Dissolved Organic Carbon Augmentation: An Innovative Tool for Managing Operational and Closure-Phase Impacts from Mining on Surface Water Resources

Charles Wisdom, PhD, Geosyntec Consultants
Felix Kristanovich, PhD, ENVIRON International Consultants
1) **Influences on water quality during mine life cycle**
   a) Direct discharges of elevated metal concentrations
   b) Modification of receiving environment through reduction in receiving environment DOC
2) **Importance of DOC in receiving environment**
3) **Modifying stream chemistry as a mine influenced water treatment approach**
4) **Proof of concept**
Influences on Water during Mine Life Cycle

- Direct discharges of elevated metal concentrations
- Modification of receiving environment through reduction in receiving environment dissolved organic carbon (DOC)
  - Loss of riparian buffer
  - Reduction in soil organic carbon pool
- The decrease in export of DOC to receiving streams and lakes from the conversion and development of mine sites can result in
  - Enhanced pollutant sensitivity
  - Reduced stream productivity
Loss of Riparian Vegetation

- Decreases litter fall, reduces carbon input to streams and lakes
- Decreases soil organic carbon pool
- Increases insolation, UV exposure
- Average of 90% of Stream DOC from Terrestrial Sources
- Average of 10-15% of Lake DOC from Terrestrial Sources
- Can shift streams and lakes from heterotrophy (carbon import) to autotrophy (algal productivity)
Water Quality through the Mine Life Cycle

Mine Life Cycle Components

- Design
- Construction
- Operation
- Closure
- Reclamation

Changes in Receiving water

- Mine operations / land use changes can reduce dissolved organic carbon (DOC) export to receiving streams, enhancing metal sensitivity and reducing stream productivity.
- Reclamation/riparian restoration can increase DOC exports to receiving waters.
Metal Bioavailability and the Biotic Ligand Model

- Bioavailability Critical Concept in Determining Toxicity of Divalent Metals
- Biotic Ligand Model
  - EPA “Best Available Science”
  - Leading scientific basis for aquatic metals toxicity
- BLM Available for Cu, Cd, Ag, Zn (Freshwater), Pb
- EPA Ag BLM Criterion and Saltwater Cu Criterion
Biotic Ligand Model

- Competing Cations
  - Ca$^{2+}$
  - Na$^{+}$
  - H$^{+}$

- Site of Action
- Inorganic Ligand Complexation
  - MOH$^{+}$
  - MHCO$_3$$^+$
  - MCl$^+$

- Organic Matter Complexation
  - M-DOC

- Free Metal Ion
  - M$^{2+}$

- M-Biotic Ligand
Non-Bioavailable and Bioavailable Copper

Dissolved Copper = Non-bioavailable + Bioavailable Fractions

Particulate Copper, non-bioavailable

DOC Bound Copper, non-bioavailable

Free Copper, bioavailable to fish

Total Recoverable Copper = Non-bioavailable + Bioavailable Fractions
Managing DOC in Mine Influenced Waters

- Use the BLM to predict the bioavailability and toxicity of metals (e.g., copper, cadmium, lead, silver, and zinc)
- Augment DOC to set cost-effective treatment goals protective of beneficial uses of streams and lakes.
- Integrate DOC management into mine reclamation activities such as erosion control and re-vegetation to
  - Preserve water quality,
  - Minimize environmental effects, and
  - Reduce overall closure costs
Treating Metals by Modifying Receiving Environment Chemistry

- Metal Toxicity is Determined by
  - Speciation
  - Bioavailability

- Bioavailability is Determined by
  - Alternative binding sites (ligands) in aquatic environment

- Reduce Bioavailability by Augmenting DOC
  - Riparian restoration
  - Soil carbon amendments
The basic approach includes:

- Establishing natural levels of DOC to establish existing deficit
- Developing short-term DOC additions approaches such as litter/compost addition either in riparian areas (soil organic carbon pool) or directly into streams
- Developing long-term DOC additions through riparian restoration to re-establish soil organic carbon pool
- Establishing appropriate treatment targets based on receiving water toxicity limits
- **GOAL** – Establish feasibility of DOC Augmentation

- **Questions:**
  - How much compost do you have to add to actually raise receiving water DOC 1 mg/L?
  - How much would this cost?
  - How often would you have to amend the riparian zone?
Proof-of-concept Case Study

