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Interactive comment on "Atmospheric processing of iron carried by mineral dust" *by* S. Nickovic et al.

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We are grateful to the reviewer for his useful comments and suggestions. Below are our replies to the general and specific comments.

General comments:

1. I would suggest reorganizing and simplifying the text of sections 2.2, 2.3 and 2.4; some concepts are repeated in these sections (mainly regarding cloud chemical processing). Although the idea of dividing Section 2 in subsections is good, the result is rather confusing, moving forward and backward in the arguments.

We accepted reviewer's suggestion. We therefore reorganized section 2. by removing subsections 2.1 - 2.4. Parts of the text related to the cloud processing of iron are reformulated (see also replies to Reviewer 2).

2. The term "weathering", broadly used in the paper, should be explained in more detail.

We explained 'weathering' in more detail and the corresponding text reads as: "Through physical weathering, parent soils are disintegrated by processes such as wetting and drying, erosion, and actions of plants and animals. Once parent soil has broken down into smaller elements, primary minerals of smaller soil particles are chemically transformed into secondary minerals such as oxides under the influence of water and/or atmosphere. "

3. Concerning the iron processing by clouds and solar radiation (described in section 2.3), the authors should assess these general considerations in terms of the specific atmospheric conditions of the study region: the Sahara, the Sahel and the subtropical North Atlantic Ocean. For example, what is the role played by the fast cloud processing over the Sahara taking into account that during Saharan outbreaks over the ocean the cloudiness is almost inexistent? In this case, which would be the role played by the slower solar radiation process?

Following the Reviewer's comments, we introduced the new Figure 7 showing the relative contribution of different iron processing components in the model, and a new paragraph listed below that comments the shown graph. Our reply is also addressed to the comment of the Reviewer 2 on the same issue.

"Although the model is applied over Northern Africa (Sahara, Sahel) and subtropical North Atlantic, the parameterization of the iron faith in the atmosphere is not specifically addressed to any particular geographic region. Certainly, the atmospheric driving forces for the iron dissolution are specific for a selected geographic domain such as much less clouds coverage than in the equatorial and mid-latitude areas (and consequently less influence on iron), or a specific incident angle of the solar radiation to the

Earth surface in the subtropics. In order to explore how in our simulations the iron processing reacts to different effects, we evaluated a set of sensitivity experiments for the M55 cruise by executing the model without clouds, with constant Fe in sources and without radiation, and then compared the results with those of the reference model containing all three effects acting together (Figure 7). The shown graph indicates that the impact of clouds is marginal due to prevailing cloud-free conditions. With the constant 3.5% iron in the sources used, the soluble values drop for up to about 20%. Finally, with no radiation effects included, the soluble iron reduces for about 40%."

4. Probably the paper is too ambitious in model validation, when the soluble iron concentration is validated against observed value. As addressed by the authors, the solubility processes are still based on insufficient information about the iron chemical transformations. On the other hand the approach used to validate iron model outputs, probably the only available at the moment, is quite risky since it is based on comparison with observed data taken from a ship moving on the southern edge of a dust cloud over the ocean where high temporal and spatial variability of dust concentration is expected, as shown in Figure 3.The authors recognize that even the "simple" validation of predicted surface dust concentration (in ug/m3) shows large errors, of one order of magnitude or more (e.g. the case of November 6, 2002, page 2707, Line 21). In these conditions, we cannot expect reasonable good results when validating the much more complex simulation of soluble iron concentration (of the order of pg/m3). The authors should put in context more clearly these limitations in the results assessment.

We accept that a reader could have an impression that comparing the simulated parameters against the observation could lead to strong conclusions about the model validation. However, we think that direct comparisons still could provide useful information on how the model performs although we are aware, as stated in the text, that sources of errors on both, modelling and observation sides. Concerning the Reviewer's comment on soluble iron concentration, it should be noted that values range in the interval of 10^3 to 10^5 pgm^{-3}.

