14. Fate and Transport of Arsenic in Contaminant Plumes
Arsenic at the Saco Landfill, Saco, ME

The Saco Landfill was operated from the early 1960s to 1989 and consists of three separate landfill areas 1, 2, and 4.
Geohydrologic section line A-A’ for Area 4. Green arrows indicate modeled flow path of arsenic concentrations.

Average ground-water velocity in the aquifer is 0.2 m/d.

Unconsolidated units include glaciomarine fine sands not in contact with bedrock, sand and gravel, and till deposits, consisting of an upper and a lower unit, over a fine-grained calcareous quartz-muscovite phyllite bedrock.

Calcareous quartz-muscovite phyllite
Landfill Areas 1 and 2 are located on the east side of Sandy Brook and have been capped since 1976 and 1989.

Natural arsenic concentrations in the bedrock and sediments beneath areas 1 and 2 are relatively low (3.0 – 6.9 mg/kg) and the average arsenic concentration in leachate-contaminated ground water is 21 μg/L (range <3.0 – 50 μg/L).

Arsenic concentrations in uncontaminated ground water up-gradient from the landfill areas range from <3.0 – 28 μg/L.
- **Landfill Area 4** is on the west side of Sandy Brook and has been inactive since 1989; it was covered with an impermeable membrane in 1998.

- The geology of Area 4 is distinctly different from areas 1 and 2; the bedrock and sediments contain greater concentrations of naturally occurring arsenic (6.8 – 51.0 mg/kg).

- Leachate from the Area 4 landfill has contaminated surficial alluvium and the upper part of the bedrock aquifer.
- Organic carbon from the landfill has caused reducing conditions as indicated by low concentrations of DO and high concentrations of DOC, Fe, Mn, NH$_3$.
- High concentrations of dissolved Fe and Mn indicate that reduction (and dissolution) of the oxyhydroxide phases of these elements by organic carbon dominate the redox potential in contaminated areas of the aquifer.
- The average arsenic concentration in area 4 leachate plume is 326 $\mu$g/L (range 52 – 647 $\mu$g/L).
- About 80 percent of the dissolved arsenic in contaminated groundwater was As(III), the remainder was As(V).
Concentrations of dissolved iron and arsenic measured in ground water contaminated by Area 4 landfill leachate

Note the correlation between increasing concentrations of dissolved iron and arsenic in the Area 4 leachate plume due to reducing conditions.
- Long-term leachate migration from the landfill has resulted in a large reservoir of organic carbon sorbed on the aquifer sediment, resulting in significant biological oxygen demand.

- As uncontaminated ground water moved through the contaminated cores, organic carbon was released from the solid phase to solution, consuming all dissolved oxygen. As a result, reducing conditions within the core were maintained, continuing the desorption processes and dissolution of hydrous ferric oxides.

- Lab experiments show this reservoir of organic carbon causes complete consumption of the influent oxygen (at 6 mg/L) for more than 200 pore volumes.
Iron decreased from 50 mg/L to 5 mg/L as iron-free uncontaminated ground water displaced the contaminated pore water. Iron then stabilized at 3 mg/L, indicating equilibrium between DOC and hydrous ferric oxide dissolution.

Experimental and modeled ferrous iron [Fe(II)] in leachate from one core
Arsenic rapidly decreased from 380 μg/L in the initial pore water to 50 μg/L by pore volume 15. Dissolution of hydrous ferric oxides and release of associated arsenic maintained arsenic concentrations at greater than 10 μg/L until conditions in the core became oxic.
Model simulated arsenic along a flow path over time after capping of the landfill. (300 m is at Sandy Brook)

Modeling shows arsenic at Sandy Brook could increase as higher concentrations migrate through the aquifer, and then gradually decrease as uncontaminated ground water moves through the aquifer. **Sixty years may be needed for As to reach sub-MCL levels.**
Summary and Conclusions

- USGS studies on the geochemistry and mineralogy of the leachate-contaminated aquifer at the Saco Area 4 landfill have shown that the source of arsenic is not the landfill itself but the sediments the leachate is moving through.

- Much of the arsenic is present adsorbed on and in hydrous ferric oxides that coat the aquifer sediments.

- The arsenic in these hydrous ferric oxides may have gradually accumulated over time as a result of adsorption of low concentrations of arsenic that occur naturally in the ground water of this area.
Summary and Conclusions contd.

