Photochemical release of humic and fulvic acid-bound metals from simulated soil and streamwater

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This study demonstrates the strong impact of photochemical degradation of soil dissolved organic matter (DOM) on its metal complexing capacity. The role of light in the fate of organically-bound metals transported from soils to surface waters was studied in laboratory experiments. We studied four humic and one fulvic acid isolates from different soil horizons in the Bohemian Forest (Czech Republic). Different concentrations of aluminium (Al) and iron (Fe) salts were added to the solutions of organic acids (initial dissolved organic carbon (DOC) concentration 0.5 mmol L\(^{-1}\)), and the samples were irradiated in a reactor equipped with 350 nm irradiation lamps for 0 to 120 min. Aliquots of irradiated samples and dark controls were analyzed for DOC, ionic and organically-bound Al and Fe (Al\(_{o}\), Fe\(_{o}\), and Al\(_{eo}\), Fe\(_{eo}\), respectively), pH, and UV-VIS spectra. The initial Fe\(_{o}\) concentrations in the samples (2.09 to 5.66 mmol L\(^{-1}\)) decreased from 21 to 52% during irradiation, while the initial Al\(_{o}\) concentrations (2.28 to 5.37 mmol L\(^{-1}\)) decreased from 7 to 41%. The greatest decrease in the organically-bound metal concentrations occurred for the fulvic acid, and the smallest decrease occurred for the humic acid from the deepest soil horizon. The extrapolation of laboratory experiments to in situ conditions suggested that the DOM’s ability to bind metals changes greatly within the first few hours after groundwater enters the stream. The rapid degradation of organically-bound Al and Fe can be an important process in first and second-order streams, and lake epilimnia.

Introduction

The export of dissolved organic matter (DOM) from soils to streams has been investigated in many studies. The major sources of DOM are the upper horizontal zones of the riparian forest zone\(^1\) and the podzol profile. Wetlands in forested watersheds significantly affect the properties of exported DOM.\(^2\) The quality and quantity of DOM exported from the soil profile depends on hydrological conditions. The percentage of humic substances in DOM increases at higher discharges. For example, humic dissolved organic carbon (DOC) increased from 20% at base flow to 80% at peak discharge in second-order streams draining watersheds in the Rocky Mountains, Colorado, USA.\(^3\)

Fulvic (FA) and humic (HA) acids and high-molecular weight organic ligands, are the most important complexing ligands for most metal ions in natural waters\(^4\) and constitute an important part of the DOM transported from terrestrial to aquatic ecosystems. The HA : FA ratio in podzolic soil decreases with increasing depth, reflecting the reduced mobility and degradation of the HA fraction.\(^5,5\) A similar vertical gradient in the HA : FA ratio occurs in cambic soils, with almost two-fold higher values in the A- and AB-horizons than in the B-horizon.\(^6\) The export of HA to fresh waters depends on soil chemistry, season, and hydrology. Dissolved FA and HA in uncolored freshwater streams commonly comprise approximately 40% and 4.5%, respectively. In significantly colored waters, the HA becomes a much higher percentage of the DOC, and the HA : FA ratio commonly increases to 1 : 4 or higher.\(^8\)

The concentration of organically-bound metals\(^9\) exported from soils to freshwaters depends on the DOC concentration and its complexing properties, pH, temperature, ionic strength, and other conditions.\(^10\) During base flow in summer, metal concentrations are generally higher than during spring run-off.\(^11\) After entering the streams, organically-bound metals undergo a series of chemical and photochemical transformations.

The influence of photochemical degradation of DOM on mobility of metals, mainly Fe, has been documented by Miles and Brezonik,\(^12\) Emmenegger et al.,\(^13\) and Howitt et al.\(^14\) Photochemical degradation of DOM decreases its ability to complex metals. Several studies have focused on the relationship between photo-oxidation of DOM and organically-bound metals. Kopáček et al.\(^15,16\) showed the decline of organically-bound Al and Fe in water from an acidic lake tributary after artificial irradiation. Kopáček et al.\(^17\) showed that in situ photochemical decomposition of organic-metal complexes of Fe and Al under solar radiation could play a significant role in water chemistry and consequently in sediment chemistry of metals. Porcal et al.\(^18\) observed a decrease of organically-bound metals in first order streams in Maine, USA after brief UV-A irradiation. Rose and Waite\(^19\) examined photo-induced degradation of...
organically-bound Fe in simulated natural waters. Shank et al. measured the sunlight-driven photodegradation of strong Cu ligands in organic-rich estuarine waters. Powell and Wilson-Finelli observed a decrease of organic iron-complexing ligands in the Gulf of Mexico.

