April 2012

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USING POLYETHYLENE PASSIVE SAMPLERS FOR THE DETERMINATION OF DISSOLVED PAHs IN GROUND WATER

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Acknowledgments

Dillon Consulting Limited	**Sean Salvatori**
Ontario MOE	**Paul Helm** **Dan Toner** **David Morse** **Eric Reiner**
Maxxam Analytics	**Bryan Chubb** **Suman Punani** **Mariana Cojocar** **Lusine Khachatryan**

Outline

- Introduction and Background
- Study Objectives
- Laboratory Trials
- Site Case Study
- Field Trials
- Next Steps

Introduction and Background

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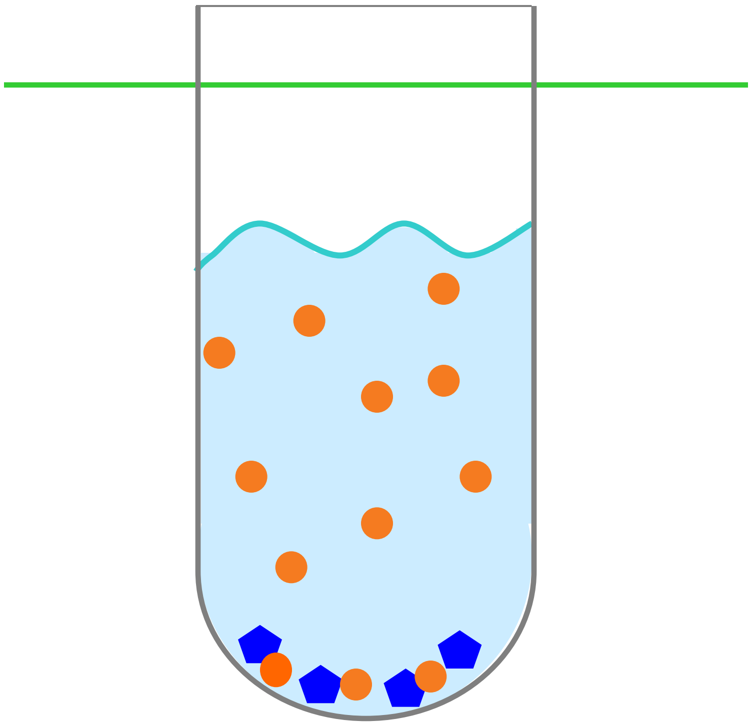

Problem Statement:

- Most environmental standards for groundwaters 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 collect samples without sediment

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Passive Sampling Devices

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- Polyethylene (PE) passive sampling devices have been used in the past to determine dissolved PAH, PCB and other hydrophobic organic compounds in other aquatic environments (Booij *et.al.* 2003; Adams *et.al.* 2007; Fernandez *et. al.* 2008; Hale *et. al.* 2010; Lohmann *et.al.* 2011;)
- Passive sampling using other media (e.g. polyoxymethylene (POM), Hawthorne *et. al.* 2009) has been investigated for sediment pore waters
- Semi-permeable membrane devices (SPMDs) have also been used in the measurement of organic chemical contamination in environmental samples (Meadows *et.al* .1998; Harman *et.al* . 2011)

Principles of Passive Sampling

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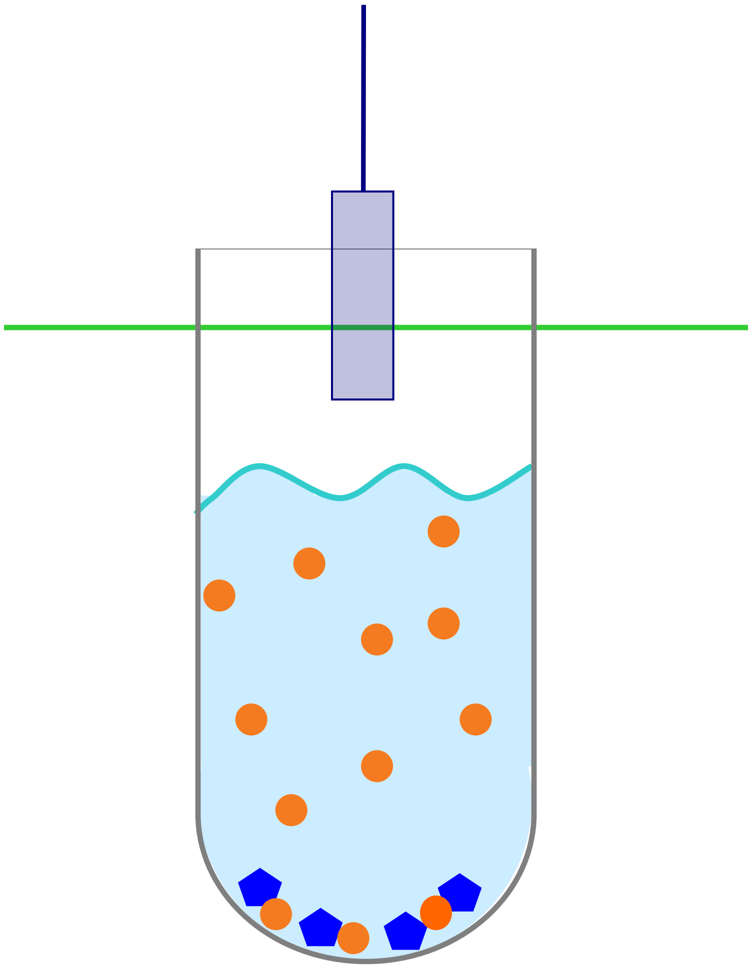

- Based on adsorption of compounds of interest from the dissolved phase onto the passive sampler medium (e.g. low density polyethylene - LDPE)

- PE/water partition coefficients at equilibrium (K_{PEW} in L/kg) can be determined as follows:

$$K_{PEW} = C_{PE} / C_W$$

Where,

C_{PE} = analyte concentration on LDPE (ug/kg)

C_W = analyte concentration in water (ug/L)

Advantages

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- Elimination of sediment problems in groundwater analysis results in the…