- Lab experiments show that dissolved organic carbon in the leachate plume is promoting reductive dissolution of hydrous ferric oxides, releasing absorbed arsenic to ground water.

- Reductive dissolution occurs because the degradation of the DOC in the plume removes oxygen and creates reducing conditions that favor the dissolution of hydrous ferric oxides and release of arsenic from the sediments.

- Predictions of arsenic fate and transport indicate that over 60 years may be needed for arsenic to decrease to drinking-water standards after the landfill is capped.
Coakley Landfill Superfund Site (NH), is a site contaminated with As, Cr, Pb, Ni, Zn, and aromatic hydrocarbons located in SE NH. Long-term field observations indicate that the concentrations of most of these contaminants have diminished as a result of treatment by monitored natural attenuation begun in 1998; however, dissolved arsenic levels increased modestly over the same interval.
Location and subsurface geology of the Coakley Superfund site (outlined in yellow) in New Hampshire.
Following landfill capping in 1998, concentrations of Cr, Ni, Pb, and Zn declined significantly, while **arsenic levels increased modestly**

**TABLE 1. Pre- and Post-Cap Average Contaminant Concentrations**

<table>
<thead>
<tr>
<th>location</th>
<th>contaminant</th>
<th>pre-cap mean</th>
<th>post-cap mean</th>
<th>change</th>
</tr>
</thead>
<tbody>
<tr>
<td>overburden</td>
<td>As</td>
<td>16.2</td>
<td>43.7</td>
<td>+169%</td>
</tr>
<tr>
<td>bedrock</td>
<td>As</td>
<td>10.7</td>
<td>9.5</td>
<td>-11%</td>
</tr>
<tr>
<td>all</td>
<td>As</td>
<td>13.8</td>
<td>21.9</td>
<td>+58%</td>
</tr>
<tr>
<td>overburden</td>
<td>benzene</td>
<td>10.9</td>
<td>2.6</td>
<td>-76%</td>
</tr>
<tr>
<td>bedrock</td>
<td>benzene</td>
<td>8.6</td>
<td>4.7</td>
<td>-46%</td>
</tr>
<tr>
<td>all</td>
<td>benzene</td>
<td>10.3</td>
<td>3.6</td>
<td>-65%</td>
</tr>
<tr>
<td>all</td>
<td>Mn</td>
<td>3160</td>
<td>107</td>
<td>-97%</td>
</tr>
<tr>
<td>all</td>
<td>Ni</td>
<td>2.5</td>
<td>&lt;0.04</td>
<td>-99.8%</td>
</tr>
<tr>
<td>all</td>
<td>Cr</td>
<td>1.3</td>
<td>&lt;0.04</td>
<td>-99.9%</td>
</tr>
<tr>
<td>all</td>
<td>Zn</td>
<td>2.2</td>
<td>0.2</td>
<td>-92%</td>
</tr>
<tr>
<td>all</td>
<td>Pb</td>
<td>25</td>
<td>4</td>
<td>-84%</td>
</tr>
</tbody>
</table>
As release with Eh changes in batch lab experiments.

Observed As changes relative to Benzene Changes.
Pre-landfill conditions indicated $\text{Fe}^{3+}$ stability. Existing conditions are indicative of $\text{Fe}^{2+}$ stability with significant As Conc.
FIGURE 5. Correlation between dissolved total As and Fe concentrations after cap construction. Arsenic concentrations generally correlate with iron concentrations until siderite solubility limits Fe levels, as indicated by shaded region.
Conclusions
- Field evidence indicates active reduction of arsenic-bearing iron hydroxide occurs at Coakley Landfill.
- Current arsenic contaminated groundwater at Coakley exhibits more reduced potentials (0 to -200 mV) within the dissolved Fe$^{2+}$ stability field, indicative of iron-reducing conditions.
- Dissolved arsenic and iron concentrations are correlated at lower concentrations, but the relationship breaks down at higher dissolved iron concentrations (Figure 5).
- The iron levels are limited by siderite solubility when the iron concentration is above about 14 mg/L; dissolved iron levels are broadly in equilibrium with siderite given the near neutral pH (6) and measured alkalinity (at least 200 mg/kg CaCO$_3$) of contaminated groundwater at the Coakley site.
Arsenic Cycling in Hydrocarbon Plumes: Secondary Effects of Natural Attenuation by Isabelle M. Cozzarelli, et. al., 2016

Study area map showing approximate extent of subsurface oil, BTEX plume, locations of redox zones, and wells and core sites.
Hydrogeologic section along the plume centerline (see location map); GW flow from left to right

Cozzarelli, 2016
Transects of groundwater concentrations for dissolved As, Fe, oxygen, and benzene (collected from 2009 to 2013), left edge mid-point in floating oil.

