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Overcoming the Technical Challenges of LDPE Passive Sampling:

Improved accuracy for the heavier and more toxic PAHs

Heather Lord, Ph.D.

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Outline

- Introduction to LDPE passive sampling
- Early results highlighting difficulty with heavy PAH
- Use of modeling to troubleshoot and plan deployments
- Use of pre-loaded standards to calibrate uptake kinetics
- Results of field deployment and comparison to models

Passive Sampling with LDPE

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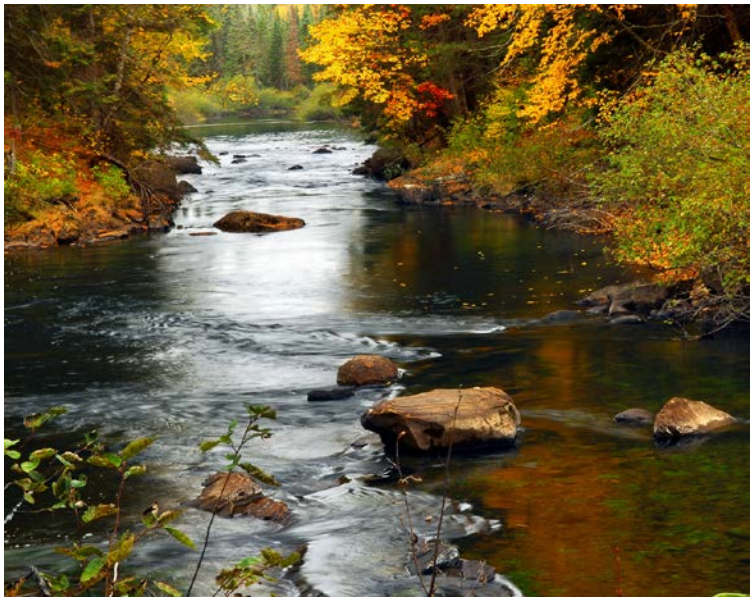
LDPE: Low Density Polyethylene

- Dissolved organics in water will concentrate in LDPE films
- Technology advances in recent months



Opportunities:

- Surface or groundwater monitoring
- Target: non-polar uncharged organics
  - polycyclic aromatic hydrocarbons
- Obtain average water concentration over time: e.g. 30 days
- Avoid interference from sediment

Concentrations in Water vs. LDPE

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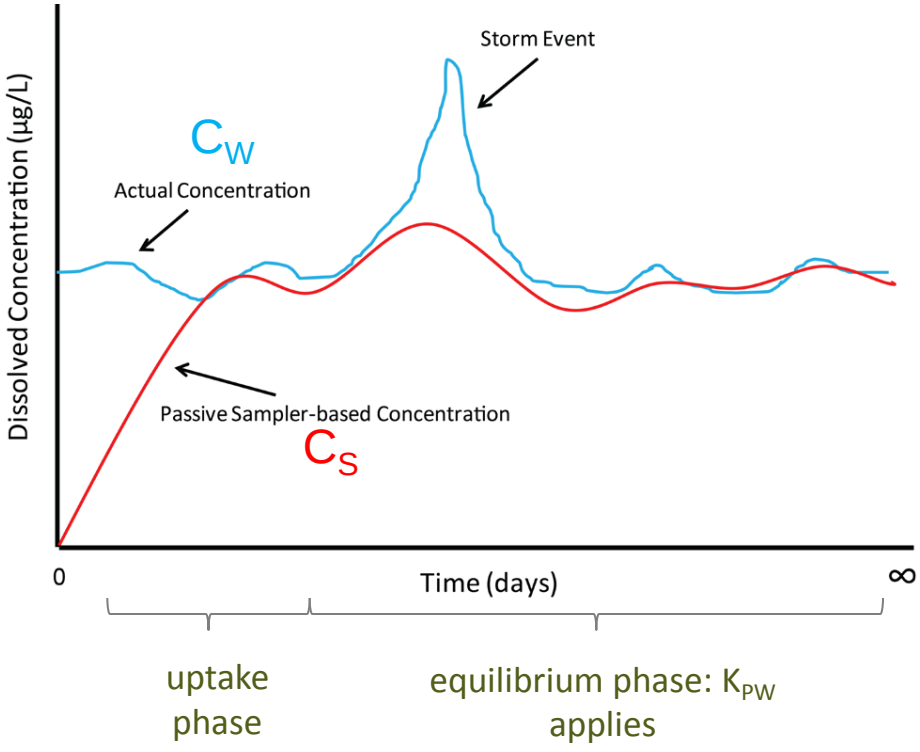

After equilibration, changes in LDPE concentration reflect moving average of past water concentrations

- according to a compound-specific partition coefficient (K_{PW}).

$$C_W = C_S / K_{PW}$$

C_S = analyte concentration on LDPE (µg/kg)

C_W = analyte concentration in water (µg/L)

Reference: EPA - OSWER Directive 9200.1-110 FS

Groundwater vs. Surface Water Sampler Designs

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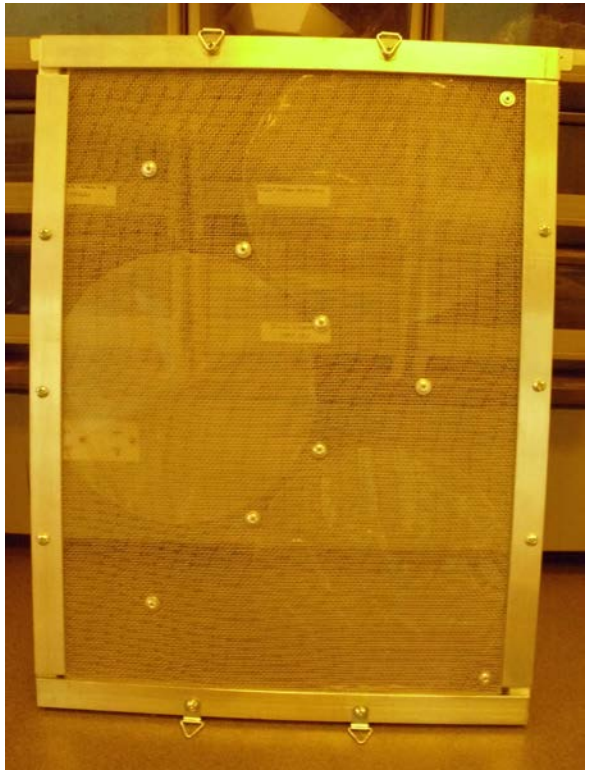

Groundwater:

- Weights hold the strip vertical in the well
- Fishing line allows operator to set depth

Surface Water

- Screening protects films from damage and keeps films flat
- Support bars and fastening clips for anchoring

K_{PW} Estimates: Literature or Experimental?