Rapid decrease in the ability of DOM to bind metals in first order streams suggested that maximum decrease could be expected within the first few hours after the soil DOM reaches the stream and is exposed to solar radiation. The aim of this study was to extend the results of a previous study to soil water and describe the changes in chemical composition as soil water emerges into a stream. The influence of photochemical processes on metal complexing properties of DOM derived from different soil horizons was evaluated.

Materials and methods

Sampling sites and isolation of humic and fulvic acids

Humic (HA) and fulvic (FA) acids were isolated from the upper O (HA2), lower O (HA4), and B (FA) soil horizons of dystric cambisol at old-growth mountain Picea abies stands in the Boubín Preserve (48°59′N, 13°48′E, elevation of 1320 m asl, the Bohemian Forest, Czech Republic). HA1 and HA3 samples were isolated from litter and humic soil horizons, respectively, of the two-mica Moldanubian granite. Detailed descriptions of soil profiles are in Table 1.

Table 1 Characterization of soil horizons from which FA, HA were isolated

<table>
<thead>
<tr>
<th>Humic, fulvic acid</th>
<th>Soil horizon</th>
<th>Depth/cm</th>
<th>Soil type</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA1</td>
<td>O</td>
<td>1–2</td>
<td>Ferro-humic podzol</td>
</tr>
<tr>
<td>HA2</td>
<td>O&lt;sub&gt;e&lt;/sub&gt;</td>
<td>2–4</td>
<td>Dystric cambisol</td>
</tr>
<tr>
<td>HA3</td>
<td>A</td>
<td>16–19</td>
<td>Ferro-humic podzol</td>
</tr>
<tr>
<td>HA4</td>
<td>O&lt;sub&gt;b&lt;/sub&gt;</td>
<td>3–5</td>
<td>Dystric cambisol</td>
</tr>
<tr>
<td>FA</td>
<td>B</td>
<td>60–70</td>
<td>Dystric cambisol</td>
</tr>
</tbody>
</table>

Soil samples were air-dried and sieved (<2 mm). HA and FA were extracted using 0.1 M NaOH at a solution : soil ratio of 20 : 1 after soil decalcification by 0.1 M HCl. FA were isolated after HA precipitation, using the standard method with a XAD8 resin column. The sodium humate and fulvate were converted into H<sup>+</sup> form and freeze-dried. FA was isolated from the B horizon because it was the dominant form of humic matter and was abundant enough for isolation in this horizon. Due to the general high mobility of FA in soils, we assume that FA extracted from this mineral horizon is characteristic of the entire soil profile.

Sample characterization with <sup>13</sup>C NMR spectroscopy

Quantitative <sup>13</sup>C liquid-state nuclear magnetic resonance (<sup>13</sup>C LS NMR) spectra of HA and FA dissolved in 0.1 M sodium deuteroxide (Sigma-Aldrich) were measured on a Bruker Avance DRX 500 spectrometer operating at 125.75 MHz using recycle delay = 5 s, number of scans = 20 000, and inverse gated decoupling. The free induction decay was processed with line broadening of 20 Hz (Fig. S1†). The <sup>13</sup>C chemical shifts were referenced to tetramethylsilane; quantification was achieved by instrumental integration of NMR peaks. The chemical shift regions 0–45, 45–110, 110–160 and 160–220 ppm were assigned to aromatic C and the sum of aromatic and aliphatic (alkyl + O-alkyl) carbons.

Table 2 <sup>13</sup>C liquid-state nuclear magnetic resonance (NMR) analysis of fulvic and humic acids; Aromaticity (f<sub>a</sub>) calculated as the ratio between aromatic and the sum of aromatic and aliphatic (alkyl + O-alkyl) carbons

<table>
<thead>
<tr>
<th>Type of C atom</th>
<th>Alkyl (%)</th>
<th>O-alkyl (%)</th>
<th>Aromatic (%)</th>
<th>Carboxyl (%)</th>
<th>Aromaticity f&lt;sub&gt;a&lt;/sub&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA</td>
<td>20.0</td>
<td>21.6</td>
<td>17.0</td>
<td>41.5</td>
<td>29.0</td>
</tr>
<tr>
<td>HA1</td>
<td>24.2</td>
<td>41.2</td>
<td>20.3</td>
<td>14.4</td>
<td>23.7</td>
</tr>
<tr>
<td>HA2</td>
<td>26.4</td>
<td>31.2</td>
<td>24.9</td>
<td>17.4</td>
<td>30.2</td>
</tr>
<tr>
<td>HA3</td>
<td>18.7</td>
<td>31.1</td>
<td>29.3</td>
<td>21.0</td>
<td>37.0</td>
</tr>
<tr>
<td>HA4</td>
<td>21.1</td>
<td>36.5</td>
<td>25.2</td>
<td>17.3</td>
<td>30.4</td>
</tr>
<tr>
<td>&quot;HA2</td>
<td>23.6–27.6</td>
<td>23.9–25.5</td>
<td>34.8–37.6</td>
<td>13.1–15.1</td>
<td></td>
</tr>
<tr>
<td>&quot;FA</td>
<td>16.5–27.6</td>
<td>26.4–38.3</td>
<td>9.9–29.6</td>
<td>24–27.6</td>
<td></td>
</tr>
</tbody>
</table>

