Case Studies of Arsenic Mobilization Related to Landfills and Superfund Sites

• Multi-group presentation
  – Columbia University SBRP and NYSDEC Region 3
  – Boston College and USEPA Region 1
  – Dartmouth College SBRP

• Steven Chillrud, Rudi Hon, Ben Bostick and their many colleagues
Arsenic in plumes of old landfills - analog for what may happen in landfill
Implications for landfill leachates

• Arsenic mobilization coupled to iron mobil.
• Mobilization tied to organic carbon sources in landfill wastes
• Regional variations of As levels in natural soils can lead to variations in gw [As], if Fe
Causes of Arsenic Contamination

• Entirely natural:
  – Arsenic in solid phase released to waters

• Entirely anthropogenic:
  – Human activities release As and contaminate soil and groundwater

• Anthropogenically induced mobilization of naturally-occurring-Arsenic:
  – Changes to groundwater chemistry allow natural As to be released from sediment to groundwater (coupling of Fe and As)

• Combination of above
Arsenic Mobilization—Geochemical Explanation

[Diagram showing the relationship between Eh (volts), ORP (mV), pH, and various arsenic species: Fe^{3+} (aq), Fe^{2+} (aq), H_3AsO_4, H_2AsO_4^-, H_3AsO_3 (aq), H_2AsO_3^-, HAsO_4^{2-}, AsO_4^{3-}, and iron oxides (s).]

[Note: The diagram illustrates how changes in Eh, ORP, and pH affect the mobilization of arsenic species.]
Arsenic & Iron vs ORP – GW Near Landfills
Central Massachusetts
Redox zonation of landfills

Baedecker & Back 1979;
Danish landfills T.H. Christensen and colleagues (mid 1990s -

(from Heron et al. 1995)
Coakley: Batch Experiments and Field Data
Coakley: Arsenic Mobilization &
Natural Attenuation

$30\text{Fe(OH)}_3 + C_6\text{H}_6 + 60\text{H}^+ \Rightarrow 30\text{Fe}^{2+} + 6\text{CO}_2 + 78\text{H}_2\text{O} \ \Delta G^o = -2359.96 \text{ kJ}$
Arsenic in Ground Water

Arsenic (ug/L) vs. dissolved inorganic carbon ppm C

Graph showing the relationship between arsenic concentration and dissolved inorganic carbon concentration.
Organic Compounds Mobilize Arsenic

Superfund Sites: Arsenic and Benzene/VOC (DOC) Sites are Highly Correlated

- **Northeast**
  - 42 of 45 As contaminated sites are contaminated with either Benzene or VOC

- **National**
  - 419/555 As sites also have aromatic hydrocarbon contamination
  - That is roughly twice the random probability
Winthrop Contamination & Remediation

1930: Dump operation begin including industrial waste
1972: Landfilling begins and serves adjacent towns
1979: Buried drums found
1982: Landfilling ceases
1987: Clay cap installed
(Capping ≠ help As)
1995: SVE and P&T remediation starts
2004: Rebound experiment begins
# Reduction Induced by Leachate

<table>
<thead>
<tr>
<th>Sed As mg kg⁻¹</th>
<th>Dissolved Species mean, mg L⁻¹</th>
<th>Cl⁻</th>
<th>DOC</th>
<th>Sulfide</th>
<th>Fe²⁺</th>
<th>Iron</th>
<th>COD</th>
<th>Water As</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 ± 1</td>
<td>Central Region</td>
<td>29 ± 6</td>
<td>26 ± 14</td>
<td>53 ± 49</td>
<td>24 ± 15</td>
<td>37 ± 9</td>
<td>35 ± 23</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td>8 ± 2</td>
<td>Upgradient Region</td>
<td>10 ± 2</td>
<td>16 ± 4</td>
<td>5 ± 2</td>
<td>2 ± 4</td>
<td>2 ± 4</td>
<td>1 ± 0</td>
<td>0.01 ± 0.005</td>
</tr>
</tbody>
</table>

![Direction of Flow](image1.png)

Winthrop As mobilization
• Al Turi Landfill- 129 Acres
  • Sections range from unlined (older) to single layer, to modern double lining
  • Leachate well characterized
  • Monitoring wells in overburden (below waste)

NYSDEC, unpublished data
Freshkills Landfill  
Staten Island, NY

Leachate monitoring wells  
(screened in waste)

Cl is conservative tracer of  
leachate strength and mixing

Sources for Fe  
acid solubilization  
redox mobilization

Sinks for Fe, Mn  
sulfide formation  
carbonate precipitation  
ion exchange  

Data from Walsh 1996
As Immobilization via Reduction
Arsenic remediation via reduction?

