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What Causes Inconsistencies among Different Labs Using Passive Sampling and How Can We Fix Them?

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Background/Objectives With the growing realization that measured freely dissolved concentrations better represent the bioavailability of hydrophobic organic compounds (HOCs) than traditional sediment-based methods, there is a need to ensure that methods to determine freely dissolved concentrations perform consistently. This is particularly important for target compound lists of regulatory interest (e.g., the parent and alkyl PAHs in the EPA's "PAH-34" list, all 209 PCB congeners). Although direct methods are available for some compound classes (e.g., ASTM D7363 for PAH-34), indirect methods using passive sampling appear likely to predominant in future. Unfortunately, there is no consensus on the best passive sampling approaches, and even labs using seemingly similar methods have arrived at varying results in sorbent/water partitioning coefficients, $K_{sorbent}$. Inconsistent, method-dependent $K_{sorbent}$ values can complicate obtaining consistent freely dissolved concentrations across different laboratories. For example, reported $K_{sorbent}$ values for a single sorbent, polyoxymethylene (POM) have varied by as much as 2 orders of magnitude among different laboratories, and thus it may not be immediately clear which $K_{sorbent}$ value to use. The goal of the present study is to determine and correct the causes of method biases in order to improve methods to determine freely-dissolved concentrations with passive samplers.

Approach/Activities This study used POM from a commercial source (76 µm) as well as prepared using a lathe in thicknesses of 17, 55, and 80 µm. Investigations included (1) selection of sorbent material and its thickness, (2) mixed vs. static exposure (e.g., lab vs. field), (3) environmental factors (4, 23, and 40^{o}C water, 0-10 wt.% salt, (4) extraction efficiencies from the sorbent, and (5) differences in analytical procedures, calibrations, etc. among different labs. All experiments were performed at EERC by the same analysts to eliminate any inconsistencies that could result from different analysis and calibration methods. All four sorbents were exposed in the same jars (done in triplicate) to two PAH-contaminated sediments at the various test conditions, followed by solvent extraction and analysis using GC/MS.

Results/Lessons Learned The results of these studies demonstrate for HOCs that:

1. *Most importantly:* Literature disagreements on Kpom values are largely a result of assuming equilibrium when it was not achieved (especially for thicker sorbents) and poor extraction efficiencies (e.g., when hexane alone is used). Mixed solvents including a polar solvent (such as hexane/acetone) are required. Approaching sorbent/water equilibrium (or knowing sorption rates) of target HOCs during the sorption process is critical to obtain consistent $K_{sorbent}$ values.

2. Mixed systems approach equilibrium MUCH faster (at least ten times) than static systems.
3. Different preparation methods and different thicknesses (17 to 80 μm) of POM do not affect results as long as equilibrium is approached. (Thinner POMs equilibrate more rapidly, but are more difficult to clean.)
4. Dissolved salt concentrations have no significant effect on Kpom values.
5. Temperature does affect sorbent/water partitioning, and further related work is needed.

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Why do passive sampling?

1. Freely-dissolved concentrations better predict bioavailability. Passive sampling is one approach to determine freely-dissolved concentrations (there are others).

2. Passive sampling can be very sensitive: ng/L (part-per-trillion) to pg/L (part-per-quadrillion !)

3. Field deployable.

4. ***Potentially*** much more "user-friendly" than other approaches to determine freely-dissolved concentrations (e.g., our ASTM D7363 direct SPME method).

What is passive sampling?

A non-depletive (weak) sorbent is allowed to equilibrate (not deplete) with the “freely-dissolved” phase in water (can also be done in air).

Analytes are extracted from the sorbent, and dissolved concentrations are calculated from previously determined water/sorbent partitioning values (Ksorbent).

Ksorbent = (conc. in sorbent) ÷ (conc. in water)

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Why has passive sampling not gained wider regulatory acceptance?

1. There are no “standard” approaches. Lots of approaches are under use and development, but no method has been approved by ASTM, EPA, etc.

2. Target compound lists are often too limited for regulatory/site management applications.

Why are there no “standard” passive sampling approaches?

1. A variety of sorbents are being used (PE, POM, PDMS)—all with different characteristics.

2. Determining Ksorbent values is laborious, and values frequently disagree among labs—especially in earlier studies.

3. Knowing exposure times to obtain sorbent/water equilibrium (or accounting for non-equilibrium, e.g., using PRCs) can be difficult, especially in the field.

4. Effects of field conditions (e.g., salt, temperature, presence of NAPLs) are not well-studied.

sorbents

Why POM?

1. Consistent polymer chemistry (fewer co-polymer variations).
2. Mechanically strong.
3. Easy to clean and keep clean (e.g., colloids, biofouling).
4. Slight polarity may help with more polar analytes.

But, it is slower than PDMS.

PE $-CH_2-CH_2-CH_2-$
POM $-CH_2-O-CH_2-O-$
PDMS $-(CH_3)_2SiO-$

POM
76 um commercial
17 to 85 µm “home-made”

EERC
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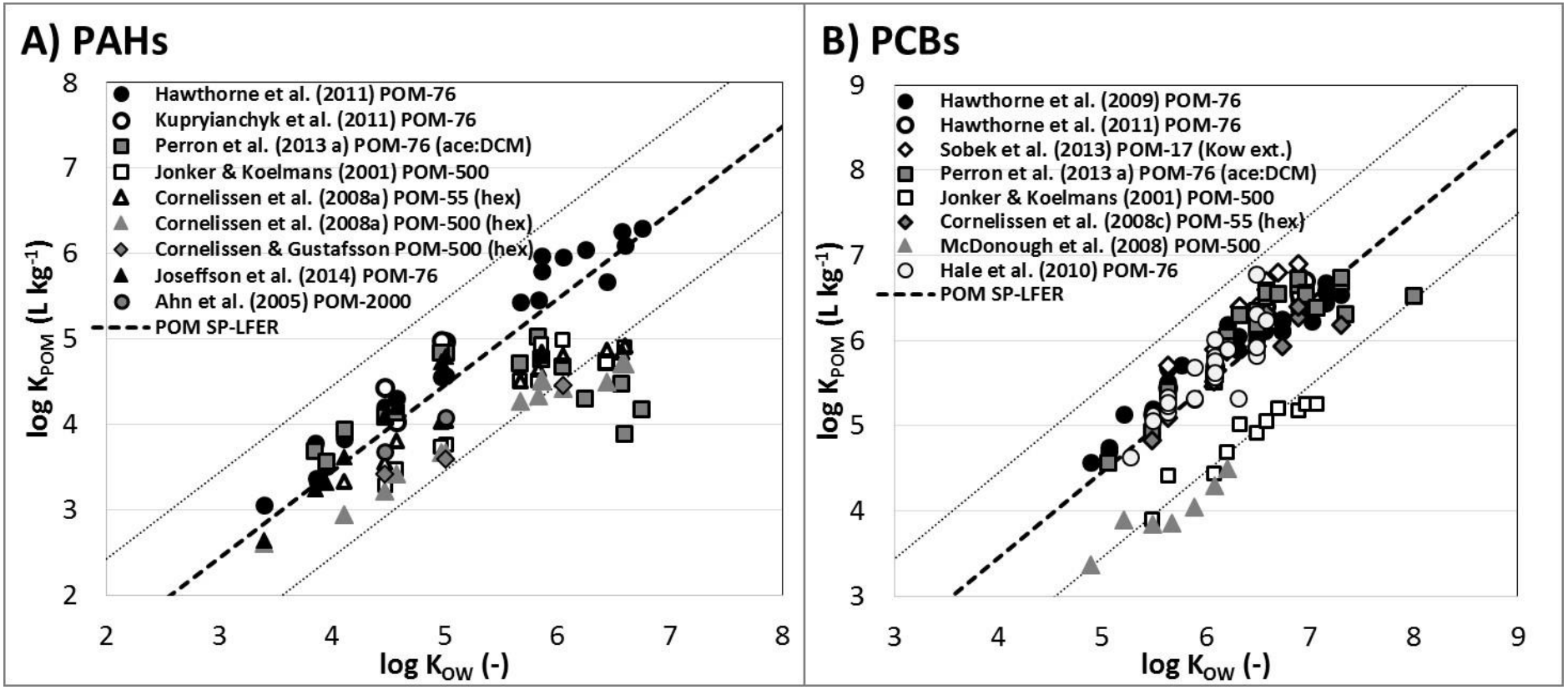
1st Problem: Ksorbent values don't always agree—why?



