Evaluating a Commercial Potassium Humate Product for the Reduction of Bioavailable Copper and Zinc in Surface Water
Erin J. Peck and S. Michele Harmon, PhD
University of South Carolina Aiken, Department of Biology and Geology

INTRODUCTION
Dissolved Organic Matter (DOM) is a crucial component in aquatic systems for the natural remediation of metals pollution. Natural organic compounds from DOM provide macromolecules which strongly attract cations such as copper, lead, zinc, and mercury. Binding with organic molecules reduces toxicity and bioavailability for metals uptake in aquatic organisms. We investigated the use of a commercially-available organic product, Borregro HA-1, to aid in metals remediation in an aquatic environment.

DOM AND BIOAVAILABILITY

**Bioavailable and Toxic**

- **Cu^{2+}**

Humic substances have no "typical" chemical structure, but they can be described as large organic molecules with areas where negatively-charged metal binding groups come together. A positively-charged metal cation will bind to these areas and be chelated by this larger molecule. The metal is then no longer bioavailable because it cannot pass through biological membranes. This makes it less toxic.

Borregro HA-1 is a carbon-rich, potassium humate product intended for use as a soil amendment in agriculture. This was to determine if Borregro HA-1 was an effective remediation approach for copper and zinc in industrial effluents.

Tests were carried out in concentrations of Borregro HA-1 that achieved a dissolved organic carbon (DOC) concentration of 2.62 mg C/L. This matched the DOC concentration of our receiving stream of interest.

**METHODS: DILUTION WATER**

Borregro HA-1 was added to two reconstituted laboratory waters:
1. soft water (≤ 25 mg/L as CaCO₃)
2. moderately hard water (55 - 90 mg/L as CaCO₃)

<table>
<thead>
<tr>
<th>Water Type</th>
<th>DO (mg/L)</th>
<th>pH</th>
<th>Alkalinity (mg/L as CaCO₃)</th>
<th>Hardness (mg/L as CaCO₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft Water</td>
<td>7.56 - 8.32</td>
<td>7.2 - 7.4</td>
<td>10 - 30</td>
<td>15 - 25</td>
</tr>
<tr>
<td>Soft Water + Borregro HA-1</td>
<td>7.34 - 8.74</td>
<td>7.0 - 7.4</td>
<td>5 - 16</td>
<td>13 - 18</td>
</tr>
<tr>
<td>Moderately Hard Water</td>
<td>7.03 - 9.54</td>
<td>6.9 - 7.4</td>
<td>54 - 80</td>
<td>86 - 89</td>
</tr>
<tr>
<td>Moderately Hard Water + Borregro HA-1</td>
<td>6.82 - 9.35</td>
<td>6.9 - 7.6</td>
<td>45 - 90</td>
<td>90 - 90</td>
</tr>
</tbody>
</table>

**RESULTS**

- **Copper toxicity** was measured using the aquatic indicator organism *Ceriodaphnia dubia*.
- **Zinc toxicity** was measured using the aquatic indicator organism *Ceriodaphnia dubia*.

**CONCLUSIONS**

- Borregro HA-1 additions reduced the toxicity of copper at both hardness levels.
- There was no change in zinc toxicity. Nominal results imply that Borregro HA-1 additions may have increased zinc toxicity in moderately hard reconstituted water.

**FUTURE WORK: USING DIFFUSION GRADIENT IN THIN FILMS (DGT) PROBES TO EVALUATE BIOAVAILABILITY**

- DGT probes are passive sampling devices
- Consist of:
  1. diffusion gel layer that selectively admits analyte molecules
  2. absorptive gel layer that binds to the contaminant of interest

Their purpose is to select and absorb only those metals that are bioavailable.

- DGT probes were suspended in surrogate test replicates
- After 48 hours, probes were dismantled and metals were extracted from the absorptive gel.
- Samples are currently being analyzed by ICP-MS. This should provide a more realistic analytical representation of metals bioavailability in these experiments.

**Acknowledgments:** Funding for this project was provided by the United States Department of Energy Office of Environmental Management and the National Nuclear Security Administration through the "Workforce Opportunities in Regional Careers (WORC)" initiative of the Savannah River Site Community Reuse Organization. Additional support and assistance was provided by Drs. Michael Paller and Anna Knox of the Savannah River National Laboratory.