

Interactive comment on “The GESAMP atmospheric iron deposition model intercomparison study” by Stelios Myriokefalitakis et al.

Stelios Myriokefalitakis et al.

s.myriok@uu.nl

Received and published: 10 September 2018

We thank the Referee#1 for the careful reading of the paper. Please find below the point-by-point answers to the referee's general and specific comments and technical corrections.

1. General comments:

Q: The authors state that this kind of modelling is the only way to estimate iron deposition (page 4 lines 11ff). But is it really impossible to utilise the large number of observations of Fe concentrations (listed in the SI) to estimate fluxes? I would like to

C1

see a better justification for this claim.

A: With our statement we do not want to devaluate the importance and the need of observations. We state that models are an excellent way to study atmospheric Fe supply to the oceans and to assess its impacts on a global scale, partly because of episodic nature of atmospheric deposition. Models enable the integration of knowledge and of discontinuous geographically and temporally observations and in synergy with observations are the appropriate tools to study the global spatial and temporal patterns of species such as Fe. We rephrased as: “The use of global biogeochemical numerical models and surface observations is an excellent way to better understand past, present and future atmospheric supply to the oceans, as well as to quantify the resultant effect on the ocean biological productivity and the carbon uptake.”

Q: The third aim of the work (page 7, top) seems circular – why would future modelling studies find the fluxes calculated in this modelling study useful, other than as comparative measures? I also miss an indication that the work described here is potentially useful in permitting prediction of changes in Fe deposition rates, for example due to anthropogenic activities.

A: The 3rd aim refers to the utility of the calculated ensemble Fe deposition as an input for the next-generation of ocean biogeochemistry modelling studies. Our study aims to provide to the scientific community with ensemble TFe and LFe deposition fluxes, as a result of state-of-the-art atmospheric models and satellite retrievals. Currently, most ocean biogeochemistry models use global dust deposition fields to derive the atmospheric Fe input (e.g., Aumont et al., 2015), usually by assuming a constant fraction by mass on dust. Furthermore, to take into account the labile fraction in Fe deposition fluxes, either a constant value is applied or Fe solubility maps from other atmospheric models are used (e.g., Mahowald et al., 2005). Such approaches mean that the ocean data will contain significant assumptions, which the current science no longer supports; e.g., the combustion Fe-containing aerosol and the heterogeneity of soil mineralogy are neglected as well as the explicitly calculation of the Fe solubilization processes (result-

C2

ing in lower Fe solubility near the dust source regions and higher Fe solubility over the remote ocean than earlier estimates, bringing closer model results to observations). Overall, models need to first be evaluated against observations though to have some level of confidence in their ability and then to use them in order to access for example the anthropogenic effects. We can further use the models for the predicting of changes in Fe deposition rates, especially for the past and the future.

2. Specific comments:

Q: Page 21, line 10 states “The TFe loading, Fe solubility, and LFe loading from the models are compared with the measurements and presented in Fig. 4.” This confuses me, since I would use the term loading to mean a flux over time (mass per unit area). The axis labels refer to concentrations, with units of mass per volume, but the text and the Figure caption use loading. Please clarify.

A: We changed the term “loading” to “concentrations”.

Q: With reference to Figure 4, if I understand correctly (and if I don't then please clarify the text) the MNB values indicate the overall bias of the predictions compared to the data, which would mean that the ensemble model overestimates LFe concentrations by a factor of five. Does it then follow that loadings to the ocean are overestimated by this factor? If so, then the proposed further work doesn't seem to address the issue – Section 5 reads more like a series of minor tweaks than addressing a major quantification problem.

