Fate of aqueous iron leached from tropospheric aerosols during atmospheric acidic processing: a study of the effect of humic-like substances

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Abstract

Humic-like substances (HULIS) are complex organic molecules that can be found in the atmosphere as components of tropospheric aerosols or suspended in atmospheric water. HULIS are chelating agents and oxidation-reduction species, therefore these substances can affect the availability of aqueous iron, a heavy metal commonly leached from atmospheric particulate matter upon acidic processing. Specifically, chelating properties allow HULIS to remove aqueous iron from atmospheric water, while their redox properties can alter iron speciation. Ultimately, wet deposition of soluble iron can be influenced not only by HULIS but also by other ubiquitous atmospheric cations. In this work, we investigate the effect of HULIS on iron leached from atmospheric particles in the presence of aluminium ions, an environmentally abundant cation also chelated by HULIS. Colorimetric methods were used to examine the cation exchange (CE) of aluminium ions with both iron (II) and (III) ions in humic acids, a model system for HULIS. An effective chelation of aqueous phase iron with humic acids was observed during suspension experiments, with aqueous iron removed from aqueous phase into a HULIS complex. In addition, the redox properties of humic acids showed no oxidation of iron (II) after chelation by humic acid, but a fraction of iron (III) was reduced into the more bioavailable iron (II). Cation exchange with aluminium suggests that bioavailable iron (II) ions chelate with HULIS in a combination of exchangeable and inexchangeable iron, with a higher proportion of exchangeable iron incidence. Additionally, HULIS interaction with iron (III) ions shows chelating properties as well a reduction potential, producing aqueous and chelated iron (II) ions.

Keywords: humic-like substances, cation exchange, iron mobility, chelation.
1 Introduction

In recent years it has become increasingly clear that atmospheric organic substances, in particular water-soluble compounds, significantly impact the properties of tropospheric aerosols [1]. One of the most ubiquitous classes of water-soluble organic compounds in the atmosphere are HUmic-LIke Substances (HULIS) [2, 3]. While lighter in molecular weight than soil and aquatic humic substances, HULIS present many characteristics that resemble aquatic humic acids [4]. Like aquatic and terrestrial humic acids, HULIS are polymeric, polyacidic materials, containing a multicomponent mixture of aromatic and aliphatic compounds with carbonyl, hydroxyl, methoxyl, and carboxyl terminal groups [4]. Taraniuk and collaborators found that HULIS, like humic acids, are powerful chelating agents, impacting the chemistry of aerosol particles [5]. Additionally, terrestrial and aqueous humic substances are dominant redox active [6]; thus, it is supposed that HULIS also play an important role in reduction-oxidation mechanisms of atmospheric pollutants [6]. Yet, many HULIS environmental implications for trace atmospheric metals, such as heavy metal mobility [7], ligand promoted aerosol dissolution [8], and the redox effect [6], have not yet been explored.

The acidic functional groups of HULIS can bind to a variety of metals ions. This chelating property is particularly important for iron, a limiting nutrient for phytoplankton in the ocean [9, 10]. Chen and Grassian proposed that ligand-promoted solubility of iron from atmospheric aerosols may play a significant role in mobilizing Fe from atmospheric dust compared with acidic processing alone [8]. Ultimately, van der Perk suggests that the humic-metal complexation enhances metal solubility [11], effectively partitioning heavy metals from tropospheric aerosols into atmospheric water. Thus, HULIS strong chelating functional groups may influence the ligand promoted solubility and further mobility of iron in tropospheric aqueous systems [12]. However, the transport and binding strength of the HULIS-Fe system is closely dependent on the relative replaceability of exchangeable cations, as described by Scheffer and Schachtschabel [13]. For instance, cation Fe$^{3+}$ chelates to HULIS terminal groups with a slightly higher strength than that of Al$^{3+}$, and overall higher strength Fe$^{2+}$ binding to HULIS, approximately following the stability order of Fe$^{3+} >$ Al$^{3+} >$ Fe$^{2+}$ [13]. Thus, a system with large excess of Al$^{3+}$ can effectively displace any exchangeable Fe$^{2+}$ complexed by HULIS, but might not be as effective to exchange with Fe$^{3+}$. Yet, metal binding to HULIS can take place on inexchangeable sites [14], making the cation exchange (CE) process more convoluted.