  …*"true" dissolved concentration*

  …potential improved data consistency

  … more representative of ground water conditions

- Elimination of the need to purge wells results in…

  …labour savings

- Small sample sizes, shipping volumes and limited risk results in…

  …decreased 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, calculating PAH-specific partition coefficients (K_{PEW})
- Using partition coefficients, determine freely dissolved PAH concentrations in groundwater
- Compare the results from LDPE samplers deployed in the field to conventional sampling methods

Sampling Media

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- Samplers (strips) of low density polyethylene cut from commercial sheeting with a thickness of 51 um (2 mil)

- Strips were cleaned for 48hrs with
  - Dichloromethane
  - Methanol
  - Water

Laboratory Trials

- % Sorption vs. PAH Solubility
- Time-to-Equilibrium Studies
- LDPE/Water Partition Coefficients (K_{PEW})
- K_{PEW} vs. Exposure Time Studies

% Sorption vs. Solubility
(10 ug/L)

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PAH Compound	MW	Solubility (ug/L)	Exposure Time				
			1hr	2hrs	4hrs	8hrs	1 day
Benzo(g,h,i)perylene	276	0.3	0%	1%	0%	0%	5%
Dibenz(a,h)anthracene	278	0.5	0%	1%	0%	5%	5%
Benzo(k)fluoranthene	252	0.8	0%	4%	3%	4%	22%
Benzo(a)pyrene	252	2.3	2%	3%	2%	3%	13%
Chrysene	228	2.8	2%	4%	3%	6%	17%
Benzo(b/j)fluoranthene	252	4.0	0%	4%	3%	4%	13%
Benzo(a)anthracene	228	10.0	3%	7%	5%	7%	24%
Indeno(1,2,3-cd)pyrene	276	62.0	0%	1%	0%	0%	7%
Anthracene	178	76.0	5%	16%	11%	18%	44%
Pyrene	202	77.0	5%	16%	12%	19%	41%
Fluoranthene	202	200	6%	18%	13%	21%	46%
Phenanthrene	178	1200	7%	22%	16%	26%	56%
Fluorene	166	1680	7%	22%	17%	26%	54%
Acenaphthene	154	1930	8%	23%	18%	27%	53%
Acenaphthylene	152	3930	8%	22%	18%	26%	44%
2-Methylnaphthalene	142	24600	8%	22%	17%	26%	49%
1-Methylnaphthalene	142	25800	8%	23%	13%	27%	48%
Naphthalene	128	31700	8%	18%	15%	20%	27%

% Sorption vs. Solubility
(10 ug/L)

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PAH Compound	Solubility (ug/L)	Exposure Time					
		2 days	4 days	8 days	12 days	30 days	60 days
Benzo(g,h,i)perylene	0.3	6%	26%	22%	14%	28%	22%
Dibenz(a,h)anthracene	0.5	5%	25%	23%	13%	27%	22%
Benzo(k)fluoranthene	0.8	23%	27%	25%	18%	39%	32%
Benzo(a)pyrene	2.3	18%	27%	28%	18%	40%	33%
Chrysene	2.8	25%	29%	27%	22%	48%	43%
Benzo(b/j)fluoranthene	4.0	23%	28%	29%	22%	46%	41%
Benzo(a)anthracene	10.0	37%	30%	32%	24%	55%	51%
Indeno(1,2,3-cd)pyrene	62.0	11%	25%	22%	14%	33%	27%
Anthracene	76.0	59%	57%	68%	65%	79%	82%
Pyrene	77.0	58%	58%	68%	59%	76%	76%
Fluoranthene	200	66%	66%	77%	70%	83%	83%
Phenanthrene	1200	73%	79%	85%	82%	86%	87%
Fluorene	1680	69%	75%	77%	76%	74%	79%
Acenaphthene	1930	63%	71%	73%	73%	71%	74%
Acenaphthylene	3930	53%	54%	54%	54%	52%	57%
2-Methylnaphthalene	24600	58%	60%	64%	61%	61%	65%
1-Methylnaphthalene	25800	57%	62%	63%	60%	59%	63%
Naphthalene	31700	30%	27%	31%	29%	27%	33%

LDPE/PAH Uptake Rates ("Time-to-Equilibrium")