A: As for the MNB values, overestimates are weighted more than equivalent underestimates. As was noted in p.24, l.24, a similar overestimate in the measured monthly averaged dust concentration from a the short-term cruise measurements was seen in the dust model intercomparison study of Huneus et al. (2011). The bias may be due to the short duration of the sampling frequencies. We added further work to address one of the major quantification problems in p.25, l.2, “due to short of the sampling frequencies. A comparison of long-term measurements with a multi-year modelling

C3

will allow assessment of the model performance to capture labile Fe concentrations under specific events” after “Note, however, that evaluation of monthly mean model results by comparison with the shorter-term (e.g., daily) observations during different sampling periods introduces uncertainties”. We also added the description of MNB in the text as following: “We use the monthly mean of model output to compare with the measurements. The normalized bias (NB) at a given grid box is calculated as follows: $NB_{i} = (C_{model,i} - C_{obs,i}) / C_{obs,i}$ (2) where, $C_{model,i}$ is the modelled aerosol concentration in grid box i , and $C_{obs,i}$ is the measured aerosol concentration in the same grid box. When discussing the multi-model results we use the mean of all models, while we also analyze the mean normalized bias (MNB) of the models against measurements (a perfect comparison would have a MNB of 0 and correlation, R , of 1). A model's MNB is derived as the arithmetic mean of all NB_i values, thus overestimates are weighted more than equivalent underestimates.”

Q: Evaluating the importance of atmospherically deposited Fe depends greatly upon assessing the fate of the metal in ocean water. According to the authors “Upon deposition to the surface ocean, this fraction of Fe from the atmosphere can either enter the dissolved Fe pool, or precipitate-out as large oxy-hydroxide particles (Meskhidze et al., 2017)”. I am surprised that the cited study, which worked with high Fe concentrations and did not explore the influence of light on iron chemistry, is considered to represent the state of knowledge in this area. I am also surprised that neither this reference nor the paper under review cites the book by Turner and Hudson “The Biogeochemistry of Iron in Seawater” (Wiley 2001).

A: The study by Meskhidze et al. (2017) was designed to represent the processes affecting the soluble Fe deposited to the open oceans through atmospheric pathways on a time scale of sec to minutes. The concentrations were selected to be representative of wet removal (i.e., rainout and washout) which is the dominant removal mechanism over the remote oceans. The reference is used here, because, as far as we know, this is the first study that explored the role of atmospheric organic ligands on Fe solubility

C4

after deposition to the surface ocean. However, we agree with the reviewer that additional references, particularly on the effects of oceanic ligands and photochemistry need to be provided. The revised manuscript now reads: "Upon deposition to the surface ocean, this fraction of Fe from the atmosphere can either enter the dissolved Fe pool or precipitate-out as large oxy-hydroxide particles (de Baar and de Jong, 2001; Boyd and Ellwood, 2010; Meskhidze et al., 2017; Turner and Hunter, 2001)."

Q: Is there any prospect of using the Fe loadings reported here to simulate Fe concentrations in the ocean? I realize that this may be outside the scope of the present paper, but some indication of possibilities would be welcome.

A: We included the following part in the conclusions: Although the calculation of the oceanic Fe concentrations is outside the scope of this paper, we do hope that the deposition fields provided by this work will be used for this purpose, since they will trigger such investigation to occur.

Q: It is not clear to me whether FeD deposited to the ocean is considered "inert" or whether it can yield significant dissolved. Maybe this could be explained. If it is not considered to be a source, then it is not so important to get the global fluxes correct, and the focus should be on the LFe.

A: Total Fe deposited in the ocean is important for the assessment of the fate of Fe in the ocean. Total Fe is needed for the comparison of particulate Fe with the measurements in the ocean biogeochemistry models (e.g., Ye and Völker, 2017). Additionally, less labile Fe in total Fe may be potentially utilized by marine organisms. Note that ocean biogeochemistry models (e.g., Aumont et al., 2015) take into account both the total and the soluble deposited Fe for chemistry calculations, assuming some fractions of less labile Fe in total Fe are dissolved in the ocean. For example, Aumont et al. (2015) considers that the particulate Fe from dust experiences dissolution in the water column, with the dissolution rate computed assuming that during sinking of mineral particles particulate Fe dissolves by about 0.01% per day (Bonnet, 2004). Therefore,

