Fluctuating Redox Conditions and Phosphorus Competition: Contributors to Arsenic Release from Wetland Tailings in Cobalt, Ontario

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Ottawa, ON
Cobalt mining camp, Ontario, Canada

- Largest Ag producer in Canada: 1904-1989
- 18 mills
- >14,000 t Ag
Legacy of > 80-yr of silver mining

- Native Ag occurred in veins with arsenides, sulfarsenides and minor sulfides
- Tailings with 0.34 - 1.50% As, discharged in or adjacent to watercourses near the mills
- Widespread contamination of watercourses by As – Percival et al. 1996
Tailings:
- As: ~1300 mg kg⁻¹
- pH 7.4

Farr Creek
- As: 0.29 mg L⁻¹
- P: 0.14 mg L⁻¹

Mill Creek
- As: 0.54 mg L⁻¹
- P: 0.25 mg L⁻¹

Field Study May 2002
Objective

- Determine the impact of the two following factors on As mobilization in wetland tailings
  - Changes in redox conditions
  - Competitive interaction between P and As
I. As and P in submerged tailings: Some field observations
May 2002: Stream Sediments (submerged tailings), confluence of Farr and Mill Creeks
Methodology

- Field deployment of anionic exchange membranes
- Chemical extraction (oxalate, water, total)
- Saturation Index:

\[
\frac{P_{o_x}}{A{I_{o_x}}+F{e_{o_x}}} \times 100
\]

\[
\frac{A{s_{o_x}}}{A{I_{o_x}}+F{e_{o_x}}} \times 100
\]
Solubility Pools of As and P in the Surface Layer of Stream Sediments, May 2002 (mean of 2 stations)

<table>
<thead>
<tr>
<th></th>
<th>As Resin ug/cm²/d</th>
<th>P Resin ug/cm²/d</th>
<th>As Saturation index %</th>
<th>P Saturation index %</th>
<th>As total mmol kg⁻¹</th>
<th>P total mmol kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Farr Ck u/s</td>
<td>0.59</td>
<td>0.07</td>
<td>1.6</td>
<td>6.0</td>
<td>4.9</td>
<td>18.1</td>
</tr>
<tr>
<td>Mill Ck</td>
<td>0.83</td>
<td>0.30</td>
<td>2.3</td>
<td>7.6</td>
<td>7.5</td>
<td>19.1</td>
</tr>
<tr>
<td>Farr Ck d/s</td>
<td>1.16</td>
<td>0.16</td>
<td>1.9</td>
<td>7.2</td>
<td>10.7</td>
<td>19.6</td>
</tr>
</tbody>
</table>
II. As and P in tailings: Impact of redox conditions
Tailings Mineralogy
(Kwong et al. 2007)

• Main constituents: quartz, feldspars, chlorite with subordinate calcite and dolomite

• Prominent primary As-species: As(-1)
  – cobaltite [(Co,Fe,Ni)AsS],
  – safflorite [(Co,Fe,Ni)As₂]
  – minor arsenopyrite [FeAsS]

• Secondary arsenates:
  – erythrite [Co₃(AsO₄)₂.8H₂O]
  – minor annabergite [Ni₃(AsO₄)₂.8H₂O]
  – scorodite [FeAsO₄.2H₂O]

• Adsorbed species?
**Approach**

- **Incubation**
  - 30-day reduction
  - reoxidation (air-drying)

- **Sediment / solution ratio of 1:10**
  - 10 mM KCl
  - 23°C, dark

- **2 profiles:**
  - Farr #3
  - Mill #12

- **3 depths/profile**
  - Surface 0 – 12 cm
  - Mid-layer 12-25 cm ± glucose
  - Bottom 25 – 50 cm
Experimental design & monitoring

- Randomized complete block design
  - Destructive sampling
  - 5 batches, 2 replicates/batch
- Reduction Day 0, 7, 14, 30
  - Eh, pH
  - Metal concentrations in solution
- Change in As speciation
  - Day 0, 30, reox
  - X18B, NSLS, BNL
Dissolution of As and P during the 30-d reduction
(Mill Creek, mid-layer)

+ Glu: Δ pH -1.2
No Glu: Δ pH -0.2
As K-XANES spectra for the mid-layer sediment (Mill) subjected to 30-d reduction followed by reoxidation

Beauchemin and Kwong 2006

E₀ = 11867 eV
P and As saturation indices as affected by change of redox conditions (Mill Creek)

\[
P_{ox} / (Al_{ox} + Fe_{ox}) \cdot 100
\]

\[
As_{ox} / (Al_{ox} + Fe_{ox}) \cdot 100
\]
Impact of P inputs on As desorption

- tailings suspension:
  - 10 mM KCl, 1:150 (w/w)
- 0, 75 to 1200 mmol P kg\(^{-1}\) tailings
- pH 8, 42 hrs, 22\(^{\circ}\)C
Impact of P inputs to the Mill Creek tailings on dissolved As (pH 8, 42 hrs)
In summary

I. Variations in redox conditions: changes in arsenic speciation readily occur in the solid phase => 30-d reduction led to rapid remobilization of arsenic into the aqueous phase

- Without soluble C input:
  - As(III) formed in the solid phase
  - dissolved P increased

- Input of soluble C
  - As(-1) formed in the solid phase
  - P is apparently being consumed

II. P competitive interaction:

- P has a higher affinity than As for the sorbing phases in the tailings
Implications for the Cobalt wetlands

- The fluctuation of flooding/drying periods in the wetlands likely enhances the release of As from sediments to water.
- Soluble C rather than P would be the limiting factor for microbial reduction of As.
- P sorbs more strongly on the substrate than As. Elevated dissolved P can thus exacerbate the mobilization of As.
- Prolonged flooding periods and the presence of sufficient soluble C could stimulate microbial reduction and favour the stabilization of As in the form of As(-1) species. Increased microbial activity might help in turn to maintain lower level of dissolved P.
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