In addition to the metal binding, HULIS are important redox agents [6]. In fact, electrochemical potentials determined by Aeschbacher and collaborators suggest that humic substances will be primarily reducing agents to iron [6]. While Fe$^{3+}$ is the most abundant species of iron in tropospheric aerosols [8, 12], the presence of HULIS in atmospheric water can reduce iron to bivalent species, which is more bioavailable. Although the reduced form of iron can be exchanged by surrounding Al$^{3+}$ in the aqueous phase, there are only a few investigations on the influence of
Fe$^{2+}$ and Fe$^{3+}$ binding to organic substances under atmospherically relevant conditions [15]. In order to better understand the redox effect of HULIS on atmospheric aqueous iron, along with the effect of Al$^{3+}$, we carried out cation exchange studies with Al$^{3+}$ under atmospherically relevant conditions for both Fe$^{3+}$ and Fe$^{2+}$ on humic acids, a proxy for atmospheric HULIS.

2 Experimental section

2.1 Materials

The HULIS solution was prepared by suspending 10.0 mg of humic acid (HA) (Sigma-Aldrich), in a 10.0 mL acidic solution of iron standard. Standard solutions of Fe$^{3+}$ were prepared by dissolving iron (III) nitrate nonahydrated (Fe(NO$_3$)$_3$)$\cdot$9H$_2$O (Sigma-Aldrich), into a solution of nitric acid to the desired final concentration. The Fe$^{2+}$ standards were prepared from a 1000 ppm stock solution of Fe$^{2+}$, obtained by dissolving primary standard Fe (NH$_4$)$_2$(SO$_4$)$_2$$\cdot$6H$_2$O (Sigma-Aldrich) in an aqueous 0.01 M HCl solution. All HULIS solutions on iron standard were prepared to a final pH of 4.

Cation exchange was carried out by adding aluminium chloride, AlCl$_3$ (Alpha-Aesar), in a large excess, for a final concentration of 0.1% w/w in Al$^{3+}$. The final solution was acidified to a final pH of 2.

2.2 Methods

HULIS suspension on iron standards were incubated at room temperature overnight and non-chelated aqueous iron was selectively analysed colorimetrically with o-phenanthroline (Alpha-Aesar) for Fe$^{2+}$ and potassium thiocyanate (Sigma-Aldrich) for Fe$^{3+}$, forming the absorbing complexes shown in reactions (1) and (2) (vide infra). Interferences from HULIS chromophores are within the margin of error of the methods, as all solutions are diluted 10 times upon analysis, which minimizes any humic substance interference. In addition, both o-phenanthroline and thiocyanate iron complexes have a maximum of absorption at 525 nm and 490 nm, respectively, well above the maximum of absorption of soluble humic acid at 220 nm. The analysis of Fe$^{3+}$ with potassium thiocyanate showed a slight HULIS interference, although quantification was still possible under experimental conditions. Non-chelated Fe$^{2+}$ is selectively analysed via colorimetry, without interference from iron chelated by HULIS, as the {HULIS-Fe$^{2+}$} and {HULIS-Fe$^{3+}$} complexes are favoured over the o-phenanthroline complex with Fe$^{2+}$ and thiocyanate complex with Fe$^{3+}$. The extraction of iron from HULIS by the colorimetric ligand has been shown to be slow, allowing the analysis of only aqueous iron (II) [16]:

$$\text{Fe}^{2+}(aq) + 3\text{o-phen}(aq) \rightleftharpoons \{\text{Fe(o-phen)}\}_3^{2+}(aq) \quad (1)$$

$$\text{Fe}^{3+}(aq) + \text{SCN}^- (aq) \rightleftharpoons \{\text{FeSCN}\}^{2+}(aq) \quad (2)$$
The colorimetric analysis of humic acid samples on iron standards after overnight passivation allowed the evaluation of the HULIS-iron complex formation.