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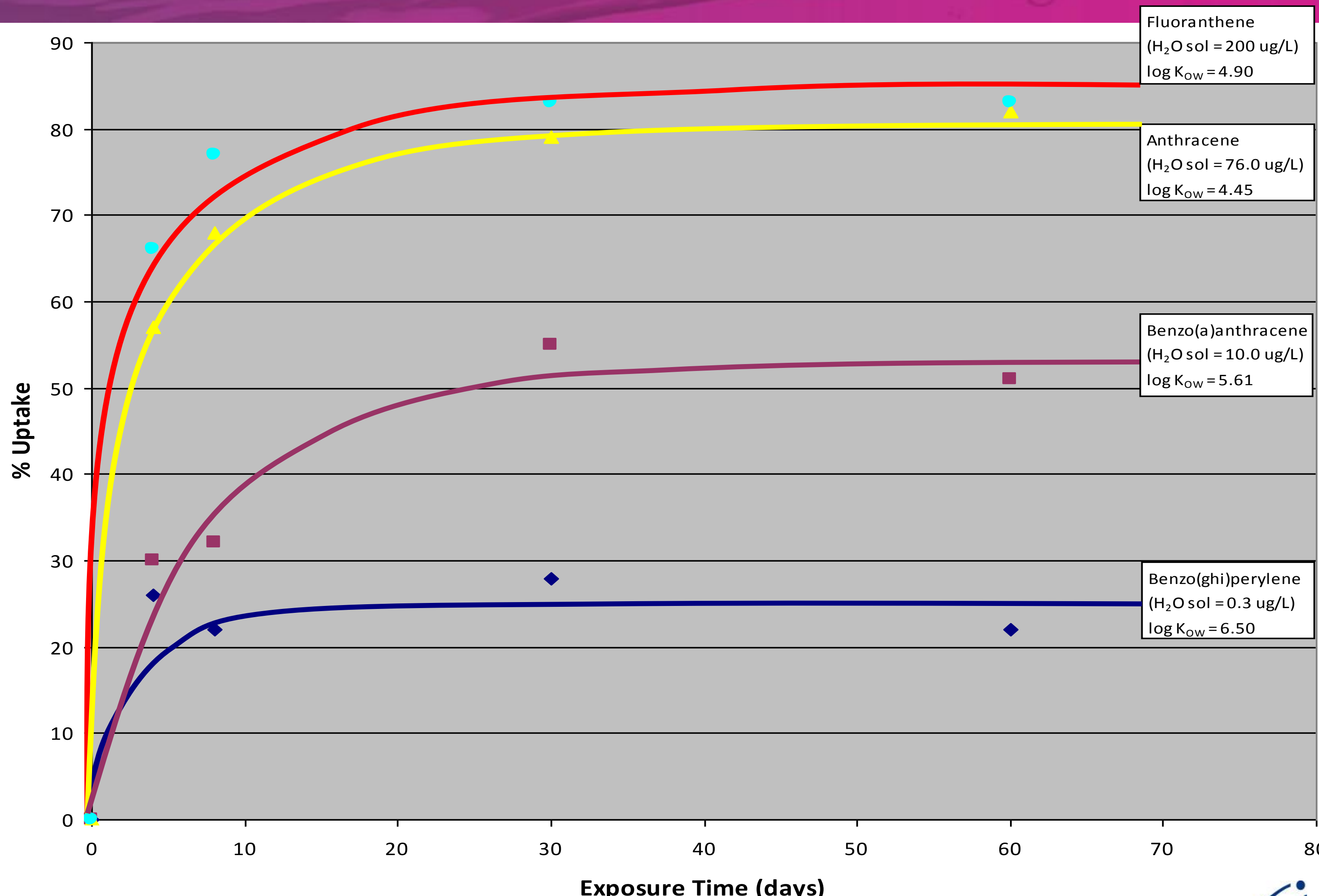

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% Standard Deviation

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PAH Compound	Exposure Time					
	2 days	4 days	8 days	12 days	30 days	60 days
Benzo(g,h,i)perylene	2	20	17	9	6	6
Dibenz(a,h)anthracene	3	20	18	9	6	6
Benzo(k)fluoranthene	3	18	16	8	1	7
Benzo(a)pyrene	2	19	18	10	2	5
Chrysene	2	18	16	11	2	3
Benzo(b/j)fluoranthene	3	18	16	11	3	4
Benzo(a)anthracene	3	17	15	10	3	2
Indeno(1,2,3-cd)pyrene	3	19	17	8	5	5
Anthracene	1	11	6	6	4	0
Pyrene	1	13	8	7	1	1
Fluoranthene	2	11	6	5	2	1
Phenanthrene	2	6	2	2	2	0
Fluorene	2	4	0	1	2	1
Acenaphthene	3	3	2	1	2	1
Acenaphthylene	2	2	2	1	3	1
2-Methylnaphthalene	3	1	1	1	2	1
1-Methylnaphthalene	2	1	2	2	3	1
Naphthalene	2	0	2	1	2	1

LDPE/Water Partition Coefficients

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LDPE/water partition coefficients at equilibrium (K_{PEW}) were determined as follows:

$$K_{PEW} = C_{PE} / C_W$$

where,

C_{PE} = concentration (LDPE) in ug/kg

C_W = concentration (water) in ug/L

$$C_W = C_{PE} / K_{PEW}$$

K_{PEW} (> 4 day exposure)

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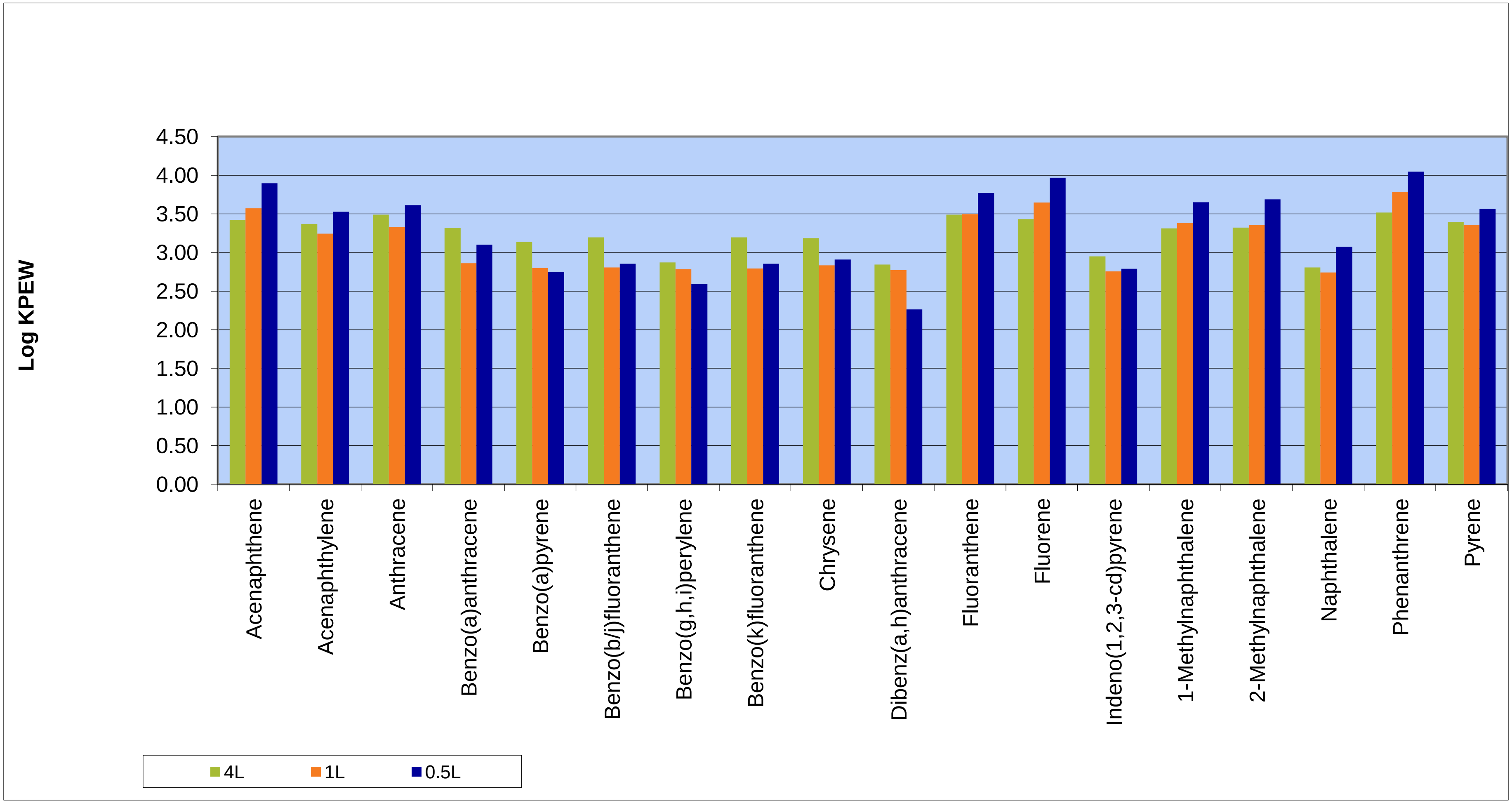