As 80-92% (III)
Fe 100% (II)
DO
Benzene

Cozzarelli, 2016
### Arsenic and Iron Sediment Concentrations

(Core 1319; see map for location)

<table>
<thead>
<tr>
<th>Elevation (m AMSL)</th>
<th>Near-Total Fe (mg/kg)</th>
<th>Near-Total As (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>423.7</td>
<td>7210 (1)</td>
<td>2.4 (1)</td>
</tr>
<tr>
<td>423.5</td>
<td>5504 (4)</td>
<td>1.3 (2)</td>
</tr>
<tr>
<td>423.1</td>
<td>3874 (5)</td>
<td>0.7 (5)</td>
</tr>
<tr>
<td>422.8</td>
<td>6800 (2)</td>
<td>1.2 (3)</td>
</tr>
<tr>
<td>422.5</td>
<td>5890 (3)</td>
<td>0.9 (4)</td>
</tr>
</tbody>
</table>

Data represent averages of triplicate digestions/analyses. Numbers in parentheses are ranking from highest to lowest.

Cozzarelli, 2016
A calculation of the maximum amount of As released to porewater can be made using the following assumptions: the As concentration in background aquifer sediment is 2.4mg/kg (μg/g), the aquifer sediment is predominantly made up of quartz, with a particle density of 2.65 g/cm³, and the aquifer has a porosity of 30%.

Thus, if all of the As from the background sediment was released to solution, the As concentration in groundwater would be 14,840 μg/L. The highest measured concentration in groundwater is 230 μg/L, which is 0.15% of the calculated maximum possible concentration.
Relationship between dissolved AsT (μg/L) and FeT (mg/L) concentrations in groundwater in 2013. Approximately 1 part As to 1,000 Fe
Time trend for (a) Dissolved Fe (mg/L) (b) dissolved As (μg/L) in three wells located in the Fe-reducing zone in 2009, 2012, and 2013.

See map and transect for location of wells.

Cozzarelli, 2016
Conclusions

1. Naturally occurring As is associated with Fe-hydroxides present in the glacially derived aquifer sediments at the Bemidji site;

2. Introduction of petroleum hydrocarbons shifts the aquifer redox environment due to the large influx of electron donor. This influx of carbon results in consumption of DO and, in the absence of DO, the reduction of As-bearing Fe-hydroxides;

3. Reduction of the As-bearing Fe-hydroxides releases dissolved FeT and AsT to groundwater;
In areas of enhanced reductive bioremediation (ERB) increased dissolved As concentrations were highly correlated with increasing Fe concentrations (p < 0.01), consistent with As release during reduction of Fe oxides and/or As removal during sorption/co-precipitation with Fe.

Tillotson and Borden, 2015
Footprints of dissolved As, dissolved OC, Eh, and dissolved Fe at a reductive dechlorination biostimulation site, Devens Reserve Forces Area, MA. Area of injection of the molasses solution and monitoring wells (solid dots) are indicated. GW flow rate ~0.34 m/d (~1.1 ft/d). (Hering et. al. 2009)
Summary

- The fate and transport of As in contamination plumes (e.g. landfills) is strongly influenced by redox conditions and the availability of various Terminal Electron Acceptors (TEAs).
- For many contaminant plumes the fate of As is tied to the fate of Fe.
- When iron oxi-hydroxides are reduced by low redox conditions produced by contaminant plume organic compound degradation (consuming all available DO and NO$_3$), then ferrous iron is released into solution, along with any co-absorbed As that may be associated with those minerals.
- If reducing conditions are strong enough, and sulfate is available, As may be immobilized as arsenic sulfides.
Summary

Attenuation of Metals via Precipitation, Redox Reactions, and Adsorption

USEPA, 2007a
Next:

Summary and Assessment