Aqueous Phase

[Graph showing the changes in acetate, alkalinity, manganese (Mn), and iron (Fe) over time, with specific data points highlighted.]
Arsenic in Ground Water (ppb) at SH Landfill
November 2004

Legend

ARSENIC

- 2.1 - 7.5
- 7.6 - 17.0
- 17.1 - 36.0
- 36.1 - 130.0
- 130.1 - 330.0
- 330.1 - 540.0
- 540.1 - 650.0
- 650.1 - 1600.0

Arsenic = non-detect
Frequency of Arsenic Levels in Soils

CENTRAL MASSACHUSETTS

Database: 510 samples
Nickel vs Arsenic in Soils -- Devens

Soil Background -- Devens

\[ y = 1.0215x \]

\[ R^2 = 0.666 \]
Arsenic in Bottom Sediments mg/Kg

Landfill
Grove Pond Bottom Sediments

Nickel in Grove Pond Bottom Sediments

\[ y = 0.6965x - 7.9309 \]

\[ R^2 = 0.8074 \]
Iron Flocs as integrating triage tool

• Seeps near old landfills easy to locate (color)
• Relatively easy to collect and analyze (compared to installing wells)

5 µm pore size absorbant pad for thin films
### CLINTON LANDFILL DATA

South Meadows Pond Seep Samples

#### Clinton Sampling Points

<table>
<thead>
<tr>
<th>Site</th>
<th>Unfiltered Total Arsenic</th>
<th>Unfiltered Total Iron</th>
<th>Unfiltered Total Manganese</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seep 1</td>
<td>600 µg/L</td>
<td>75,000 µg/L</td>
<td>8,200 µg/L</td>
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<tr>
<td>Seep 2</td>
<td>71 µg/L</td>
<td>30,000 µg/L</td>
<td>1,700 µg/L</td>
</tr>
<tr>
<td>Seep 3</td>
<td>4,100 µg/L</td>
<td>120,000 µg/L</td>
<td>6,700 µg/L</td>
</tr>
<tr>
<td>Monitoring Well</td>
<td>Dissolved As</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW6</td>
<td>429 µg/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW7</td>
<td>427 µg/L</td>
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</tr>
<tr>
<td>MW5</td>
<td>1209 µg/L</td>
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Adopted from http://www.state.ma.us/mgis

- Seep collection points
- Monitoring Wells
~150 old landfills in Region 3 (2M people) => thousands nationwide

NYSDEC Region 3 landfill locations (open stars) 47 of ~150 inactive landfills are shown with census track population densities. Seven landfill sites (filled stars) have been sampled for Fe floc chemistry by state personnel and Columbia SBRP researches in 2004-2005.
Implications for iron residuals

• Field and laboratory data consistent with
  – widespread impacts of landfill organics on Fe, Mn, As
  – groundwater [As] range from 10s to 1000s of µg/L
    higher levels in Central MA w/ higher soil [As]
  – publications that indicate TCLP not an appropriate
    test for Arsenic leachability for arsenic bearing iron
    residuals
  – Predict large mobilization of As from ABRs, will
    this lead to high [As]?
  – sulfide and carbonate precipitation, limiting
    dissolved [As]?; complicated by thioarsenites
Implications (continued)

- Any liner failures could result in future assessments needing to separate out two sources (leachate As & induced mobilization of As)

- As toxicity to methanogens @ As(III) > 300 ppb?
  - Spatial separation of methanogenesis and iron mobilization suggests that field data from Central MA monitoring wells (not in waste) not necessarily applicable to laboratory results of As toxicity of methanogens at As > 300 ppb
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The End