BIG problem with passive sampling: The accuracy of dissolved concentrations depends on Kpom (or Kpe or Kpdms) values.

Why did early Kpom values for the same HOC sometimes vary by orders of magnitude?

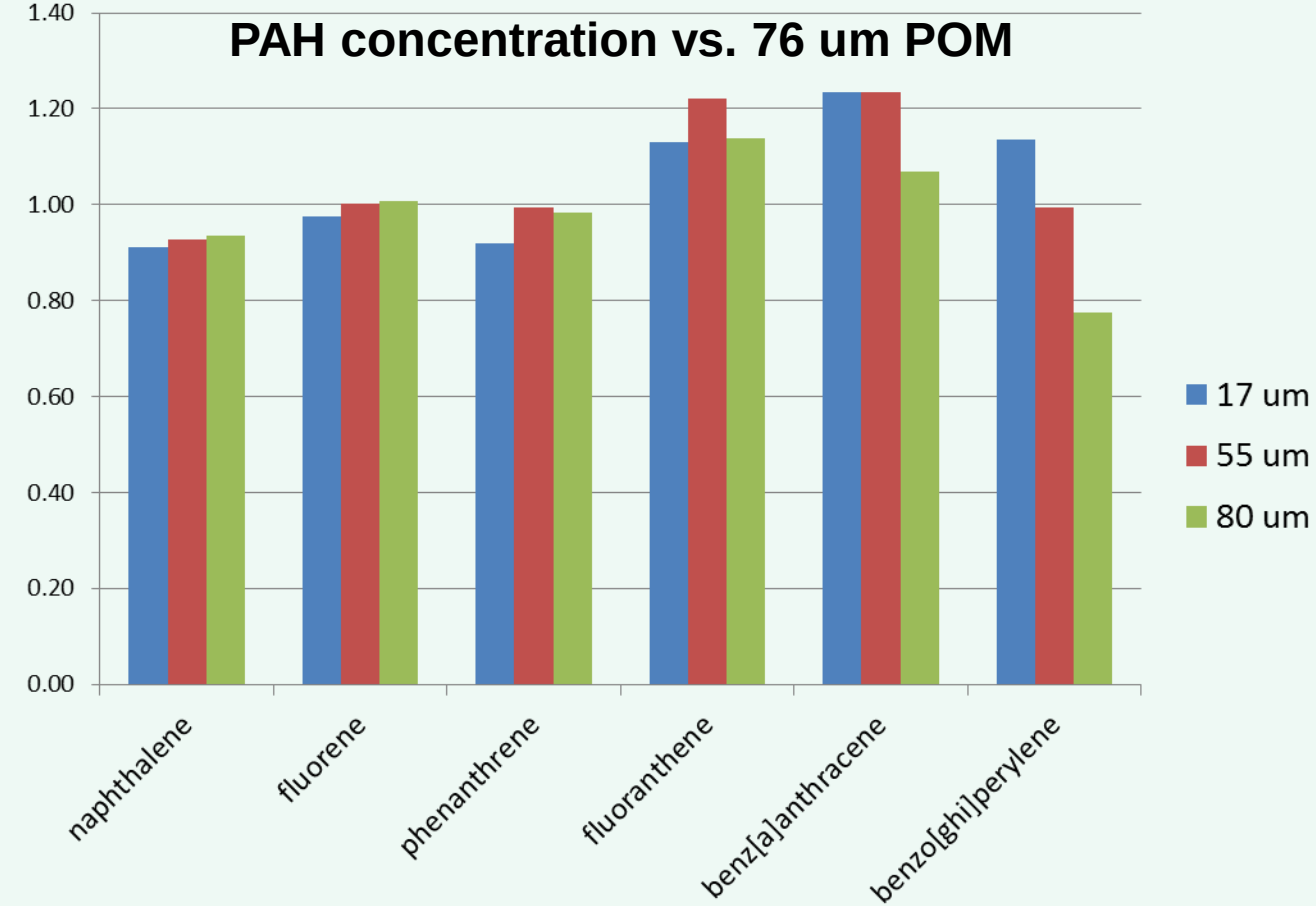
1. Sorbent not at equilibrium (e.g., 500 µm POM). Problem is largely solved by using thinner POM sheets (76 µm is the thinnest commercially available, home-made as thin as 17 µm).

2. Even the "same" sorbents can have different characteristics (especially PDMS). Potential for different behavior from different POM sources.

3. Inefficient extraction of sorbed HOCs (surprisingly common).

Are all POMs created equal?
(different thicknesses, different sources, effects of milling?)

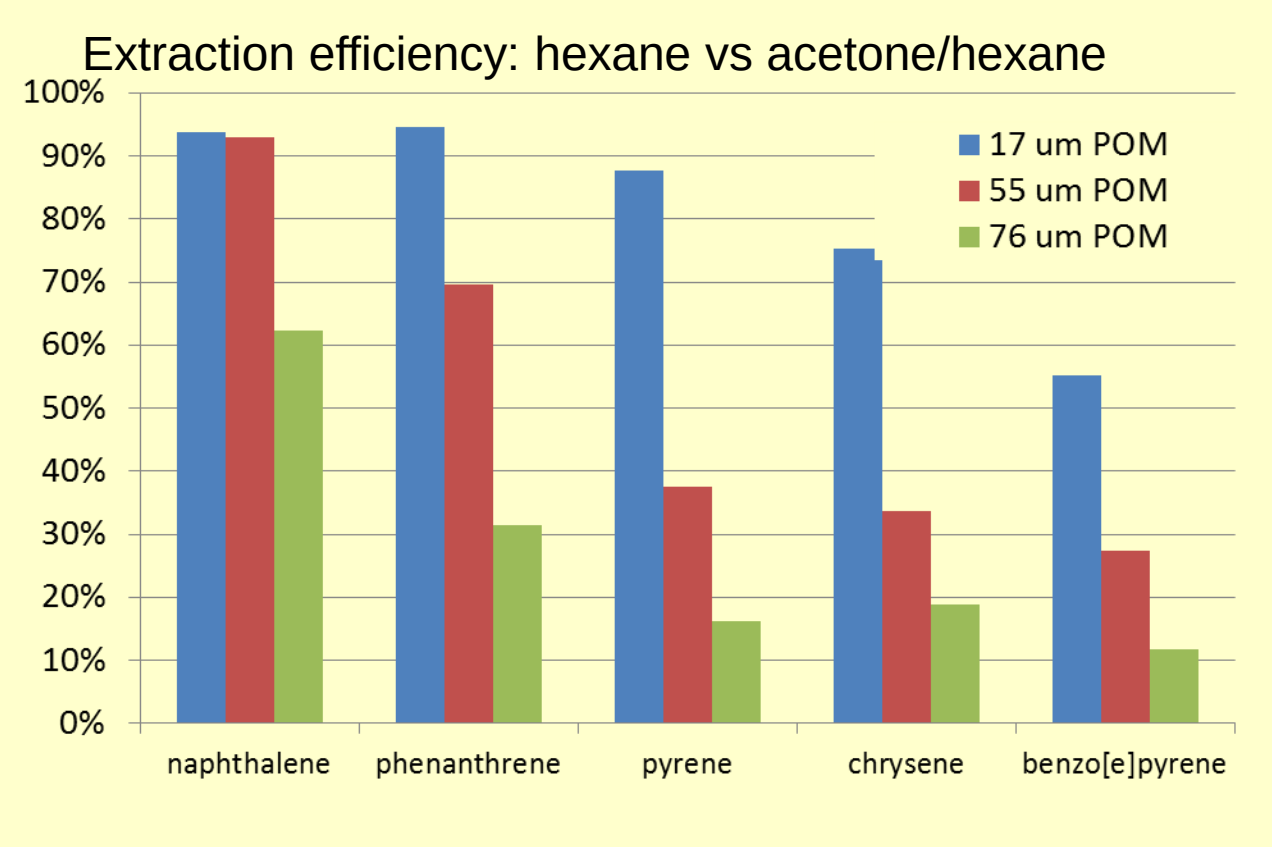
PAH concentrations after 28-days in "home-made" POM showed good agreement with commercial 76 um POM



Many early Kpom values are too low, because of inefficient solvent extraction.