C5

both the total and the labile Fe deposition fluxes are needed. However, the dissolution of Fe from FeD is species dependent and affected by spatiotemporal variations in the ocean. The following explanation has been added in the text in the introduction: "Both the TFe and LFe atmospheric deposition can be used in ocean biogeochemical modelling. For example, total Fe is needed for comparisons of particulate Fe with the measurements in the ocean biogeochemistry models (e.g., Ye and Völker, 2017), while LFe can be assumed as readily available to the marine ecosystem. Note that the less labile fraction of Fe in TFe can be slowly dissolved from particulate Fe in the ocean during sinking of mineral particles (e.g., roughly 0.01% per day; Bonnet, 2004), with the dissolution of Fe, however being species dependent and affected by spatiotemporal variations in the ocean"

Q: As I understand it, a similar loading (to LFe) of dissolved Fe to the oceans comes from rivers. Could the authors briefly explain why this is not considered as important as the atmospherically-deposited form?

A: According to the recent study of Tagliabue et al. (2016), riverine inputs are considering 1-2 order of magnitudes smaller than the atmospheric dust deposition to the global ocean. We included the following part in the manuscript (introduction), to further refer to the other known sources of Fe in the global ocean: "However, significant Fe inputs from continental margins and hydrothermal vents are also supplied to the global ocean, regulating the ocean biogeochemical cycles. Moreover, riverine Fe inputs are currently estimated 1-2 orders of magnitudes smaller than the atmospheric pathway (e.g., Tagliabue et al., 2016), affecting mainly coastal regions, while icebergs and glaciers could also be important to the polar oceans (Raiswell et al., 2016)."

Q: Section 2.1.2 introduces the presence of oxalate in aerosols, without explanation of its sources and why other carboxylic acids are not considered. I am not at all expert in this area, it appears as though oxalate is assumed or known to be dominant – if so then its strong solubilising properties are clearly important. I would appreciate some references to justify the assumption that oxalate is truly dominant in governing aerosol

C6

Fe solubility.

A: Indeed, numerous organic compounds, such as acetate, formate, oxalate, malonate, succinate, glutarate, glycolate, lactate, tartrate and humic like substances (HULIS) can be found in atmospheric waters. However, oxalate, malonate, tartrate and humic acid have been observed to enhance Fe solubility (e.g., Paris et al., 2010, 2011). For all these organic ligands, positive dependences of iron solubility to organic concentrations were observed and revealed that the extent of organic complexation on iron solubility decreased in the following order: oxalate > malonate = tartrate > humic acid (Paris et al., 2011). Therefore, this study confirmed that among the known atmospheric organic binding ligands of Fe, oxalate is the most effective ligand in promoting dust iron solubility under atmospheric conditions. Furthermore, observations in the atmosphere, point to oxalate as the most abundant organic ligand (e.g., Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999). Oxalate originates from multiphase chemistry of organics, but has also weak anthropogenic primary sources (see Myriokefalitakis et al., 2011 and Lin et al., 2014 for a comprehensive global modelling study of atmospheric oxalate). Therefore, atmospheric models use oxalate to study the effect of organic ligands on Fe dissolution. However, the lack of experimental data for Fe-containing minerals mixed with a variety of organic ligands in solution is an important source of uncertainty. For clarity, in Sect. 2.1.2 we added after the first sentence the following explanatory text: “Oxalate is, however, used in models as a proxy of all organic ligands for ligand-promoted dissolution since 1) it is the most abundant in the atmosphere (e.g., Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999) originating mainly from secondary sources and only a weak contribution from combustion primary sources (e.g., Myriokefalitakis et al., 2011) and 2) it is the most effective ligand in promoting iron solubilisation (e.g., Paris et al., 2011). We note, however, that more work is required to elucidate the role of other ligands that may promote Fe dissolution in future studies.”.