K_{PEW} vs. Time (Acenaphthene)

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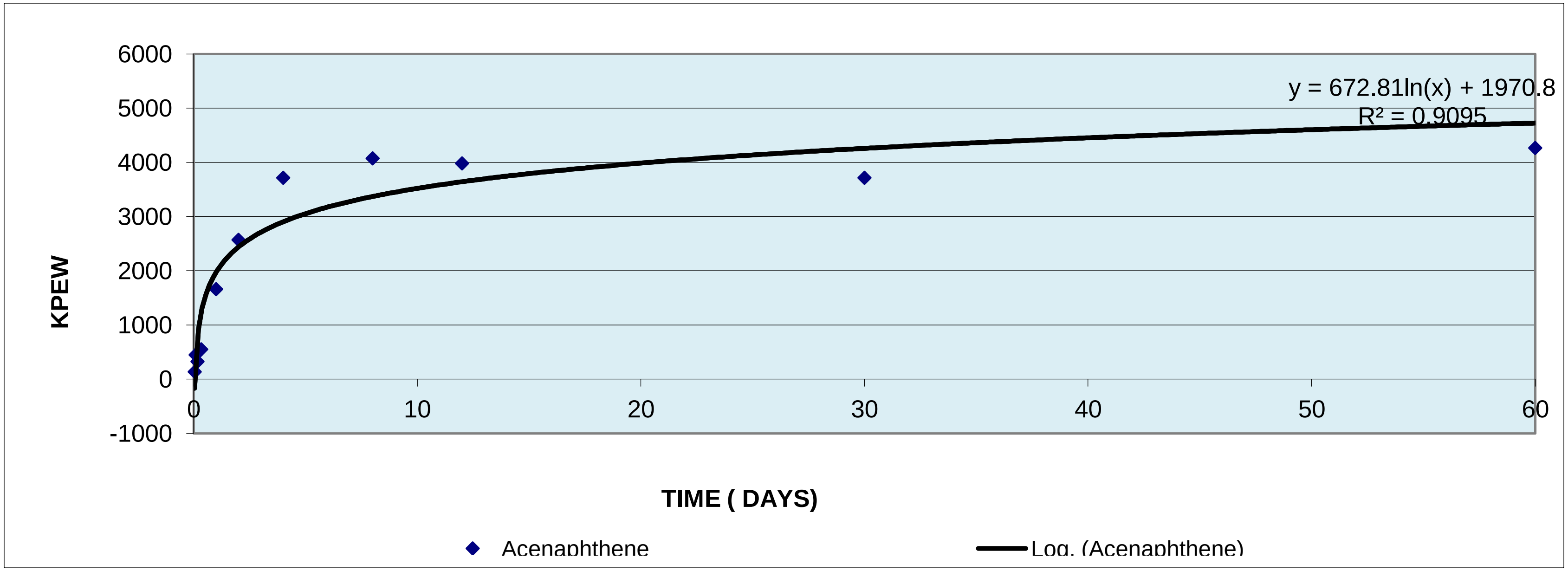

K_{PEW} (12 day) = 3981

K_{PEW} (30 day) = 3715

K_{PEW} (60 day) = 4266

$K_{PEW} = 672.81 \ln(t) + 1971$ ($r^2 = 0.9095$)

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K_{PEW} vs. Time (Phenanthrene)