POM requires a "wetting" solvent to extract HOCs

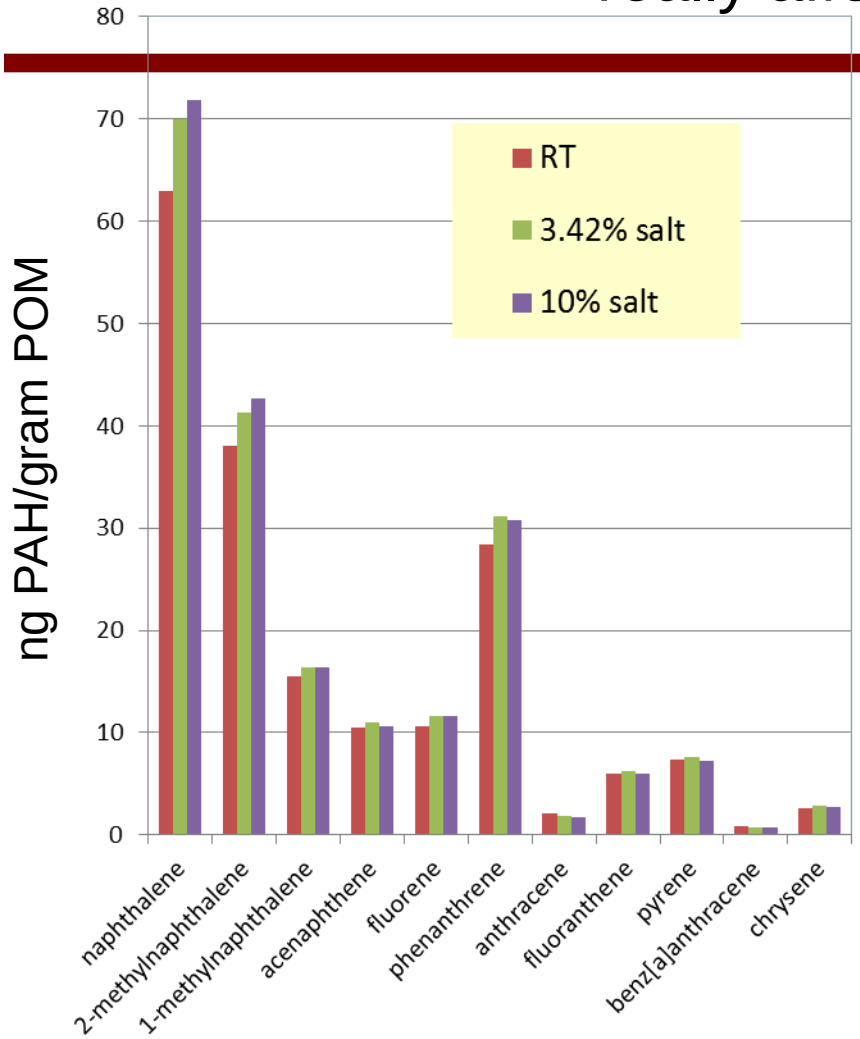
Acetone/hexane gives much higher recoveries than pure hexane.
Recoveries drop with MW and POM thickness.



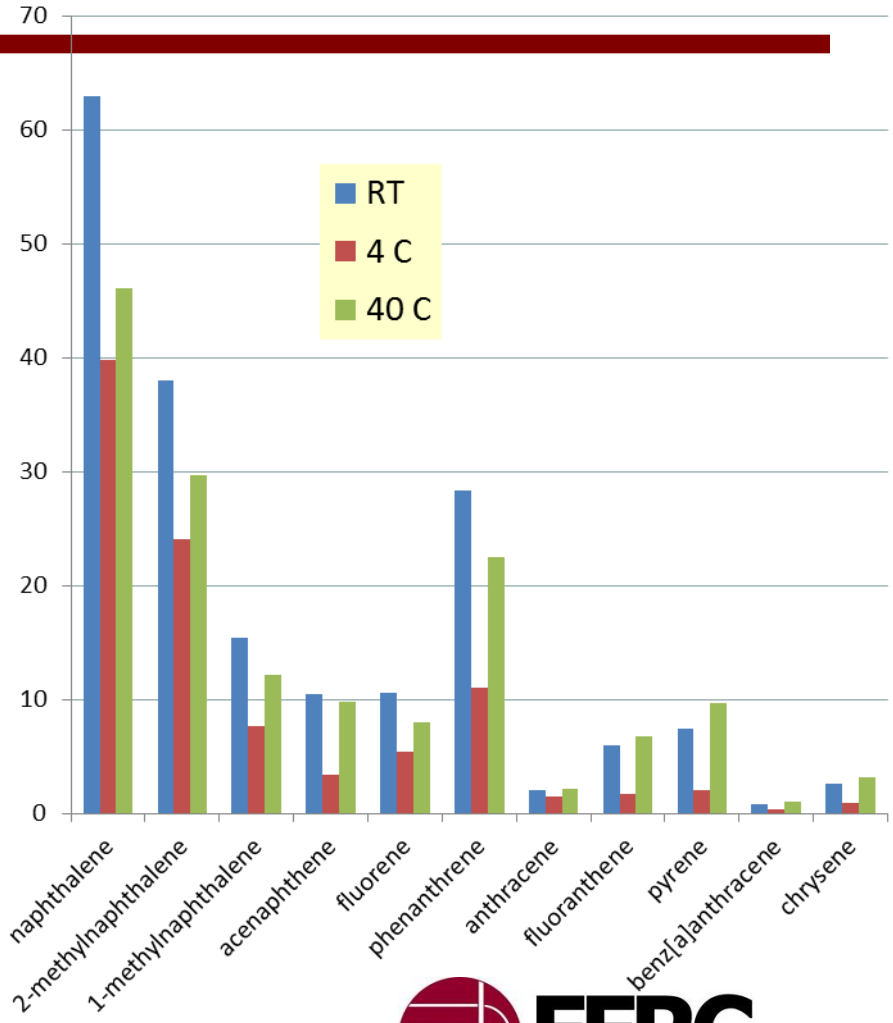
3 hour sonication or 48 rotation both work with mixed solvent.

What about water temperature and salinity?

Water salinity has little effect on POM sorption of PAHs, but lower temperatures depress sorption rates (but didn't really affect Koc).



