Atmos. Chem. Phys. Discuss., 13, C766–C770, 2013
www.atmos-chem-phys-discuss.net/13/C766/2013/

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

Anonymous Referee #1

Received and published: 25 March 2013

The manuscript describes laboratory experimental results of iron dissolution from a dust analog (< 20 um Sahelian soil) in the presence of various potential iron-binding organic compounds typically present in atmospheric waters. Results indicate a linear correlation between iron solubility (associated with an increase in dissolved Fe(II)) and the concentration of four of the organic compounds tested (oxalate, malonate, tartrate and a humic acid). This linear relationship was interpreted as the result of reductive ligand-promoted dissolution, and this mechanism was considered important in "the estimation of atmospheric iron fluxes".

General comments: There is a continuum from weak to strong iron binding ligand classes in natural waters. The organic compounds tested in this study represent compounds in the weak iron-binding ligand class (Table 1), with the exception of the Suwa-

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nee River humic acid standard. The authors suggest that in addition to complex formation, reductive ligand-promoted dissolution plays an important role in aerosol iron solubility, and conclude that through this mechanism “oxalate is indeed the most effective atmospheric ligand, enhancing iron dissolution in cloud and rain water” and that aerosol “dissolved Fe could be mainly as organic Fe(II) complexes”. However, the dissolution effect of strong iron binding ligands with low molecular weights, and the reductive dissolution by photochemical processes were not assessed in the study. 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.

A natural strong iron binding organic ligand class has been observed in rain samples (Cheize et al., 2012. Iron organic speciation determination in rainwater using cathodic stripping voltammetry. Analytica Chimica Acta 736, 45-54) 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 1uM oxalate and $\sim$ 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. 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. The diel variability in soluble FeII from Saharan dust samples collected in Barbados (Zhu et al., 1997) (Journal of Geophysical Research), 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. 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 ($\sim$ 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.

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. 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 4. The type of labware used to collect the leachate after filtration. 5. A brief description of the cleaning protocol for the

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Comments about writing style: The manuscript is generally well organized and easy to follow. A “Discussion” section is not explicitly included. However some of the text in the “Results” section (3) is appropriate as part of the discussion. Sections 3 and 4 could be merged as three separate subsections under “3 Results and discussion”. Several awkward phrases need attention. I have included here some examples from the Abstract, Introduction, and Materials and methods sections, but others can be found throughout the manuscript.

Abstract, lines 14-15 “ligand playing on dust iron solubility. . .” Suggested change: “ligand promoting dust iron dissolution. . .”

Introduction, 3182, line 17 Remove “the” from “ promote the iron”

Introduction, 3182, line 22 Replace “are” with “were” in “compounds are often”

Introduction, 3182, lines 27-28 Rearrange sentence for clarity Suggested change: “The aim of this paper is to test the effect of previously identified atmospheric iron binding ligands on the solubility of iron from mineral dust,. . .”

Introduction, 3183, line 5 Remove “really”

Material and method, 3183, line 9 Replace “Material and method” with “Materials and Methods”

Material and method, 3184, line 1 Make “Leaching solution” plural as several leaching solutions were prepared and tested.

Material and method, 3184, line 8 Replace “was” with “were” in “solutions was prepared”

Material and method, 3184, line 15 Replace “no” with “none of the” in “no studied organic”

Material and method, 3184, line 16 Insert “the” before “dissolved phase”

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