Following the Reviewer's comment, we made several changes in the article. We first changed the Section title from "Model validation" to "Model performance". Second, we added a new paragraph to elaborate the model comparison against observations which reads: "There are significant sources of errors in both modelling and observations. In the dust model intercomparison study for example Uno et al. (2005) and Todd et al. (2008) report that the predicted surface level concentration of tested models sometimes shows a difference of at least an order of magnitude. On the observational side, aerosol concentrations in general and in particular iron fraction and/or its soluble part are difficult to measure accurately at low concentrations observed (Mahowald et al., 2009; Baker and Croot, 2008). Additional uncertainty in observations is originating from the fact that the total Fe was often assessed assuming its fraction in dust mass concentration to be 3.5% (e.g. Baker and Croot, 2008; Mahowald et al., 2009; Sholkovitz et al., 2012). Therefore, when accuracy of dust-iron models is assessed, one has to draw conclusions with caution. Yet, there is a necessity to understand modeling performance in direct comparison against observations, because large gaps in iron-related observations could be at least partly compensated by information from model simulations. Several studies report on direct point-to-point model-observations comparisons (Luo et al., 2005; Hand et al., 2004; Luo et al., 2008; Mahowald et al., 2009). Based on several model studies used to extrapolate observation data, Mahowald et al. (2009) concluded that annual averaged model iron surface concentrations and daily averaged observations differ by a factor of 50–1000%. On the other hand, their study shows that in direct point-to-point comparison, scattering along the individual cruises is much smaller than for the annual averages (with most of the points falling within $\pm$ one order of magnitude interval). Their results also indicate that the model overpredicts iron especially in places with very low concentrations and depositions. Following the mentioned approach of direct comparison of simulated and observed parameters along the cruises, we show performance of the near-surface model total iron concentration T, the soluble iron concentration S and the iron solubility ($s_{\%}$)..."

Specific comments

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1. Page 2701: The solar radiation effect is in terms of temperature tendencies. Why? It makes sense the dependence of radiation with the temperature tendency for short wavelengths (solar range)?

The relevant paragraph was reformulated and clarified in our response to Reviewer 2 on the same issue.

3. Page 2702: Please, check the following sentences (line 25): "The free-total iron ratios in the samples ranged from 0.13 (Libya) to 0.6 (Niger). The Sahel soils (Niger sites and Mali) which were mostly weathered had the highest Spot values". These sentences seem to be contradictory with the previous sentence: "There was considerable spatial variability among the samples in the free-to-total iron ratio, with generally higher ratios in less weathered soils". These sentences are not in concordance with results shown in Figures 1b and 1c.

There was an error in our ACPD text. The relevant paragraph was reformulated and clarified in our response to Reviewer 2 on the same issue.

4. Page 2705: Page 17. Could you, please, specify what means "dominated by the Saharan dust"? Could you quantify this assessment?

We cannot precisely quantify the statement "dominated by Saharan dust". Instead, we replace it with the text that reads: ". . .the aerosol likely to originate from Saharan dusts sources. Namely, datasets JCR, ANT23-1, PEL, M55 (1) and M55 (2) include only samples which had visible Saharan dust on the filters and should therefore have dust as a major component of the total aerosol (A. Baker, personal communication, 2012). Similarly, BUCK data include only samples marked as Saharan for the air mass regime (Table 1 in Buck et al., 2012)"

5. Page 2705: Line 20. Could you, please, describe more in detail the group of Observations G2?

This group relates to the Atlantic Ocean data shown in figures 5 and 6 by Sholkovitz et al. (2012). We added a reference to these figures.

6. Figure 3a; Since total iron doesn't play an important role in the iron solubilization process, why not to use dust concentration to describe better the dust intrusion over the ocean?

Dust concentration could be considered as a first-guess proxy for the total iron. Since we use iron fraction in soil sources based on the heterogeneous geographic distribution rather than frequently used constant 3.5% Fe assumption, it makes sense to simulate the total iron field through an additional tracer equation for T(as done in our study), although, in general, patterns of dust and iron concentrations have similar but not identical shapes.