2-ring ---------- 5-ring



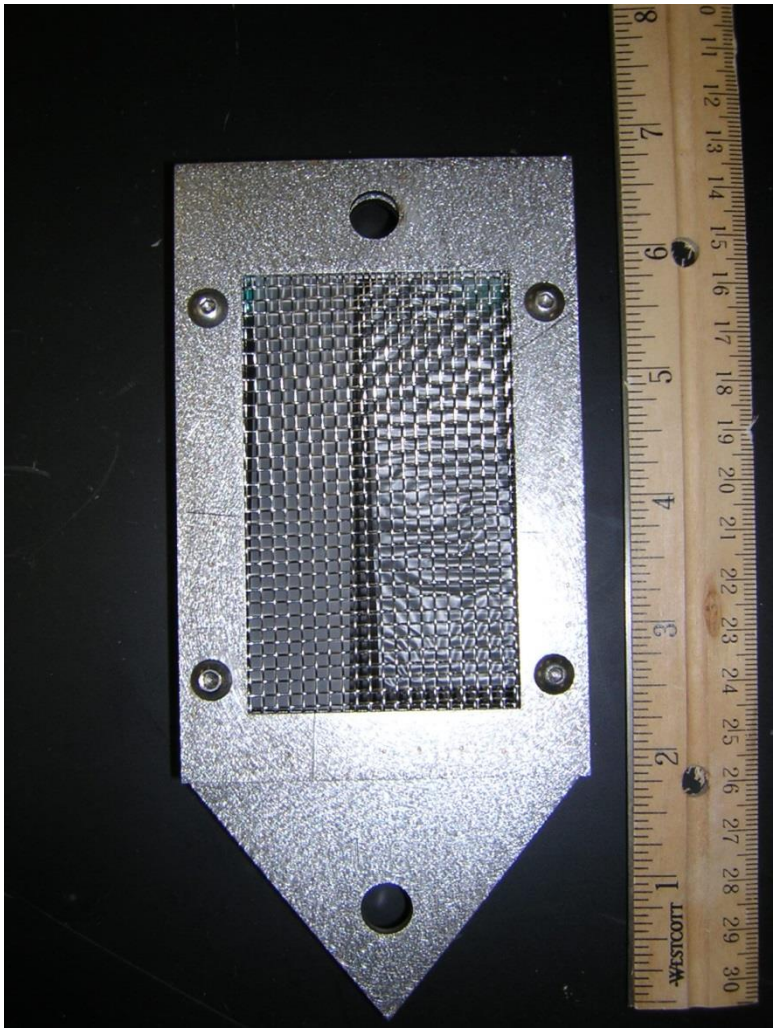
2-ring ---------- 5-ring

Field vs Lab Equilibration Times

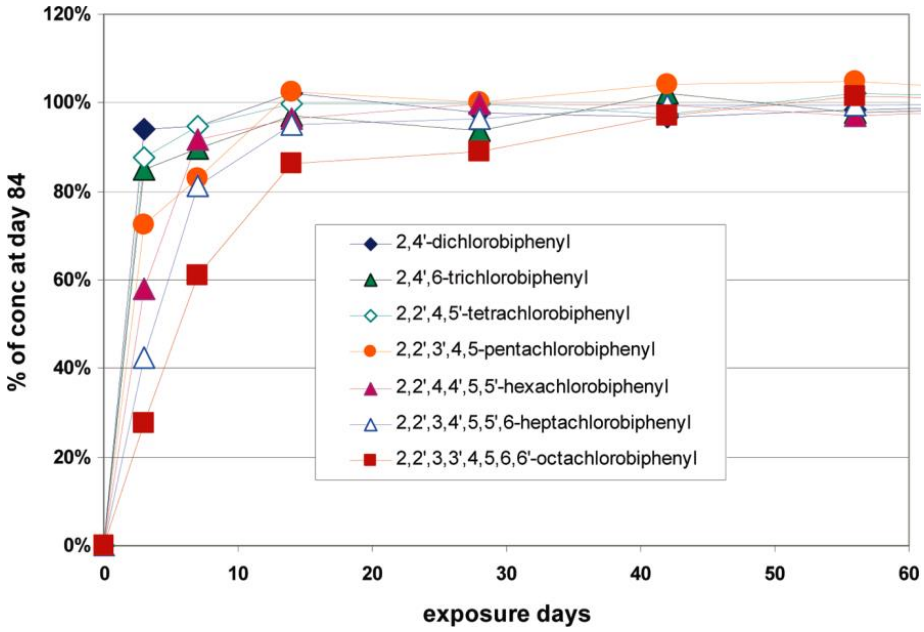
Lab Method: Sorbents are placed directly in the sediment/water slurry, and mixed.

In the field, “mixing” depends on site conditions.

POM/PE sampling “sword”

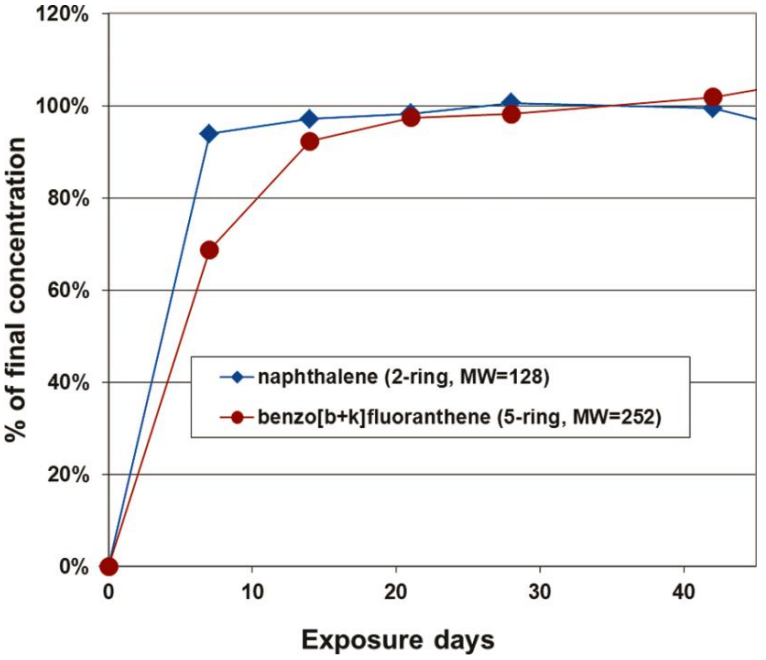


Constant mixing makes lab POM (76 µm) equilibration times consistent and easier to measure. 28 days is sufficient for PAHs and PCBs.