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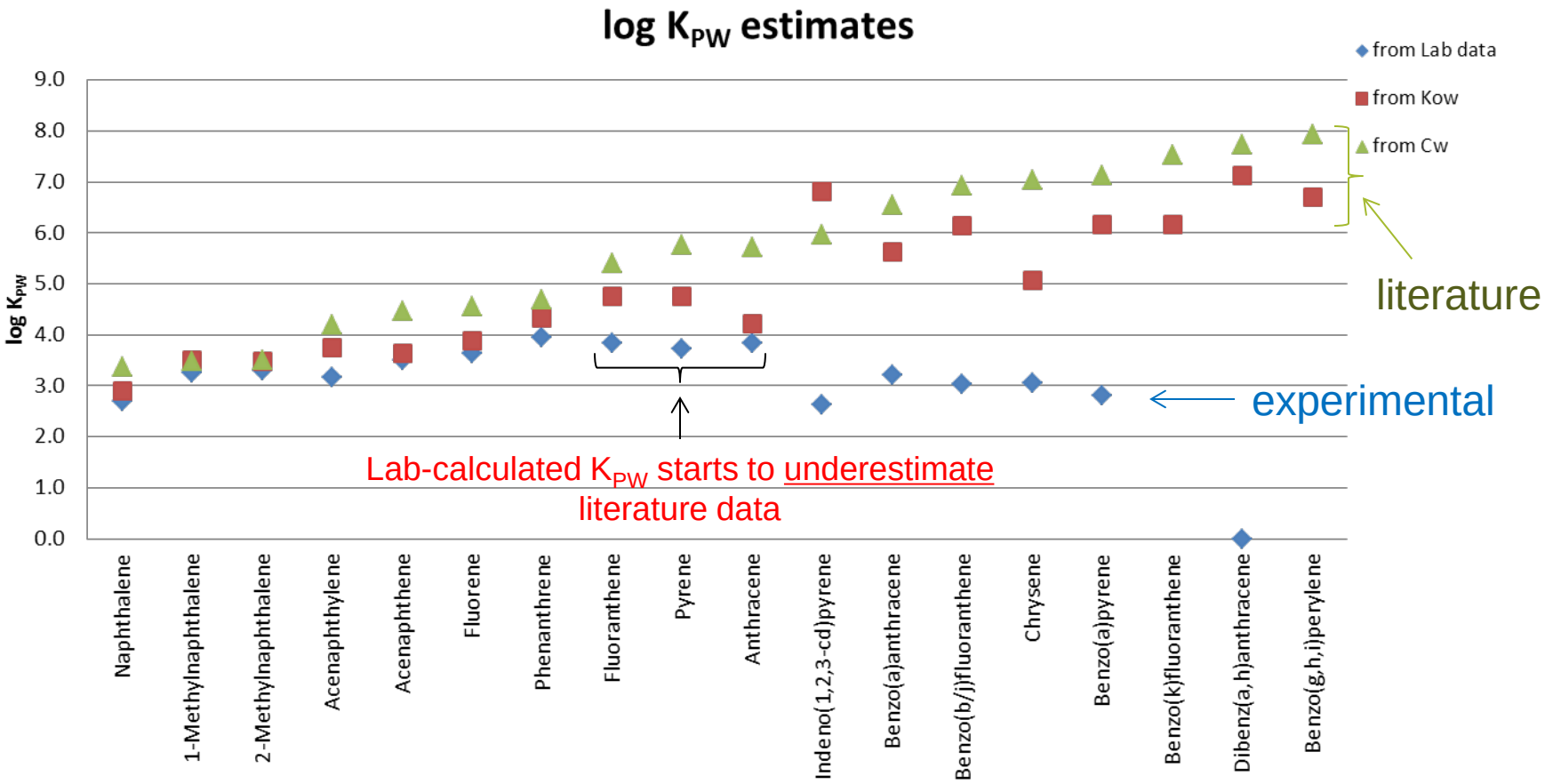