7. Figure 6 is quite interesting showing that Iron solubility is higher than about 8% only when dust concentration is lower than 1 ug/m3. This scenario does not correspond really with typical dust concentration associated to dust intrusions in which we might record concentrations two orders of magnitude higher. This low value might be result of dust gravitational settling taken place far away from the sources, or long after the intrusion near sources. Does it mean that the major iron solubility would take place preferable far away from dust sources, in this case, near the Americas? Does it mean that iron solubility would keep always low near the African coast during and after a dust intrusion, and only might be significantly higher long time after dust intrusions? Please, assess scientifically the results of Figure 6.

The Reviewer raised the important question of physical sorting of dust aerosol along their path trough the atmosphere. Several authors dealt with the issue and hypothesized why the negative correlation is observed between the dust concentration and the iron solubility. Following the Reviewer's comments, we added a new paragraph to elaborate the effect of physical particle sorting on the Fe solubilization. We also redraw Figure 6 by marking values of the aerosol originating from Sahara in order to provide easier comparison with the model values. The new text reads as: "Baker and Jickells

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(2006) hypothesized that size reduction of the transported aerosol Is a result of higher deposition rate of larger particles due to gravitational settling, and consequently related to decreasing concentration during transport to regions remote from desert sources. In parallel, smaller particles being longer time exposed to chemical processing have a larger probability to enhance its iron solubility. Thus, higher solubility for smaller concentrations is likely to be a combined effect of the particle size effects and the acid processing reactions. In Figure 6, we plot together their data and our simulated values. The model values are concentrated in the lower right quadrant (higher C and lower $s_{\%}$) in general follow the observed trend. Actually, the model values group mainly around those being from Saharan dust. On the other and – where the solubility gets higher values, the samples are collected at least five days over the ocean before collection (see A. Baker's description at http://www.uea.ac.uk/ e780/solubility.htm)."

8. Concerning the model validation with in-situ observations, it should be taken into account the fact that a strong acid digestion procedure is normally used to determine total Fe using an ammonium acetate leach at pH 4.7 (see Baker et al., (2006); Marine Chemistry 98, 43–58), what does not seem to fit seawater pH (around 8). Could you, please, assess this potential limitation in observations for model validation?

Following the Referee's comment, we added a new paragraph addressed to the issue of solubilities in the atmosphere and in the ocean. The new text reads as: "Laboratory studies have shown that repeated cycling of aerosol by acid processing between high and low pH will enhance iron solubility (e.g. Spokes et al., 1994; Zhu et al., 1997; Baker et al., 2006). These cycles should simulate the dust cycling of dust between aerosols and clouds. For example, Baker et al. (2006) used pH 4.7 for the laboratory aerosol processing. Furthermore, Shi et al. (2011a) performed experiments by exposing soil samples to acidic conditions in order to simulate the atmospheric conditions. Exposure of soil samples was performed through multiple pH cycling applied between acidic (pH 2) and circumneutral pH (pH 5–6) conditions. Establishment of standard tools (reference materials and protocols) as stated by Baker and Croot (2008) could help reducing differences in solubility estimation between current methods. In the mentioned studies, the iron solubility has been estimated although these methods do not really reproduce the conditions under which iron is released from aerosol particles once they are deposited onto the surface of the ocean where pH is around 8. They more show the trends in solubility that might be expected in the behavior of the aerosol in the seawater (Baker et al., 2006). With such methods, being internally consistent, the observed relative changes in iron solubility could most probably indicate tendencies in solubility process in seawater (Baker et al., 2006). In our study, we are focused on simulating iron solubilities in dust aerosol before it is deposited onto the ocean. When the simulations are compared against laboratory estimates of solubility, one should bear in mind that some variability between different laboratory methods dust processing might exist."

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 2695, 2013.

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