ACKNOWLEDGMENTS

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- Challenges with Conventional PAH Sampling and Analysis
- Site Case Study
- Objectives and Experimental Design
- Results
- Next Steps
Problem Statement:

- Most environmental standards for groundwater are based on “dissolved” analyte concentrations.
- Conventional analytical methods do not measure freely dissolved concentrations because of the difficulty in partitioning or removing the solids from groundwater samples without impacting the integrity of the data.
- Difficult to obtain samples without sediment.
- Varying sediment levels can lead to scattered data (i.e., Waterra vs. peristaltic pump).
- Lead to biased high results and an overestimation of risk.
Test Site:

- Peterborough, Ontario
- Operated as a coal gas manufacturing facility, carburetted gas plant and propane facility from the 1860's to mid-1950s
- Adjacent to the Otonabee River
- Current use:
  - Provincial Courthouse;
  - Parking lot;
  - Electrical transformer station; and
  - Park
Existing and Historical Monitoring

- Environmental data available since mid 1980's
- Environmental impacts include soil and groundwater contamination with PAHs and PHCs
- LNAPL and DNAPL are present on the site and adjacent properties
- Discharge of LNAPL to the Otonabee River has been observed
- DNAPL extends partially below river
Current activities:
• Develop remediation objectives and a remedial action plan for the site and adjacent properties (Dillon, 2011)
• Investigation includes:
  – Soil, groundwater, surface water and soil vapour sampling
  – Delineation of LNAPL and DNAPL using Laser Induced Fluorescence technology
  – Development of remediation objectives for the site through risk assessment
  – Review of potential remedial options and selection of preferred option, including conceptual design
Polyethylene Membrane Devices (PMDs) have been used in recent studies to determine dissolved PAH, PCB and other hydrophobic organic compounds in surface water (Booji et.al. 2003; Adams et.al. 2007; Fernandez et. al. 2008; Hale et. al. 2010; Lohmann et.al. 2011;)

PMDs used as the sampling technology to conclude in the “Schindler Report” Oil Sands Development Contributes Polycyclic Aromatic Compounds to the Athabasca River and its Tributaries, 2009

PE sampling for groundwater has not been validated

Other passive samplers include Polyoxymethylene (POM), Passive Diffusion Bags (PDBs) and Semi-permeable Membrane Devices (SPMDs)
Principles of Passive Sampling

- PAHs will adsorb onto the polyethylene from the dissolved phase until equilibrium is achieved with dissolved concentration in GW
- PAHs bound to particulate or with organic matter will stay fixed
- After exposure, analysis of PE is completed by solvent extraction, GC/MS (results in ug PAH/g of PE)
- Published PE/water partition coefficients are used to quantify results in ug/L
Passive Diffusion Bags vs PE Samplers

**PDBs**
- Used for VOCs
- Filled with organic free water
- Principle of the technology is that VOCs will diffuse across PE membrane and “contaminate” the water in the PDB
- Deployed for ~ 2 weeks to reach equilibrium

**PE Samplers**
- Used for SVOCs
- Are not filled with water
- Principle of the technology is that SVOCs will adsorb to the PE
Sampling Media

- Strips of low density polyethylene cut from commercial sheeting with a thickness of 51 um (2 mil)
- Surface area = 145 cm²
- Dimensions altered to fit a 2” well and to capture across a 18” well screen
- Strips were cleaned for 48hrs with
  - Dichloromethane
  - Methanol
  - Water
Advantages

- Elimination of sediment problems in groundwater analysis results in the...
  ...“true” dissolved concentration
  ...potential improved data consistency over time

- Longer deployment time can lead to more representative data

- Hanging multiple PE samplers could provide stratification data

- Elimination of the need to purge wells...field time and cost savings

- No need to dispose of contaminated purge water...time and cost savings

- Reduced cross contamination potential from purging pumps and other field equipment

- Small sample sizes, shipping volumes and reduced breakage risk and decreased shipping costs
Study Objectives

- Determine applicability of low density polyethylene (LDPE) samplers for measuring freely dissolved PAH concentrations in groundwater
- Determine the time to reach equilibrium for each individual compound
- Compare the results from PE samplers deployed in the field to conventional sampling methods
## Experimental Design

<table>
<thead>
<tr>
<th>Preparation</th>
<th>Exposure</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Phase I: Laboratory Trials</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- 1L deionised water in amber glass bottles</td>
<td>- 4 days</td>
<td>- LDPE Samplers</td>
</tr>
<tr>
<td>- Spiked 10 ug/L PAHs</td>
<td>- 8 days</td>
<td>- Spiked water after exposure</td>
</tr>
<tr>
<td>- LDPE in spike water</td>
<td>- 12 days</td>
<td></td>
</tr>
<tr>
<td><strong>Sample 1:</strong></td>
<td>- 30 days</td>
<td></td>
</tr>
<tr>
<td>- 1L groundwater in amber glass bottles</td>
<td></td>
<td>- Groundwater (Conventional PAH analysis)</td>
</tr>
<tr>
<td>- LDPE in glass bottles with sample</td>
<td></td>
<td>- LDPE Sampler (from bottled sample)</td>
</tr>
<tr>
<td><strong>Sample 2:</strong></td>
<td></td>
<td>- LDPE Sampler (from monitoring well)</td>
</tr>
<tr>
<td>- LDPE in monitoring well</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Phase 1 Results: Lab Spiking Study

