



Atmospheric organic
complexation and
iron solubility

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Effect of atmospheric organic complexation on iron-bearing dust solubility

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Abstract

Recent studies reported that the effect of organic complexation may be a potentially important process to be considered in models to estimate atmospheric iron flux to the ocean. In this study, we investigated this effect by a series of dissolution experiments on iron-bearing dust in presence or absence of various organic compounds typically found in the atmospheric waters (acetate, formate, oxalate, malonate, succinate, glutarate, glycolate, lactate, tartrate and humic acid as an analogue of humic like substances (HULIS)). Only 4 of tested organic ligands (oxalate, malonate, tartrate and humic acid) caused an enhancement of iron solubility which was associated with an increase of dissolved Fe(II) concentrations. For all of these organic ligands, a positive linear dependence of iron solubility to organic concentrations was observed and showed that the extent of organic complexation on iron solubility decreased in order oxalate > malonate = tartrate > humic acid. This was attributed to the ability of electron donors of organic ligands and implied a reductive ligand-promoted dissolution. This study confirmed that oxalate is the most effective ligand playing on dust iron solubility and showed, for the first time, the potential effect of HULIS on iron dissolution in atmospheric conditions.

1 Introduction

Iron bioavailability has been shown to limit or co-limit primary productivity in a large portion of the world ocean (Martin et al., 1994). A significant external iron source to the open ocean is atmospheric input and particularly the atmospheric deposition of mineral dust from continental regions (Jickells et al., 2005). The wet deposition seems to be the major dust removal process over ocean region (Sarhou et al., 2003) and is the most efficient for input of nutrients to the oceans since a significant part of the dust can be previously dissolved in droplets. Presently, the mechanisms controlling the release of Fe from atmospheric particles into the aqueous phase are not well understood. Measurements of iron solubility during atmospheric dust cycle suggest a much higher

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solubility in transported aerosols implying substantial atmospheric chemical processing. Atmospheric chemical processes affect Fe speciation and solubility (Desboeufs et al., 2001; Hand et al., 2004), and hence its bioavailability in the ocean. Among these processes, organic complexation enables both to enhance the iron solubility, in particular with oxalate (Sulzberger and Laubscher, 1995; Paris et al., 2011), and to stabilise iron in dissolved form after wet deposition in seawater (Kieber et al., 2005). Thus, the atmospheric organic complexation of iron in cloud or rain water could be essential to estimate the supply of bioavailable iron to the ocean (Shi et al., 2012).

In marine systems, increased Fe solubility is known to result from complexation with prokaryotic-released organic matter (OM) such as siderophores as well as low molecular weight polycarboxylate compounds (Barbeau, 2006), humic substances (Laglera and van den Berg, 2009) and saccharides (Hassler et al., 2011). While siderophores are not produced in atmospheric aqueous phase, (poly)carboxylic acids, humic substances or sugars have been detected in rainwater or in the water soluble fraction of aerosol particles (Wiley et al., 2008). However, the presence of sugar seems to be limited to biomass burning aerosols (Mayol-bracero et al., 2002) or primary biological aerosol particles (Graham et al., 2003). Carboxylic acids contribute significantly to atmospheric water acidity in urban areas (Peña et al., 2002), and can be the main contributor to acidity (70 %) in remote (dusty) areas (Gioda et al., 2009; Desboeufs et al., 2010). Formic and acetic acids constitute the most abundant carboxylic acids in the cloud and rainwater (Peña et al., 2002). In all the regions, oxalic (c2), malonic (c3) succinic (c4) and glutaric (c5) acids are usually the most abundant dicarboxylic acids, more concentrated than ketoacids such as glyoxalic acid or hydroxyacids as glycolic or lactic acids (Sempéré and Kawamura, 1996; Desboeufs et al., 2010). The contribution of organic acids to total dissolved organic carbon (DOC) ranges from only 14–36 % (Altieri et al., 2009). A large part of the rainwater DOC has been attributed to macromolecular organic matter, termed humic like substances (HULIS) because of properties similar to terrestrial and aquatic humic and fulvic acids (Graber and Rudich,

2006). These HULIS are usually identified in rain and cloud waters, but not quantified (e.g. Muller et al., 2008).