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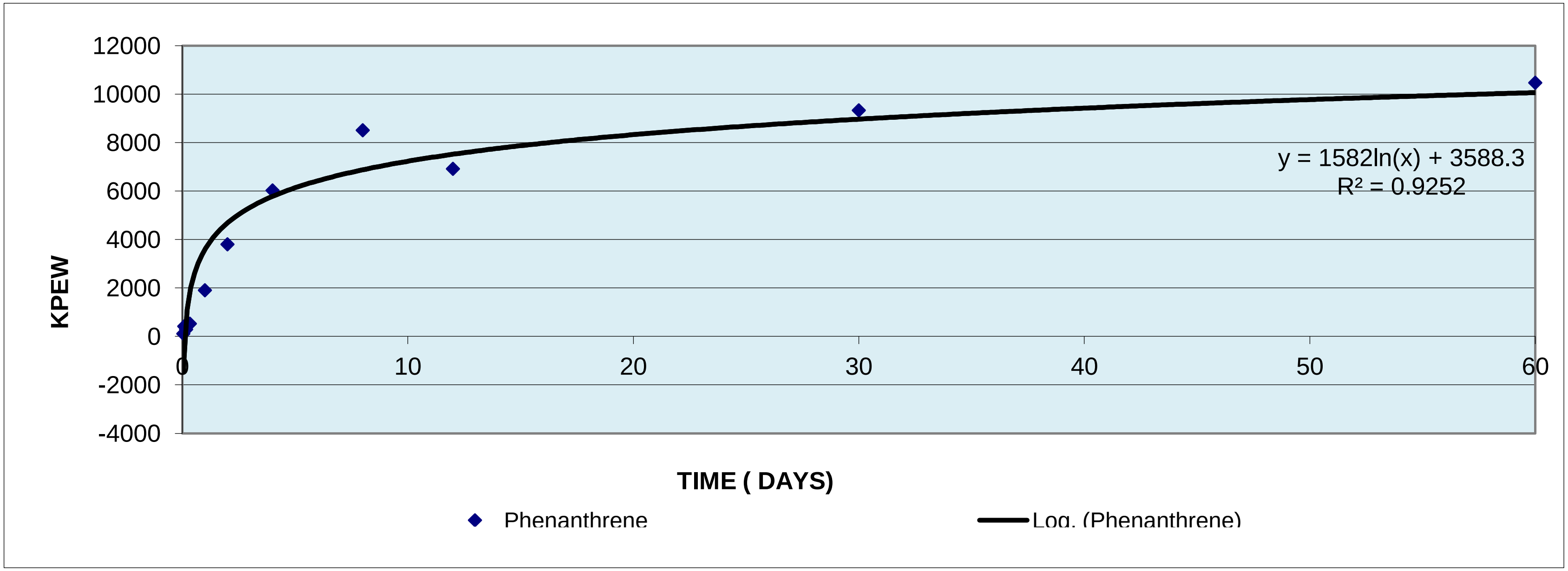


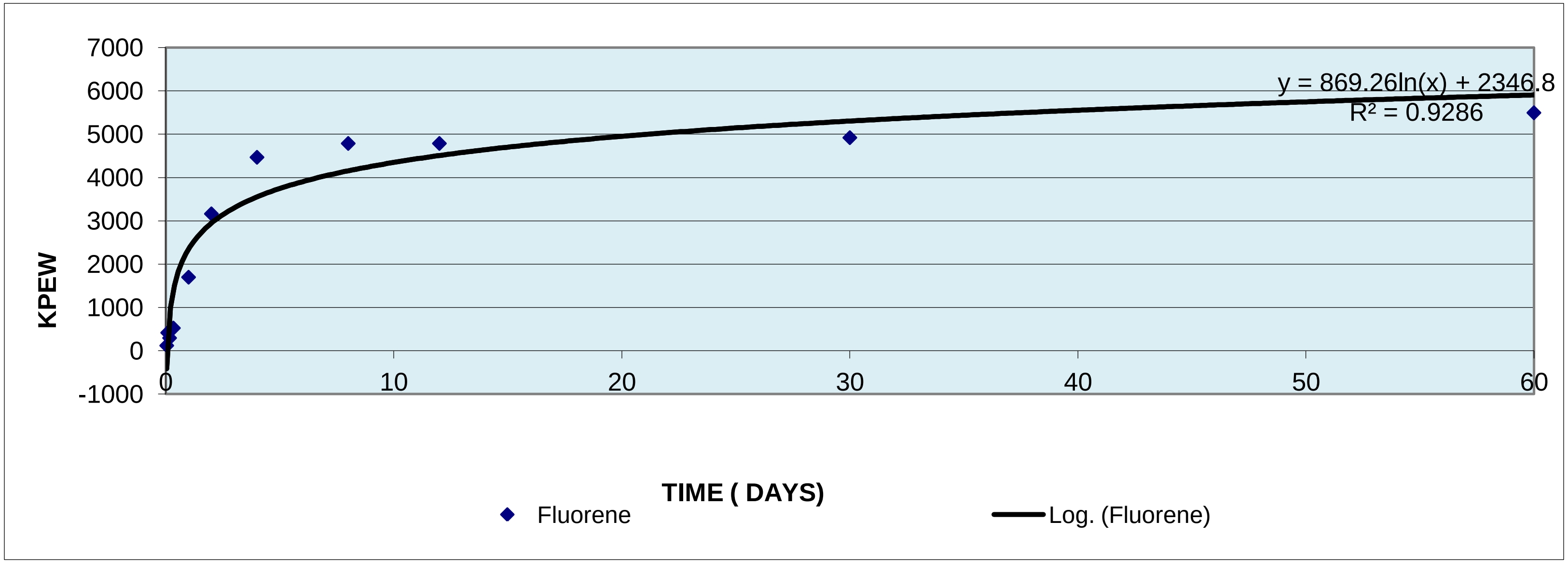
K_{PEW} (12 day) = 6918

K_{PEW} (30 day) = 9333

K_{PEW} (60 day) = 10471

$K_{PEW} = 1582\ ln(t) + 3588.3$ ($r^2 = 0.9252$)

K_{PEW} vs. Time (Fluorene)



K_{PEW} (12 day) = 4786

K_{PEW} (30 day) = 4920

K_{PEW} (60 day) = 5495

$K_{PEW} = 869.26 \ln(t) + 2346.8$ (r^2=0.9286)

Conclusions (Laboratory Trials)

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- Based on % sorption, equilibrium is reached within 4 days of exposure for PAH compounds having solubility > 76 ug/L

- log K_{PEW} vs. log K_{OW} and log K_{PEW} vs. log C_W^{sat} (L) compare well with literature values (Lohmann et. al., 2012)

- K_{PEW} calculated at various exposure times, i.e.,

  $$K_{PEW} = a\ ln(t) + b$$

  offers a potential approach to determine the dissolved concentration of the compound of interest at time *t*.