Data Comparison - Groundwater: Lab vs. Literature Partition Coefficients

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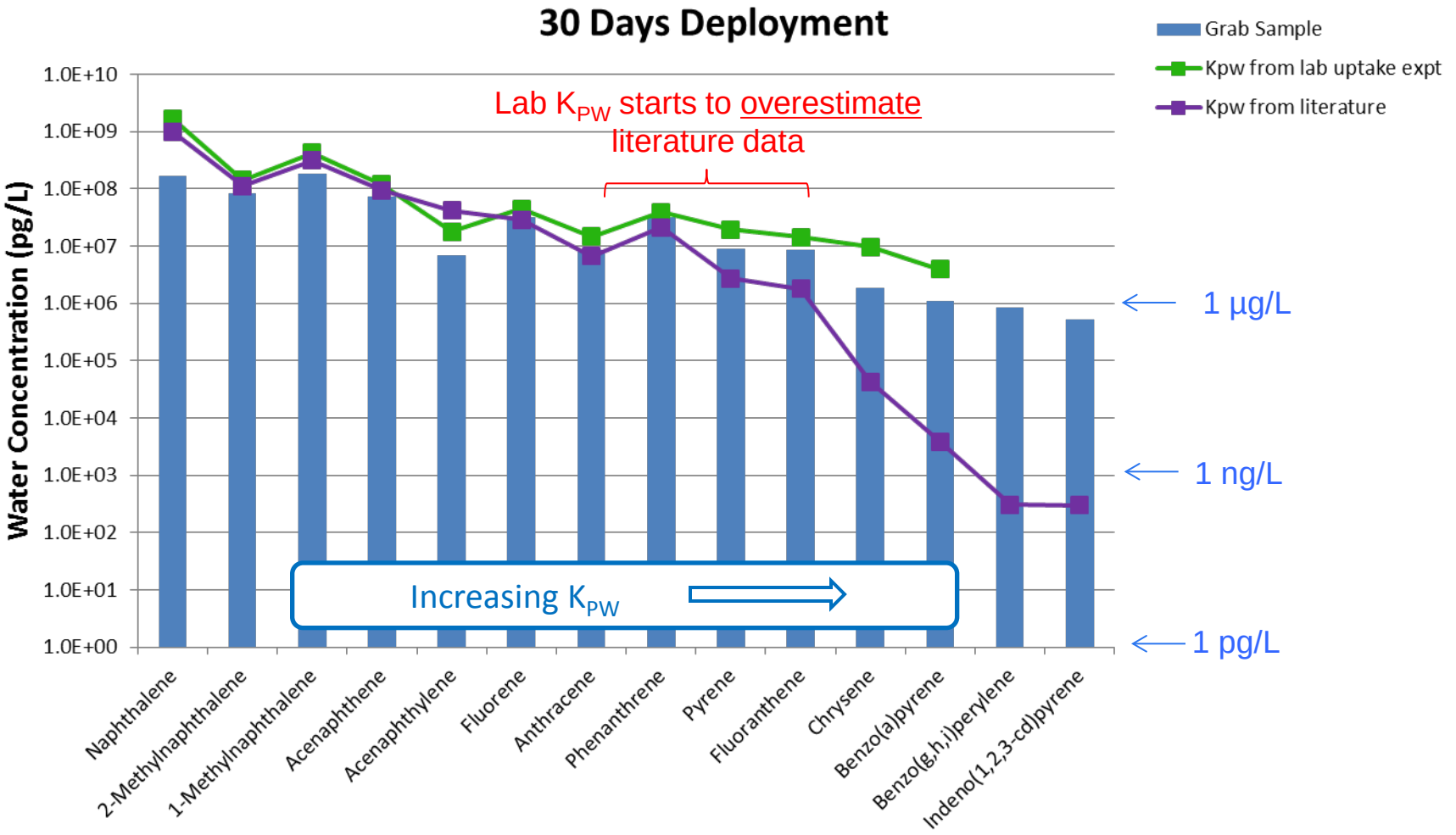
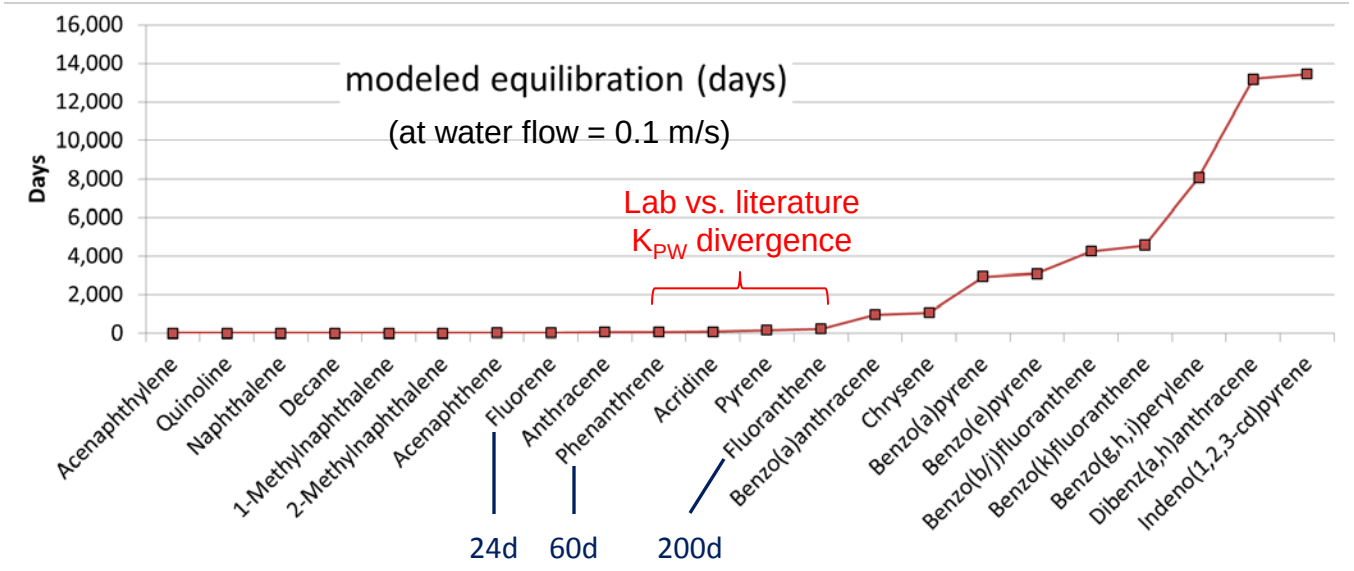


Why the difficulty in laboratory determination of K_{PW}?

- Water solubility
  - water solubility gets v. low: < 10 µg/L, analytically challenging
- High K_{PW} compounds stick to bottle walls etc.
  - free water concentration is difficulty to accurately determine
- For high K_{PW}, equilibration can take a very long time