Among the organic compounds found in rainwater, Okochi and Brimblecombe (2002) studied, by theoretical calculations, the potential ligands of iron in atmospheric conditions. They reported that the simple monocarboxylic acids (e.g. formic and acetic) do not complex substantial amounts of metal under typical atmospheric conditions. On the contrary, the dicarboxylic oxalic and malonic acids, which are strong acids and have high Henry's law constants and large stability constants, lead to substantial iron complexation at very low concentrations (around ppt). The hydroxylated dicarboxylic acids, as glycolic and tartaric acids, are less volatile and relatively strong acids could be more effective than monocarboxylic acids to complex iron under atmospheric conditions. Humic substances are known to provide binding sites, due to the presence of phenolate or carboxylate groups, for iron in aquatic systems (Allard et al., 2004; Weber et al., 2006). Similar complexation could be observed for HULIS in the atmospheric waters. Thus, it appears that some of the most important organic compounds present in the aerosols and aqueous phase of the atmosphere are potentially preferred ligands of iron. Practically, it has been observed that some organic ligands could promote the iron dissolution from iron-bearing minerals and ambient aerosols (Pehkonen et al., 1993; Siefert et al., 1994; Majestic et al., 2006; Xu and Gao, 2008; Upadhyay et al., 2011; Paris et al., 2011). However, these works are limited to the main organic carboxylic acids found in the atmospheric waters; i.e. formate; acetate and oxalate. Moreover, the used concentrations of organic compounds are often 50 to 600 times higher than atmospheric concentrations in rain water. This makes extrapolation of the conclusions of these works to atmospheric conditions difficult. Thus, despite the profound significance of the Fe-organic ligands in rainwater, virtually nothing is known regarding the nature of the ligand(s) and the quantification of complexation effect on Fe solubility.

The aim of this paper is to test the effect of the potential iron atmospheric ligands identified by the previous works on iron-bearing dust solubility, i.e. monocarboxylate (acetate and formate), dicarboxylate (oxalate, malonate, succinate and glutarate),

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hydroxylated dicarboxylate (glycolate, lactate and tartrate) and humic acid as an analogue of HULIS. Fe solubility is affected by the origin of aerosol, which determines the mineralogical speciation of aerosol iron (Journet et al., 2008), the resulting extract pH (Desboeufs et al., 2003a) and the size of particles (Ooki et al., 2009). In consequence, it is important to control the particulate matter in order to be able to really compare the effect of organic ligands. Thus, dissolution studies were conducted with leaching solutions of organic ligands at typical concentrations found in rainwater on a proxy for Sahelian dust close to emission region.

2 Material and method

2.1 Material source

The experiments were carried out with the sieved fraction of Sahelian soil ($< 20 \mu\text{m}$) used as analogue of dust. The soil sample has been collected in the area of Bani-zoumbou, Niger ($13^{\circ} 31' \text{N}$; $2^{\circ} 38' \text{E}$) which is a source region of Sahelian dust. It corresponds to the first millimetres of soils that are prone to wind erosion. The finest fraction of soil with a diameter less than $20 \mu\text{m}$ is representative of naturally produced dust (Alfaro and Gomes, 2001). The elemental chemical analysis of sieved soil has been performed by Wavelength dispersive X-ray fluorescence (WD-XRF) using a PW-2404 spectrometer by Panalytical based on the protocol described in Guieu et al. (2010). The finest fraction of soil from Niger is composed of $3.1 \pm 0.2\%$ Fe and $4.9 \pm 0.7\%$ Al. The aerosol-adapted Citrate Bicarbonate Dithionite (CBD) method described by Lafon et al. (2004) emphasizes that 70 % of iron is present as iron oxide. The Fe, which is not oxide, is mainly present as illite, a typical clay found in dust aerosols (Paris et al., 2011). The fraction of organic matter in soil has been estimated by loss-on-ignition method (Konen et al., 2002) and corresponds to 7.3 % of total mass of material.