The sodium humate and fulvate were converted into H<sup>+</sup> form and freeze-dried. FA was isolated from the B horizon because it was the dominant form of humic matter and was abundant enough for isolation in this horizon. Due to the general high mobility of FA in soils, we assume that FA extracted from this mineral horizon is characteristic of the entire soil profile.

Table 2 <sup>13</sup>C NMR characteristics of these samples were within characteristic ranges of FA and HA samples isolated from different mineral soil horizons.

In the Bohemian Forest soils, carboxylic C atoms in FA samples were nearly twice as abundant as those in HA samples. In contrast, HA had a higher content of O-alkyl and aromatic C. All the <sup>13</sup>C NMR characteristics of these samples were within characteristic ranges of FA and HA samples isolated from different mineral soil horizons.

Sample preparation

HA and FA isolates were dissolved in Milli-Q water to an approximate concentration of 0.5 mmol L<sup>−1</sup> DOC. The initial concentrations of total Al and Fe in diluted samples were 0.2 to 2 and 0.4 to 2 μmol L<sup>−1</sup>, respectively. Aluminium chloride (AlCl<sub>3</sub>) and iron chloride (FeCl<sub>3</sub>) were added to the samples to form organically-bound complexes with HA and FA, following the procedure suggested by Nierop et al. Both metals were added to all samples; additional experiments with only added Al or Fe were performed with samples HA1 and HA3. The pH was adjusted to ~5, and the samples were stored at 4°C for 48 hours. The samples were then filtered through a 0.4 μm polycarbonate membrane filter (Millipore) and promptly passed through a column filled with strong cation-exchange resin (DOWEX HCR-W2) to remove ionic and labile forms of metals from the solution.

The elevated Al and Fe concentrations, after addition of their chloride salts, were from 4.0 to 11.6 μmol L<sup>−1</sup> and from 2.1 to 5.8 μmol L<sup>−1</sup>, respectively. Samples were adjusted to a similar optical density before irradiation, such that the difference in absorbance at 254 nm was ±2% among all samples at the beginning of irradiation. Immediately after cation exchange, the metals were present only in the organically-bound form. However, during the following storage (24 h), a new equilibrium between organic and inorganic forms of metals was established (Table 3, Table 4). The only source of inorganic unbound metals...
The temperature inside the reactor was 25–35 °C. Natural solar radiation in the summer solstice, spring or autumn laboratory simulation is equivalent to 0.3, 0.6, and 2.7 days of midsummer. The amount of energy in the 120 min irradiation was computed by 120 min irradiation. We used the model of temperature on stability of organically-bound metals during photochemical experiments.

Photochemical experiments

Photochemical experiments were carried out in an irradiation reactor (RAYONETT-RMR 100, The Southern New England Ultraviolet Company, USA). The reactor was equipped with RPR-3500A lamps emitting radiation in the UV-A range with an intensity of 1.25 W m⁻². The temperature inside the reactor was 25–35 °C. The influence of temperature on stability of organically-bound metals during irradiation was tested using dark controls in preliminary experiments (not shown). It was shown that temperature had no significant effect on metal speciation for at least 24 h of incubation at 40 °C.

The total irradiation energy used in this experiment was approximately 0.49 MJ m⁻², estimated as intensity of irradiation multiplied by 120 min irradiation time. We used the model developed by the Norwegian Institute for Air Research to estimate the incident UV-A radiation at 50 °N 15 °E on a horizontal surface for winter solstice, spring and autumn equinox, and summer solstice. The amount of energy in the 120 min laboratory simulation is equivalent to 0.3, 0.6, and 2.7 days of natural solar radiation in the summer solstice, spring or autumn equinox, and winter solstice, respectively. Each sample was divided into seven sub-samples: one sub-sample was a dark control and the others were irradiated in quartz flasks for 15 to 120 min. After irradiation, all sub-samples were filtered through 0.4 µm polycarbonate membrane filters, and analyzed for DOC, Al and Fe speciation, pH, and UV-Vis spectra.