Modeled equilibration time used to correct water concentration estimates

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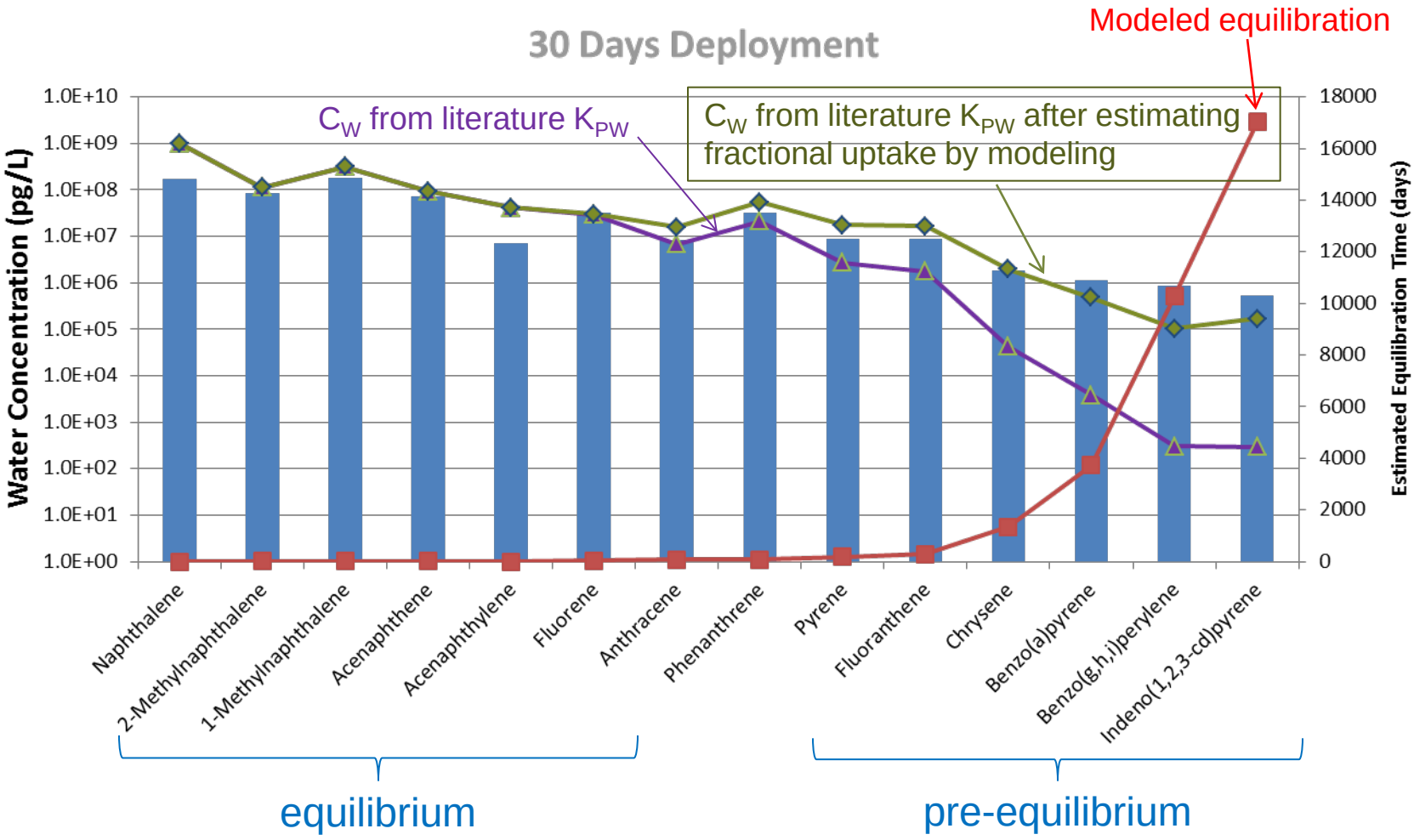

What else can modeling tell us?
Preferred Water Flow

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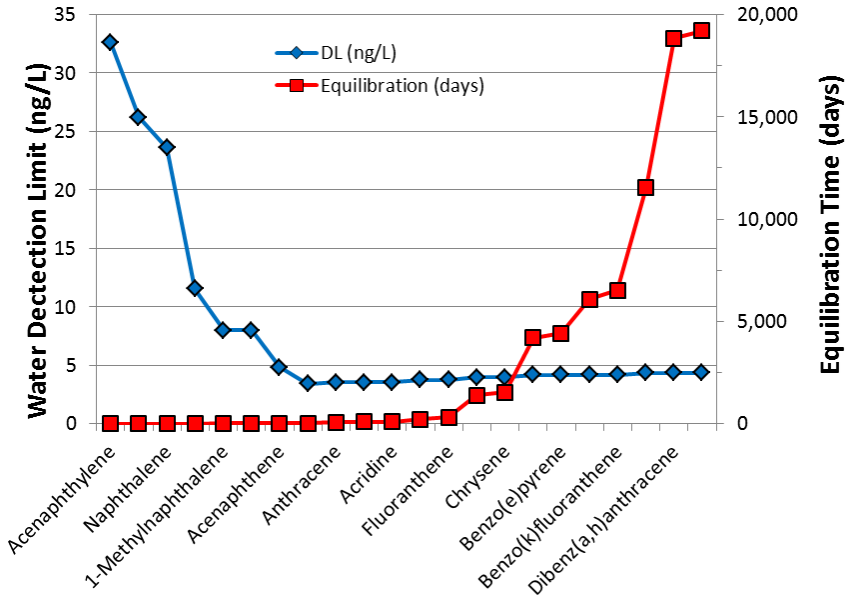
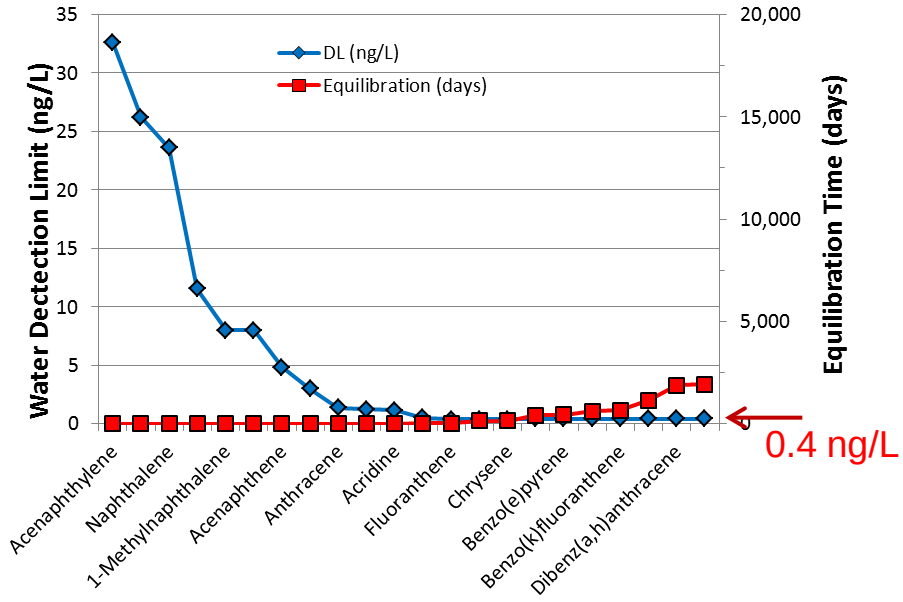
Water Flow: 0.1 cm/s