- Predictive model to
  - Estimate bulk carbon application rates
  - Soil organic matter pool formation
  - DOC soil export rates
- Assessed treatment targets for a variety of receiving water conditions in six western states
  - pH
  - Temperature
  - Hardness
  - Cations
  - Anions
BLM Parameters

- pH
- DOC
- Calcium
- Magnesium
- Sodium

- Potassium
- Sulfate
- Chloride
- Alkalinity

Laboratory Costs

- $125-$173 per BLM suite
## Average BLM Parameters for 6 Western States

<table>
<thead>
<tr>
<th>State</th>
<th>Temp (°C)</th>
<th>pH</th>
<th>Ca (mg/L)</th>
<th>Mg (mg/L)</th>
<th>Na (mg/L)</th>
<th>K  (mg/L)</th>
<th>SO₄ (mg/L)</th>
<th>Cl  (mg/L)</th>
<th>Alkalinity (mg/L)</th>
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<td>2.6</td>
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<td>OR</td>
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<td>7.4</td>
<td>12.1</td>
<td>4.1</td>
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<td>13.0</td>
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From USGS NAWQA Database
## DOC Levels in Six Western States

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<thead>
<tr>
<th></th>
<th>Mean</th>
<th>Max</th>
<th>Min</th>
<th>StDev</th>
<th>n</th>
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<td>Alaska</td>
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</table>

From USGS NAWQA Database
Proof of Concept
Modeled Receiving Stream

1,000 m
6 m
3.4 m

Compost amended buffer strips

100 cfs
Riparian Amendment

- Two buffer strips on each side of the target stream
  - Width 10 meters each side (20 meters total)
  - Length 1,000 meters
  - Depth 20 centimeters
  - Total 5 acres amended

- Carbon mineralization rate - 0.41 mg C/ g C day (Ahn et al. 2009)

- 200,000 pounds of organic matter/acre per 1% increase in stable organic matter (USDA NRSC)
<table>
<thead>
<tr>
<th>DOC Level (mg/L)</th>
<th>Percent of TOC of Soil</th>
<th>Tons of Organic Matter to add to 5 acres</th>
<th>Cost of Compost/Acre</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 mg/L</td>
<td>7.8%</td>
<td>3,898</td>
<td>$27,287</td>
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<tr>
<td>4 mg/L</td>
<td>15.6%</td>
<td>7,796</td>
<td>$54,575</td>
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<td>6 mg/L</td>
<td>23.4%</td>
<td>11,695</td>
<td>$81,862</td>
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<td>8 mg/L</td>
<td>31.2%</td>
<td>15,593</td>
<td>$109,149</td>
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<td>10 mg/L</td>
<td>39.0%</td>
<td>19,491</td>
<td>$136,437</td>
</tr>
</tbody>
</table>

Assuming the carbon source is 20% -50% recalcitrant, this would represent 3.5 - 5.5 years of carbon supply.
Influence of DOC on Copper LC50

For every 1 mg/L increase in DOC levels in receiving environment, on average, there is a 78 µg/L increase in the FHM Cu LC50.
For every 1 mg/L increase in DOC levels in receiving environment, on average, there is a 68 µg/L increase in the FHM Zn LC50.
For every 1 mg/L increase in DOC levels in receiving environment, on average, there is a 2 µg/L increase in the FHM Cd LC50.
Augmenting stream and lake DOC can be an element of an integrated treatment approach for mine runoff, process water discharges, and industrial stormwater.

DOC augmentation offers a comprehensive way to:

- Develop cost-effective approach to treatment goals and effluent limits
- Establish off-site mitigation strategies for mine and metal fabrication operations
- Integrate closure restoration efforts with water quality management
- Enhance habitat restoration valuation
- Create water quality trading credits
Restoring DOC inputs through direct augmentation and riparian restoration after establishing DOC targets through use of the Biotic Ligand Model (BLM) is a promising tool for mitigating mine operational effects and setting mine closure goals and conditions.

Needs and Next Steps

- Widespread adoption and implementation of BLM-based water quality criteria in Canada, the US, and the EU
- Conduct a field pilot study at an existing mine site
Interaction of pH and DOC on FHM Cu LC50

Changes in FHM Cu LC50 with Changes in Receiving Water pH

Dissolved Organic Carbon, mg/L

Copper LC50, ug/L

pH 4
pH 5
pH 6
pH 7
pH 8