2.2 Leaching solution

The leaching solution was prepared to mimic atmospheric rain water by acidifying 18.2 mΩcm ultra-pure water (Elga® Purelab) with sulphuric acid (Ultrapure, Norton 2, Prolabo®) at pH 4.7, typical pH of remote rainwater samples (Heartsill-Scalley et al., 2007) and by diluting a working solution of the studied organic compound. Stock organic solutions (10^{-2} mol L⁻¹) were prepared by dissolving pure powder organic salts (Table 1) in ultra pure water then diluted to the concentration of 10^{-4} mol L⁻¹ as working solution. All organic solutions were prepared in sterilised glass flasks and stored before experiment (max. 2 weeks in the refrigerator). The used concentration of the leaching solution during the dissolution experiments corresponds to the range of measured concentrations in the rainwater from 0.5 to 8 μM (Table 1). The humic acid concentrations have been estimated on the basis that HULIS represent 50 % of typical marine rainwater DOC (Sempéré and Kawamura, 1996). Initial organic ion concentrations (except HULIS) have been checked by ionic chromatography using a Professional IC 850 by Metrohm® with a Metrosep A Supp 7–250 columns. Moreover, no studied organic compounds were detected via ionic chromatography in dissolved phase after leaching of Niger dust by ultra pure water in ambient laboratory conditions (temperature and light).

2.3 Dissolution experiments

In order to measure iron solubility in dust particles, 15 ± 0.2 mg of the sieved fraction of soil were put into 1 L of the leaching solution. This amount of soil material represents 0.465 ± 0.006 mg of iron (Fe_{tot}). This dust : water ratio of 15 mg L⁻¹ is consistent with the observed cloud or rain conditions (Desboeufs et al., 2010). Each experiment was set for one organic compound. After 60 min of contact with an automatic shaking and under laboratory light (with no UV properties), the leaching solutions were filtered through a 0.2 μm Nucleopore® polycarbonate filter for dissolved iron analysis. This time is consistent with the lifetime of cloud droplets (Warneck, 1988). Moreover, previous studies on dissolution rates of dust showed that the highest rates are obtained

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in the first ten minutes and hence that most Fe was released in the solution in about 60 min (Desboeufs et al., 1999). All experiments were made in triplicate. The experimental conditions enabled us to use very low concentrations of about $\mu\text{g L}^{-1}$ (ppb) or less. To avoid extraneous contamination and to ensure very low detection limits, all dissolution experiments and analyses were conducted in a clean room (class < 1000) and with laminar-flow ultraclean benches (class < 10), using ultraclean material based on the cleaning protocol detailed in Desboeufs et al. (2003b). The temperature in the clean room was maintained between 20 °C and 22 °C. In order to check the potential contaminations, 3 blank experiments were conducted in leaching solutions for each organic species but without soil addition. Dissolved iron concentrations (DFe_T) obtained for these blank experiments ranged from no measurable (< 0.6 nM, the detection limits of the instrument) to 0.9 nM. If the mean DFe_T of the blank experiments of an organic species were measurable, this blank value was deducted to the measured DFe_T of corresponding dissolution experiments. Niger soil does not contain calcite or carbonated minerals and hence its buffering capacity is insignificant. However, as the used solution is not buffered, the pH is measured in the initial solution and at the end of the experiment to check that it is fixed at 4.7. For all experiments, this pH was stable.

2.4 Dissolved iron measurement

Dissolved iron concentration (DFe_T) was analyzed by a Perkin Elmer Optima 3000 XL ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometer), which the detection limit for Fe is 0.6 nM (Desboeufs et al., 2003b). The iron solubility (% SFe) is calculated as follows: $\% \text{SFe} = 100 \times (\text{DFe}_T / \text{Fe}_{\text{tot}})$. For some experiments, the dissolved Fe(II) ($\text{DFe}(\text{II})$) was determined by a modification of spectrophotometric ferrozine method (Kieber et al., 2005). Absorbance of the iron ferrozine complex was read at 562 nm using a 1 m liquid wave-guide capillary cell attached to a JAZ spectrometer (Ocean Optics, World Precision Instruments). Absorbance measurements were referenced to a nonabsorbing wavelength (700 nm) in order to compensate for turbidity and instrument drift. Preliminary analysis of each tested organic species solution spiked

with known Fe(II) content showed that the formation of iron-ferrozine complex was not affected by the presence of studied organic ligand in the solution. The detection limit of the Fe(II) method is 2 nM. DFe(III) was determined by the difference between DFe_T and DFe(II).