Table 3 Percentage of organically-bound metals in the samples before (dark control at 0 min) and after (120 min) irradiation. 100% represents the total concentration of metal at the beginning of the experiment after passing through a cation exchange column, time between cation exchange and irradiation was 24 h.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Irradiation time/min</th>
<th>A₁₀⁰/A₅₆₅</th>
<th>E₄/E₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA</td>
<td>0</td>
<td>4.30</td>
<td>6.14</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>5.39</td>
<td>7.84</td>
</tr>
<tr>
<td>HA1</td>
<td>0</td>
<td>4.08</td>
<td>6.45</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>3.55</td>
<td>5.57</td>
</tr>
<tr>
<td>HA2</td>
<td>0</td>
<td>3.27</td>
<td>6.26</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>3.62</td>
<td>6.41</td>
</tr>
<tr>
<td>HA3</td>
<td>0</td>
<td>2.98</td>
<td>12.48</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>3.25</td>
<td>8.54</td>
</tr>
<tr>
<td>HA4</td>
<td>0</td>
<td>3.21</td>
<td>8.71</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>3.73</td>
<td>6.85</td>
</tr>
</tbody>
</table>

Table 4 Concentrations of DOC, Al, and Fe, and pH, in the dark control (t = 0) and after 120 min irradiation (t = 120).

<table>
<thead>
<tr>
<th>Sample</th>
<th>DOC/mmol L⁻¹</th>
<th>Al/µmol L⁻¹</th>
<th>Fe/µmol L⁻¹</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA</td>
<td>0.43</td>
<td>5.67</td>
<td>4.08</td>
<td>4.30</td>
</tr>
<tr>
<td></td>
<td>0.37</td>
<td>7.32</td>
<td>2.40</td>
<td>120</td>
</tr>
<tr>
<td>HA1</td>
<td>0.16</td>
<td>1.76</td>
<td>2.28</td>
<td>4.20</td>
</tr>
<tr>
<td></td>
<td>0.16</td>
<td>1.86</td>
<td>2.11</td>
<td>120</td>
</tr>
<tr>
<td>HA2</td>
<td>0.47</td>
<td>2.37</td>
<td>5.27</td>
<td>4.82</td>
</tr>
<tr>
<td></td>
<td>0.45</td>
<td>2.74</td>
<td>4.82</td>
<td>120</td>
</tr>
<tr>
<td>HA3</td>
<td>0.31</td>
<td>1.30</td>
<td>5.38</td>
<td>4.82</td>
</tr>
<tr>
<td></td>
<td>0.27</td>
<td>1.67</td>
<td>5.01</td>
<td>120</td>
</tr>
<tr>
<td>HA4</td>
<td>0.47</td>
<td>6.60</td>
<td>4.97</td>
<td>4.19</td>
</tr>
<tr>
<td></td>
<td>0.45</td>
<td>6.90</td>
<td>4.19</td>
<td>120</td>
</tr>
</tbody>
</table>

* Only Al was added to the solution. † Only Fe was added to the solution.

The total radiation energy used in this experiment was approximately 0.49 MJ m⁻², calculated as intensity of irradiation multiplied by 120 min irradiation time. We used the model developed by the Norwegian Institute for Air Research to estimate the incident UV-A radiation at 50 °N 15 °E on a horizontal surface for winter solstice, spring and autumn equinox, and summer solstice. The amount of energy in the 120 min laboratory simulation is equivalent to 0.3, 0.6, and 2.7 days of natural solar radiation in the summer solstice, spring or autumn equinox, and winter solstice, respectively. Each sample was divided into seven sub-samples: one sub-sample was a dark control and the others were irradiated in quartz flasks for 15 to 120 min. After irradiation, all sub-samples were filtered through 0.4 µm polycarbonate membrane filters, and analyzed for DOC, Al and Fe speciation, pH, and UV-Vis spectra.

Total dissolved and organically-bound Al (A₁₀⁰, A₅₆₅, and Fe (Fₑₙ, Fₑo) were determined according to Driscoll: the strongly acidic cation exchange resin (DOWEX HCR-W2) was used to separate the positively-charged inorganic Al and Fe forms from their neutral and/or negatively-charged metal-DOM complexes. The resin column was rinsed with 45 mL of filtered sample prior to processing a sample for analysis of A₁₀⁰ and Fₑo. Concentrations of DOC, Al, and Fe (DOC, Al, and Fe) were calculated as the difference between Al₁₀⁰ and Fe₀, and Al₀ and Fe concentrations, respectively. Particulate Al and Fe (Alₚ and Feₚ) produced during irradiation were the difference between the Al₁₀⁰ and Fe₀ before and after the irradiation.

