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Atmospheric Chemistry and Physics Discussions

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

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A. General comments:

The results obtained from this study add to the knowledge of atmospheric processing of aerosols by showing that reductive dissolution can take place without photo-induced processes, and that several organic compounds found in atmospheric waters can be involved in the reductive dissolution of aerosol iron. However, results should be placed in context with other dissolution processes, and not assumed to be the only and most important process taking place.

Response: We agree with this statement. In the purpose to replace our results in a largest context of dissolution process in presence of organic species, we added several paragraphs and modified the conclusion by including various points of discussion emphasized by the various publications mentioned by the reviewer (see below).

(i)A natural strong iron binding organic ligand class has been observed in rain samples (Cheize et al., 2012) with stability constants similar to the siderophore deferoxamine mexylate (DFOB). The work of Cheize et al. (2012) showed that 80% or more of the dissolved Fe present in the rain samples was bound by this natural strong iron binding ligand class. Because of their experimental conditions, Cheize et al. (2012) were unable to detect weak iron-binding ligands such as oxalate.However in artificial rain water containing 1μM oxalate and 10 nM DFOB 100% of the dissolved Fe was found to be complexed by the strong ligand class (i.e. DFOB). Additionally, they observed high concentration of dissolved iron ($\sim$74 nM and $\sim$ 99 nM) in the filtered rain samples, suggesting that the presence of strong iron-binding ligands is necessary to maintain high concentrations of dissolved iron in solution.

Response: This missing reference has now been added and the results of Cheize et al. (2012) on the presence of strong Fe(III)-binding ligand in rain water has developed in "1. Introduction": " The organic speciation of Fe (II) and Fe(III) in rain waters has only highlighted in natural conditions by thermodynamical calcultation (Okochi and Brimblecombe, 2002) or by indirect ferrozine method (Kieber et al., 2005). However, recent works of Cheize et al. (2012) showed by cathodic stripping voltammetry that 80% or more of dissolved Fe(III) present in rain samples was bound with natural strong organic binding ligand, which stability constant is close to siderophore. These results pointed the potential role of organic complexation on the dissolved iron concentrations in rain waters." A paragraph on the interested of their method has been added in the conclusion: "However for this purpose, very few data exists on the characterisation of iron-complexing organic ligands in atmospheric waters limiting the incorporation of organic complexation in modeling. In this domain, the method developed by Cheize et al. (2012) on the identification of organic forms of Fe(III) in rain waters need to be adapted to other class of iron organic binding ligands."

(ii)Buck et al. (2010) (Marine Chemistry) also observed high concentrations of dissolved iron (1-160 nM) in rain samples collected over the Atlantic Ocean which contained crustal Fe:Al ratios, and did not observe a significant correlation between aerosol oxalate and aerosol iron solubility in their DI water leaches, suggesting that compounds other than oxalate were involved in the dissolution of iron from aerosols.

Response: The introduction was focused on the link between iron solubility and organic concentrations in a context of laboratory studies, since it is the kind of experiments carried out in these studies. However, we agree with the reviewer that we need to precise the state of knowledge on this link including field studies. In consequence, we added a paragraph in the introduction about field observations: " The conclusions obtained from field measurements are also unclear since some studies suggested a positive effect of organic complexation on dust iron solubility (Zhu et al., 1993; Johansen et al., 2000; Chen and Siefert; 2004), whereas other works do not get correlation between aerosol iron solubility and oxalate concentrations in the collected rain samples or in the water soluble fraction of aerosols (e.g. Buck et al., 2006, 2010; Paris et al., 2010). Nevertheless, the destruction of oxalate associated to the production of soluble iron (Siffert and Sulzberger, 1991; Zuo 1995, Cwiertny et al., 2008) could explain this lack of correlation. Moreover, during field studies, several factors regarding the iron solubility measurements could play simultaneously, as acid species, photochemical reactions, dust mineralogical composition (Baker and Croot, 2010), making difficult the determination of involved processes in the dissolution of iron."

(iii)The diel variability in soluble FeII from Saharan dust samples collected in Barbados (Zhu et al., 1997) suggests that photochemical processes contribute a similar amount of FeII as obtained in the absence of light (day samples contained about 2x the amount found in night samples). Zhu et al. (1997) also concluded that the variability in FeII solubility did not affect the total Fe solubility in their Saharan dust samples, suggesting that solubility is controlled by non-reductive dissolution processes. In the surface

ocean, the diel concentrations of Fe(II) are minor components of the dissolved Fe pool (e.g. Hansard et al., 2009), which in turn is controlled by the availability of strong iron binding organic ligands (L1 class) (e.g. Buck et al. 2007). These observations indicate that atmospheric Fe(II) complexes (such as the ones discussed in this manuscript) are not stable, and do not accumulate in the surface ocean.