3 Results

3.1 Iron solubility and redox speciation

We have carried out 6 dissolution experiments without organic species and it has been determined that the mean solubility for Niger aerosol analogues, is about 0.04 ± 0.01 %, i.e. 180 ± 40 ng of dissolved iron for each experiments (Table 2). This shows that the fine fraction of soil, analogue of dust collected before atmospheric transport, is poorly soluble. This result is consistent with previous works on dust-iron solubility from proxies for mineral dust (e.g. Desboeufs et al., 2005; Mackie et al., 2006). This solubility corresponds to a release of dissolved iron 3.22 ± 0.72 nM. The redox speciation of the dissolved iron shows that DFe(II) is below the limits of detection of LWCC method of 2 nM. This result shows that less than 2 nM of DFe_T is present as Fe(II), i.e. DFe(II) represents less than 60 % of DFe_T.

The results obtained in presence of organic compounds are detailed in the Tables 2. For the 10 studied organic compounds, it appears that the iron solubility obtained for 6 of these compounds is 0.04 %, i.e. the same as the one determined without organic compounds, meaning no significant effect on dust iron solubility. This is the case of acetate, formate, glycolate, succinate, glutarate and lactate, whereas for 4 organic compounds, an increase of iron solubility is observed, i.e. oxalate, malonate, tartrate and the analogue of HULIS. As previously mentioned as motivation of this paper, very few data exists on the effect of atmospheric organic compounds. The promoting effect of oxalate on iron solubility, in dark condition, is consistent with other works carried out from pure minerals or from fine fraction of soil (Xu and Gao, 2008 (hematite); Paris

et al., 2011 (goethite, illite, various Saharan dust analogues)). In contrast, our results are not in agreement with the observations of Pehkonen et al. (1993), Siefert et al. (1994) and Upadhyay et al. (2011) which emphasize the positive effect of acetate and formate on the iron solubility from iron oxyhydroxides and ambient aerosols. It is known that the origin of iron (dust-bearing or anthropogenic) is crucial to estimate its solubility (Desboeufs et al., 2005). The aerosol particles used by Upadhyay et al. (2011) or Siefert et al. (1994) have been collected in regions of anthropogenic influence whereas our particulate matter is soil matter. In consequence, the effect of organic compounds could be dependent on the origin of iron. Pehkonen et al. (1993) and Siefert et al. (1994) carried out dissolution experiments under UV light. Pehkonen et al. (1993) attributed the promoting effect of acetate and formate on iron dissolution to the photo-production of Fe(II) from Fe(III)-oxyhydroxides, process which is impossible in our study carried out under no-UV light. However, to explain the difference of results, it is important to take also into consideration that the studied concentrations in these works are 60 to 600 higher than in our study, i.e. much higher than the atmospheric concentrations. For these studies, the amount of Fe extracted in acetate and formate solutions increases by a factor of 10 in the best case. We have found that iron solubility increases from 0.04 % to 0.26 % (Table 2a) in presence of atmospheric concentrations of oxalate, i.e. by a factor of 6.5. In consequence, our results emphasize that the organic complexation by oxalate is also effective on iron solubility that in these works carried out for formate and acetate in extreme conditions. Thus, even if formate and acetate are the two major carboxylic acids in the atmospheric aqueous phase, they are not good candidates to consider in the studies of iron dust solubility at the difference of malonate, tartrate and macroorganic ligands, type HULIS, which the promoting effect in rainwater conditions has been identified for the first time in this study.

Due to the proximity of dissolved iron concentrations with the detection limit of Fe(II) method, the measurements of redox iron speciation have been only determined for the experiment with the highest concentrations of organic compounds. The DFe(II) concentrations have been below the detection limit for all organic compounds which did

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not increase iron solubility. The percentages of dissolved Fe(II) for the organic compounds playing on iron dissolution range from 66 % for humic acid to 78 % for oxalate. This means an increase of release of Fe(II) in comparison to experiments without organic compounds. These Fe(II) ratings are in the same order of magnitude than those reported in the literature, where $D\text{Fe(II)}/D\text{Fe}_T$ mean ratios higher than 50 % are observed in the atmospheric waters (Behra and Sigg, 1990; Özsoy and Saydam, 2001). Since Fe(II) is thermodynamically unstable in rain water (Zuo, 1995), the role of organic macromolecules, as humic substances, to stabilize iron in its reduced form via complexation has been proposed by various authors (Kieber et al., 2005; Willey et al., 2008). Our results confirm that the organic ligands could play a critical role in the stabilization of dissolved Fe(II) in the aqueous phase.

