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DETERMINATION OF PAHs IN GROUNDWATER AT A FORMER COAL GASIFICATION PLANT USING POLYETHYLENE PASSIVE SAMPLERS

Bryan Chubb, B.Sc., C.Chem

Sean Salvatori, P.Geo (ON)

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Tom Grimminck

Ontario

Paul Helm

Dan Toner

David Morse

Maxxam

Terry Obal

Suman Punani

Mariana Cojocar

OVERVIEW

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

Introduction and Background

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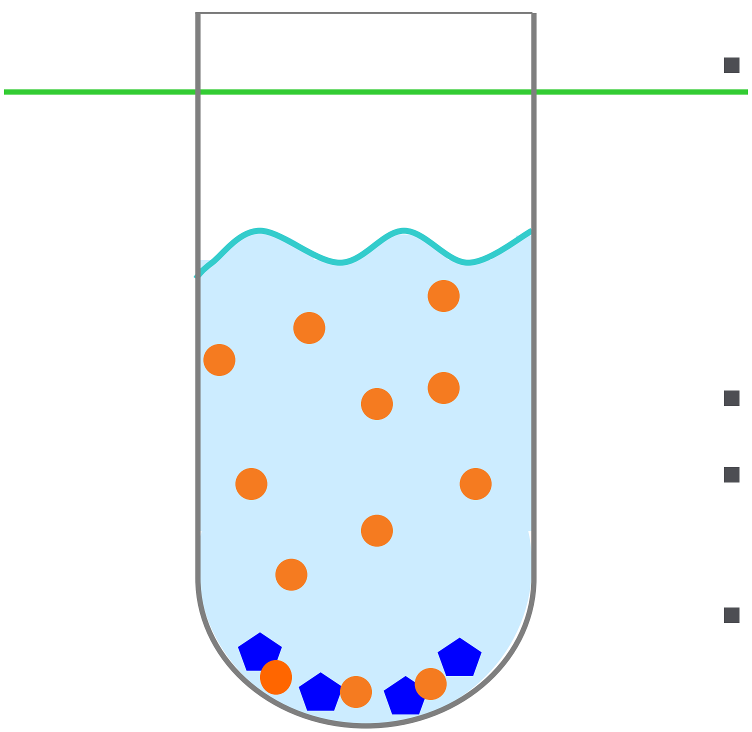

Problem Statement:

- 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 (ie Waterra vs peristaltic pump)
- Lead to biased high results and an overestimation of risk

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Peterborough Gas Works
Simcoe Street Facility

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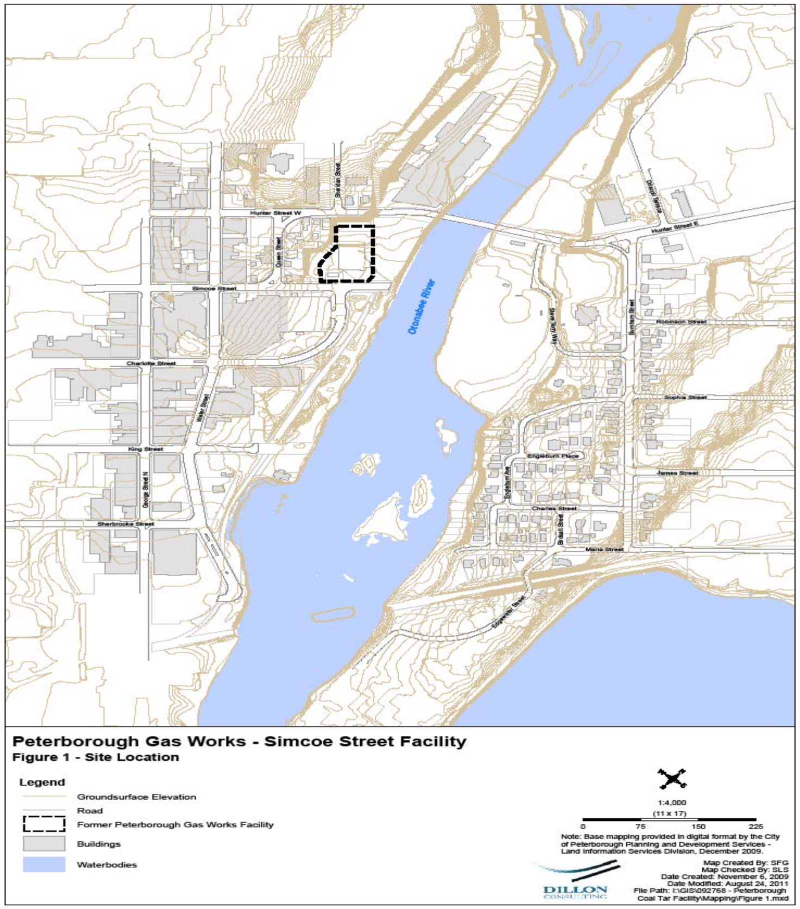

<u>Test Site</u>:

- 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

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Existing and Historical Monitoring