To investigate the CE, AlCl$_3$ was added to the HULIS-Fe complex solutions until a final concentration of 0.1% w/w of Al$^{3+}$. Aluminium binds strongly with HULIS. In the presence of an excess of aluminium, the CE leads to the following reaction:

$$\{\text{HULIS} - \text{Fe}^{n+}\}(aq) + \text{Al}^{3+}(aq) \rightleftharpoons \{\text{HULIS} - \text{Al}^{3+}\}(aq) + \text{Fe}^{n+}(aq)$$  \hspace{1cm} (3)

where $n$ is the oxidation state of iron (2+ or 3+). Reaction (3) leaves iron available in aqueous phase for colorimetric analysis with o-phenanthroline or potassium thiocyanate (reactions (1) and (2)). Exchanged iron was determined immediately after the addition of Al$^{3+}$, as cation exchange takes place instantaneously [11]. However, based on the stability order of the HULIS-metal complex (vide supra) [13], reaction (3) is not favoured for iron in the oxidation state $n=3+$, limiting the concentrations of Fe$^{3+}$ exchanged. Finally, for the CE reaction (3) to be analytically useful, the concentration of Al$^{3+}$ needs to be in excess, so the equilibrium is displaced towards the products. The pH of CE used for all the iron concentrations examined was pH = 2, acidified by the hydrolysis of AlCl$_3$.

3 Results and discussion

3.1 Characterization of HULIS Model System and HULIS-metal binding

The solutions of HULIS, as well as HULIS treated in an iron standard solution before and after cation exchange (CE) with aluminium, were dried and analysed using an attenuated total reflection (ATR), in a germanium crystal (Pike Technologies), with a Fourier transformed infrared (FTIR) spectrometer (Thermo, 6700). A thin film of the humic sample, with and without metal complexation, were prepared by applying the aqueous sample onto the ATR crystal and placed in a dry air purged sample compartment; as water evaporated, a thin film of the HULIS/HULIS-metal sample was homogeneously deposited on the surface of the ATR crystal. Figure 1 shows three different FTIR spectra: humic acid with no iron or aluminium (HULIS), humic acid in a 15 ppm solution of Fe$^{2+}$ (HULIS+Fe$^{2+}$), and the solution after CE (HULIS+Al$^{3+}$). All FTIR spectra are averages of 100 scans with a 4 cm$^{-1}$ resolution.

ATR-FTIR spectrum of the samples revealed a typical pattern of humic materials. The broad and intense peak ranging from 3100 to 3500 cm$^{-1}$ is assigned to O-H stretching with inter- and intra-molecular hydrogen bonding characteristic of polymeric alcohols, phenols, and carboxylic acids [4, 17]. The relatively high intensity of this OH band in the presence of aluminium indicates that humic materials are protonated due to the acidic environment during CE. This equilibrium protonation can also be observed in the clear band at 2920 cm$^{-1}$, assigned to C-H stretching vibration of aliphatic acids and in the band centred at 2474 cm$^{-1}$ for protonated carboxylic acids [4].
The carboxylic band at 1608 cm\(^{-1}\) shows a shift of \(\Delta \nu = 24\) cm\(^{-1}\) in excess of aluminium, indicating that metal chelation takes place with binding in the carboxylic group [4, 17]. In addition, there is a significant shift (\(\Delta \nu = 42\) cm\(^{-1}\)) in the C-H aromatic ring stretch, at 1402 cm\(^{-1}\) [18], suggesting that aromatic rings also participate in the metal chelation process. Given the low concentrations of iron chelated in HULIS, no significant shifts are observed on the carboxylic or aromatic bands. However, an iron chelation is observed in a significant Fe-O band growth at 1379 cm\(^{-1}\) along with a small but observable band at 1030 cm\(^{-1}\) assigned to the Fe-OH stretch [19]. In addition, the disappearance of the peak at 1240 cm\(^{-1}\) as metals are added to the HULIS mixture indicates that OH in phenyl groups also participate in the chelation of metals [18, 20]. The peak assignment for HULIS solutions is summarized in Table 1.