Response: We are aware that the atmospheric concentrations of Fe(II) complexes are controlled by photochemical processes. However, we argued that various works showed that these concentrations are not dependent on diel cycle. We added a paragraph to adress this point in the section "3.1. Iron solubility and redox speciation": " Thus, our results suggest that the initial dissolved iron is mainly as Fe(II)-organic complex in dark conditions. These Fe(II) ratings are in the same order of magnitude than those reported in the literature, where DFe(II)/DFeT mean ratios higher than 50% are observed in the atmospheric waters (Behra and Sigg, 1990; Özsoy and Saydam, 2001; Kieber et al., 2001). It is known that iron redox species are involved in numerous (photo)chemical reactions in cloud and rain drops, such as the oxidation of S(IV), the budget of H2O2, the formation of free radicals (OH, HO2/O2-) or the oxidation of ozone, (Erel et al, 1993; Deguillaume et al., 2004; Ben'ko and Lunin, 2010). This modifies the redox cycling between Fe(II) and Fe(III) and implies a temporal pattern of Fe(II) and Fe(III) partition with predominance of Fe(II) throughout the day (Zhu et al., 1997; Siefert et al., 1998; Kieber et al., 2001, Deutsch et al., 2001). Thus, the organic Fe(II)-complexes released by dissolution could be not stable. Nevertheless, recent works of Deguillaume et al. (2010) showed that the initial DFe(II)/DFeT ratio issued from dissolution of incorporated aerosols in cloud droplets predominates on the chemical reactions to determine the concentrations of Fe(II) during daytime. Moreover, Kieber et al. (2005) observed that 25% of the Fe(II)-complexing ligands in rainwater is strong enough to prevent and slow oxidation in seawater, suggesting that organic complexation enables to stabilize iron as Fe(II), probably via organic macromolecule binding ligands (Willey et al., 2008). This implies that the dissolved Fe(II) concentration could be significant in the aqueous phase even during the night due to the organic complexation.". Moreover, the question about the fate of Fe(II) after deposition to seawater is addressed in the conclusion by adding a sentence: " In this purpose, the photochemical redox cycling of dissolved Fe in atmospheric waters needs to be considered similarly to iron solubility in the assessment of atmospheric iron fluxes."

(iv)The authors indicate that during their experiments the highest dissolution “rates are obtained in the first ten minutes and hence that most Fe was released in the solution in about 60 min (Desboeufs et al., 1999)”. With this in mind, and given the excess in ligand concentrations used (2 orders of magnitude for oxalate) one would expect the amount of soluble Fe to not increase linearly with ligand concentration, but to increase towards a maximum dissolved iron value. If the additional Fe released at higher ligand concentrations is not from impurities in the ligand stock solution, as indicated by the blank experiments, then the maximum solubility of this dust analog was not obtained with the typical concentrations of oxalate found in atmospheric waters. Thus, suggesting that other processes are likely to contribute to the solubility of dust during atmospheric processing as well as after deposition to surface waters.

Response: We agree with the reviewer that we expected logically to reach a maximum of iron solubility with the increase of oxalate or other organic species playing on dissolution. As mentioned in the paper, to explain the linear correlation, we could think that even if the oxalate is in excess, only a part of this oxalate can form Fe-oxalate complex in surface. To check really the part of active oxalate, we need to predict iron complexed by oxalate in surface (e.g. see Xu and Gao, Applied Geochemistry, 2008). However, we worked with soil compound by various minerals and hence compound by various elements, among which ones other trace metals than iron as Cu, Mn... of which the oxalate is also a ligand. Another hypothesis, as though by the reviewer, could be a control by the kinetic of dissolution reaction. The dissolution rates could be increased by the presence of organic ligands and the linearity could be due to the effect of this increase. Thus, for all these reasons, we think that it is very complicated to conclude on the cause(s) involved in the linearity of iron solubility with ligands concentrations. In this

purpose, it will be necessary to make further investigation (kinetic experiments) and consider numerical simulation of ligand reactivity in the aqueous phase, with iron but also other dissolved elements. We had thought that this interpretation being unclear, it risked to complicate the conclusion. However, the fact that the reviewer points the question shows that this discussion is necessary. Thus, in order to take into account the difficulty of interpretation of our results, we added in section "3.2; Dependence to the organic compounds concentration": "In atmospheric conditions, the formation of iron surface complexes with oxalate on hematite has been highlighted by an adsorption isotherm method (Xu and Gao, 2008). However, in our case, the prediction of surface complexes is made difficult by the use of soil compound by various minerals. These minerals probably release various elements in solution such as transition metals (Cu, Mn, Cr..) which could form complexes with organic ligands and hence modify their reactivity with iron. Another hypothesis to explain the linear relation could be due to an increase of dissolution rates in presence of organic ligands, as previously observed by the pH effect (Desboeufs et al., 1999). As we worked for a fixed time (60 min.), the maximum of dissolved iron amount could not be reached at this time and the linearity could so directly be associated to the temporal linearity of the increase of dissolution rates. Consequently, we need further studies, as kinetic studies or numerical simulation to conclude on the cause of the linearity."

B. Comments about methodology: It would be useful for the reader to specify:

1.Whether the dissolution experiments were carried out in the glass flasks or in acid washed plastic bottles. 4. The type of labware used to collect the leachate after filtration. 5. A brief description of the cleaning protocol for the polycarbonate filters.

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 ultra-pure water. The collected sample solutions were acidified at pH 1 with ultrapure Prolabo™ Normatom® HNO3 to allow proper analyses. "

2. Whether the specific labware used in a particular set of blank experiments was then used during the same particular set of aerosol dissolution experiment. 3. Whether the blank experiments were also filtered.

Response: By definition a blank experiment is based exactly on the same protocol that the dissolution experiments and in a same set of measurements. Here, we precised that blank experiments are experiments without soil, including logically that they were based on the same protocol that the dissolution experiments in a same set of experiments. In consequence, we don't think that we need to specify the points mentioned by the referee.

C. Comments about writing style: The sections 3 and 4 have been merged under one section "Result and discussion", including 3 subsections: "Iron solubility and redox speciation", "Dependence to the organic compounds concentration", "Dissolution process". All technical corrections suggested by the reviewer have now been corrected, and a careful read of the paper has been made to try to correct all awkward phrases.

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