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Using Passive Sampling at Contaminated Sites for Human and Ecological Risk Assessments

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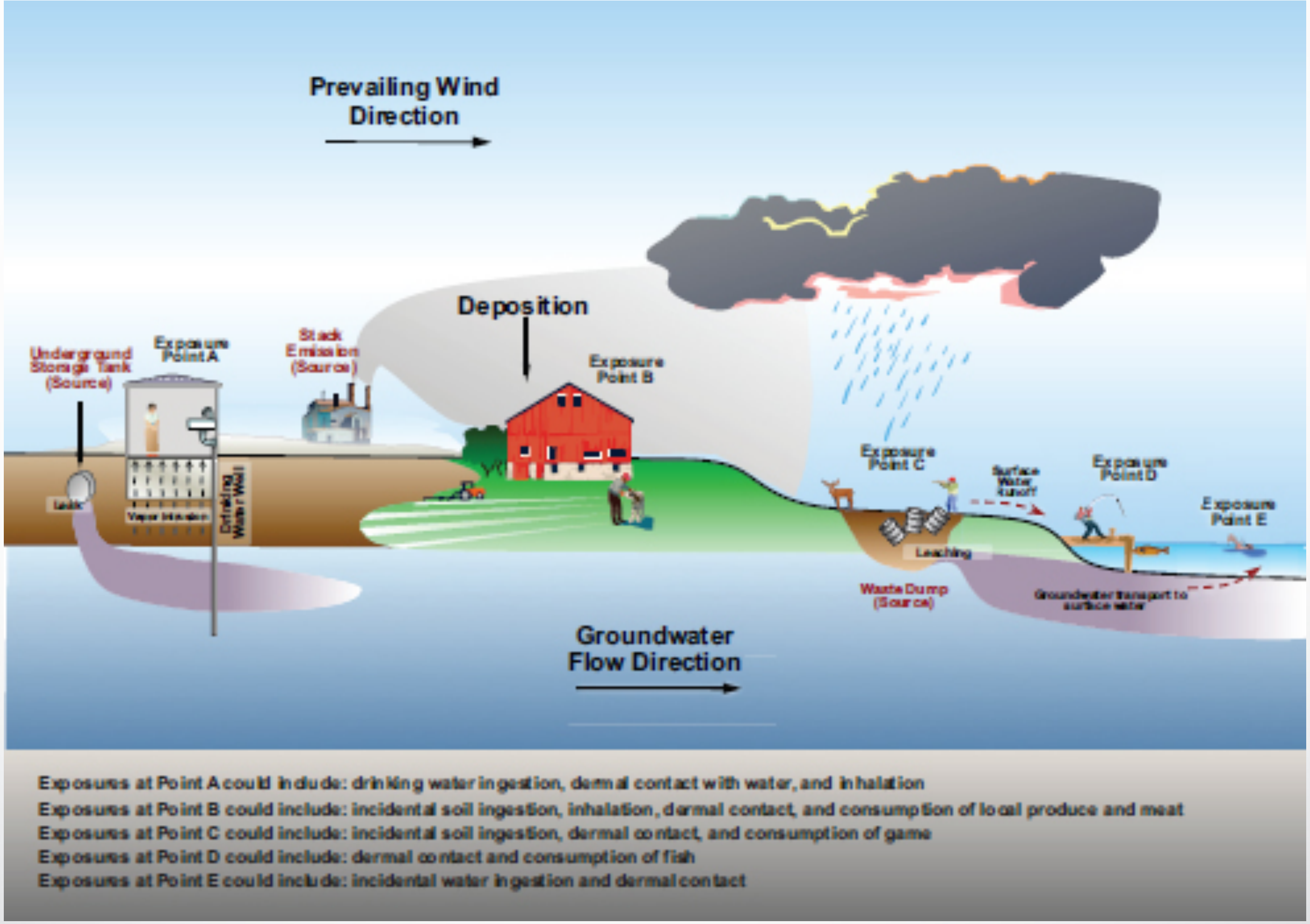
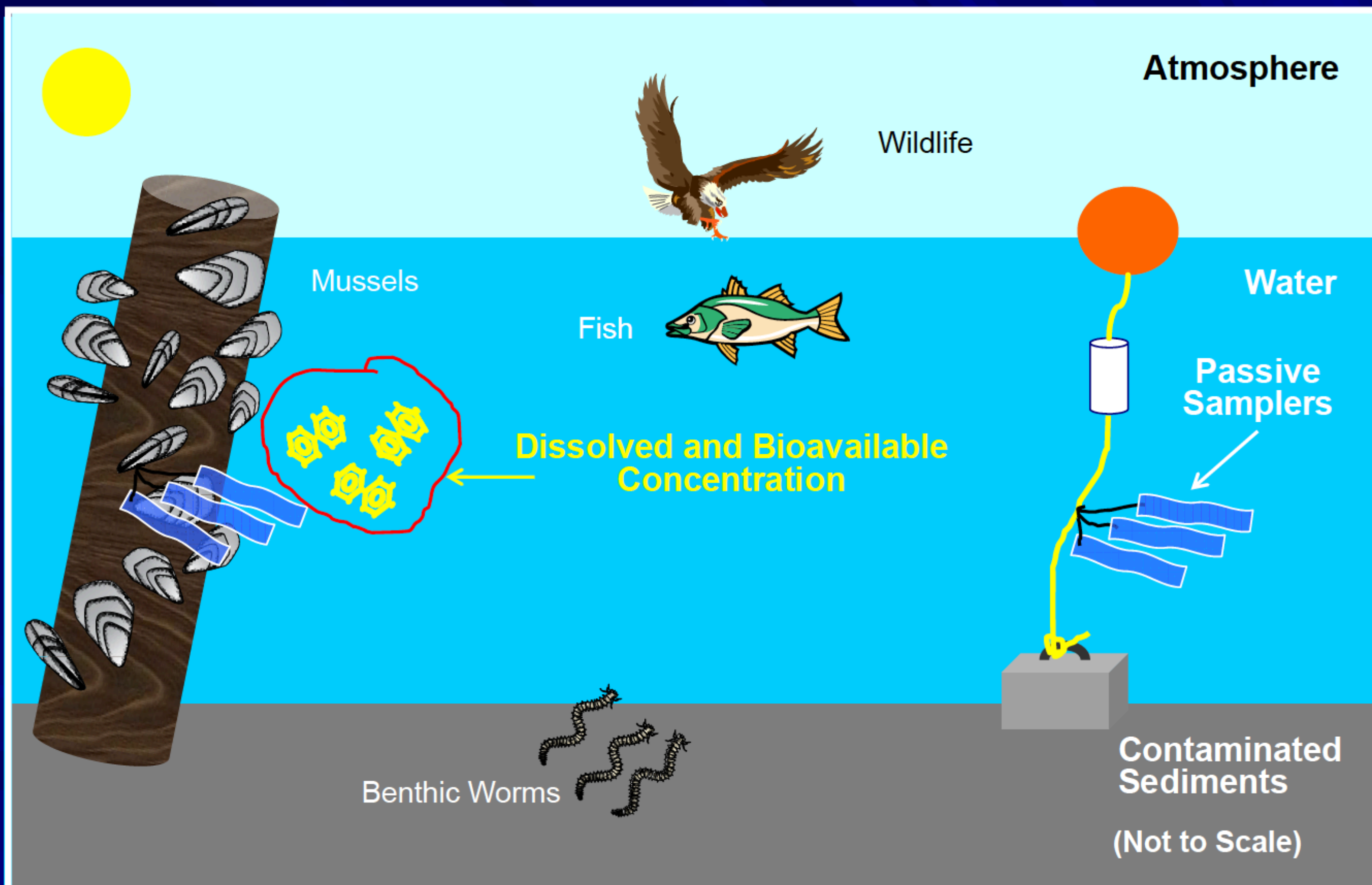
Outline of presentation