Figure 2 shows the UV-Vis spectrum (Perking-Elmer Lambda 35) of the humic fractions with and without metal treatment. In general, the HULIS proxy shows a strong absorbance, mainly in the UV range, from 190 nm to 400 nm, due to the presence of aromatic chromophores. Upon addition of metal, the UV absorptivity around 220 nm decreased, characteristic of the \(\pi-\pi^*\) transitions in substituted benzenes or polyphenols [22]. This relative loss of absorptivity indicates that aromatic C=C undergoes distortion and electron density loss during metal binding. Some red shift is also observed as shoulders when iron and aluminium are chelated by the humic substance, supporting that the aromatic rings in HULIS also participate in metal chelation, as suggested by the FTIR spectra.
Table 1: ATR-FTIR peak assignments for HULIS samples.

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3390</td>
<td>H-bonded OH</td>
<td>[4, 17, 21]</td>
</tr>
<tr>
<td>2920</td>
<td>C-H stretching of aliphatic acids</td>
<td>[4, 17, 21]</td>
</tr>
<tr>
<td>2474</td>
<td>O-H (v_{as}) (COOH)</td>
<td>[17, 20]</td>
</tr>
<tr>
<td>1702</td>
<td>C=O (v_{as}) (COOH)</td>
<td>[4, 17, 21]</td>
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<tr>
<td>1608/1638</td>
<td>C=O (v_{as}) (COO(^-))</td>
<td>[17]</td>
</tr>
<tr>
<td>1450–1370</td>
<td>C-H ring stretch</td>
<td>[18]</td>
</tr>
<tr>
<td>1379</td>
<td>Fe-O stretch</td>
<td>[19]</td>
</tr>
<tr>
<td>1240</td>
<td>Ph-OH and Ph-COOH stretch</td>
<td>[20, 21]</td>
</tr>
<tr>
<td>1130</td>
<td>C-O(C=O) (v_{as})</td>
<td>[21]</td>
</tr>
<tr>
<td>1030</td>
<td>Fe-O stretch</td>
<td>[19]</td>
</tr>
<tr>
<td>1005</td>
<td>C-H Polysaccharides stretch</td>
<td>[4, 21]</td>
</tr>
</tbody>
</table>

Figure 2: UV-Vis spectra of humic solutions. Aqueous phase humic acid (HULIS solution); humic acid in 15 ppm of iron (II) standard (\{HULIS-Fe\(^{2+}\}\}); humic acid after cation exchange with excess of aluminium (III) (\{HULIS-Al\(^{3+}\}\)).

An elemental analysis of the organic sample (CHN analyzer, Costech Instruments) revealed an organic composition of the humic substance used as HULIS proxy of (38±2)%, (3.34±0.08)%, (0.84±0.05)%, in carbon, hydrogen, and nitrogen, respectively. The C/H and C/N rations are similar to those proposed by the Steelink humic monomer [23]. In addition, X-ray fluoresce (XRF) spectroscopy (Bruker) showed the presence of trace metals in the untreated sample, with a relatively large presence of iron. Analysis with atomic absorption spectrophotometer (Perkin Elmer) showed (1.07±0.03)% total iron, with estimated concentration of calcium, strontium, and titanium <0.5%, and copper, nickel, zinc, phosphorous and sulphur <0.05%.
3.2 HULIS chelation of iron

As observed by spectroscopic evidence in the preceding section, more than one functional site of HULIS chelates both iron and aluminium. Under atmospherically acidic conditions of pH below 4 [24], the moderately acidic functional groups of HULIS tend towards protonation, with a variable negative density charge [11]. In addition, at pH below 4, aqueous phase aluminium is predominantly in the Al\(^{3+}\) form [11]. These conditions promote the CE as described by reaction (3), in which a large excess of Al\(^{3+}\) will exchange with exchangeable Fe\(^{2+}\) or Fe\(^{3+}\). Cation exchange is a relatively fast process, which allows for the instantaneous analysis of iron in solution upon CE.