3.2 Dependence to the organic compounds concentration

In the case of a promoting effect of organic species, it appears that a positive linear dependence between iron bearing-dust solubility and ligand concentrations in the range of atmospheric concentrations (Fig. 1). The positive linear correlation between dissolved iron and oxalate concentrations has been already observed on typical pure minerals bearing iron in dust aerosols: hematite (Xu and Gao, 2008), goethite and illite (Paris et al., 2011), but also on various analogues of Saharan dust (Paris et al., 2011). Our experiments show that the slope of the positive correlation is different for each compound meaning that the effectiveness to promote iron solubility is dependent on the nature of ligands. Oxalate is the most effective with a slope around 14 fold superior to the one of humic acid, which is the less effective. For solution with an organic compound concentration of 1 μM , the increase of iron solubility is 126 %, 42 % and 10 % for oxalate, malonate = tartrate and humic acid, respectively. Thus, our results show a dependence of iron solubility both on the nature of organic compounds and on their ranges of atmospheric concentrations. This linear behaviour could be explained by a limitation of the iron dissolution by the concentrations of available ligands to complex iron. However, the number of moles of organic ligands in solution is always

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much higher than that of the dissolved iron concentrations (Table 2a), suggesting that the ligand concentrations are not limiting. The linear relation of dissolved metals with ligand concentrations is known from the studies on aquatic surface chemistry and is attributed to the dependence of dissolution to the formation of surface complexes and hence to the surface concentrations of ligands (Stumm and Morgan, 1996). However, to extrapolate this theory to the domain of atmospheric waters, we need to consider a dissolution determined by surface reaction.

4 Dissolution process

Under no-UV conditions, two mechanisms of ligand-promoted dissolution have been proposed in the case of dissolution of iron oxide in aquatic environment: a non reductive ligand-promoted dissolution (Stumm and Morgan, 1996) and a reductive ligand-promoted dissolution (Stumm and Sulzberger, 1992). In the first case, the organic compounds acting as ligands form relatively strong metal-organic surface complexes, which destabilize the Fe-O bond and lower the energy barrier for dissolution. This type of dissolution increases Fe release through the generation of dissolved forms of Fe(III), e.g. $\text{Fe}(\text{C}_2\text{O}_4)_n$ in the presence of oxalate. In the second mechanism, the organic compounds play both a role as ligand, i.e. complexing agent, and as electron donor, i.e. reducing agent. The reductive dissolution is characterized by the formation of surface iron organic complexes, which lead to electron transfer in the metal-organic surface complexes reducing Fe(III) to more soluble Fe(II) and to the subsequent detachment of free Fe(II) in solution.

Our results show that the capacity for one organic ligand to promote iron-dust dissolution is not exclusively linked to its capacity to form a complex with Fe, i.e. to its stability constant of Fe(III)- or Fe(III)-ligand complex. For example, malonate is a better iron ligand than tartrate (Table 1), but their effect on iron dissolution is similar (Fig. 1). This observation excludes the assumption of a non-reductive ligand-promoted dissolution. On the contrary, the increase of dissolved Fe(II) in the leaching solution shows a reduction