DOC was determined by wet oxidation with persulfate (1010 TOC analyzer, OI Corporation). The precision for DOC analyses (±3%) was estimated using a coefficient of variation (n = 3). Metal concentrations were determined by inductively coupled plasma optical emission spectrometer (ICP-OES; Perkin-Elmer Optima 3300XL) with axially-viewed plasma and ultra sonic nebulizer (CETAC International, Inc.). Samples were measured in triplicate. Detection limits were 0.05 and 0.1 µmol L⁻¹ for Al and Fe, respectively.

UV-Vis spectra were measured for each DOC sample from 200 to 700 nm using a 1 cm quartz cell with a HP 8452A diode array spectrophotometer. Specific UV-A absorbance at 254 nm (SUVA₂₅₄) was calculated as the ratio of absorbance (A₂₅₄) and
DOC concentration (mg L\(^{-1}\)). The ratios between absorbances at 250 and 365 nm (\(A_{250}/A_{365}\)), 254 and 436 nm (\(A_{254}/A_{436}\)), and 465 and 665 nm (\(E_6/E_0\)) were also calculated.\(^{31,32}\)

Pseudo first-order photodegradation rate constants for degradation of DOC (\(k_{\text{DOC}}\)), \(\text{Al}_0\) (\(k_{\text{Al}}\)), and \(\text{Fe}_0\) (\(k_{\text{Fe}}\)) were calculated from

\[
C = (C_0 - C_t)e^{-kt} + C_t
\]

where \(k\) is the pseudo first-order constant for each observed component, \(t\) is time (min), \(C_0\) is the initial concentration of DOC, \(C\) is the DOC concentration at any time \(t\), and \(C_t\) is the concentration of the recalcitrant fraction that does not degrade during the irradiation experiment.

Each irradiation experiment was carried out only once. The high degree of repeatability of our experimental protocol was established previously with river water (data not shown). The variability of DOC concentrations for 8 h of irradiation was <1\% (\(n = 6\)).

### Results and discussion

#### DOC

The concentration of DOC in samples prepared for irradiation ranged from 0.16 to 0.47 mmol L\(^{-1}\). Initial absorbance at 254 nm differed by only ±2%. The concentration of DOC decreased after irradiation from negligible to 13\%. The highest percent decrease in DOC concentration occurred in the FA sample, while almost no change occurred in sample HA1 (Table 4). The decrease in DOC concentration was higher in samples with added metals than in samples without added metals (t-test, \(p < 0.05\)). The fact that \(\text{Fe}^{2+}\) increases the rate of DOM photodegradation has been reported previously.\(^{11-13}\) Despite the changes in the DOC concentration after irradiation are relatively low, the decreasing trend is obvious. Eqn (1) was used to model the decrease in DOC due to irradiation. Table 6 shows the best fits to the parameters in Eqn (1).

The irradiation of DOM results not only in its oxidation to carbon oxides but also in changes in structure\(^{44,45}\) and formation of lower molecular weight organic acids.\(^{36,37}\) Concordantly, the spectral characteristic of soil HA and FA samples changed during irradiation (Table 5): (i) The \(A_{250}/A_{365}\) ratio increased in all samples, except HA1, indicating decreases in their molecular weight.\(^{38}\) The different behavior of HA1 could be explained by the highest content of O-alkyl groups (Table 2). The increased absorbance of these groups could mask the effect of decreasing molecular weight on the \(A_{250}/A_{365}\) ratio. Similar changes associated with the decrease in aromaticity and molecular size were observed during irradiation of marine humic samples.\(^{39}\) (ii) The \(E_6/E_0\) ratio decreased during irradiation in all HA samples except for HA2. The difference between absorbance spectra before and after irradiation of HA2 samples was obvious only at wavelengths <400 nm, and the spectra at higher wavelengths remained unchanged. The \(E_6/E_0\) ratio in HA (an indicator of humification\(^{31}\)) and percentage of DOC decrease during irradiation were strongly positively correlated (\(r = 0.90, p < 0.05\)) (Table 5). High \(E_6/E_0\) ratios can be related to a high molecular weight\(^{31}\) and decreasing \(E_6/E_0\) ratios indicate DOM decompositions.\(^{32}\) (iii) SUV \(A_{254}\) increased after irradiation in all samples probably due to the decrease of DOM molecular size.\(^{40}\) Such a decrease in molecular size is commonly emphasized by formation of lower molecular size acids.\(^{41}\)

#### Aluminium and iron

Photochemical changes of DOM structure affect its binding properties and, consequently, release of \(\text{Al}_0\) and \(\text{Fe}_0\) from their complexes with DOM.\(^{32}\) During the experiments, the \(\text{Al}_0\) and \(\text{Fe}_0\) concentrations decreased by 25\% to 75\% and 24\% to 54\%, respectively. This decrease was compensated by a reciprocal increase in their ionic and particulate forms (Fig. 1, Fig. S2 and S3\(^\text{†}\)).