Figure 3 shows the fraction of Fe\(^{2+}\) standard that remains free after chelation by HULIS with respect of the initial concentration of Fe\(^{2+}\) standard ([Fe\(^{2+}\)]\(_0\)). It is clearly observed that, a significant fraction of the aqueous Fe\(^{2+}\) remains in solution as free Fe\(^{2+}\) after the equilibrium in reaction (4) has been reached:

\[
\text{HULIS}(aq) + \text{Fe}^{2+}(aq) \rightleftharpoons \{\text{HULIS-Fe}^{2+}\}(aq) \quad (4)
\]

![Figure 3: Free and exchangeable Fe\(^{2+}\) from a HA suspension on Fe\(^{2+}\) standards. The area under the dashed line represents the concentration of Fe\(^{2+}\) remaining in solution (free Fe\(^{2+}\)) after HULIS chelation of available iron. The area under the solid line represents free Fe\(^{2+}\) after the addition of 0.1% w/w of Al\(^{3+}\), once CE has been completed. Finally, the area under the dotted line represents the total Fe\(^{2+}\) present in solution before the addition of HULIS. The insert represent the ratio between the concentration of \{HULIS-Fe\(^{2+}\}\} and free Fe\(^{2+}\). Each point is the mean of triplicate measurements and the error bars represent the standard deviation.](image.png)
As the HULIS binding sites get occupied, the formation of the \{HULIS — Fe$^{2+}$\} complex reaches a limit given by the saturation of HULIS chelating sites. Under our experimental conditions, the HULIS chelating capacity reaches a maximum at a [Fe$^{2+}$]$_0$ threshold of around 10 ppm. Above this threshold concentration, a constant amount of Fe$^{2+}$ will complex with HULIS.

Because HULIS is present in a relatively large concentration (1000 mg/L) with respect of [Fe$^{2+}$]$_0$, [HULIS] remains relatively constant over the course of the reaction. Thus, the equilibrium constant for equation (4) can be expressed as $K_{eq}'$, or the ratio between of remaining aqueous Fe$^{2+}$ (free Fe$^{2+}$) with respect of [HULIS — Fe$^{2+}$]:

$$K_{eq} = \frac{[HULIS - Fe^{2+}]}{[HULIS][Fe^{2+}]} \Rightarrow K_{eq}' = [HULIS]K_{eq} = \frac{[HULIS - Fe^{2+}]}{[Fe^{2+}]} \quad (5)$$

Upon saturation of HULIS chelating sites, the concentration of Fe$^{2+}$ in aqueous phase ([Fe$^{2+}$]) increases with [Fe$^{2+}$]$_0$, and thus the $K_{eq}'$ decreases. The change in the equilibrium constant is, therefore, driven by the ratio between the concentration of \{HULIS-Fe$^{2+}$\} and free Fe$^{2+}$ ($K_{eq}'$) and it is represented in the insert of Figure 3.

This HULIS-Fe$^{2+}$ complex is highly soluble, increasing the environmental mobility of iron. Therefore, HULIS complexing of iron is a significant factor in the transport and wet deposition of atmospheric iron. However, based on the Scheffer and Schachtschabel [13] chelate stability, the ubiquitous Al$^{3+}$ can break the HULIS-Fe$^{2+}$ interaction for the most favoured \{HULIS-Al$^{3+}$\}, particularly under Al$^{3+}$ excess, a common environmental occurrence during tropospheric aerosol dissolution.