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of initial Fe(III), suggesting rather a reductive ligand-promoted dissolution. In this case, the difference of the effect by organic species on dissolution can be attributed to their ability to act as electron donor. Indeed, it is known that bidentate ligands, as carboxylate groups, are Lewis bases which are good electron donors. However, the capacity of organics as electron donor is directly related to the structure of ligand molecules. We observe a decrease of iron solubility with the increase of the number of carbon atoms in the studied organic molecules, i.e. for di-carboxylate species: oxalate (C_2) > malonate (C_3) > succinate (C_4) = glutarate (C_5), the former couple of longest compounds having no effect on the dissolution. Stumm and Morgan (1996) reported that the effect of bidentate ligands (type carboxylate) on the extent of dissolution of Fe oxides decreases with the increase in the length of chain for aliphatic ligands. The inductive effect of the chain of carbon atoms increases the electronegativity of COO^- cluster, inhibiting the electron donor capacity. In consequence, the longer the aliphatic chain, the weaker is the capacity of the organics to donate an electron. This is the reason why oxalate and malonate promote dissolution whereas succinate and glutarate are ineffective on dissolution. In the case of the tartrate molecule (C_4), the presence of $-OH$ groups on the chain of carbon atoms decreases the inductive effect and could explain its impact on iron solubility. In spite of the complexity of the humic acid structure, it is known that the large variety of carboxylate groups makes humic substances good electron donors and hence they have an important role in the control of iron bioavailability in the surface waters and in soils (Allard et al., 2004). Thus, the combination of the ability as electron donor and ligand could explain the promoting effect of HULIS analogue. However, the humic acid is less effective in iron dissolution than aliphatic organic ligands. The reductive ligand-promoted dissolution is typically controlled by surface-process (Stumm and Morgan, 1996). Thus, the dissolution will be dependent on the numbers of complexes (Fe-L) formed at the surface of particles. Due to the size of humic acid in comparison to aliphatic ligands, the difference in the extent of Fe dissolution can be attributed to the steric hindrance of these molecules limiting the access at the surface site. Thus, the

dependence of iron solubility to organic ligand concentrations is related to the nature of ligands due to its ability to form surface complexes as suggested above.

From the assumption of a mechanism of ligand-promoted dissolution, the ineffectiveness to promote dissolution by such organic compounds can be also explained.

5 Among studied organic compounds, the stability constants of monocarboxylic acids (formic, acetic and glycolic acid) and lactic acid are not known with Fe(II) and are very low with Fe(III) (Okochi and Brimblecombe; 2002). No significant effect on dust iron solubility for these compounds could be observed due to their very low ability to form complex with iron in our experiments. However, this low ability could be compensated
10 by the very high concentrations of these compounds or by the anthropogenic origin of the Fe-containing aerosol materials (Upadhyay et al., 2011). The results of Pehkonen et al. (1993) suggest that the photo-production of Fe(II) in the UV experiments could also compensate the low ability of these species as iron ligands. Nevertheless, these experiments were carried out for high formate and acetate concentrations (6 mM) in
15 comparison of their usual atmospheric content. This makes difficult the estimation of the effect of photo-reduction compared with the effect of high concentrations.

5 Conclusion and comments

Our results show for the first time that under atmospheric conditions, organic ligands, other than oxalate, promote iron-dust solubility even without photo-induced processes.
20 The increase of solubility corresponds to a linear relationship between dissolved iron and organic ligands concentrations and is systematically associated with an increase of dissolved Fe(II) concentrations. This study confirms that oxalate is indeed the most effective atmospheric ligand, enhancing iron dissolution in cloud and rain water. However, oxalate is not unique: tartrate, malonate and HULIS influence also the dissolution
25 of this trace metal. We have found that iron solubility increases by a factor of 6.5 in presence of organic species, i.e. ranges from 0.04 % to 0.26 %. This value is consistent with the previous observed increases yielded by reactions of dust with acidic species

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or with oxalate (Hand et al., 2004; Meskhidze et al., 2005; Fan et al., 2006; Solmon et al., 2009; Luo et Gao, 2010; Paris et al., 2011). That confirms that the effect of atmospheric chemical processing does not allow for dust to reach the high iron solubility values of anthropogenic aerosols (Sholkovitz et al., 2012). However, it is important to note that a factor of 6.5 could be important on the estimation of the atmospheric fluxes of dissolved dust iron by wet precipitation to the ocean, notably if rain dissolved iron is prone to be more bioavailable than particulate dust iron. Indeed, the increase of dissolved Fe(II) concentrations observed during our experiments suggests that dissolved Fe could be mainly as organic Fe(II) complexes. This point is particularly relevant to studying the fate of dissolved iron deposited by rain after contact with seawater and its subsequent bioavailability. In this purpose, the stability of the atmospheric organic Fe(II) complexes identified in this study after contact with seawater should be tested, for example on the base of the protocol of Kieber et al. (2005). Humic substances being known to complex Fe in the ocean (Laglera and van den Berg, 2009), the role of HULIS in the stabilization of atmospheric iron after contact with seawater should be the next step in addressing the bioavailability of atmospheric dissolved iron input.