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Field Trials

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- Determination of dissolved phase PAHs *in situ* and *ex situ:*
  - Based on equilibrium K_{PEW} (10 day/30 day exposure)
  - Based on K_{PEW} vs. Exposure Time Curves
- Comparison with conventional sampling and analysis protocols

Peterborough Gas Works Simcoe Street Facility

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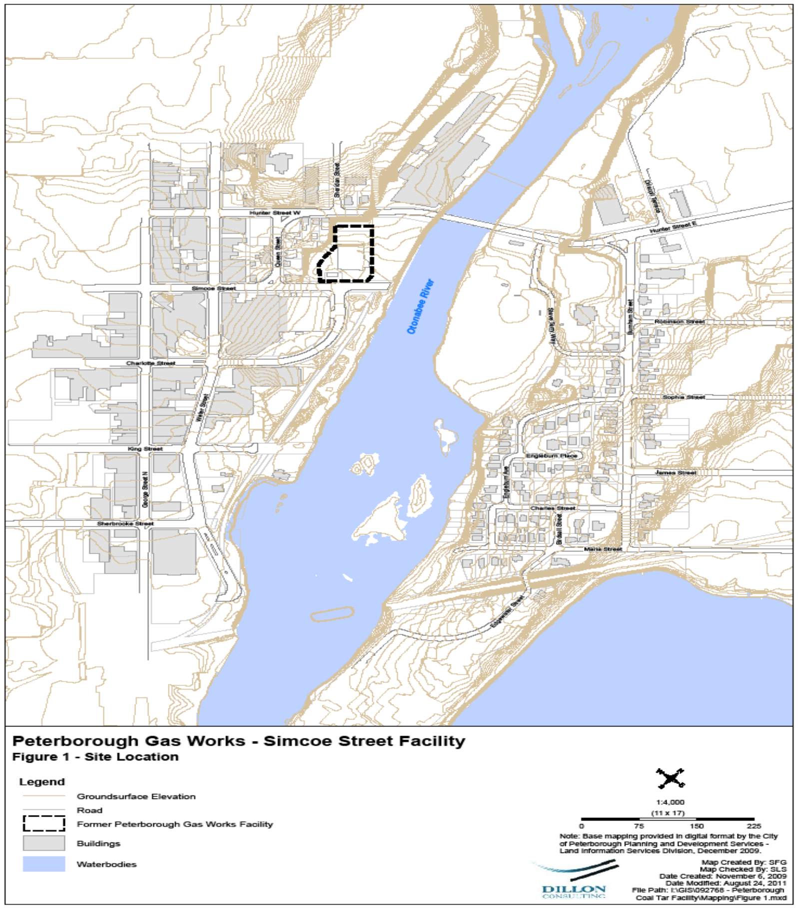

Test Site:

- 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

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Data Comparison (BH07-6; Sep/11): 10 Day vs 30 Day Exposure

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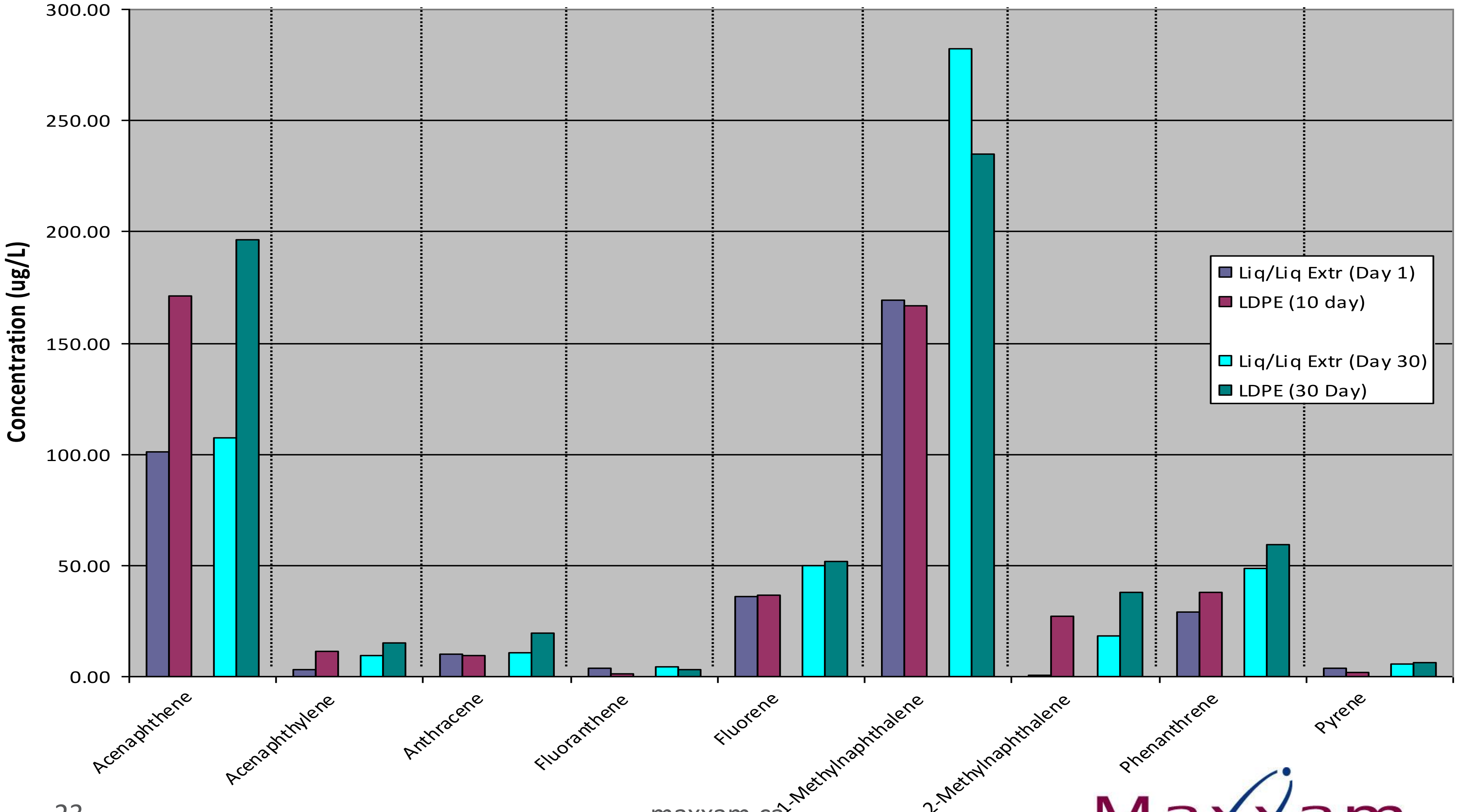