PCBs

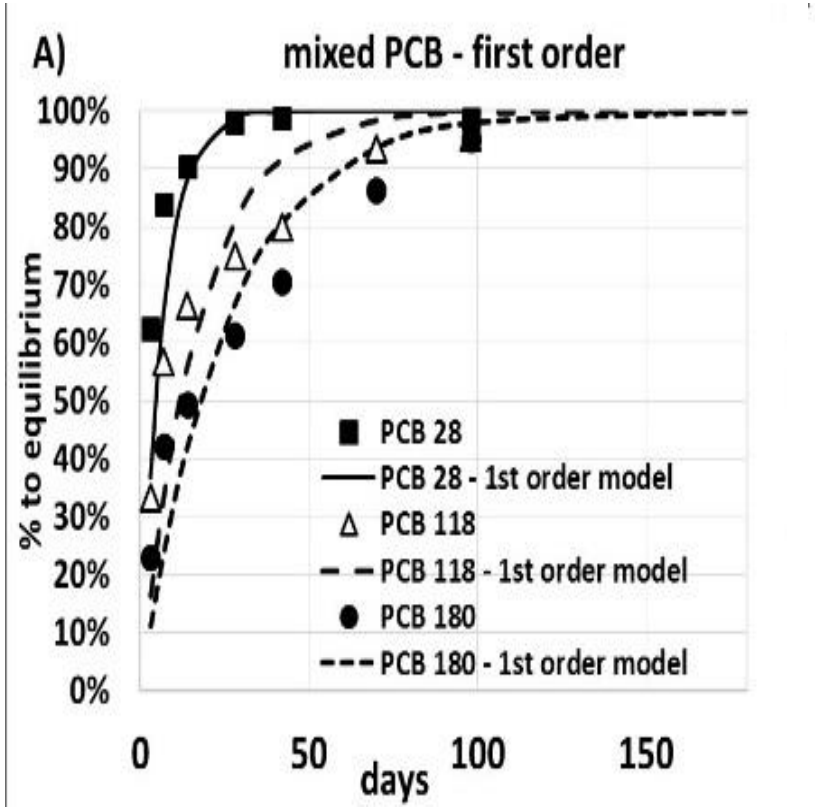
Hawthorne et al. **Anal. Chem.** 2009

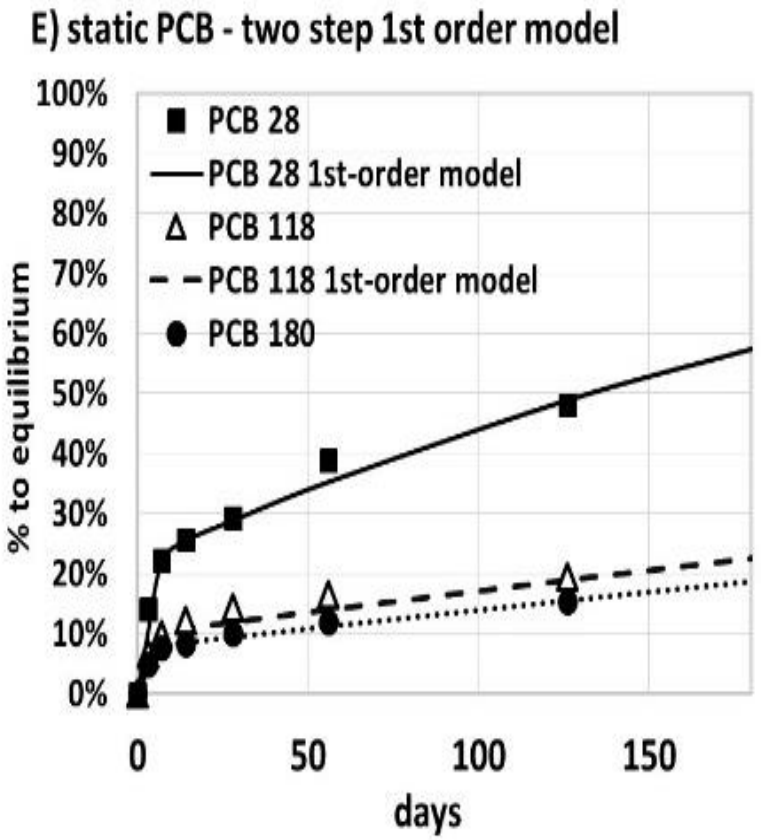


PAHs

Hawthorne et al. **Anal. Chem.** 2011

Mixed vs. static changes equilibrium time.





Mixed systems approach equilibrium MUCH faster (at least ten times) than static systems.

How do we account for field sampling rates (equilibrium)?

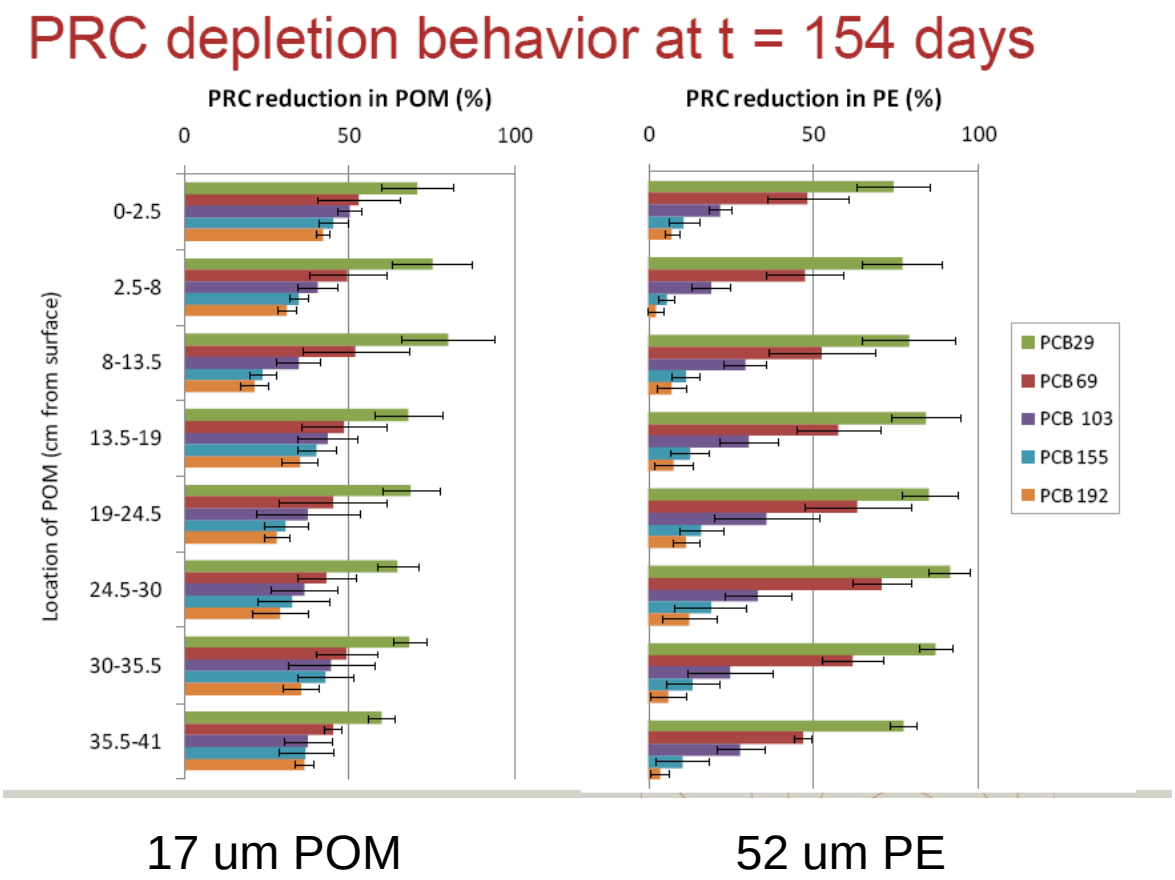
1. **PRCs (performance reference compounds) ??**
   - **Need to represent range of target analytes.**
   - **Some question about desorption vs sorption rates.**

2. **Deploy two different sorbent thicknesses and compare analyte concentrations.**
   - **Twice the analyses.**

3. **Wait a long time.**

4. **Develop sorption rate models.**

Field – in situ exposure in sediment (no mixing)



17 um POM

52 um PE

Oen et al. ES&T 2011 concluded PRC behavior was not as expected.

-Did not observe full depletion of PRC after 160 days of exposure to sediment in situ (no mixing)