2 mil film, 15 cm dia, 10 °C



Water Flow: 10 cm/s

2 mil film, 15 cm dia, 10 °C



What else can modeling tell us?
Preferred Film Thickness

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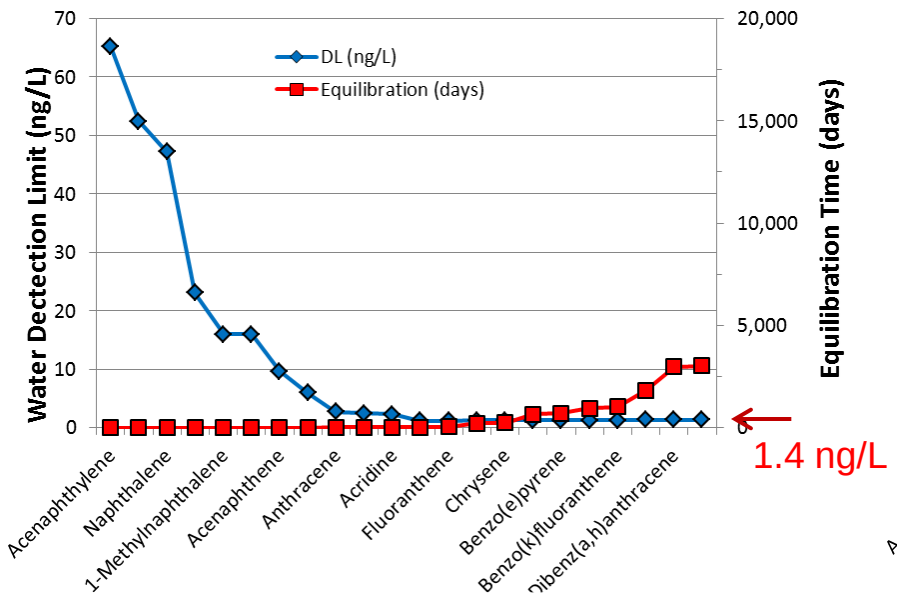
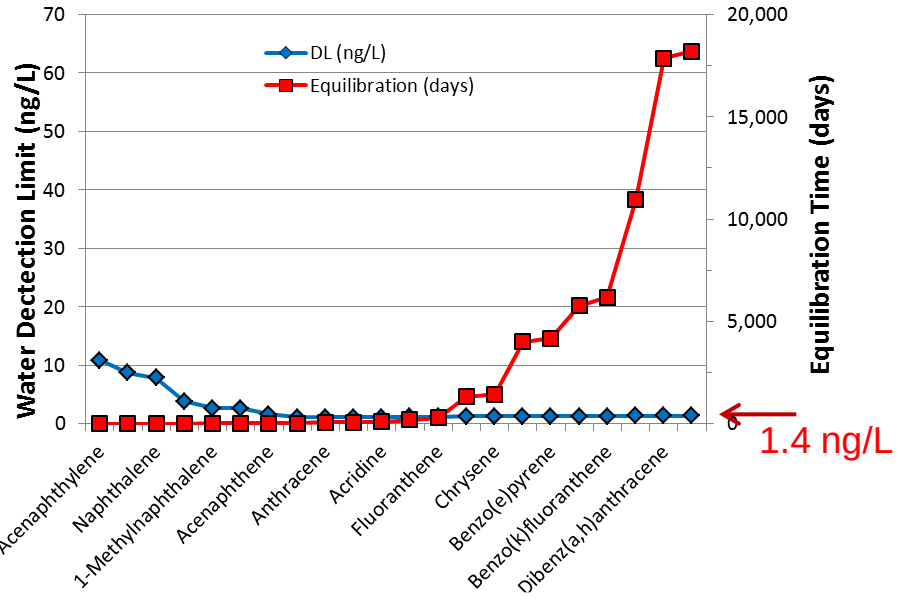
Film Thickness: 1 mil

1 cm/s, 150 cm^2, 10 °C



Film Thickness: 6 mil

1 cm/s, 150 cm^2, 10 °C



Do we know if different films are the same?
Film Crystallinity Study

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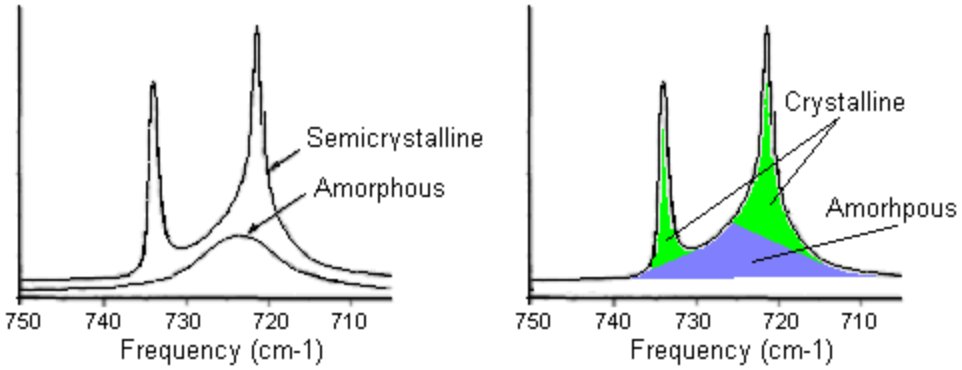
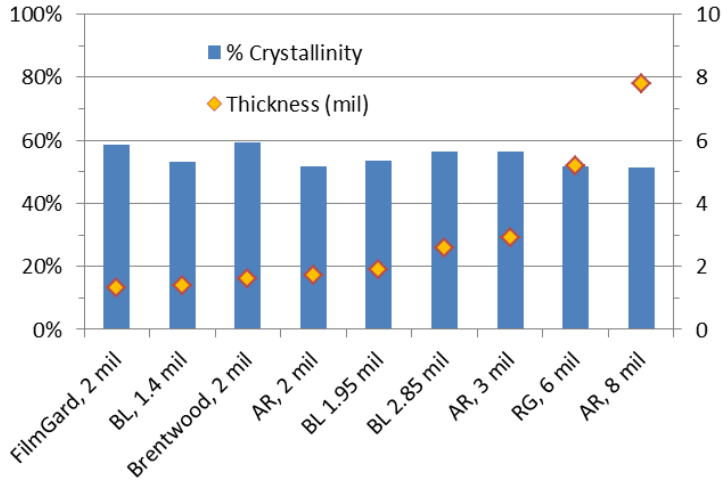
- LDPE is composed of crystalline and amorphous regions
- Uptake associated primarily with the amorphous regions
- FTIR spectroscopy was used to investigate the degree of crystallinity