Data Comparison (BH07-5; Sep/11): 10 Day vs. 30 Day Exposure

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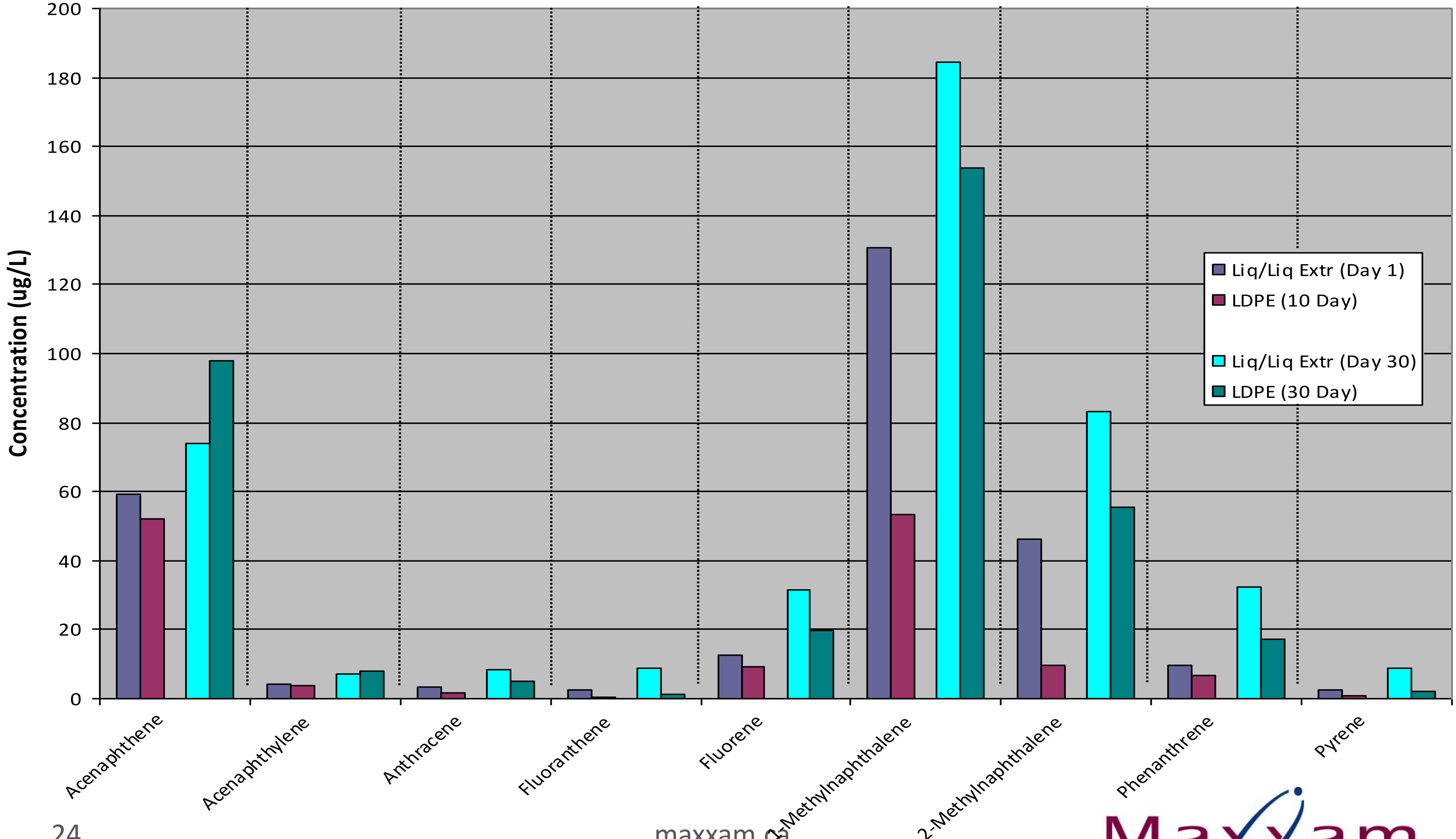

“Dissolved” PAHs
(LDPE vs. Grab Samplling)