Q: The right-hand maps in Figure S4 are not informative. Is it possible – or do the

C7

authors consider it worthwhile? – to show primary sources of LFe?

A: As we state in the text, not all the models simulate the LFe primary and secondary sources in the same manner of dust and combustion aerosols. For a fairer comparison in Fig. S4, we show the primary (i.e., emissions) and secondary (i.e., atmospheric processing) sources together. As we state in the manuscript “the models use significantly different assumptions to describe the total LFe source to the atmosphere and therefore primary (emissions) and secondary (atmospheric processing) sources cannot be accurately separated” for all models. A detailed description of models’ parameterizations as well as the differences among them with regard to the LFe sources, are also presented in Sect. 2.1.

3. Technical Corrections:

Q: Page 5 line 15 This sentence needs improvement.

A: We rephrased the text between lines 13-19 as follows: “During atmospheric transport coating of Fe-containing dust particles by acidic compounds (e.g., sulfates and nitrates) increase the Fe solubility. When this process is taken into account in model simulations (e.g., Meskhidze et al., 2005) it aids in explaining the observations. Indeed, measurements of the fresh dust particles present low (<1%) initial solubilities (Chuang et al., 2005; Fung et al., 2000; Hand et al., 2004; Sedwick et al., 2007), while high aerosol solubilities are commonly observed at lower dust concentrations far from sources (Baker and Jickells, 2006; Sholkovitz et al., 2012; Oakes et al., 2012). Atmospheric processing of dust (Kumar et al., 2010; Meskhidze et al., 2003; Srinivas et al., 2014) is considered as the best candidate to explain these observations.”

Q: Table S3. What does “NaN” mean? (not analysed I guess, but please say).

A: NaN is replaced with “-”, which means that data are not available. We have also modified and explain it now in the Table S3 caption.

Q: Figure S7 should have “continuous” not “continues”.

C8

A: Done

Q: Page 21 line 19. I assume that SH = southern hemisphere? Is this so very well known?

A: We replaced “SH” with “the Southern Hemisphere”.

Q: Page 21 line 22. Should it read 0.50-0.56?

A: The value is correct. The differences in Fe solubility trend between CAM4 and TM4-ECPL can be partly seen from Fig. 5.

4. References

Aumont, O., Ethé, C., Tagliabue, A., Bopp, L. and Gehlen, M.: PISCES-v2: an ocean biogeochemical model for carbon and ecosystem studies, *Geosci. Model Dev.*, 8(8), 2465–2513, doi:10.5194/gmd-8-2465-2015, 2015. de Baar, H. J. and de Jong, J. T.: ‘Distributions, sources and sinks of iron in seawater’, 2001. Baker, A. R. and Jickells, T. D.: Mineral particle size as a control on aerosol iron solubility, *Geophys. Res. Lett.*, 33(17), L17608, doi:10.1029/2006GL026557, 2006. Baker, A. R., French, M. and Linge, K. L.: Trends in aerosol nutrient solubility along a west–east transect of the Saharan dust plume, *Geophys. Res. Lett.*, 33(7), L07805, doi:10.1029/2005GL024764, 2006. Bonnet, S.: Dissolution of atmospheric iron in seawater, *Geophys. Res. Lett.*, 31(3), L03303, doi:10.1029/2003GL018423, 2004. Boyd, P. W. and Ellwood, M. J.: The biogeochemical cycle of iron in the ocean, *Nat. Geosci.*, 3(10), 675–682, doi:10.1038/ngeo964, 2010. Chuang, P. Y., Duvall, R. M., Shafer, M. M. and Schauer, J. J.: The origin of water soluble particulate iron in the Asian atmospheric outflow, *Geophys. Res. Lett.*, 32(7), L07813, doi:10.1029/2004GL021946, 2005. Fung, I. Y., Meyn, S. K., Tegen, I., Doney, S. C., John, J. G. and Bishop, J. K. B.: Iron supply and demand in the upper ocean, *Global Biogeochem. Cycles*, 14(1), 281–295, doi:10.1029/1999GB900059, 2000. Hand, J. L., Mahowald, N. M., Chen, Y., Siefert, R. L., Luo, C., Subramaniam, A. and Fung, I.: Estimates of atmospheric-processed