Crystallinity is estimated by subtracting the amorphous region from the total crystalline peak

H. Hagemann, et al., *Macromolecules*, **22**, 3600 (1989)



- % crystallinity is similar for all films (50-60%)
- A significant difference between stated and actual thickness is noted for some films

Calibration Options: Equilibrium vs. Pre-Equilibrium

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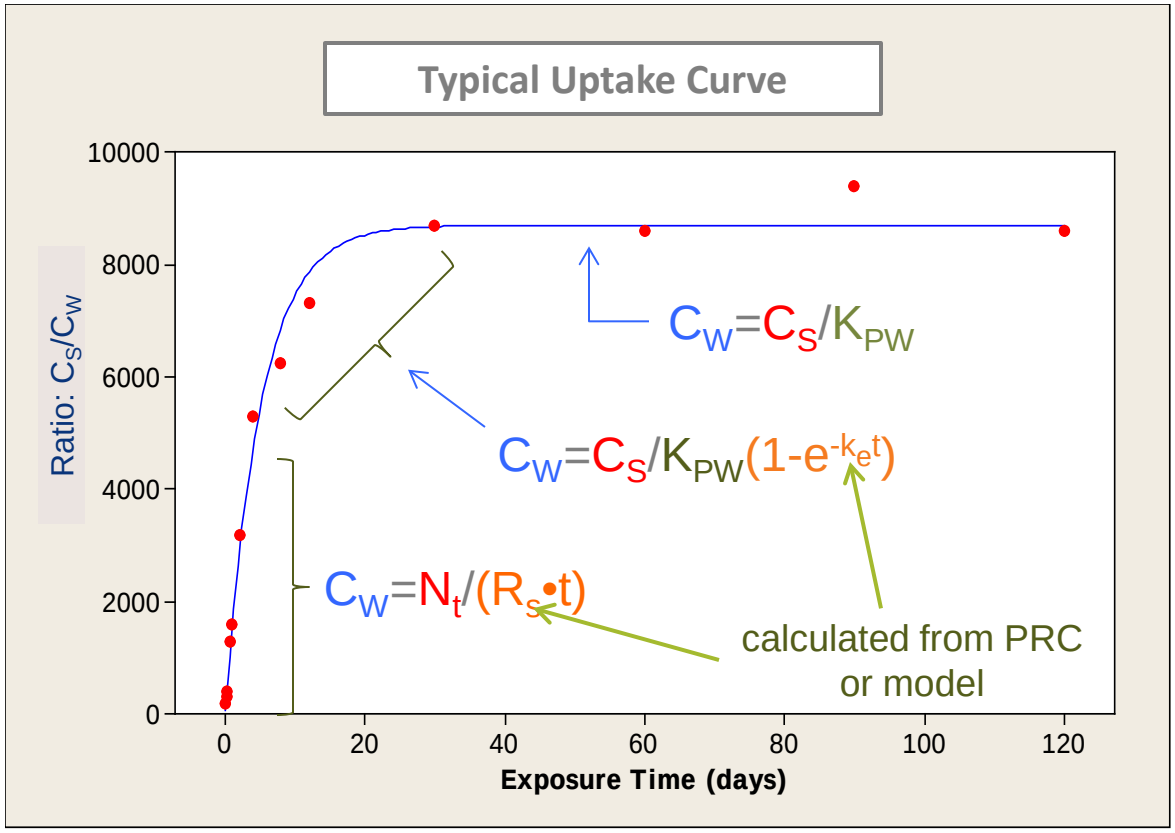

Different equations are used to estimate C_w depending on uptake phase

- Equilibration ($f > 0.95$)
- Transition
- Linear ($f < 0.5$)

PRC: Performance reference compounds

- pre-loaded standards
- PRC loss used to determine uptake rates and fractional uptake

ISO (2011) Water quality – sampling – part 23: Guidance on passive sampling in surface waters, 5667-23:2100 (E).

How to use PRC to measure uptake in the field?

- Deuterated PAH loaded in the film before deployment
- Amount of PRC loss correlates to degree of uptake:

PRC	Log K_{PW}
Fluorene-d10	3.83
Fluoranthene-d10	4.75
Benzo(a)anthracene-d12	5.37
Benzo(e)pyrene-d12	5.85

$$k_e = \ln \frac{n_0}{n_t} \Big/ t$$

$$R_s = k_e K_{PW} V_S$$

n_0 = mass of PRC loaded
n_t = mass of PRC remaining at end of deployment time (t)

Use PRC to Estimate Kinetics for Other PAH:

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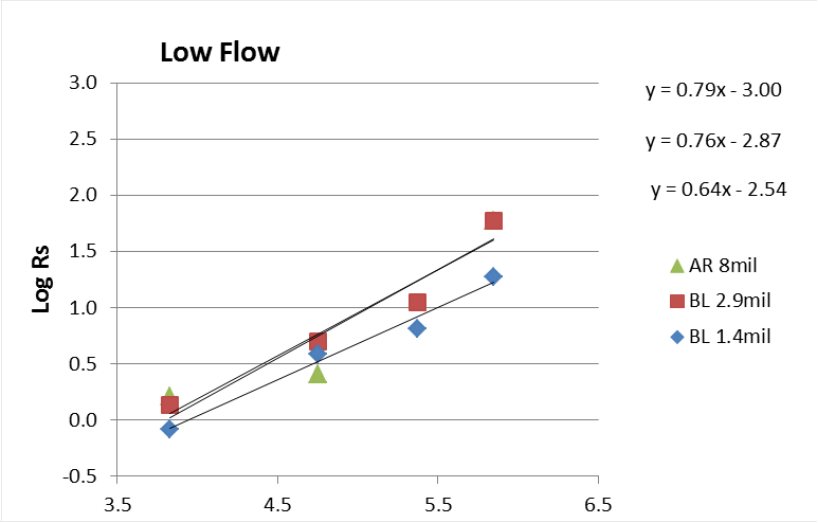