% Sorption vs. Solubility Spiked at 10ug/L

<table>
<thead>
<tr>
<th>Polynuclear Aromatic Hydrocarbons</th>
<th>MW</th>
<th>Solubility in water (ug/L)</th>
<th>4 days</th>
<th>8 days</th>
<th>30 days</th>
<th>60 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo(g,h,i)perylene</td>
<td>276</td>
<td>0.3</td>
<td>26%</td>
<td>22%</td>
<td>28%</td>
<td>22%</td>
</tr>
<tr>
<td>Dibenz(a,h)anthracene</td>
<td>278</td>
<td>0.5</td>
<td>25%</td>
<td>23%</td>
<td>27%</td>
<td>22%</td>
</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
<td>252</td>
<td>0.8</td>
<td>27%</td>
<td>25%</td>
<td>39%</td>
<td>32%</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>252</td>
<td>2.3</td>
<td>27%</td>
<td>28%</td>
<td>40%</td>
<td>33%</td>
</tr>
<tr>
<td>Chrysene</td>
<td>228</td>
<td>2.8</td>
<td>29%</td>
<td>27%</td>
<td>48%</td>
<td>43%</td>
</tr>
<tr>
<td>Benzo(b/j)fluoranthene</td>
<td>252</td>
<td>4.0</td>
<td>28%</td>
<td>29%</td>
<td>46%</td>
<td>41%</td>
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<tr>
<td>Benzo(a)anthracene</td>
<td>228</td>
<td>10.0</td>
<td>30%</td>
<td>32%</td>
<td>55%</td>
<td>51%</td>
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<tr>
<td>Indeno(1,2,3-cd)pyrene</td>
<td>276</td>
<td>62.0</td>
<td>25%</td>
<td>22%</td>
<td>33%</td>
<td>27%</td>
</tr>
<tr>
<td>Anthracene</td>
<td>178</td>
<td>76.0</td>
<td>57%</td>
<td>68%</td>
<td>79%</td>
<td>82%</td>
</tr>
<tr>
<td>Pyrene</td>
<td>202</td>
<td>77.0</td>
<td>58%</td>
<td>68%</td>
<td>76%</td>
<td>76%</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>202</td>
<td>200</td>
<td>66%</td>
<td>77%</td>
<td>83%</td>
<td>83%</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>178</td>
<td>1200</td>
<td>79%</td>
<td>85%</td>
<td>86%</td>
<td>87%</td>
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<tr>
<td>Fluorene</td>
<td>166</td>
<td>1680</td>
<td>75%</td>
<td>77%</td>
<td>74%</td>
<td>79%</td>
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<tr>
<td>Acenaphthene</td>
<td>154</td>
<td>1930</td>
<td>71%</td>
<td>73%</td>
<td>71%</td>
<td>74%</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>152</td>
<td>3930</td>
<td>54%</td>
<td>54%</td>
<td>52%</td>
<td>57%</td>
</tr>
<tr>
<td>2-Methylnaphthalene</td>
<td>142</td>
<td>24600</td>
<td>60%</td>
<td>64%</td>
<td>61%</td>
<td>65%</td>
</tr>
<tr>
<td>1-Methylnaphthalene</td>
<td>142</td>
<td>25800</td>
<td>62%</td>
<td>63%</td>
<td>59%</td>
<td>63%</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>128</td>
<td>31700</td>
<td>27%</td>
<td>31%</td>
<td>27%</td>
<td>33%</td>
</tr>
</tbody>
</table>
### Data Comparison: Field Sampling (LDPE) vs. Lab Sampling (LDPE)

<table>
<thead>
<tr>
<th>Polynuclear Aromatic Hydrocarbons</th>
<th>RDL’s</th>
<th>Conventional Analytical Methods*</th>
<th>PE Sampler (deployed in lab)</th>
<th>PE Sampler (field deployed in well)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Water (Replicate 1)</td>
<td>Water (Replicate 2)</td>
<td>Strip (Replicate 1)</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>0.05</td>
<td>1.06</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>0.05</td>
<td>0.24</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>0.05</td>
<td>0.17</td>
<td>0.09</td>
<td>0.12</td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.05</td>
<td>0.19</td>
<td>0.12</td>
<td>0.17</td>
</tr>
</tbody>
</table>

**Notes:**
* Samples collected in 1L amber bottles and extracted as a whole including particulate
* Samples collected using peristaltic pump
* All results reported in (ug/L)
NEXT STEPS

- Evaluate PE samplers in different subsurface conditions (low vs high permeable soils)
- Evaluate potential naphthalene evaporation loss
- Investigate the use of using isotopically labeled performance reference compounds (PRCs) to correct data for % sorption vs using sorption coefficients
- Analyze additional general chemistry (TDS, TSS, DOC, TOC)
- Build a statistically significant dataset
- Validate ideal deployment time (ie 4 days)