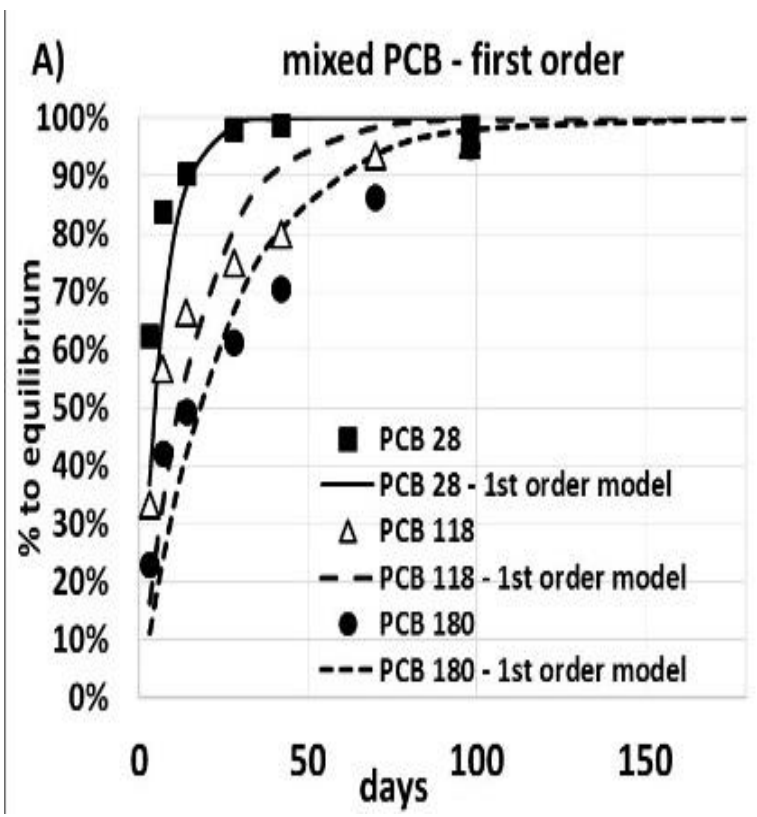
-"Steady state depletion" observed

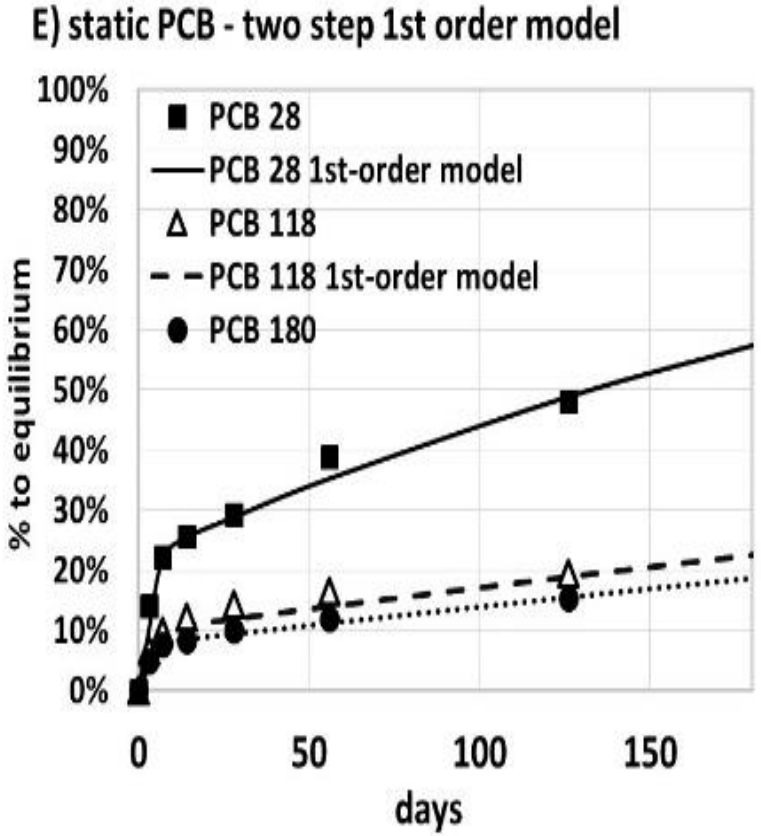
-Hypothesis is the method of adding PRC – by soaking POM in PRC loaded solvent – is problematic.

-Method needs improvement. Future work will try soaking POM in PRC loaded water.

Mixed vs. static changes equilibrium time.

Mass transfer (boundary layers) more rate limiting than diffusion in the polymer?



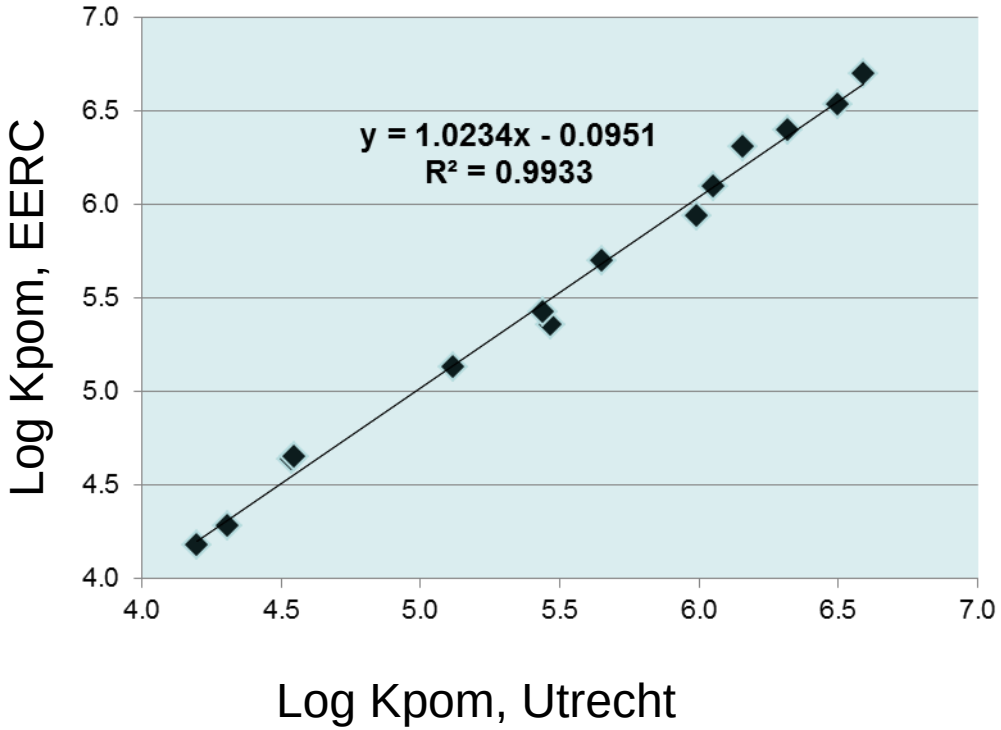


Mixed systems approach equilibrium MUCH faster (at least ten times) than static systems.

How do inter-lab Kpom values agree, if we are careful to achieve equilibrium, and high extraction efficiencies?

Kpom = (conc. in POM) ÷ (conc. in water)

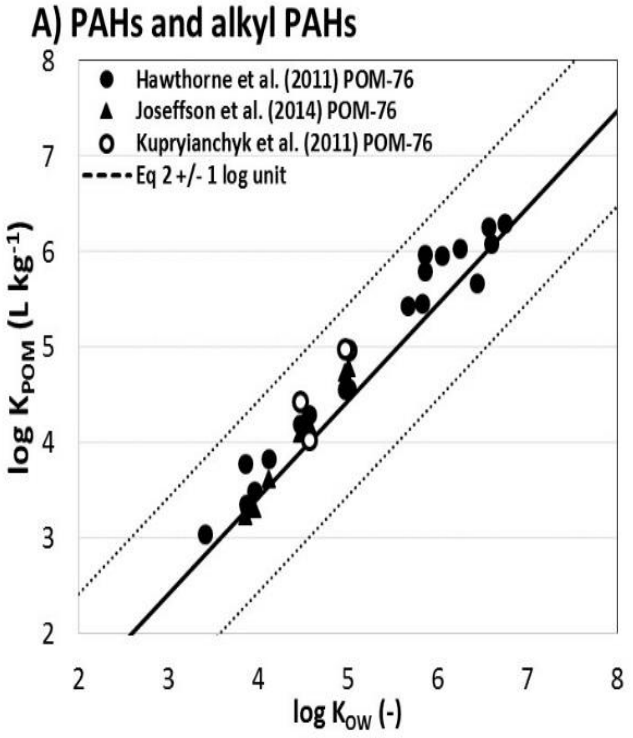
Kpoms determined by Jonker et al. (13 pure PAHs, 5 PCB congeners) and at EERC (contaminated sediments) agree well, with slope of 1 and intercept near zero.