1. Overview and theory of passive sampling
2. Examples with surface and groundwater
3. Examples with sediment and soil
4. Regulatory implications and potential impact

Passive sampling can be used in any environmental medium

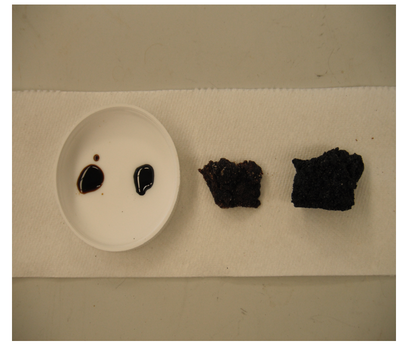


Conceptual Model of Relationship Between Contaminated Sediments and Aquatic Life



Octanol-water (and other) partition coefficients

$K_{OW} = C_{octanol} / C_{water}$



$K_{OIL} = C_{oil} / C_{water}$

$K_{d,\ soil} = C_{soil} / C_{w} = f_{OC}\ K_{OC}$

f_{OC} is the mass fraction of organic carbon in the soil, K_{OC} is the OC-water distribution coefficient

Because K_{OW} values range ~9 orders of magnitude for chemicals we are interested in, we use $\log_{10}$ scale, or log K_{OW}

Simplified model of the partitioning processes that control the bioavailability of PAH

P: Parent PAH

M: PAH metabolites (oxy-PAH)

K_{PSW} and K_{MSW}: PSD-water partition coefficients of P and M

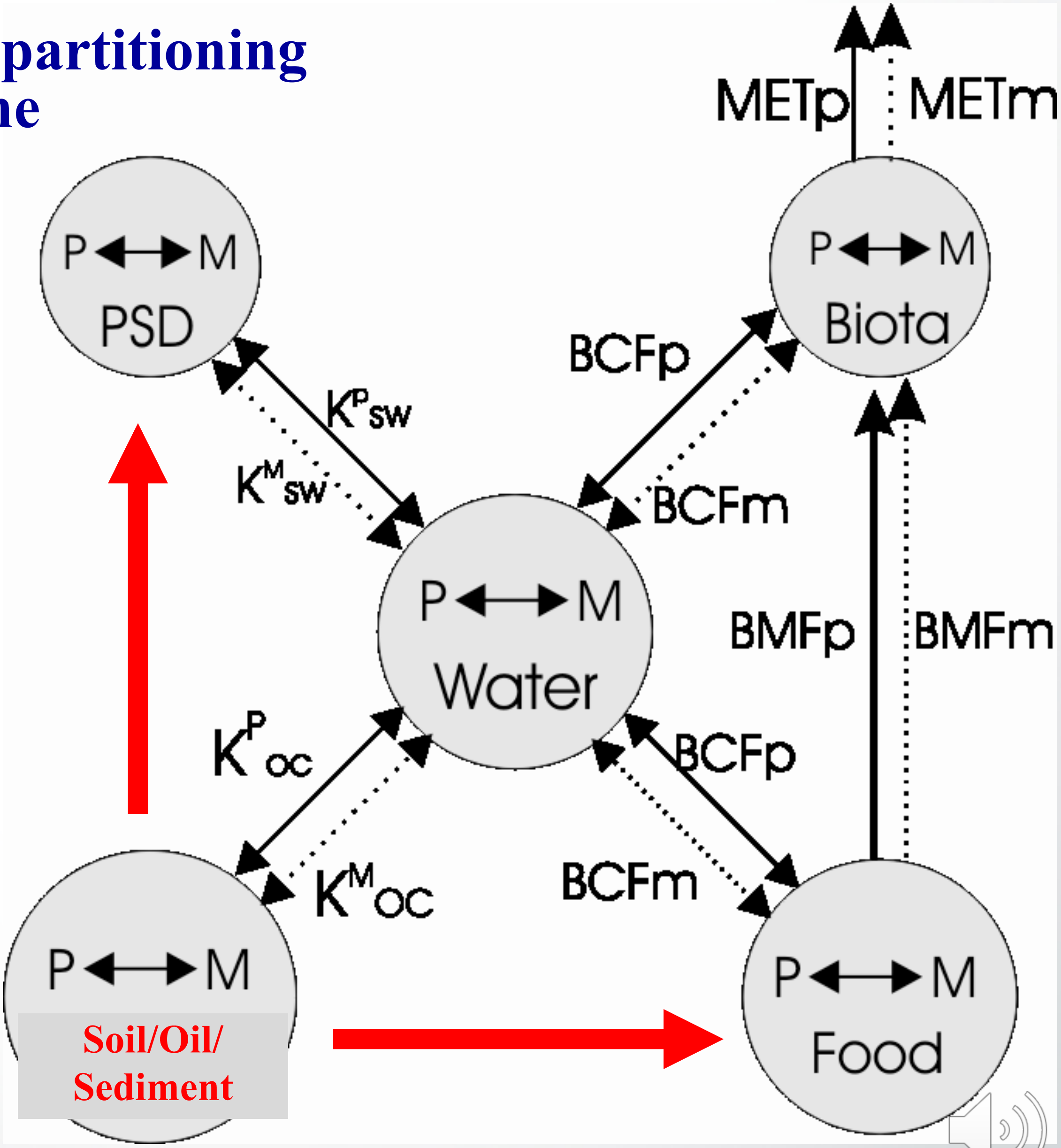
K_{POC} and K_{MOC}: oil or other organic carbon sorption coefficients of P and M