C9

soluble iron from observations and a global mineral aerosol model: Biogeochemical implications, *J. Geophys. Res.*, 109(D17), D17205, doi:10.1029/2004JD004574, 2004. Kawamura, K. and Ikushima, K.: Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, *Environ. Sci. Technol.*, 27(10), 2227–2235, doi:10.1021/es00047a033, 1993. Kawamura, K. and Sakaguchi, F.: Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics, *J. Geophys. Res. Atmos.*, 104(D3), 3501–3509, doi:10.1029/1998JD100041, 1999. Kumar, A., Sarin, M. M. and Srinivas, B.: Aerosol iron solubility over Bay of Bengal: Role of anthropogenic sources and chemical processing, *Mar. Chem.*, 121(1–4), 167–175, doi:10.1016/j.marchem.2010.04.005, 2010. Lin, G., Sillman, S., Penner, J. E. and Ito, A.: Global modeling of SOA: the use of different mechanisms for aqueous-phase formation, *Atmos. Chem. Phys.*, 14(11), 5451–5475, doi:10.5194/acp-14-5451-2014, 2014. Mahowald, N. M., Baker, A. R., Bergametti, G., Brooks, N., Duce, R. A., Jickells, T. D., Kubilay, N. N., Prospero, J. M. and Tegen, I.: Atmospheric global dust cycle and iron inputs to the ocean, *Global Biogeochem. Cycles*, 19(4), GB4025, doi:10.1029/2004GB002402, 2005. Meskhidze, N., Chameides, W. L., Nenes, A. and Chen, G.: Iron mobilization in mineral dust: Can anthropogenic SO₂ emissions affect ocean productivity?, *Geophys. Res. Lett.*, 30(21), 2085, doi:10.1029/2003GL018035, 2003. Meskhidze, N., Chameides, W. L. and Nenes, A.: Dust and pollution: A recipe for enhanced ocean fertilization?, *J. Geophys. Res. D Atmos.*, 110(3), 1–23, doi:10.1029/2004JD005082, 2005. Meskhidze, N., Hurley, D., Royalty, T. M. and Johnson, M. S.: Potential effect of atmospheric dissolved organic carbon on the iron solubility in seawater, *Mar. Chem.*, 194, 124–132, doi:10.1016/j.marchem.2017.05.011, 2017. Myriokefalitakis, S., Tsigaridis, K., Mihalopoulos, N., Sciare, J., Nenes, A., Kawamura, K., Segers, A. and Kanakidou, M.: In-cloud oxalate formation in the global troposphere: a 3-D modeling study, *Atmos. Chem. Phys.*, 11(12), 5761–5782, doi:10.5194/acp-11-5761-2011, 2011. Oakes, M., Ingall, E. D., Lai, B., Shafer, M. M., Hays, M. D., Liu, Z. G., Russell, A. G. and Weber, R. J.: Iron Solubility Related to Particle Sulfur Content in Source Emission and Ambient