The total changes in \(\text{Al}_0\) and \(\text{Al}_i\) proportions and concentrations in the samples after metal addition to DOM are interpreted as a combination of three processes: (i) establishment of a new equilibrium between organically bound and ionic species after passing through the cation-exchange resin, (ii) changes induced by irradiation, and (iii) precipitation of \(\text{Al}_i\).\(^{44}\)

Numerous studies have described binding properties of DOM. Two main concepts were developed to recognize extreme heterogeneity of DOM binding sites (ref. 43 and references therein). In the NICA-Donnan model (e.g. ref. 44, 45), the heterogeneity is described with continuous functions, whereas in Model VI a collection of chemical reactions is used.\(^{46}\) The combination of both models seems to be the best explanation of processes described in our experiment. Tipping\(^{48}\) reviewed cation binding in DOM and grouped the binding sites for metal cations into three main categories: (1) Non-specific sites, binding at which is due to electrostatic attraction; (2) Weak sites formed by oxygen-containing ligands; (3) Stronger sites formed by combinations of O, N and S.

The establishment of a new equilibrium between ionic and organically-bound forms of metals during storage after cation exchange and irradiation was more significant for \(\text{Al}\) than \(\text{Fe}\). Fe was bound more strongly in organic complexes; a maximum of 8\% of \(\text{Fe}_0\) was converted to \(\text{Fe}_i\) (Table 3), while the original \(\text{Al}_0\)

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**Table 6** Pseudo first order reaction constants (\(k\)) for DOC, \(\text{Al}_0\), \(\text{Fe}_0\). N/C = does not fit pseudo first order reaction equation

<table>
<thead>
<tr>
<th>DOC</th>
<th>(C_0/\text{mmol L}^{-1})</th>
<th>(k_{\text{DOC}}/\text{h}^{-1})</th>
<th>(C_1/\text{mmol L}^{-1})</th>
<th>(R^2)</th>
<th>(C_0/\text{µmol L}^{-1})</th>
<th>(k_{\text{Al}}/\text{h}^{-1})</th>
<th>(C_1/\text{µmol L}^{-1})</th>
<th>(R^2)</th>
<th>(C_0/\text{µmol L}^{-1})</th>
<th>(k_{\text{Fe}}/\text{h}^{-1})</th>
<th>(C_1/\text{µmol L}^{-1})</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA</td>
<td>0.43</td>
<td>0.633</td>
<td>0.35</td>
<td>0.95</td>
<td>4.07</td>
<td>4.265</td>
<td>2.55</td>
<td>0.97</td>
<td>5.63</td>
<td>4.700</td>
<td>3.27</td>
<td>0.86</td>
</tr>
<tr>
<td>HA1</td>
<td>N/C</td>
<td>N/C</td>
<td>N/C</td>
<td>N/C</td>
<td>2.28</td>
<td>7.971</td>
<td>2.05</td>
<td>0.47</td>
<td>2.09</td>
<td>4.009</td>
<td>1.41</td>
<td>0.84</td>
</tr>
<tr>
<td>HA2</td>
<td>0.47</td>
<td>0.101</td>
<td>0.36</td>
<td>0.89</td>
<td>5.24</td>
<td>0.468</td>
<td>4.54</td>
<td>0.74</td>
<td>4.71</td>
<td>0.140</td>
<td>0.00</td>
<td>0.97</td>
</tr>
<tr>
<td>HA3</td>
<td>0.31</td>
<td>3.009</td>
<td>0.28</td>
<td>0.80</td>
<td>5.36</td>
<td>0.787</td>
<td>4.95</td>
<td>0.95</td>
<td>3.13</td>
<td>1.156</td>
<td>2.45</td>
<td>0.96</td>
</tr>
<tr>
<td>HA4</td>
<td>0.47</td>
<td>0.101</td>
<td>0.36</td>
<td>0.89</td>
<td>4.97</td>
<td>0.247</td>
<td>4.30</td>
<td>0.91</td>
<td>4.27</td>
<td>1.114</td>
<td>2.17</td>
<td>0.97</td>
</tr>
</tbody>
</table>
concentration decreased by 19 to 58%. In natural environments, the non-specific sites of the DOM may be occupied by major cations and cationic Al species under acidic conditions.43 These non-specific sites may preferentially release Al during the establishment of new equilibrium after ion exchange. In the samples to which only Al was added, the decrease in the Al fraction was similar to the case when both metals were added.