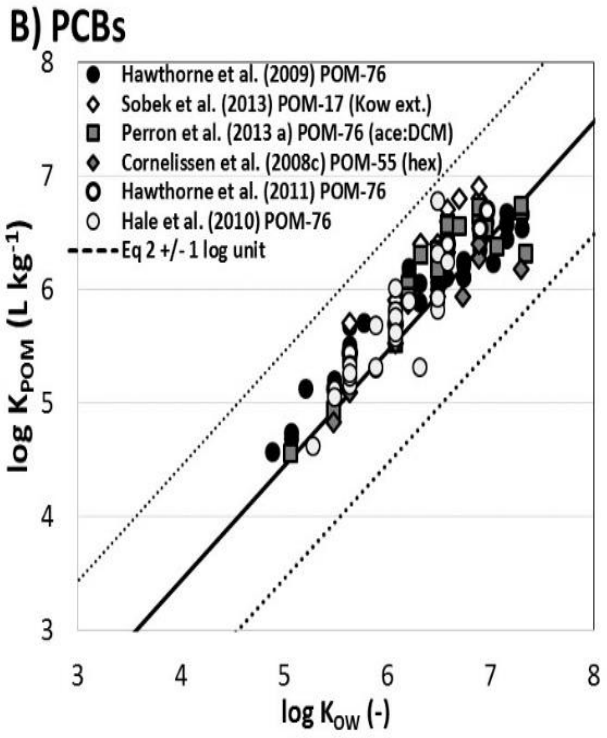


Recent comparisons with Jonker et al., and Cornelissen et al. show generally good agreement for PAH and PCB Kpom values.

Concentrations will vary by 2-29% based on Kpom differences between the two labs.

Accounting for POM reproducibility across labs



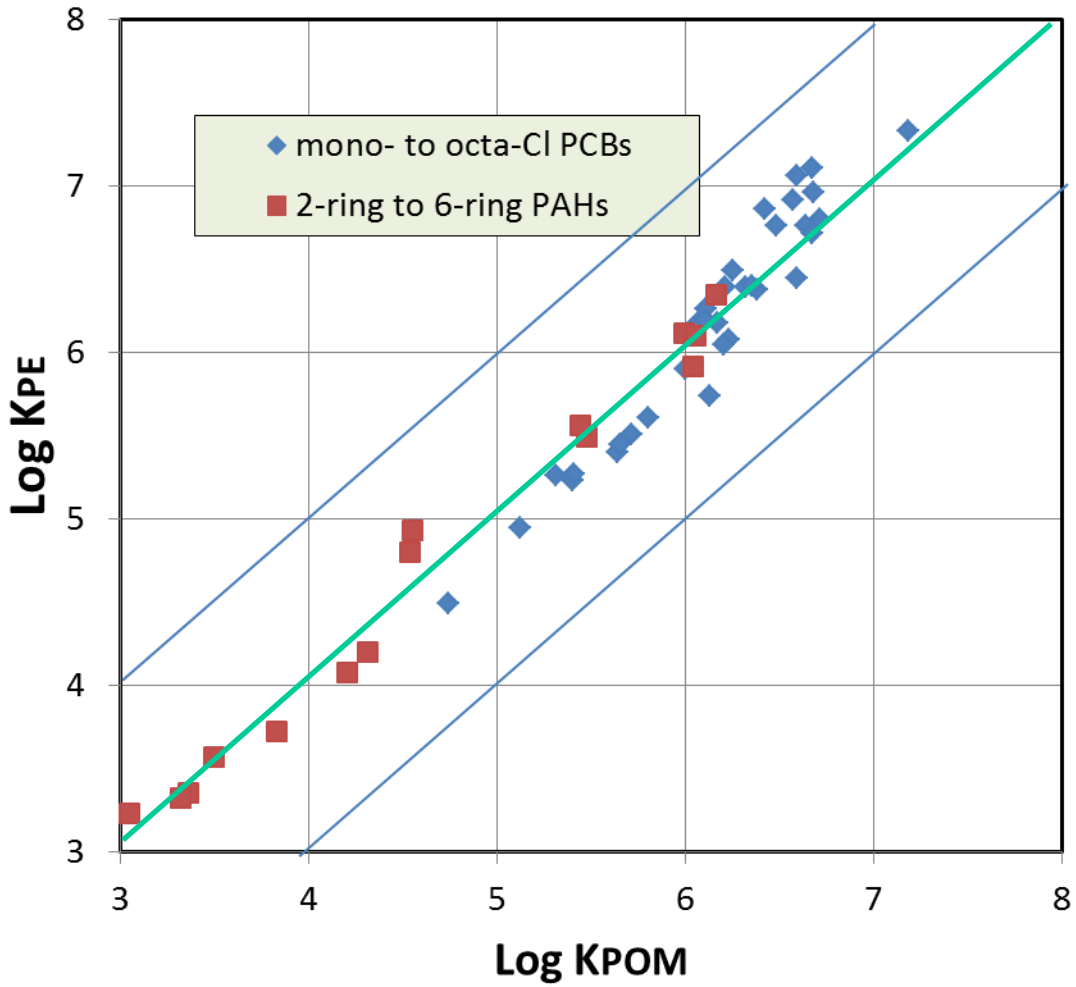


Good reproducibility in the literature when:

Thickness: POM 17 – 80
Extraction Solvent: hex:ace similar
Extraction method: shaking or stronger (sonication, Soxhlet)
Temperature: 15 to 30 °C
Salinity: 0 – 10%
Exposure to sediment: shaking 28 days or longer

Can’t we all just be friends?
POM and PE

Independently-determined Kpom and Kpe values correlate very nicely for PAHs and PCBs



Log KPE: Choi et al., EST, 2013

Log KPOM, Hawthorne et al., EST 2009, 2011

rsq PCBs = 0.94
rsq PAHs = 0.98

Co-deployment of POM and PE at the Kotzebue Airport.

BTEX and PAH-34

NOAA “hockey-puck” sampler.

2.6 g 500 um PE,
0.4 g 25 and 76 um POM

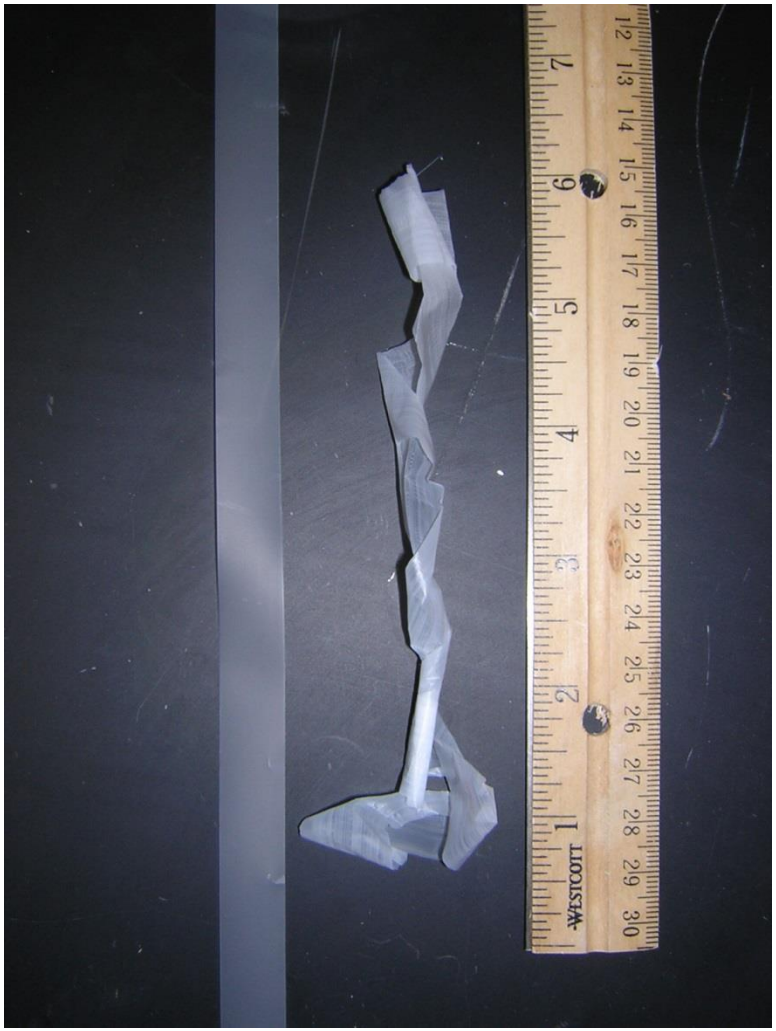
45 day groundwater (tidal flow) deployment

- Only very low concentrations detected making comparisons difficult.
- POM had better detection of low MW species (esp. benzene).
- Agreement between 25 and 76 um POM indicate near equilibrium.
- PE vs POM agreement was reasonable for most species.
- “Curly” lathe-cut POM had poorer detection limits for some species (higher GC/MS background?) .

