Monitored Natural Attenuation at a Municipal Solid Waste Landfill Near Sulphide Bearing Mine Tailings

Leslie Hardy, M.Sc., P.Eng.
Dean Wall, M.Sc., P.Eng.

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Introduction

- Case History
  - Five Year Hydrogeology Review
- Evaluation of Sub-Surface Conditions
  - Water level and temperature monitoring
  - Biogeochemical cycling
    - Biogenic gases
- Sampling and analytical limitations
  - Sulphide, arsenic, dissolved oxygen
Site Location and History

- Landfill operated by the Regional District
  - Municipal Solid Waste
  - Septage (1,000 m³/year)
  - Serves approximately 100,000 people
  - Started in 1983
  - First hydrogeology study in 1999

- Mine
  - Operated from 1912 to 1978
  - Pb, Zn, Ag, Cd, Au, and talc
  - 30 hectares (over 70 acres) of tailings
Oblique View of Site

- Tailings Pond and Dam
- Landfill
- Valley Bottom
- Tailings
- Septage
- Creek and Road
Hydrogeology

- Generally coarse grained sediments over bedrock
  - Up to 18 m of sand and gravel
  - Bedrock (phyllite, or metasediment)

- Depth to groundwater varies
  - Above ground surface (i.e. artesian well)
  - Maximum DTW of about 19 m below grade

- Previous interpretations assumed unfractured bedrock with all groundwater flow being through sand and gravel
Chloride

- Total ion concentrations in groundwater are low
- Minor amounts of chloride in groundwater

- Chloride is normally considered a conservative tracer
  - Moves at speed of groundwater flow and is unaffected by biological or chemical reactions
- Historically, contaminant hydrogeologists and landfill engineers have viewed this as an iron clad assumption
  
  No chloride = No leachate = No problem

- More recently, this assumption has been called into question
  - Landfill gas can affect groundwater without chloride
  - Korom and Seaman, When Conservative Anionic Tracers Aren’t, Groundwater, Nov/Dec 2012
Water Level Monitoring

- Monitor water level changes to evaluate potential hydraulic connections between monitoring wells
  - Barometric pumping
  - Like a groundwater pumping test
  - Easiest way to evaluate wells completed in fractured bedrock

- Data loggers measure:
  - Time
  - Temperature
  - Total Pressure
  - Manual DTW measurements to scale response to elevation
  - Compensate for fluctuations in barometric pressure
  - These graphs show about 40 days of data at 10 minute intervals
Data Logger Barometric Compensation

Difference in before and after manual readings versus barometrically compensated logger readings is considered indicative of a gas phase present in the groundwater.

Manual elevation measurement is used as the calibration point where Delta Baro is set to 0.00 m. Changes in barometric pressure from this point are subtracted from the total pressure reading from the Levelogger to determine the water elevation.

Note that normally the final manual elevation measurement will match the barometrically compensated water elevation. The fact that these readings don't match is indicative of the presence of a gas phase that is affecting water levels.
Change in Water Elevation - Overburden

Change in Groundwater Elevation - Overburden Wells

- MW-01-2004 (S)
- MW-01B-03
- 5-MW-2
- MW99-3(S)
- MW99-7D

Change in Elevation from Initial Calibration Point (m)

Change in Water Elevation - Bedrock

Change in Groundwater Elevation - Bedrock Wells

- MW-01-2004(D)
- MW-02-2004(D)
- MW99-2(S)
- MW99-3D
- MW99-1(D)

Change in Elevation from Initial Calibration Point (m)

Change in Water Elevation - Downgradient Bedrock Wells
Water Level Data

Large variation in water level responses.

Final manual DTW differed from barometrically compensated logger reading at most locations.

Two major storm events over this timeframe.

River elevation changes shown in lower right corner.

Horizontal grid 10 days. Vertical grid 0.25 m.
Summary of Water Level Observations

- Variety of water level responses
  - Logger readings calibrated to initial manual DTW reading
  - Difference between compensated logger reading and final DTW indicative of a separate gas phase below the water table
    - Dissolved gases don’t affect water levels
    - Presence of bubbles in an aquifer can affect water levels
      - Bubbles can form when total dissolved gas pressure exceeds confining pressure
- Storm events had large changes in barometric pressure
  - Drop in confining pressure resulted in discharge of gas from aquifer
  - Most wells were under suction when J-plug was removed
- Gas phase in groundwater is starting to be acknowledged as an issue that hydrogeologists have historically ignored
  - Groundwater, July/August 2013
    - Focus on the Deep Subsurface and Gas in Groundwater
Landfill Redox Zonation

Schematic illustration of redox zonation in soil gas and groundwater near a landfill. The pore scale close-up illustrates biogeochemical processes active in the saturated zone below the water table.