Figure 3 shows the relative increase of aqueous free Fe$^{2+}$ after the addition of Al$^{3+}$ to the \{HULIS-Fe$^{2+}$\} solution. However, the amount of Fe$^{2+}$ measured after CE (solid line) is less than the original amount of Fe$^{2+}$ added (dotted line). Since no Fe$^{3+}$ was detected, suggesting no oxidation of Fe$^{2+}$ by HULIS, some Fe$^{2+}$ must remain chelated in HULIS. This indicates two types of binding sites, one exchangeable and one inexchangeable. The inexchangeable sites of HULIS are favoured as suggested by the binding observed for 5 ppm of Fe$^{2+}$ solutions, where exchanged Fe$^{2+}$ was only (1.2±0.2) ppm, or around 27% of the initial aqueous Fe$^{2+}$. In general, the inexchangeable iron in HULIS, [Fe$^{2+}$]$_{inx}$, seems to be fairly constant as evidenced by the relatively constant slope of free iron after C.E, particularly after the 10 ppm threshold. Under our experimental conditions, [Fe$^{2+}$]$_{inx}$ reaches a maximum of 5 ppm for every [Fe$^{2+}$]$_0$ examined, after which inexchangeable sites are no longer available.

Increasing the initial concentration of aqueous Fe$^{2+}$ to concentration above a threshold of 10 ppm, where both HULIS sites become saturated, showed a relatively higher iron recovery ($\phi_R$):

$$\phi_R \approx \frac{[Fe^{2+}]_0 - [Fe^{2+}]_{inx}}{[Fe^{2+}]_0} \quad (6)$$
Where iron recovery is the ratio of the concentration of free $\text{Fe}^{2+}$ after CE divided by the initial concentration of $\text{Fe}^{2+}$, $[\text{Fe}^{2+}]_0$. At relatively higher concentrations of initial $\text{Fe}^{2+}$, the percentages of exchanged iron rose to 29%, 65%, 75% and 92% for initial $\text{Fe}^{2+}$ concentrations of 10 ppm, 15 ppm, 30 ppm, and 50 ppm, respectively. Clearly, $[\text{Fe}^{2+}]_{\text{in}}$ depends on the concentration of HULIS. Higher concentrations of HULIS in atmospheric water will increase the inexchangable sites available to irreversible chelate $\text{Fe}^{2+}$. Thus, it can easily be shown that the CE yield can be expressed by the logical statement in equation (7):

$$[\text{Fe}^{2+}]_0 > [\text{Fe}^{2+}]_{\text{in}} \leftrightarrow \phi_R = 1 - \frac{[\text{Fe}^{2+}]_{\text{in}}}{[\text{Fe}^{2+}]_0} \quad (7)$$

Equation (7) implies that as $[\text{Fe}^{2+}]_0$ increases, the iron recovery will be larger.

3.3 HULIS redox of iron

Incubation of HULIS with $\text{Fe}^{2+}$ yields only $\text{Fe}^{2+}$, either chelated or free. In contrast, suspension of HULIS in $\text{Fe}^{3+}$ standard yields both $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$. Table 2 shows the effect of HULIS proxy suspension in a solution of 18 ppm of $\text{Fe}^{3+}$ standard. Here, HULIS reduction potential is enough to form free $\text{Fe}^{2+}$.

Table 2: HULIS on $\text{Fe}^{3+}$ standard.

<table>
<thead>
<tr>
<th>$(\text{Fe}^{3+})_0$ (ppm)</th>
<th>$(\text{Al}^{3+})$ (% w/w)</th>
<th>Free $(\text{Fe}^{3+})$ (ppm)</th>
<th>Free $(\text{Fe}^{2+})$ (ppm)</th>
<th>Free $(\text{Fe})_{\text{total}}$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>0</td>
<td>1.8±0.2</td>
<td>1.2±0.4</td>
<td>2.0±0.6</td>
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<tr>
<td></td>
<td>0.1</td>
<td>2.1±0.2</td>
<td>2.4±0.7</td>
<td>4.5±0.9</td>
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<tr>
<td>30</td>
<td>0</td>
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<td>1.1±0.1</td>
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</tr>
<tr>
<td></td>
<td>0.1</td>
<td>2.4±0.9</td>
<td>5.6±0.5</td>
<td>7.9±1</td>
</tr>
<tr>
<td>50</td>
<td>0</td>
<td>0.6±0.09</td>
<td>2.5±0.5</td>
<td>3.1±0.6</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>3.0±0.7</td>
<td>6.7±0.3</td>
<td>9.7±1</td>
</tr>
</tbody>
</table>