Freely-dissolved concentrations, ppb (ug/L)

	Sediment A				Sediment B		
	PE	76 um POM	25 um POM		PE	76 um POM	25 um POM
benzene		1.8	1.5			1.2	1.1
naphthalene		0.13	0.28		0.02	0.13	0.14
2-methylnaphthalene	0.005	0.023	0.037		0.01	0.02	
1-methylnaphthalene	0.003	0.009	0.015		0.004	0.007	
acenaphthene	0.008	0.007			0.012	0.009	
fluorene	0.007	0.007	0.010		0.010	0.006	
phenanthrene	0.007	0.006	0.006		0.010	0.006	0.006
fluoranthene	0.002	0.004	0.003		0.002	0.003	0.003
pyrene	0.001	0.003	0.003		0.001	0.002	0.003
benz[a]anthracene	0.00002	0.00003			0.00002	0.00004	
chrysene	0.00003	0.00007			0.00005	0.00010	
"corrected"							
fluoranthene	0.003	0.004	0.003		0.003	0.003	0.003
pyrene	0.003	0.003	0.003		0.003	0.002	0.003

New approach using a “gold roller” yields smooth 25 um POM, rather than curly lathe-cut POM.



If Ksorbent values are so difficult ($$$) to measure, how are models doing?

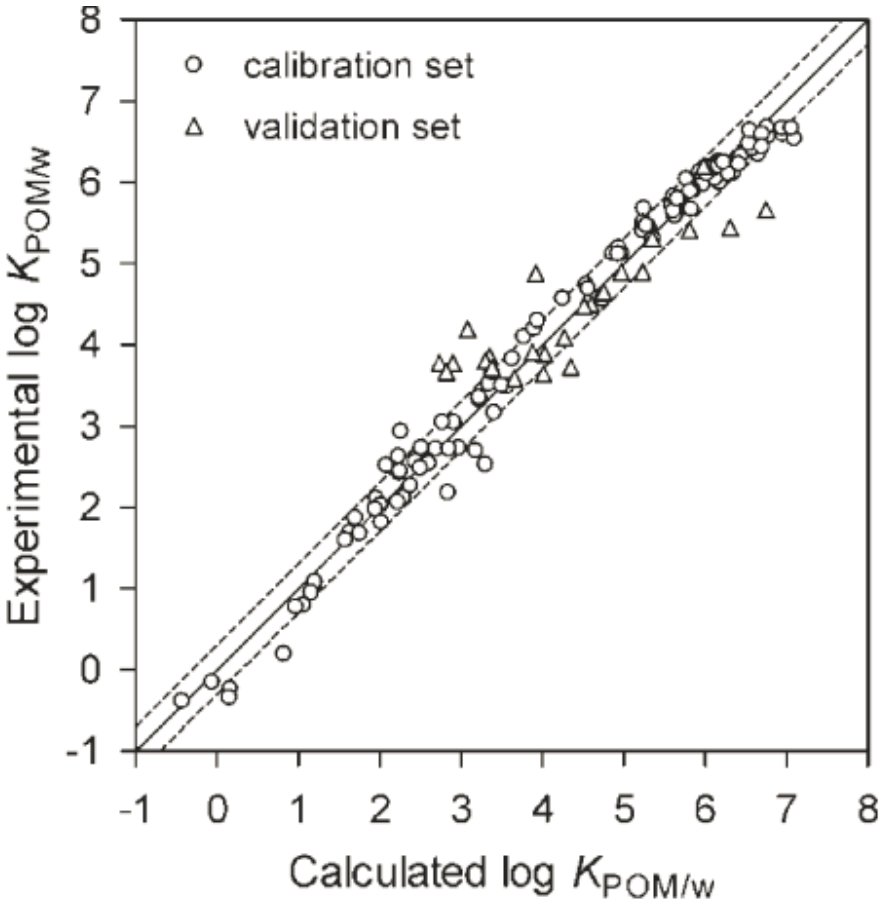
K_{POM} predictive models

PP-LFER model predicts reasonable Kpom values for polar and non-polar organics.

K_{POM} vs PP-LFER K_{POM} (n=116)

r^2 = 0.986

SD = 0.24



Key stats:

No. PCB = 53
No. PAH =20
No. Pesticides = 13
No. Other cmpds =43

Model can estimate K_{POM} usually within a factor 2 – 3, and nearly always within a factor 10.

Endo et al. ***ES&T*** 2011

$$\log K_{POM/w} = -0.24(0.12) + 0.27(0.04)L + 0.17(0.12)S - 0.62(0.15)A - 4.03(0.09)B + 2.10(0.19)V$$

Passive sampling has focused on hydrophoic organics (high Kow), but Endo's model successfully includes very soluble molecules.

	log Kpom
n-heptane	3.05
n-octane	3.52
n-nonane	4.10
2,2,4-trimethylpentane	2.70
cycloheptane	2.18
cyclooctane	2.53
1-nonene	3.66
1-heptyne	2.43
trichloromethane	1.69
trichloroethene	2.11
tetrachloroethene	2.58
di-*n*-butyl ether	1.68
di-*n*-pentyl ether	2.54
2-octanone	1.60
2-nonanone	2.03
2-decanone	2.57
methyl phenyl sulfoxide	−0.23
tri-*n*-butyl phosphate	1.87
1-heptanol	1.04
3-ethyl-3-hexanol	0.80

	log Kpom
2-butoxyethanol	−0.38
1,4-dibromobenzene	3.17
ethyl benzoate	1.98
valerophenone	2.49
benzophenone	2.73
di-*n*-propyl phthalate	2.72
2-nitrotoluene	2.12
2,4-dinitrotoluene	2.52
2,4,6-trinitrotoluene	2.94
4-nitroanisole	2.07
2,5-dimethylpyrazine	−0.34
caffeine	−0.15
diazepam	1.82
4-chlorobenzyl alcohol	1.09
phenol	0.78
4-iodophenol	2.27
1-naphthol	2.45
2-phenylphenol	2.74
bisphenol A	2.63
2-methylaniline	0.95
acetanilide	0.20
carbazole	3.49
estrone	2.72

Endo et al., EST, 2011

Analytical considerations

Large sets of measured Kpom values are available for:

59 PCB congeners (Hawthorne et al., 2009)
PAH-34 (Hawthorne et al. 2011)
56 polar to non-polar organics (Endo et al., 2011)

For PCBs and PAHs:

- 28 day equilibration with mixing (76 µm POM) is close enough
- 4-5 orders of magnitude linearity
- 0.1 to 100 pg/L detection limits (for PCBs and PAHs) with 100 mg POM.

Compounds with lower Kow values have poorer detection limits, because Kpom values are lower.

Conclusions/Observations

1. Passive sampling is one way (but not the only one) to determine freely-dissolved HOC concentrations.

2. Poor extraction efficiencies and failure to come to equilibrium (thicker sorbents) explain earlier disagreeing Kpom values, but:

3. Consistent multi-lab values now exist.

4. All POMs behave similarly (or pretty close !)

5. Water salinity did not measurably change POM uptake.

6. Water temperature is important to uptake, and not well understood.

7. Pretty good agreement between co-deployed PE and POM, and similar K values are encouraging.

Biggest needs to implement passive sampling more widely ?

1. More and better Ksorbent values.

2. Better “vetting” of analytical methods (e.g., solvent extraction)

3. Better understanding of matrix issues (temperature, marix/colloid contamination, biofouling, etc.)

4. Consistent sorbent materials and procedures so that many labs can use one set of Ksorbent values.

5. Better models for estimating Ksorbent values.

6. Better understanding of equilibrium times, and methods (like PRCs, sorption rate models) to compensate for non-equilibrium sampling.