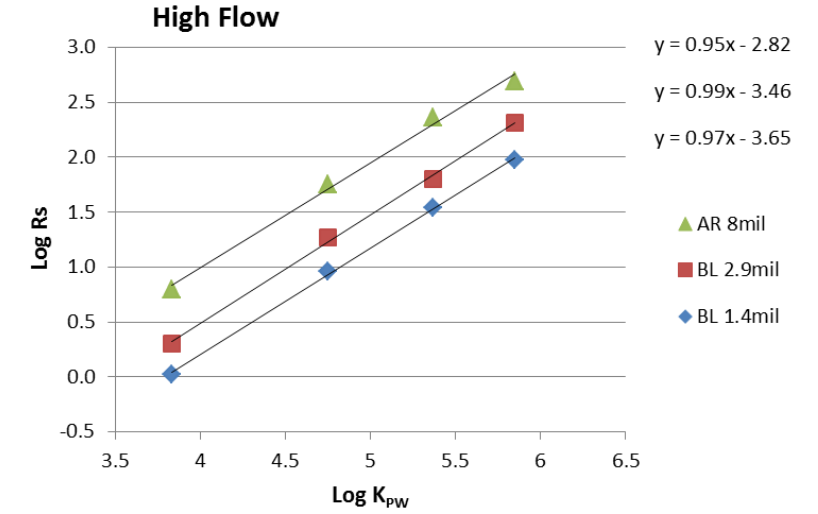

R_S vs. K_{PW} correlation

- R_s data are plotted vs. K_{PW} to establish relationship

$$R_s = K_{PW}{}^{a}\beta$$

$$LogR_S = a \bullet LogK_{PW} + Log\beta$$

Example Results

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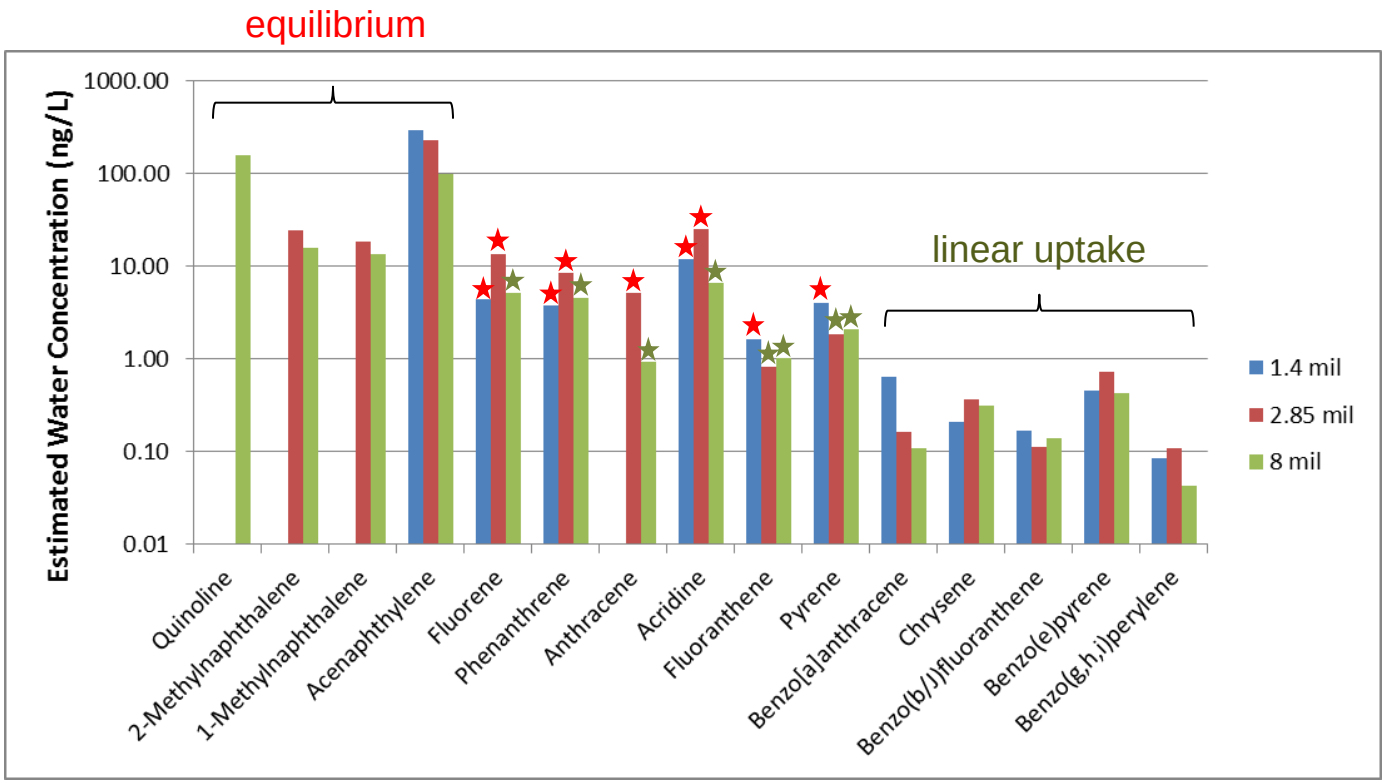

