Influence of Dissolved Organic Carbon Molecular Weight and Structure on Copper Complexation

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Dissolved Organic Carbon

Organic carbon that passes through 0.45µm pore size filter

(Sutton and Sposito, 2006)
Determine which MW fraction of DOC preferentially complexes Cu?

- Shafer et al. (2004) ES&T
- deZarnuk et al. (2007) Chemosphere

Identify factors responsible for Cu-DOC complexation.

Ho: Cu complexation increases in LMW DOC with oxygen functional groups

Ho: Aromatic moieties in DOC provide strong Cu-binding sites

### Standardized Humic Substances with known molecular structure

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>S</th>
<th>P</th>
<th>Aromaticity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suwannee River HA</td>
<td>52.63</td>
<td>4.28</td>
<td>42.04</td>
<td>1.17</td>
<td>0.54</td>
<td>0.013</td>
<td>31</td>
</tr>
<tr>
<td>Suwannee River FA</td>
<td>52.34</td>
<td>4.36</td>
<td>42.98</td>
<td>0.67</td>
<td>0.46</td>
<td>0.004</td>
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<tr>
<td>Suwannee River NOM</td>
<td>52.47</td>
<td>4.19</td>
<td>42.69</td>
<td>1.1</td>
<td>0.65</td>
<td>0.02</td>
<td>23</td>
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<tr>
<td>Nordic Reservoir NOM</td>
<td>53.17</td>
<td>5.67</td>
<td>nd</td>
<td>1.1</td>
<td>nd</td>
<td>nd</td>
<td>19</td>
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<tr>
<td>Aldrich HA</td>
<td>68.98</td>
<td>5.26</td>
<td>43.45</td>
<td>0.74</td>
<td>4.24</td>
<td>&lt;0.05</td>
<td>26</td>
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</tbody>
</table>
### Solid Phase Extraction

#### Cartridge ID | Cartridge Type | SPE Media | Retention Mechanisms | Molecular Weight Cutoff
--- | --- | --- | --- | ---
Anion-F | BioRad AG MP-1 | Quaternary ammonium - styrene divinylbenzene copolymer (fluoride counterion) | Anion Exchange | none
Anion-1kDa | BioRad AG 1 X8 | Quaternary ammonium - styrene divinylbenzene copolymer (fluoride counterion) | Anion Exchange | 1kDa
Cation | BioRad Chelex 100 | Iminodiacetic acid exchange - styrene divinylbenzene copolymer | Cation Exchange | none

#### Retention Mechanisms

1. **Trace metal and carbon clean**
2. **Molecular weight fraction**
3. **No chemical treatments altered both DOC and trace metal complexation**
4. **Simultaneous quantification** of DOC and Cu-DOC complexation

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**Ligand Size**

\[ LS = \frac{M_F - M_X}{M_X} \]

- \( M_F \) – metal retained by Anion-F cartridge
- \( M_X \) – metal retained by Anion-1kD cartridge

**MW Binding Site Density**

\[ MW BSD = \frac{M_F - M_X}{C_F - C_X} \cdot \frac{C_X}{M_X} \]

- \( M_F \) – metal retained by Anion-F cartridge
- \( M_X \) – metal retained by Anion-1kD cartridge
- \( C_F \) – organic carbon retained by Anion-F cartridge
- \( C_X \) – organic carbon retained by Anion-1kD cartridge
Cu is preferentially complexed by **HMW** fractions of DOC

\[ \text{MW BSD ratio} = 0.3 (\%\text{Aro}) - 2.7 (\%\text{O}) + 57.6 \quad (r^2 = 0.99) \]
The **strength** of Cu-DOC complexation increases with aromatic structure.

Nordic Reservoir NOM (●), Suwannee River FA (● Suwannee River HA (●), and Suwannee R NOM (●), and Aldrich HA (○).

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**Cu-DOC complexation** related to molecular structure:

1. Cu is preferentially complexed by **HMW** DOC

2. Complexation with **HMW** DOC increases with **aromatic** structure

3. Complexation with **LMW** DOC increases with **oxygen** functional groups

4. **Aromatic** moieties provide **strong** Cu-binding sites
Thank You

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