The dissolution process is a reductive dissolution implying the formation of organo-ferric surface complexes, as it has been underlined with pure minerals, such as oxides and hydroxides iron. The capacity of an organic compound to dissolve iron is linked to the ability as Fe-ligand and as electron donor. On this basis, the effect of atmospheric organic ligands could be estimated. Thus, the results of this paper provide a concrete basis of work to consider the organic complexation effect in the estimation of atmospheric iron fluxes, by identifying both the effective organic species and the involved dissolution processes. However for this purpose, very few data exists on the characterisation of organic species and iron ligands in atmospheric waters limiting the incorporation of organic effect in modelling. This is particularly the case of HULIS which are not quantified in the cloud or rain water, even if they could represent a large part of the dissolved organic carbon. Finally, if the effectiveness of the organic species by reductive ligand dissolution has been showed in this work, the effect of organic ligands

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to promote iron dissolution by photo-production of Fe^{2+} , previously identified by Pehkonen et al. (1993), remains to investigate in atmospheric conditions.



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K. V. Desboeufs**Table 1.** Chemical characteristics of organic compounds and the range of concentrations measured in rainwater collected in various environments.

Compounds	Supplier (purity)	Dentate form at pH 4.7	Acid dissociation ¹		log K_{FeL} ²		Rainwater concentration (μM) ³
			pK _{a1}	pK _{a2}	Fe ²⁺	Fe ³⁺	
Formate	Aldrich® (ACS grade, > 99 %)	H-COO ⁻	3.7			3.1	0.6–13
Acetate	Aldrich® (ACS grade, > 99 %)	CH ₃ -COOH/CH ₃ -COO ⁻	4.8			3.4	0.2–15
Glycolate	Acros organics (97 %)	CHO-COO ⁻	3.8	–	1.9	3.5	No data
Oxalate	Prolabo® (Normapur, 99.8 %)	⁻ OOC-COO ⁻	1.3	4.3	4.2	9.4	0.3–5
Malonate	Prolabo® (Rectapur, 99 %)	⁻ OOC-(CH ₂)-COOH	2.8	5.7	3.3	9.4	0.02–2
Succinate	Fischer Chemical (extrapur, > 99 %)	⁻ OOC-(CH ₂) ₂ -COOH	4.2	5.6	2.4	8.8	0.04–1.3
Glutarate	Acros Organics (99 %)	⁻ OOC-(CH ₂) ₃ -COOH	4.3	5.4	–	8.7	0.01–0.7
Tartrate	Prolabo® (Normapur, 99.8 %)	⁻ O ₂ CCH(OH)CH(OH)CO ₂ ⁻	3.0	4.4	2.6	6.9	No data
Lactate	Acros Organics (99 %)	CH ₃ -CH ₂ (OH)-COO ⁻	3.9	–	–	–	1.3–6
Humic Acid	IHSS, Suwannee River HA (Standard II)		–	–	5.0–5.6	21.3	No data

¹ Values at 25 °C;² Okochi and Brimblecombe (2002); Fujisawa et al. (2011); Pandey et al. (2000);³ Sempéré and Kawamura (1996); Pena et al. (2002); Avery et al. (2003); Hegg et al. (2002); Desboeufs et al. (2010).

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Table 2a. Dissolved iron concentrations (nM) obtained for the dissolution experiments from Niger dust at pH 4.7 and for various atmospheric concentrations of organic ligands.

Organic concentration (μM)	Formate DFe (±)		Acetate DFe (±)		Glycolate DFe (±)		Oxalate DFe (±)		Malonate DFe (±)		Succinate DFe (±)		Glutarate DFe (±)		Tartrate DFe (±)		Lactate DFe (±)		Humic Acid DFe (±)	
0	3.22	0.72	3.22	0.72	3.22	0.72	3.22	0.72	3.22	0.72	3.22	0.72	3.22	0.72	3.22	0.72	3.22	0.72	3.22	0.72
0.5							5.71	0.94	3.94	0.09	3.12	0.49	2.51	0.18						
1					3.05	0.18	7.01	0.93	4.83	0.36	3.58	0.36	3.22	0.18	6.09	0.18				
2							8.59	0.54	5.19	0.18	3.04	0.18	2.86	0.36						
3					3.26	0.18	11.15	0.50							6.27	0.18	3.15	0.08		
3.6																			3.76	0.41
5					3.1	0.18	17.42	0.77							7.88	0.18	3.25	0.18		
8	2.88	0.31	3.76	0.42			22.43	0.65									3.40	0.09		
10.9																			4.83	0.36
21.8																			7.70	0.19

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Table 2b. Iron solubility obtained for the dissolution experiments from Niger dust at pH 4.7 and for various atmospheric concentrations of organic ligands.