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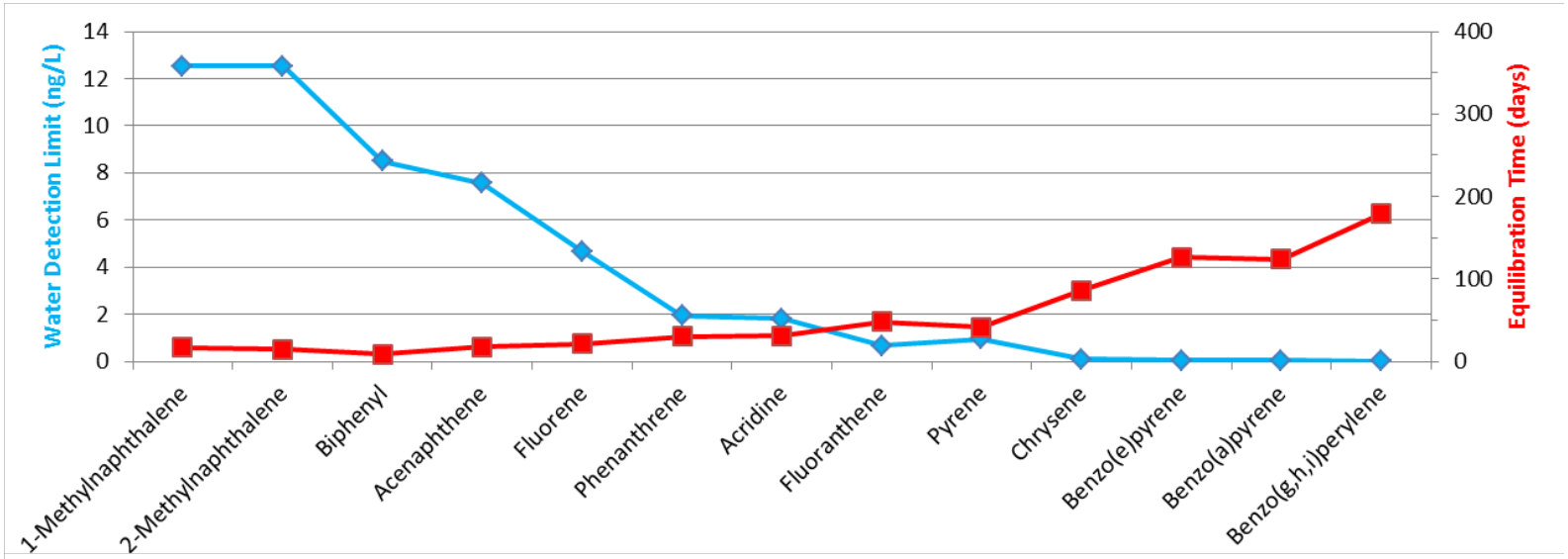
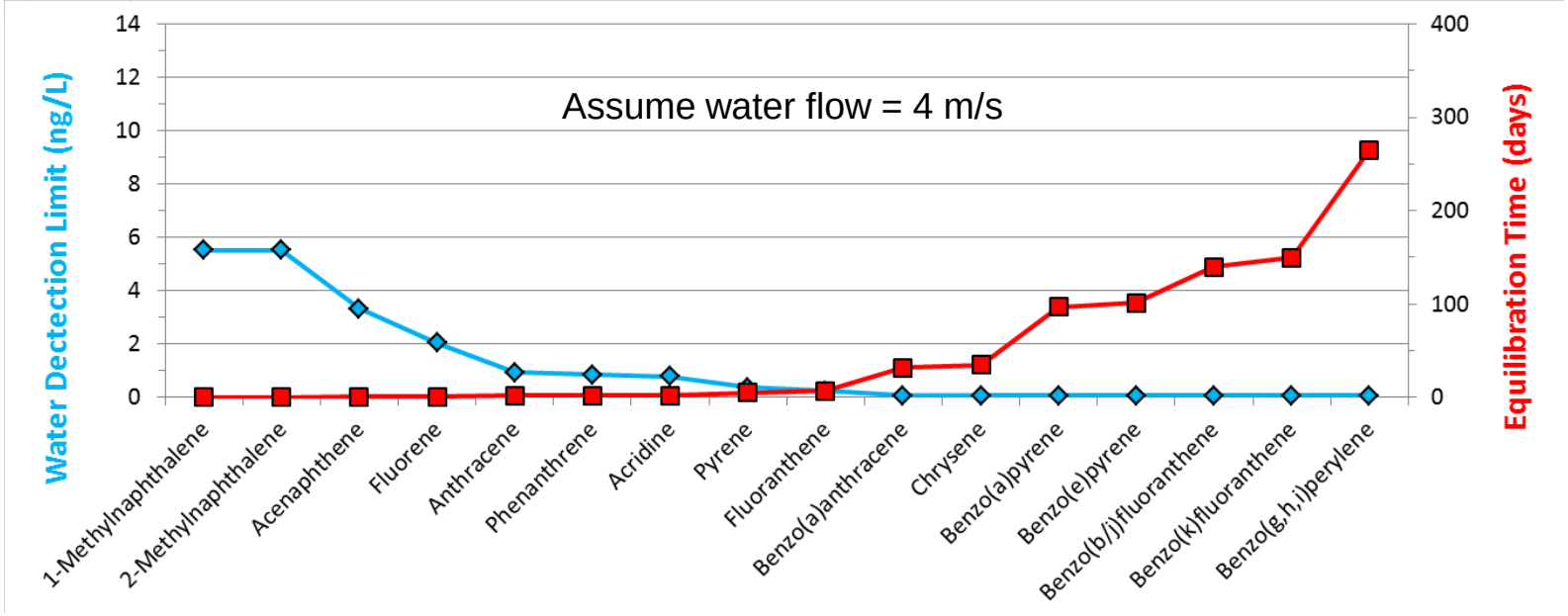
Comparison of Observed Data vs. Model

Med. Flow Site, 2.9 mil film

Expt. Data



Model



Conclusions:

1. LDPE samplers are inexpensive, easy to deploy & process
2. Literature data for K_{PEW} are available
   - Effective calibration only for the lighter PAH
3. Heavier PAH don't equilibrate, need to measure uptake rate
   - Deuterated PAH loaded in film
   - Used to estimate uptake rates of all PAH
4. Modeling is helpful to guide deployment planning

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Questions?

Heather Lord
hlord@maxxam.ca