C10

Fine Particles, *Environ. Sci. Technol.*, 46(12), 6637–6644, doi:10.1021/es300701c, 2012. Paris, R., Desboeufs, K. V., Formenti, P., Nava, S. and Chou, C.: Chemical characterisation of iron in dust and biomass burning aerosols during AMMA-SOP0/DABEX: implication for iron solubility, *Atmos. Chem. Phys.*, 10(9), 4273–4282, doi:10.5194/acp-10-4273-2010, 2010. Paris, R., Desboeufs, K. V. and Journet, E.: Variability of dust iron solubility in atmospheric waters: Investigation of the role of oxalate organic complexation, *Atmos. Environ.*, 45(36), 6510–6517, doi:10.1016/j.atmosenv.2011.08.068, 2011. Raiswell, R., Hawkings, J. R., Benning, L. G., Baker, A. R., Death, R., Albani, S., Mahowald, N., Krom, M. D., Poulton, S. W., Wadham, J. and Tranter, M.: Potentially bioavailable iron delivery by iceberg-hosted sediments and atmospheric dust to the polar oceans, *Biogeosciences*, 13(13), 3887–3900, doi:10.5194/bg-13-3887-2016, 2016. 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, *Geochemistry, Geophys. Geosystems*, 8(10), 1–21, doi:10.1029/2007GC001586, 2007. Sholkovitz, E. R., Sedwick, P. N., Church, T. M., Baker, A. R. and Powell, C. F.: Fractional solubility of aerosol iron: Synthesis of a global-scale data set, *Geochim. Cosmochim. Acta*, 89, 173–189, doi:10.1016/j.gca.2012.04.022, 2012. Srinivas, B., Sarin, M. M. and Rengarajan, R.: Atmospheric transport of mineral dust from the Indo-Gangetic Plain: Temporal variability, acid processing, and iron solubility, *Geochemistry, Geophys. Geosystems*, 15(8), 3226–3243, doi:10.1002/2014GC005395, 2014. Tagliabue, A., Aumont, O., DeAth, R., Dunne, J. P., Dutkiewicz, S., Galbraith, E., Misumi, K., Moore, J. K., Ridgwell, A., Sherman, E., Stock, C., Vichi, M., Völker, C. and Yool, A.: How well do global ocean biogeochemistry models simulate dissolved iron distributions?, *Global Biogeochem. Cycles*, 30(2), 149–174, doi:10.1002/2015GB005289, 2016. Turner, D. R. and Hunter, K. A.: *The biogeochemistry of iron in seawater*, J. Wiley. [online] Available from: <https://www.wiley.com/en-us/The+Biogeochemistry+of+Iron+in+Seawater-p-9780471490685> (Accessed 27 August 2018), 2001. Ye, Y. and Völker, C.: On the Role of Dust-Deposited Lithogenic Particles for Iron Cycling in the Tropical and Subtropical Atlantic, *Global Biogeochem. Cycles*, 31(10), 1543–1558, doi:10.1002/2017GB005663, 2017. Zhu, X., Prospero, J. M., Savoie, D. L., Millero, F. J., Zika, R. G. and Saltzman, E. S.: Photoreduction of iron(III) in marine mineral aerosol solutions, *J. Geophys. Res. Atmos.*, 98(D5), 9039–9046, doi:10.1029/93JD00202, 1993. Zhuang, G., Yi, Z., Duce, R. A. and Brown, P. R.: Link between iron and sulphur cycles suggested by detection of Fe(n) in remote marine aerosols, *Nature*, 355(6360), 537–539, doi:10.1038/355537a0, 1992.

C11

Cycles, 31(10), 1543–1558, doi:10.1002/2017GB005663, 2017. Zhu, X., Prospero, J. M., Savoie, D. L., Millero, F. J., Zika, R. G. and Saltzman, E. S.: Photoreduction of iron(III) in marine mineral aerosol solutions, *J. Geophys. Res. Atmos.*, 98(D5), 9039–9046, doi:10.1029/93JD00202, 1993. Zhuang, G., Yi, Z., Duce, R. A. and Brown, P. R.: Link between iron and sulphur cycles suggested by detection of Fe(n) in remote marine aerosols, *Nature*, 355(6360), 537–539, doi:10.1038/355537a0, 1992.

Interactive comment on *Biogeosciences Discuss.*, <https://doi.org/10.5194/bg-2018-285>, 2018.

C12