

Interactive comment on “Effect of atmospheric organic complexation on iron-bearing dust solubility” by R. Paris and K. V. Desboeufs

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The authors thank the anonymous reviewer for his(her) comments.

1) While this process may very well be extremely important in the atmosphere, the data presented here does not support some of the strong statements made in this MS. As the authors note, photochemical reduction of Fe has been shown to increase Fe solubility > 10x, while the most efficient organic donor used in this study (oxalic acid) only increased soluble Fe by a factor of 6.5. It is true that photochemical expts have tended towards higher concentrations of e⁻ donor, but one cannot conclude from this that photochemistry is less important. A good example of this is on page 3187, line 21-25. This was quite a surprising statement considering that all of the previous photochemical work has, in fact, shown that photoreduction is a very important reduction process.

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This is even more surprising given that formic and acetic acids are in greater abundance than oxalate and all of the other compounds tested in this study and those are the most photoactive. In short, I think that the authors have generated very interesting data, but are overstating its importance based on the current level of knowledge.

Response: We agree with the reviewer, maybe we have been a little bit too much enthusiastic for our results. In consequence, we have rewritten the paragraph (p3187, line 21-25): "Knowing the impact of photochemical process in presence of formate and acetate on iron solubility, studies of iron dust solubility under UV irradiation in presence of oxalate, malonate, tartrate and macroorganic ligands, type HULIS should be carried out." Moreover, in the section "conclusions", some sentences of the conclusions have been re-written to be more precise, e.g. p3191, L22: "This study shows that among the identified atmospheric iron organic binding ligands, oxalate is the most effective ligand enhancing iron dissolution in cloud and rain water, at least under no UV irradiation." Sentences have been also added (P3192, L4): " Nevertheless, this factor could be underestimated since our experiments are been made without UV light."

2) In the HULIS standard, were any formic, acetic, etc acids detected?

Response: As mentioned in the paper, the analyses by ionic chromatography were not made for HULIS standard. Thus, a possible contamination of other organic ligands is possible. A chemical characterization of our HULIS standard is available on the web site of the provider IHSS (<http://www.humicsubstances.org/sources.html>). It appears that HULIS standard, SRHA, contains carbohydrate and amino-acid and that the carboxylic groups predomine on phenolic groups with a ratio around 3.5. Thus, it is difficult to conclude on how these groups are implied in the iron complexation, it is probably a partition between the various binding ligand groups contained in the SRHA. However, the presence of potential contaminants as formic or acetic acid is probably negligible in comparison of these various active groups. We added the site web reference in the Table 1.

3) The material of the experimental/extraction vessel needs to be stated. If glass, then, expts examining Fe loss to surfaces need to be completed.

Response: P3185, L6: We rewrote the sentence on the labware used for the dissolution experiments in the purpose to specify these points: "All leaching and sample solutions were collected in polyethylene bottles that were carefully acid washed in accordance with the cleaning protocol detailed in Desboeufs et al. (2003b). Filters were also washed by rinsing once with ultrapure 0.2 M HCl then 3 times with ultrapure water. The collected sample solutions were acidified at pH 1 with ultrapure ProlaboTM Normatom[®] HNO₃ to allow proper analyses. "

4) page 3187, line 6: The authors state that the particles used in Upadhyay et al (2011) had significant anthropogenic influence. After perusing this article, I am not sure if this is correct. Roughly 1/2 of these particles were collected in the Southwest USA deserts. Although there is probably some anthropogenic influence in the PM_{2.5} fraction, many studies have shown that the coarse particles in this region are almost exclusively a result of wind-blown dust. This is the primary reason that this region suffers from exceedences from the regulated PM₁₀ standard.

Response: We cannot follow the reviewer on this point. The three main sites of sampling discussed in the paper of Upadhyay et al. (2011) are: the site of TYL which " is a semi-closed parking structure (300 parking spaces) with a steady state of daytime traffic flow during the classes at the University", the site of LSA which "is representative of a suburban site within a large urban area surrounded by the road arteries within a few hundred meters and influenced by vehicles/machines/unknown point sources in the campus premises.", and the site of NOG, which "is a city of about 20,000 inhabitants (on the US side), heavily impacted by cross-border transport of pollution from both anthropogenic and desert sources.". So, we think that we did not overstate when we wrote "anthropogenic influence", all the more reason that the dissolution experiments were mainly carried out on PM_{2.5} fraction. Even if the dust could constitute an

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important part of the collected PM, the values of solubility observed by Upadhyay et al. (2011) are consistent with values of solubility obtained for anthropogenic iron and the relation between Fe(Sol) to total Fe content (Figure 6) present the same pattern that the relation compiled by Sholkovitz et al. (2012), suggesting higher solubility associated to lower total iron content. On this figure, the NOG samples are potentially the only ones with a predominance of iron issued from dust. However, the authors wrote that " The ratio of Fe(sol) in PM >2.5-to-PM_{2.5} were $10.8 \pm 5.7\%$ at NOG and $3.2 \pm 1.2\%$ at TYL (Table S2) which suggests that >90% of the soluble Fe is associated with the smaller particulates (PM_{2.5}).". This means, in our opinion, that the anthropogenic influence on soluble iron could be not excluded and that the dust iron release is not significant in comparison to the anthropogenic iron dissolution.

5) p 3192, lines 2-4: starting "That confirms that the effect of atmospheric chemical processing..." Again, I think this is an overstatement. The author's data suggests that solubilization of Fe by SMALL CHAIN ORGANIC ACIDS and HULIS does not allow for soluble Fe in dust to reach those of anthropogenic aerosols. What about SO₂, HNO₃, PAH, or other redox active and acid/base compounds which were not tested in this study? And, as mentioned above, what about photochemistry? There are too many other unknowns to make such a strong statement.

Response: Sholkovitz et al. (2012) estimates from a global data compilation on fractional solubility of iron in the bulk marine aerosol that iron solubility values of dust aerosol reaches 2%, whereas this value ranges from 4 to 95% for anthropogenic aerosols. Thus, if we apply the factor 6.5 to higher values of iron dust solubility (corresponding to already transported dust), we find that the organic complexation could produce a dust iron solubility around 13%, which is in the lowest values obtained for anthropogenic aerosols. Moreover, in Paris et al. 2011, we compared the effect of oxalate and acid processing in extreme conditions (pH 2) on iron dissolution. These effects were similar, so we do not think that it is possible to reach the solubility observed for anthropogenic iron. However, to take into account the overstatement of this

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sentence, we modify it by " Even if the effect of atmospheric chemical processing is significant on iron dust solubility, the organic complexation does not seem to allow for dust to get the high iron solubility values attributed to anthropogenic aerosols reaching 95% (Sholkovitz et al., 2012)." Moreover, this sentence is followed directly to the paragraph of the photochemical effect to balance the conclusions: " Nevertheless, this factor could be underestimated since our experiments are been made without UV light. Thus, the effect of photo-induced dissolution in presence of organic species, previously identified by Pehkonen et al. (1993), remains to be investigated in atmospheric conditions. Moreover, the potential synergetic effect of the different atmospheric processes needs also to be estimated. Thus, the organic complexation could significantly affect the global distribution of the atmospheric Fe deposition fluxes to the oceans, and this process needs to be further studied."

6) Technical corrections: All technical corrections suggested by the referee have now been corrected.

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