Spectroscopic Studies of Aluminum Ion Binding by Soil Derived Humic Material: Fluorescence Enhancement

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$M^{x+} = \text{metal ion, toxic or non, of charge } x^+ \text{ (e.g., } Cu^{2+}, Al^{3+}, \text{ etc.)}$

$NOM^{y-} = \text{natural organic matter of varying negative charge } y^-$
$M^{x+} + \text{NOM}^{y-} \leftrightarrow M\text{-NOM}^{(x-y)-}$

$$K = \frac{[M\text{-NOM}^{(x-y)-}]}{[M^{x+}][\text{NOM}^{y-}]}$$

$K =$ equilibrium constant describing complexation reaction

$M\text{-NOM}^{(y-x)-} =$ metal complex of natural organic matter
Metal Speciation = determination of the forms of metal in equilibrium with NOM

Measurement must not disturb equilibrium
Fluorescence Quenching

Fluorescence Emission scans of NOM with varying Cu$^{2+}$ excited at 340 nm
Fluorescence Quenching Curves

Cu-NOM titrations at pH 5 (○), 6 (▼) & 7 (□)

Added Copper Concentration (M x10$^5$)

Relative Fluorescence Intensity
Fluorescence binding curves for Cu, Co, Mn & Al at pH values of 4-8

- very sensitive
- does not disturb equilibrium
- few metals
Fluorescence Enhancement

15 mg/L Fulvic Acid at pH 4
(a) 112 μM Al³⁺  (b) 0 μM Al³⁺

Emission Wavelength in nm with 360 nm Excitation
Fluorescence Enhancement

15 mg/L Fulvic Acid at pH 4
(a) 112 μM Al\(^{3+}\)  (b) 0 μM Al\(^{3+}\)

Emission Wavelength in nm with 340 nm Excitation
Excitation Emission Matrix

15 mg/L Fulvic Acid at pH 4 with no Al(III)
Excitation Emission Matrix

15 mg/L Fulvic Acid at pH 4 with Al(III)
Fluorescence Enhancement Curve with One-Site Model

15 mg/L of Fulvic Acid with increasing Al(III) concentrations at pH 4 (o)
Fluorescence Enhancement Curve with Two-Site Model

15 mg/L of Fulvic Acid with increasing Al(III) concentrations at pH 4 (o)
Individual Fluorescence Intensities Making Up the Overall “I”

\[ I = I_{L1} + I_{ML1} + I_{L2} + I_{ML2} \]
Hypothetical Fluorescence Intensity Curves Showing Component Intensities
### Binding Data for Al$^{3+}$ & FA
(15 mg/L)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.00</td>
</tr>
<tr>
<td>log $K_1$</td>
<td>6.56 ± 0.30</td>
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<tr>
<td>log $K_2$</td>
<td>5.16 ± 0.12</td>
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<tr>
<td>$C_{L1}$</td>
<td>13.1 ± 1.5 μM</td>
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<tr>
<td>$C_{L2}$</td>
<td>6.0 ± 0.9 μM</td>
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<tr>
<td>$f_1$</td>
<td>0.07 ± 0.02</td>
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<tr>
<td>$I_{RES}$</td>
<td>186.2 ± 9.7</td>
</tr>
</tbody>
</table>
Conclusions

- Al-NOM speciation can be measured by fluorescence enhancement & $^{27}$Al NMR
  - Fluorescence sensitive – natural waters
  - NMR not sensitive – soil solutions

- Both techniques are sensitive to the complexed Al species

- Data modeled for predictive purposes

- Al$^{3+}$ binds strongly as expected

- Multiple Al species present