Organic concentration (μM)	Formate SFe (%) (±)	Formate (±) (%)	Acetate SFe (%) (±)	Acetate (±) (%)	Glycolate SFe (%) (±)	Glycolate (±) (%)	Oxalate* SFe (%) (±)	Oxalate* (±) (%)	Malonate SFe (%) (±)	Malonate (±) (%)	Succinate SFe (%) (±)	Succinate (±) (%)	Glutarate SFe (%) (±)	Glutarate (±) (%)	Tartrate SFe (%) (±)	Tartrate (±) (%)	Lactate SFe (%) (±)	Lactate (±) (%)	Humic Acid SFe (%) (±)	Humic Acid (±) (%)
0	0.04	0.01	0.04	0.01	0.04	0.01	0.04	0.01	0.04	0.01	0.04	0.01	0.04	0.01	0.04	0.01	0.04	0.01	0.04	0.01
0.5							0.06	0.01	0.047	0.001	0.04	0.01	0.030	0.002						
1					0.037	0.002	0.08	0.01	0.058	0.004	0.043	0.004	0.039	0.002	0.073	0.002				
2							0.10	0.01	0.062	0.002	0.037	0.002	0.034	0.004						
3					0.039	0.002	0.13	0.01							0.075	0.002	0.038	0.001		
3.6																			0.045	0.005
5					0.037	0.002	0.21	0.01							0.095	0.002	0.039	0.002		
8	0.035	0.004	0.045	0.005			0.27	0.01									0.041	0.001		
10.9																			0.058	0.005
21.8																			0.092	0.005

* Data for “Oxalate” are issued from Paris et al. (2010) and are completed by new experiments with 0.5 and 2 μM oxalate solutions.

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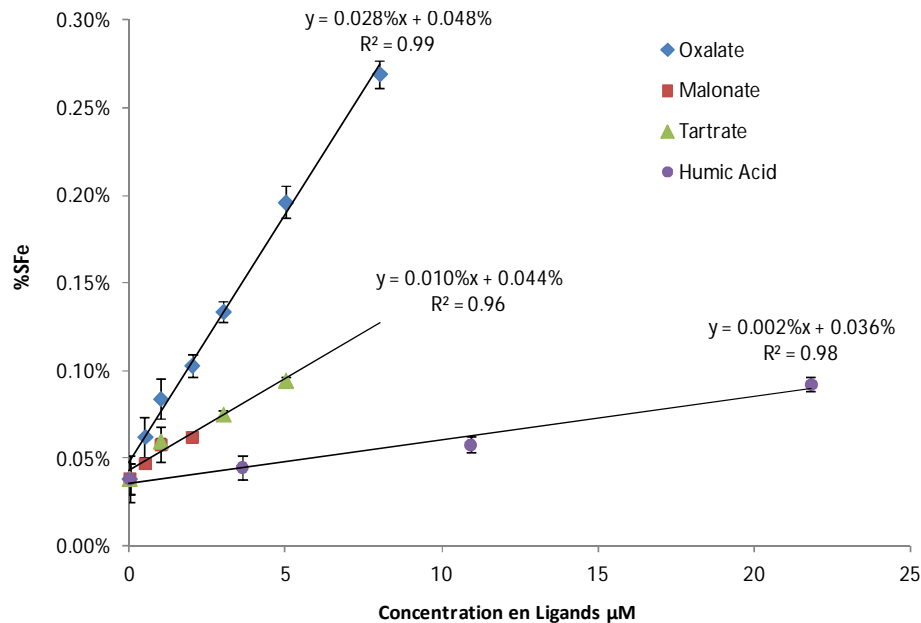


Fig. 1. Iron solubility (%) vs. organic species concentrations (μM) for the 4 species affecting iron solubility at pH 4.7. Uncertainties represent one standard deviation of triplicate experiments.