Geochemical modeling of Copper (II) speciation in MSWI bottom ash leachates

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Outline

• Introduction bottom ash and Cu leaching

• Literature findings on mechanisms

• DOC fractionation

• Titration results and modelling of Cu binding

• Conclusions
Introduction

- MSWI bottom ash is widely produced and increasingly re-used
- Leaching of Cu is one of the bottlenecks in re-use practice (NL, BE)
- Understanding of leaching mechanisms important for development of quality improvement technologies
Extraction of humic substances

Humic substances

Alkaline extraction

Humin (non-soluble)

(Soluble fraction)

Acidification

Humic acid (precipitate)

Fulvic acid (soluble)
Modelling Cu-DOC binding in MSWI bottom ash leachates (1)

Conclusion:
• Fulvic acid is present in bottom ash leachates
• Fulvic acid explains over 90% of observed Cu complexation
Modelling Cu-DOC binding in MSWI bottom ash leachates (2)

Conclusion:
• Fulvic acid explains 30% of Cu complexation
• Hydrophilic acids explain about 50% of observed Cu complexation

Arickx et al. (2007) Waste Manage. 27, 1422-1427
Modelling Cu-DOC binding in MSWI bottom ash leachates (3)

Conclusion:  
• Hydrophilic acids contribute substantially to observed Cu complexation  
• Fulvic acids are also important

Rationale for this study

No full consensus on the importance of different DOC fractions responsible for Cu complexation in MSWI bottom ash leachates:

- Van Zomeren and Comans (2004): fulvic acid explains Cu leaching
- Arickx et al. (2007): mainly hydrophilic acids and also fulvic acids explain Cu leaching
- Olsson et al. (2007): mainly hydrophilic acids and also fulvic acids explain Cu leaching

"If you can't beat them, join them!"
DOC fractionation method (ISO FDIS 12782-5)

→ Humic acids (HA)
   (precipitate at pH =1)

→ Fulvic acids (FA)
   (bind to DAX-8, desorbed with NaOH)

→ Hydrophobic neutrals (HON)
   (bind to DAX-8, not desorbed with NaOH)

→ Hydrophylc acids (Hy)

* van Zomeren & Comans, ES&T 41, 6755-6761 (2007)
Effects of different fractionation methods on DOC speciation

<table>
<thead>
<tr>
<th>Method</th>
<th>HA (mg C/L)</th>
<th>FA (mg C/L)</th>
<th>Hy (mg C/L)</th>
<th>DOC (mg C/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>van Zomeren &amp; Comans, 2007</td>
<td>0.09</td>
<td>6.2</td>
<td>5.5</td>
<td>11.8</td>
</tr>
<tr>
<td>Leenheer, 1981</td>
<td>0.01</td>
<td>3.3</td>
<td>7.2</td>
<td>10.5</td>
</tr>
</tbody>
</table>

→ Higher FA and lower Hy with rapid batch method

→ Differences due to pH and amounts of DAX-8 resin used
pH-static copper titrations

- Experiments on cation-exchanged fractions
- Titrations at pH 6 and 8.5
- I = 0.12-0.18 M NaNO3
- CuT = 6E-7 to 1.5E-4 M
- Cu-ISE: Radiometer
- Experiments under N2
Copper titrations on bottom ash leachate

![Graphs showing copper titrations on bottom ash leachate at pH 8.5 and pH 6.](image)
Copper titrations on fractions

• Fulvic acid versus hydrophilic acids
• BA1 shows distinction in binding capacity at pH 8.5: FA gains in importance
Modelling of Cu titration data

BA1 leachate

log Cu bound (mol/kg DOC)

log\{Cu^{2+}\}

BA2 leachate

log Cu bound (mol/kg DOC)

log\{Cu^{2+}\}
Modelling of Cu titration data

- Good prediction at pH6, over prediction at pH 8.5
Modelling of Cu titration data

- Optimisation of parameters improves description: binding parameters of BA differ from natural organic matter
Putting results in perspective...

• Van Zomeren and Comans (2004): fulvic acid explains Cu leaching
  At high pH and in environment with competing ions

• Arickx et al. (2007): mainly hydrophilic acids and also fulvic acids
  explain Cu leaching
  Low resin/volume ratio to isolate DOC fractions

• Olsson et al. (2007): mainly hydrophilic acids and also fulvic acids
  explain Cu leaching
  Low resin/volume ratio to isolate DOC fractions; in environment
  without competing ions; pH 6-8.5
Conclusions

• Differences in DOC fractionation procedures (definition of Hy and FA)

• Hydrophilic acids do also contribute significantly to Cu binding in systems with no competing ions and at pH <8

• Indications for more important role of FA at higher pH values (phenolic sites)

• Variability in binding properties: MSWI bottom ash has specific properties that differ from natural DOC

• development of a generic parameter set for MSWI bottom ash
Thanks for your attention!
Major differences in fractionation schemes for NOM

- Thurman & Malcolm (1981); **column procedure** for natural waters, adopted by the International Humic Substances Society (IHSS)
- Leenheer (1981); **column procedure** for natural water
- Swift (1996); **column procedure** for soil samples, adopted by the IHSS
- van Zomeren & Comans (2007), **rapid batch procedure** for solid and aqueous samples

### Fractionation Schemes

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Aquatic</th>
<th>Aquatic</th>
<th>Aquatic/soil</th>
<th>Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample pH</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k’ (first) XAD-8 step</td>
<td>2</td>
<td>first adsorb on XAD-8, then acidify to pH2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Flow rate (bv/h)</td>
<td>100</td>
<td>50</td>
<td>4</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>30</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td><strong>Typical features:</strong></td>
<td>Low sample pH: adsorption of HA, FA, HON on XAD-8 in first step; relatively large sample/resin ratio = less intense contact</td>
<td>Neutral sample pH: adsorption of HoB on XAD-8 in first step (desorbed with acid)</td>
<td>HA precipitated prior to contact with resin; low sample pH (=1); relatively low sample/resin ratio = more intense contact, relatively high FA and lower HA recovery</td>
<td>HA precipitated prior to contact with resin; low sample pH (=1); relatively high sample/resin ratio = similar HA and lower FA recovery than van Zomeren &amp; Comans (2007)</td>
</tr>
</tbody>
</table>

$k' = \text{dimensionless ratio between sample and resin volume}$
First attempt to explain different conclusions

• Different fractionation methods were used

• Experiments under different conditions (e.g. leachate with and without competing ions)

• Differences in pH domain

• Cooperation started with SLU/Ecoloop to resolve this scientific challenge
Modelling of Cu titration data

![Graphs showing the relationship between log Cu bound (mol/kg DOC) and log Cu2+ for BA1-HY and BA2-HY samples.](image)
Modelling of Cu titration data

• Reasonable prediction, except for BA2 at pH8.5
Modelling of Cu titration data

- Optimised parameter set improves prediction for BA2
Modelling of Cu titration data

- Over prediction for FA. Optimisation leads to improvement at pH 8.5: less phenolic binding sites