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Date strips deployed in wells	Grab Samples			LPDE Sampler			LPDE Sampler		
Exposure time for strips	Sampling Date 15-Sep-11	Sampling Date 27-Oct-11	Avg Conc. (ug/L)	K_{PEW} vs. Exposure Time Calculation (10 day exposure)	Calculated K_{PEW}	Calculated Conc. (ug/L) 10 day Exp.[1]	K_{PEW} vs. Exposure Time Calculation (32 day exposure)	Calculated K_{PEW}	Calculated Conc. (ug/L) 32 day Exp.[2]
Acenaphthene	98.0	32.6	65.3	y=672.81ln10 +1970.8	3520	66.5	y=672.81ln32 +1970.8	4303	64.2
Acenaphthylene	12.1	3.9	8.0	y=267.28ln 10 +1047.3	1663	7.9	y=267.28ln 32 +1047.3	1974	7.6
Anthracene	15.3	1.5	8.4	y=885.61ln 10 +1841.5	3881	3.9	y=885.61ln 32 +1841.5	4911	4.0
Benzo(a)anthracene	5.6	0.8	3.2	y=226.09ln 10 +541.46	1062	3.4	y=226.09ln 32 +541.46	1325	2.5
Benzo(a)pyrene	3.1	0.5	1.8	y=130.99ln 10 +313.03	615	1.6	y=130.99ln 32 +313.03	767	1.1
Benzo(b/j)fluoranthene	2.3	0.8	1.5	y=164.58 ln10+373.15	752	2.0	y=164.58 ln 32+373.15	944	1.6
Benzo(g,h,i)perylene	1.0	0.2	0.6	y=87.978 ln 10+206.14	409	0.0	y=87.978 ln 32+206.14	511	0.0
Benzo(k)fluoranthene	0.8	0.0	0.4	y=122.2ln 10 +312.58	594	1.2	y=122.2ln 32 +312.58	736	0.0
Dibenz(a,h)anthracene	3.4	0.8	2.1	y=1237.8 ln10 +1925.8	4776	0.6	y=1237.8 ln32 +1925.8	6216	0.6
Chrysene	0.3	0.0	0.1	y=172.61ln 10 +403.16	801	0.0	y=172.61ln 32 +403.16	1001	0.0
Fluoranthene	13.1	2.1	7.6	y=1110.6 ln 10 +2390.5	4948	2.4	y=1110.6 ln 32 +2390.5	6240	2.9
Fluorene	32.5	8.9	20.7	y=869.26 ln10 +2346.8	4328	17.4	y=869.26 ln32 +2346.8	5360	18.1
Indeno(1,2,3-cd)pyrene	1.3	0.2	0.7	y=127.66 ln 10+169.71	468	0.8	y=127.66 ln 32+169.71	614	0.0
1-Methylnaphthalene	266.8	64.4	165.6	y=377.66 ln 10 +1295.2	2165	35.2	y=377.66 ln 32 +1295.2	2604	318.4
2-Methylnaphthalene	103.1	7.2	55.1	y=403.55 ln10 +1346.4	2276	33.6	y=403.55 ln32 +1346.4	2745	41.1
Naphthalene	1272.6	99.0	685.8	y=68.825 ln 10 +448.87	607.3	729.7	y=68.825 ln 32 +448.87	687.4	1328.1
Phenanthrene	44.3	1.0	22.6	y=1582ln10 +3588.3	7231	7.6	y=1582ln32 +3588.3	9071	7.5
Pyrene	15.9	3.1	9.5	y=700.95ln 10 +1624	3238	5.6	y=700.95ln 32 +1624	4053	5.3

Notes:
(1) Sep 15/11 - Sep 25/11
(2) Sep 25/11 - Oct 27/11

Conclusions
(Field Trials)

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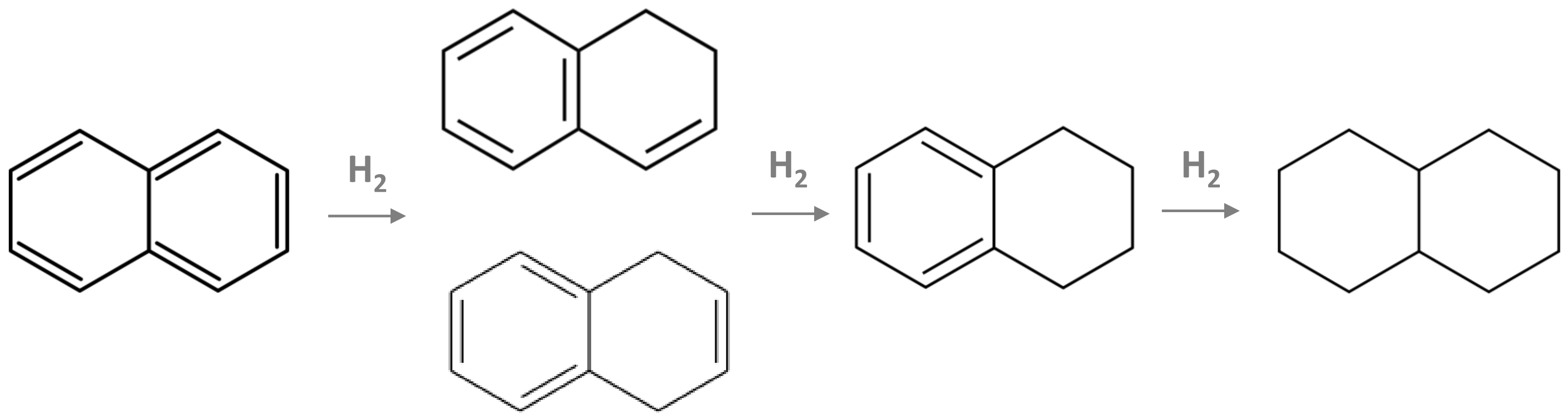
- Results compare reasonably well for some compounds between conventional sampling and strips deployed in wells
- Samples collected by traditional methods are not homogeneous as shown from the grab samples
- Data on the strip is a time weighted average, data by conventional methods is a point-in-time

A Word About Naphthalene…

- The data obtained for naphthalene suggest the need for additional study
- In some samples, where naphthalene was expected…it was not observed
- Spiking studies and subsequent mass balance calculations indicated significant decreases in napthalene concentrations
- *Where did it go?*

A Word About Naphthalene…

- Under certain conditions, naphthalene (and potentially methylnaphthalenes, acenaphthene and acenaphthylene) can undergo hydrogenation:



- Confirmed elevated levels of the dihydronaphthalene(s) in the spiked samples by GC/MS
- Site specific phenomenon?

On-going Studies
(not reported here)

- Investigation of exchange rate coefficients (k_e) using labeled performance reference compounds (PRCs) as an alternate to equilibrium partition coefficients (K_{PEW})

$$k_e = ln[C_{PE,0} / C_{PE,t}] \times t^{-1}$$

then

$$C_W = C_{PE,t} / (1 - e^{ke,t}) \times K_{PEW}$$

Potential Advantages:

- *Shorter exposure periods (faster sampling)*
- *Alternate approach to calculating analyte concentrations before equilibrium is reached*

- Investigation of effects of concentration and surface area on % sorption and partition coefficients

Next Steps

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- Time Weighted Average Studies based on more frequent conventional grab sampling
- Continued validation and optimization of LDPE sampling and using K_{PEW} vs. exposure time values as a means of calculating freely dissolved PAH concentrations
- Compare investigative results using K_{PEW} values (30-day exposure) against results using exchange rate coefficients (7-day or less exposure)
- Expand Study to include other sites
- Investigate applicability of LPDE passive sampling systems for other organic contaminants of concern

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