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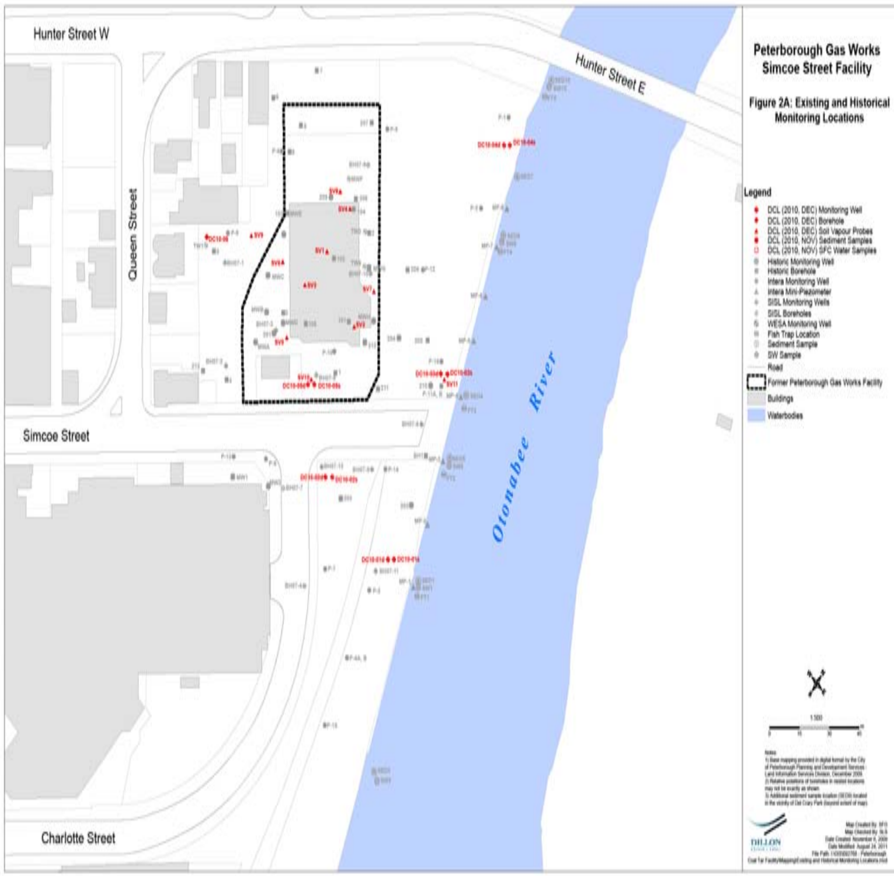

- Environmental data available since mid 1980's
- Environmental impacts include soil and groundwater contamination with PAHs and PHCs
- LNAPL and DNAPL are present on the site and adjacent properties
- Discharge of LNAPL to the Otonabee River has been observed
- DNAPL extends partially below river

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Current Investigation

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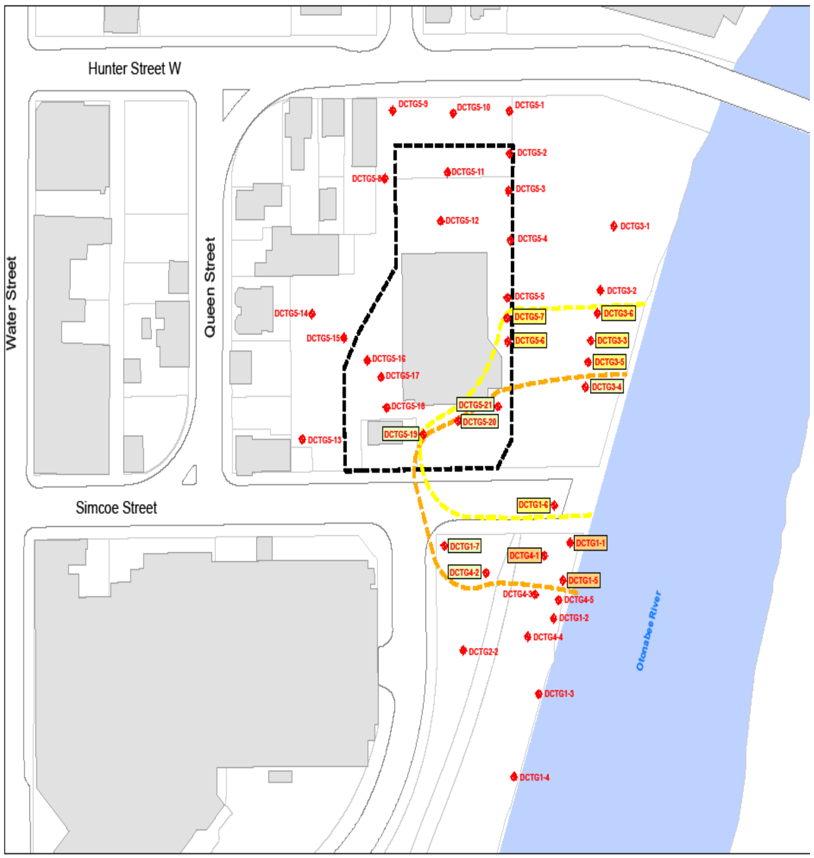