The decrease in the ratio of organically-bound to ionic metals caused by establishment of the new equilibrium was greatest in FA, and lowest in HA3 (Table 3), which had the highest content of aromatic C (Table 2). We hypothesize that similar changes in Al could occur also in the field, after the soil water emerges into the streams. A partial precipitation of Al could occur by pH increase due to degassing of carbon dioxide43 or after mixing with less acidic water.44 Alp formation decreases Al fraction, changing the original proportion between concentrations of Al and Al0 in soil water. This results in the transformation of some Al0 to Alp.17

Compared to the dark controls after establishment of the new equilibrium, irradiation decreased Al0 and Feo concentrations in all samples by 7% to 41% and 21% to 52%, respectively (Table 3, Fig. 1, Fig. S2 and S3†). The FA and HA are operationally defined distinct fractions of DOM which not only differ in their structural parameters but also in their photochemical properties. The highest photo-liberation of Al0 and Feo occurred in FA, while the lowest was in HA3. The FA had the highest concentration of carboxylic C groups, lowest aromatic C concentration, and highest A254/A436 ratio. Irradiation of Fe2+ carboxylate complexes leads to transfer of one electron from carboxylate to Fe3+ resulting in the formation of Fe3+ and R-CO2• radical which may undergo decarboxylation.39 The higher carboxylic content of FA was thus likely to be the major reason for its higher photo-reactivity compared to HAs. The decrease in Al0 and Feo concentrations correlated with the A254/A436 ratio in all samples, with r = 0.91 and p < 0.05 for Al0, and r = 0.71 and p < 0.05 for Feo. DOM with higher A254/A436 ratio is more sensitive to photochemical degradation, and metal complexes with such DOM are more sensitive to photochemical liberation, probably due to a higher energy absorption in the UV range. The A254/A436 ratio describes the slope of spectral curve43 and the higher A254/A436 DOM exhibits higher UV-light absorption.

The liberation of Al0 and Feo differed by the operative dominant mechanism. The establishment of new equilibrium was more important for Al, and the photochemical release was more important for Fe.49 The partial release of Al0 and Feo during irradiation indicates the presence of different binding sites. The non-specific binding sites are significant during establishing of new equilibrium, while the weaker and stronger binding sites may play important role in the photochemical release of Al0 and Feo. Plankey and Patterson49 found that Al could be bound in organic complexes by weak and strong binding sites. We hypothesize that weaker binding sites were altered during our short-term irradiation. Metal binding at these sites parallels binding to simple organic acids with oxygen functionalities.43 The stronger (but less abundant) sites formed by combination of O, N and S could exhibit a wide range of affinities and relative abundance and differentiate among metals more than the weaker (but abundant) sites.44 The higher decrease in Feo than Al0 observed during irradiation could also result from the autocatalytic effect of Fe during photodegradation.13,14,38

Production of particulate matter

Production of Alp and Fe p was significant in only HA2 and HA4 and represented 17% to 62% of decline of Al0 and Feo in these samples, despite only small changes in pH during the irradiation (Table 4). Both HA samples were from the dystric cambisol (Table 1). We hypothesize that the formation of Alp and Fe p was caused as follows:

(i) Table 4 shows that in HA2 and HA4 samples, a higher amount of Fe p than Alp was formed. The release of trivalent cations (Al3+ and Fe3+) during irradiation and formation of fresh Fe–OH complexes (a product of partial Fe3+ hydrolysis) could cause DOM coagulation, as well as coprecipitation and formation of Fe p. Only the hydrolysis of Fe3+ to Fe(OH)3+ (pK = 2.2) and Fe(OH)2+ (pK = 3.48)60 and formation of positively-charged Fe hydroxyl-complexes was possible under the experimental conditions. Formation of these hydrolysis species lowers the solubility of Fe(OH)3+. However, for Alp to form, pH of the...
irradiated samples (4.1 and 4.7; Table 4) was too low to allow Al hydrolysis to Al(OH)$^{3+}$ ($pK = 4.95$) and precipitation of significant amounts of Al(OH)$_3$.

(ii) Irradiation causes the oxidation of DOM and formation of lower-molecular-weight organic acids.$^{36,37}$ These changes could also decrease the concentration of carboxylic groups per mass of HAs, thus increasing their hydrophobicity and, consequently, causing their precipitation at stable pH.