BCF: bioconcentration factor

BMF: biomagnification factor

MET: metabolic clearance

K_{POM} and $K_{D\ (sediment)}$ determined via POM in equilibria with water and sediment using two-phase equilibria model (EqP)



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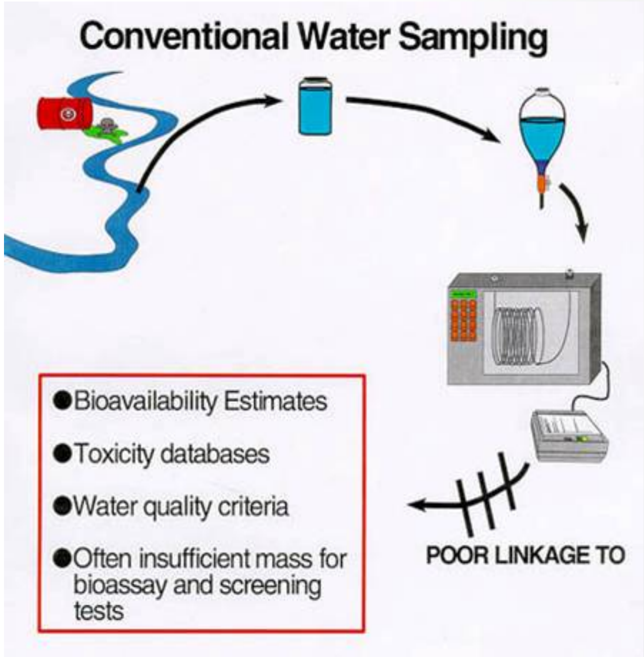
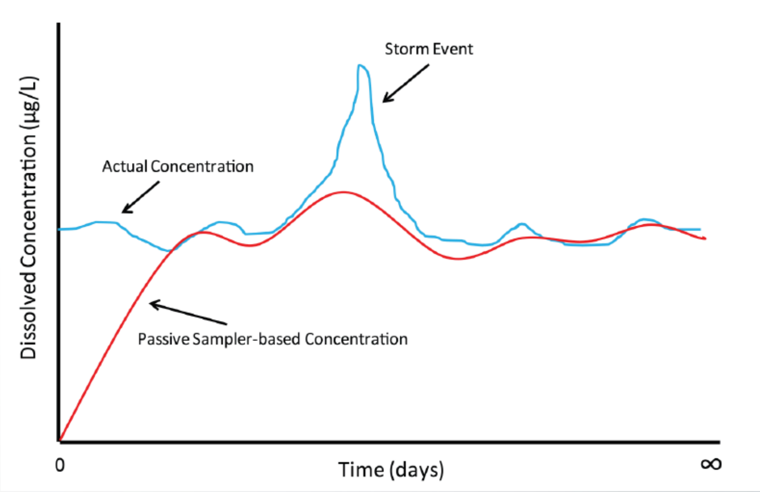
Grab Sampling

Collect water, transport to lab, extract, pre-concentrate, analyze

Offers "accepted" approach and time-point data, but has disadvantages

- "Snapshot" in time
- No information on chronic exposure
- No information on bioavailability
- Large amount of water and solvent needed (not very green)
- Often has insufficient sensitivity
- Multiple samples/extraction needed for different class of chemicals