Redox zonation occurs in both groundwater and soil gas.
Landfill Gases (Biogenic Gases)

Gas Water Partitioning (Henry’s Law)

### Biogenic Gas

<table>
<thead>
<tr>
<th>Biogenic Gas</th>
<th>Henry's Law Constant L^*atm/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen Gas</td>
<td>N\textsubscript{2}</td>
</tr>
<tr>
<td>Methane</td>
<td>CH\textsubscript{4}</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O\textsubscript{2}</td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td>NO\textsubscript{2}</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>CO\textsubscript{2}</td>
</tr>
<tr>
<td>Hydrogen Sulphide</td>
<td>H\textsubscript{2}S</td>
</tr>
</tbody>
</table>

- Formation of N\textsubscript{2} creates high gas partial pressures
- Gas bubbles can form when total gas pressure > confining pressure
- Separate gas phase contributes to total pressure in aquifer
Artesian conditions (i.e. water level above ground surface) due to combination of physical setting and gas pressure.
Artesian Well

Bedrock Wells MW99-2(D) and MW99-2(S)

Note how rapid pressure changes in the deep well correspond to peaks and troughs in pressure in the shallower well. These results are indicative of a gas phase present at the deep well screen (screened at 20.5 to 23.5 m below grade), and the release of gas to the atmosphere near the shallow well screen (screened at 2.3 to 3.9 m below grade in bedrock).
Dissolved Oxygen Readings

Equilibrium concentration with air for dissolved oxygen in freshwater at 700 m elevation at 10°C is 10.6 mg/L.
Temperature

Groundwater temperature is typically average ambient temperature

Wells downgradient of tailings increased by up to 3 degrees

Sulphide oxidation?
Sulphide and Arsenic

- **Dissolved metals**
  - Acidify with Nitric Acid
- When sulphide is present in water, most metals will precipitate at neutral pH as metal sulphides
  - Not arsenic
- Arsenic can precipitate from solution when nitric acid is added to sulphide rich water (Smieja & Wilkin, 2003)
- Collect and analyze unacidified metals samples to determine in-situ arsenic concentration when sulphide is present

**Table 1** Final dissolved arsenic and sulfide concentrations (ppm) after treatment with HNO₃

<table>
<thead>
<tr>
<th>H₂S</th>
<th>As(III)</th>
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</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.358 ± 0.011</td>
<td>0</td>
<td>1.94 ± 0.03</td>
<td>0</td>
<td>10.06 ± 0.02</td>
</tr>
<tr>
<td>0.28 ± 0.21</td>
<td>0.348 ± 0.010</td>
<td>0.50 ± 0.01</td>
<td>1.78 ± 0.01</td>
<td>0.23 ± 0.01</td>
<td>7.05 ± 0.04</td>
</tr>
<tr>
<td>1.18 ± 0.09</td>
<td>0.299 ± 0.002</td>
<td>1.04 ± 0.07</td>
<td>0.70 ± 0.03</td>
<td>0.33 ± 0.13</td>
<td>3.70 ± 0.05</td>
</tr>
<tr>
<td>2.52 ± 0.03</td>
<td>0.145 ± 0.006</td>
<td>3.1 ± 0.23</td>
<td>0.140 ± 0.004</td>
<td>2.20 ± 0.15</td>
<td>0.28 ± 0.02</td>
</tr>
<tr>
<td>4.67 ± 0.00</td>
<td>0.027 ± 0.001</td>
<td>6.44 ± 0.07</td>
<td>0.063 ± 0.006</td>
<td>9.09 ± 0.33</td>
<td>0.093 ± 0.005</td>
</tr>
<tr>
<td>10.74 ± 0.08</td>
<td>0.011 ± 0.001</td>
<td>13.00 ± 0.38</td>
<td>0.051 ± 0.016</td>
<td>17.45 ± 0.18</td>
<td>0.073 ± 0.002</td>
</tr>
</tbody>
</table>

The reported uncertainty is one standard deviation of replicate measurements. aInitial As(III) concentration = 0.35 ppm. bInitial As(III) concentration = 2.0 ppm. cInitial As(III) concentration = 10.0 ppm.
Follow Up Sampling Interpretation

- No sulphide present
  - Consistent with presence of dissolved oxygen
  - Reported arsenic results are correct
- Why did the temperature downgradient of tailings increase?
  - Exothermic chemical reaction
  - Organic acids present
    - Comparing Total Alkalinity versus Total Inorganic Carbon and Total Organic Carbon
- Possibly due to Serpentinization of bedrock
  - Low temperature, low pressure (retrograde metamorphosis)
- Could explain temperature increase and large extent of gas phase noted during water level monitoring
- Serpentinization as the explanation is just a hypothesis
Conclusions

- Landfills should be evaluated on more than just chloride and a few other indicator parameters
  - Landfill Gas
  - Landfill Leachate
- Water level monitoring is an effective way to evaluate hydraulic connections between wells
  - Barometric pumping
  - Better understanding of aquifer and flowpaths
- Presence of a gas phase can be identified using water levels in some situations
  - Biogenic gases
- Temperature increase is not due to sulphide oxidation
  - Possibly a regional scale metamorphic process