The decrease in Al$_o$ (7 to 41%) and Fe$_o$ (21 to 51%) during irradiation is consistent with laboratory and in situ experiments with natural tributary water to acidic Plešné Lake, Czech Republic. There, the percentage decrease was 54%–61% and 64%–70% for Al$_o$ and Fe$_o$, respectively, for irradiation at 300 nm up to 12 h.$^{17,18}$ Photochemical experiments conducted with first order stream water in Maine, USA, resulted in a decrease in Al$_o$ (26%–76%) and Fe$_o$ (63%–100%) concentrations (irradiation at 350 nm, intensity $\sim$68 W m$^{-2}$, irradiation time up to 8 h.$^{19}$

**Kinetics of DOC, Fe$_o$, and Al$_o$ photochemical changes**

The pseudo first-order rate constants, $k$, were higher for Al$_o$ than for Fe$_o$ in samples HA1, HA2, and HA4, whereas in samples FA and HA3 the rate constants were higher for Fe$_o$ than for Al$_o$ (Table 6, Fig. 2). The calculated decline (difference between initial concentration $C_0$ and concentration of recalcitrant fraction $C_r$) was higher for Fe$_o$ (24%–54%) than for Al$_o$ (9%–38%) in all samples (Table 6). The greater decrease in Fe$_o$ may be partly explained by the autocatalytic effect of Fe on photo-degradation.$^{13,35,14}$ Dissolved Fe participates in a series of photochemically-initiated reactions to produce radical species, including peroxyl, superoxide, and hydroxyl.$^{51,52}$ The formation of Fe$_p$
during irradiation of samples HA2 and HA4 (Table 4) could have accelerated photochemical degradation of DOM by the heterogeneous reactions on the surfaces of Fe(III) hydroxides.15

The rate constants observed for DOM (Table 6) can be compared to those measured for a first-order stream in Maine, USA,19 with values ranging from 1.8 to 5.5 h⁻¹ for Feo and 0.1 to 0.5 h⁻¹ for Alo. Compared to the rate constants for the stream, the rate constants are higher in soil water for Alo and are similar for Feo (Table 6).

Laboratory experiments versus natural conditions

Laboratory experiments enable precise control of both irradiation and sample environment, but their interpretation and interpolation to natural conditions is problematic. Some experiments used whole spectrum solar light simulators (e.g. ref. 35, 53), while others used a particular range of wavelengths (e.g. ref. 14, 15, 17, 18, 37). One meaningful comparison among different methods is the total light energy during irradiation.53 For our experiments, the 2 h irradiation was equal to 0.3 to 2.7 days, depending on the season (sun angle). These results with DOM isolated from European mountain forest soils are in good agreement with the response of DOM in headwater streams in Maine, USA.19 The maximum rate of change in DOM’s ability to bind metals occurs within the first few hours after groundwater enters the stream. Thus, a significant effect of solar radiation on de-complexation of organically-bound metals can be expected not only in lakes, but also in the first- or second-order streams draining to these lakes.

We assume that the amount of photochemically liberated metals in streams depends on both the amount and quality of DOM exported to waters from soils. The transport of DOM from soil to stream usually increases during high discharge episodes.3 The higher photo-degradability of FA than HA suggests that the photochemical properties of DOM exported to the streams from soil may also change with a changing discharge.84 The contribution of DOM from individual soil horizons is driven by flow conditions,1 with a relatively greater importance of mineral soil horizons during base flow conditions, and a greater importance of upper organic or litter horizons during hydrologic events. The major part of the DOM found in the surface waters at low to intermediate flow conditions consists of leachates from mineral soil horizons rather than of leachates from humus layers or humic top soil horizons.57 Shumacher et al.58 showed that the composition of the aquatic DOM in boreal forest catchments was rather constant during low to intermediate flow, and its composition with mean DOC distribution of 26%, 42%, 10%, and 18% of alkyl C, O-alkyl C, aromatic C, and carboxylic C, respectively, was more similar to our HA than FA (Table 2).

Conclusions

Our results show the influence of photochemical processes, and also suggest a significant influence, mainly on Alo, of other processes, such as degassing of carbon dioxide and/or pH change that can affect metal speciation in metal-saturated soil DOM after emergence to surface waters. The changes in metal binding by DOM can occur very rapidly, reflecting flow condition (and thus stream water residence time), and sunlight intensity. The chemical equilibrium established in soil can change rapidly in streams leading to the precipitation of metal hydroxides (e.g. ref. 47, 48). As a new equilibrium between ionic and organically-bound metals is achieved, concentrations of organically-bound metals decrease. We hypothesize that the release of weakly-bound metals is an important process during high flow events (spring snow-melt, rain storms), primarily due to the lower pH during these events. In contrast, photochemical degradation of DOM and reduction of Alo and Feo concentrations in stream water is likely more significant in summer, when the intensity of natural solar radiation is higher and discharge is lower. The widespread decrease in acid deposition in Europe and Northern America has resulted in increasing DOC concentrations at many sites.86 At relatively stable Alo : DOC ratios in natural waters86,44 we can expect increasing export of Al from soils to freshwaters. The degradation of Alo may represent an Al buffer, maintaining potentially toxic concentrations of Al in aquatic habitats77 and delaying biological recovery in fresh waters recovering from acidification.

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