Once again, HULIS does not chelate all the amount of iron available. Before CE, a significant fraction of $\text{Fe}^{3+}$ standard, $[\text{Fe}^{3+}]_0$, is chelated by HULIS. In addition, 4–7 % of the $\text{Fe}^{3+}$ standard is converted into free $\text{Fe}^{2+}$. The chelation and exchange of iron by HULIS can be summarized as follows:

$$\text{HULIS(aq)} + \text{Fe}^{3+} (aq) \rightarrow \{\text{HULIS} - \text{Fe}^{3+}\}(aq) \quad (8)$$

$$\text{HULIS(aq)} + \text{Fe}^{3+} (aq) \rightarrow \text{Fe}^{2+}(aq) + [\text{HULIS}]^+ (aq) \quad (9)$$

$$\text{HULIS(aq)} + \text{Fe}^{2+} (aq) \rightarrow \{\text{HULIS} - \text{Fe}^{2+}\}(aq) \quad (10)$$

$$\{\text{HULIS} - \text{Fe}^{n+}\}(aq) + \text{Al}^{3+}(aq) \rightleftharpoons \{\text{HULIS} - \text{Al}^{3+}\}(aq) + \text{Fe}^{n+} \quad (11)$$

In equation (9) HULIS transfers an electron to reduce $\text{Fe}^{3+}$, producing $\text{Fe}^{2+}$ which can be chelated by HULIS. As a consequence, the charge density of HULIS becomes less negative, diminishing its capacity to effectively bind iron. However, given the higher stability of the $\{\text{HULIS-Fe}^{3+}\}$, iron recovery is lower than
observed in the presence of only Fe$^{2+}$, around 25% total iron recovery, which is significantly lower than the recovery observed for Fe$^{2+}$ alone. This is supported by the low amount of Fe$^{3+}$ exchanged in every concentration examined, consistent with the chelate stability observations of Scheffer and Schachtschabel [13]. Given the large excess of Al$^{3+}$, this low CE suggests that Fe$^{3+}$ binds to HULIS stronger than Al$^{3+}$. Most iron exchanged corresponds to the reduced species of iron, Fe$^{2+}$. In fact, the concentration of aqueous Fe$^{2+}$ increases significantly after CE with Al$^{3+}$.

As the \{HULIS − Fe$^{3+}$\} complex is more stable, a higher HULIS induced mobility is expected for Fe$^{3+}$ than that for Fe$^{2+}$. In fact, given the values of [Fe$^{2+}$]$_{\text{in}}$ (5 ppm) under our experimental conditions, it can be assumed that Fe$^{3+}$ is the larger fraction of inexchangeable iron that results from the interaction of HULIS with Fe$^{3+}$ standard. However, HULIS can also decrease the relative concentration of Fe$^{3+}$ in atmospheric water in favour of Fe$^{2+}$.

4 Atmospheric implications

In the past decade, it has been suggested that atmospheric acidic processing of tropospheric aerosols leaches mostly Fe$^{3+}$ into atmospheric water [25]. However, the presence of HULIS suggests that a fraction of aqueous Fe$^{3+}$ leached from atmospheric dust will undergo reduction to form the bioavailable Fe$^{2+}$. In addition, the higher solubility of the HULIS-Fe complexes can induce further aerosol dissolution. Thus, the presence of HULIS will not only increase the concentration of aqueous iron in atmospheric water but increase the transport of iron species in the troposphere. Ultimately, since Fe$^{2+}$ is bioavailable and a limiting phytoplankton nutrient, during atmospheric acidic processing HULIS can induce and/or boost plankton blooms.

Nonetheless, environmental factors can directly impact the role of HULIS in the transport, chelation, and reduction of iron. Cations such as Al$^{3+}$, also leached from acidic dissolution of atmospheric dust, induce cation exchange, which partition Fe$^{2+}$ to the aqueous phase. Given that both metals, aluminium and iron, are common components of atmospheric dust, HULIS will induce a relatively larger concentration of Fe$^{2+}$ than initially expected in the aqueous phase of tropospheric water.

References


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