a) and dissolved Fe (Fig. 5b) associated with atmospheric aerosols over the Atlantic Ocean (Baker et al., 2013) and the Indian Ocean (Witt et al., 2006) as compiled by Sholkovitz et al. (2013)."*

- Iron solubility calculated by the model with observations are now also depicted in Fig. 5. *"Figure 5c also presents the comparison of daily solubility fractions of the above observations versus the respective calculated fractions by the model."*

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

- The spatial distribution of %SFe for dust aerosol has been added in the supplementary figures S6a (see comment 14).
- Although we use separate species for each type of mineral-released Fe, for computational efficiency reasons, we do not track the dissolved Fe from each mineral pool, so we cannot produce a figure for the spatial distribution of iron solubility for each iron type.

17) *Could you show the comparison of iron solubility?*

- This has been added (Figure 5c).

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

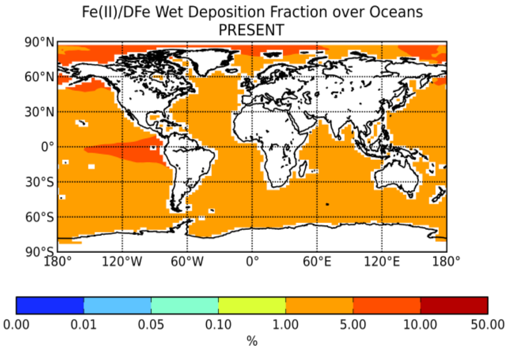
- Mean pH values of surface aerosol and cloud at 850hPa are added in the supplement (figure S2) (see comment 14)

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

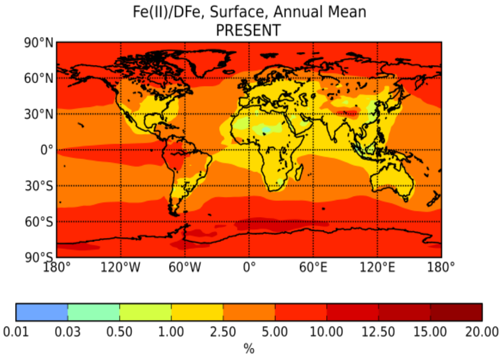
- Proton- and ligand- dissolution are separated processes in our model. Since each type of dissolution is a kinetic process – it is parameterised like a separate chemical reaction and its reaction budget can be derived from the model output.
- Iron speciation is based on the chemical scheme used for this study. Fig. S5, shows the spatial distribution of Fe(III) - sum of Fe^{3+} and Ferric-Oxalato complexes, and Fe(II) - sum of Fe^{2+} and Ferrus-Oxalato complexes and Fe(II)

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

- The observations we dispose in our database (see answer 15) do not provide information on the Fe speciation. The figures provided herebelow show that the modelled Fe(II)/DFe ratio in wet deposition (a) follows the distribution of the surface Fe(II)/DFe concentration ratio (b). The model calculates high fractions of Fe(II)/DFe deposition fluxes over the equatorial Pacific due to large scale precipitation and to relatively enhanced Fe(II) concentrations as also seen in the Fe(II)/DFe surface concentrations fraction.



(a)



(b)

21) *Figure 8 and Figure S8 are confusing. If Figure 8(e) and 8(f) represent mineral dust only, why the changes in DFe are so large in the Southern Hemisphere? If Figure 8(e) and 8(f) represent the total DFe, what is the difference from Figure S8(a) and S8(b)? Please explain more clearly.*

- We thank the reviewer for finding this double posting and for pointing us the missing caption for figures 8e and 8f. These figures have removed from the main text and are now only in the supplement as Figures S9e and S9f. They show the differences in deposition fluxes of DFe from all sources (combustion, dust and mineral dissolution) – not only mineral dust - of PAST and FUTURE from PRESENT simulations.

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

- Following the earlier comments of both reviewers that helped us improve the clarity of the manuscript, this part of the discussion has been rephrased as follows. *"The percentage differences of calculated PRESENT DFe deposition fluxes over oceans from the PAST and FUTURE simulations are depicted in Fig. 9c and 9d, respectively. The model in general calculates for both PAST and FUTURE simulations lower DFe deposition fluxes over oceans. DFe deposition fluxes are calculated to be ~80% higher in the PRESENT than in the PAST simulation (Fig. 9c), which can be attributed both to the increase of i) mineral Fe dissolution (almost 3-fold) and ii) primary DFe emission (from both fossil fuel combustion (6-fold) and biomass burning sources (almost an order of magnitude)). Furthermore, based on emission projections following air quality legislation, decreases of about 30-60% in DFe deposition are calculated for the FUTURE simulation over the Northern Pacific and Atlantic oceans, the Arabian Sea, the Bay of Bengal and the East Mediterranean Sea and lower reductions (less than 20%) over the remote* *tropical Pacific and Atlantic Oceans and the Southern Ocean These smaller changes from the PRESENT simulation calculated for the FUTURE (globally about 45% reduction) than for the PAST (globally almost 3-fold change) are attributed to the projected increase of Fe biomass burning emissions (about 20%) that partially counterbalance the more than 5-fold reduction in anthropogenic emissions of Fe. Overall, these sensitivity PRESENT-to-FUTURE simulations clearly support that changes in i) atmospheric acidity and ii) Fe combustion sources, both driven by anthropogenic pollutants emissions, affect significantly DFe deposition over the oceans, and therefore they have the potential to also perturb open-ocean phytoplankton growth and thus the carbon biogeochemical cycling."*