Current activities:

- 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

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Passive Sampling Devices

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- 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

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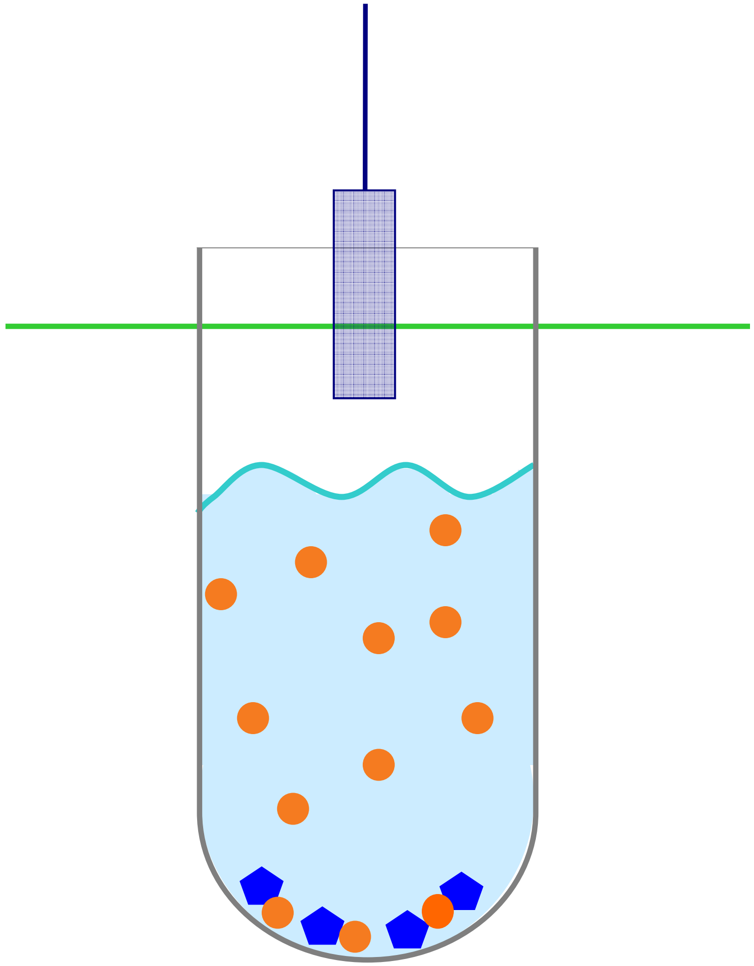

- PAHs will adsorb onto the polyethylene from the dissolved phase until equilibrium is achieved with dissolved concentration in GW
- PAHs bound to particulate or with organic matter will stay fixed
- After exposure, analysis of PE is completed by solvent extraction, GC/MS (results in ug PAH/g of PE)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

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Passive Diffusion Bags vs PE Samplers

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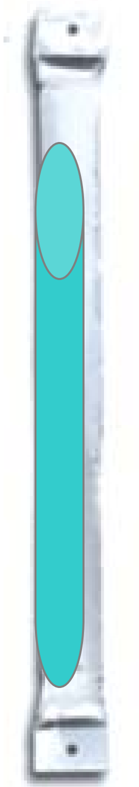

PDBs

- 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

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Sampling Media

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- Strips of low density polyethylene cut from commercial sheeting with a thickness of 51 um (2 mil)
- Surface area = 145 cm^2
- 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

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- 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***

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Study Objectives

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- 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

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	Preparation	Exposure	Analysis
Phase I: Laboratory Trials	- 1L deionised water in amber glass bottles - Spiked 10 ug/L PAHs - LDPE in spike water	- 4 days - 8 days - 12 days - 30 days - 60 days	- LDPE Samplers - Spiked water after exposure
Phase II: Field Trials	**Sample 1:** - 1L groundwater in amber glass bottles - LDPE in glass bottles with sample **Sample 2:** - LDPE in monitoring well	- 30 days	- Groundwater (Conventional PAH analysis) - LDPE Sampler (from bottled sample) - LDPE Sampler (from monitoring well)

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Phase 1 Results :Lab Spiking Study
% Sorption vs. Solubility Spiked at 10ug/L

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

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Data Comparison: Field Sampling (LDPE) vs. Lab Sampling (LDPE)

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Polynuclear Aromatic Hydrocarbons	RDL's	Conventional Analytical Methods*		PE Sampler (deployed in in lab)			PE Sampler (field deployed in well)
		Water (Replicate 1)	Water (Replicate 2)	Strip (Replicate 1)	Strip (Replicate 2)	Strip (Replicate 3)	Strip
Acenaphthene	0.05	1.06	<0.05	<0.05	<0.05	<0.05	<0.05
Acenaphthylene	0.05	0.24	<0.05	<0.05	<0.05	<0.05	0.19
Fluoranthene	0.05	0.17	0.09	0.12	0.12	0.14	0.08
Pyrene	0.05	0.19	0.12	0.17	0.16	0.19	0.20

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

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- 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 statisically significant dataset
- Validate ideal deployment time (ie 4 days)

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