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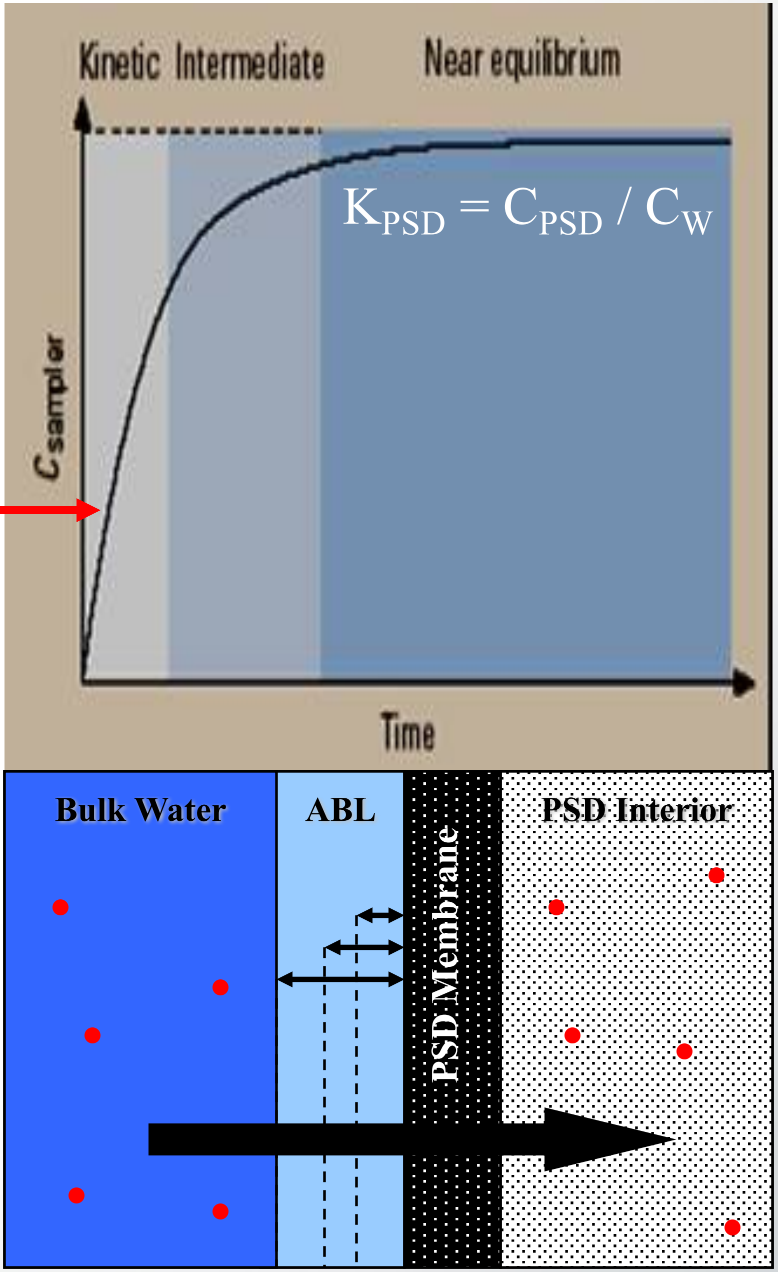
Uptake Model

Integrative Approach

- Provides estimation of TWA during a specific exposure period
- Chemical residues from episodic chemical events are retained
- Only occurs in linear phase
- Requires calibration data
  - Effective Sampling Rate (Rs)
- $R_s = N / C_w * t$
- $C_w = N / R_s * t$
- Deuterated PRC to account for variation due to environmental processes (biofouling, shear flow)



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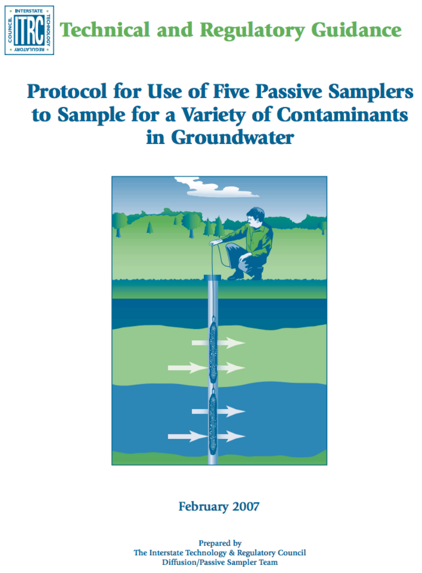
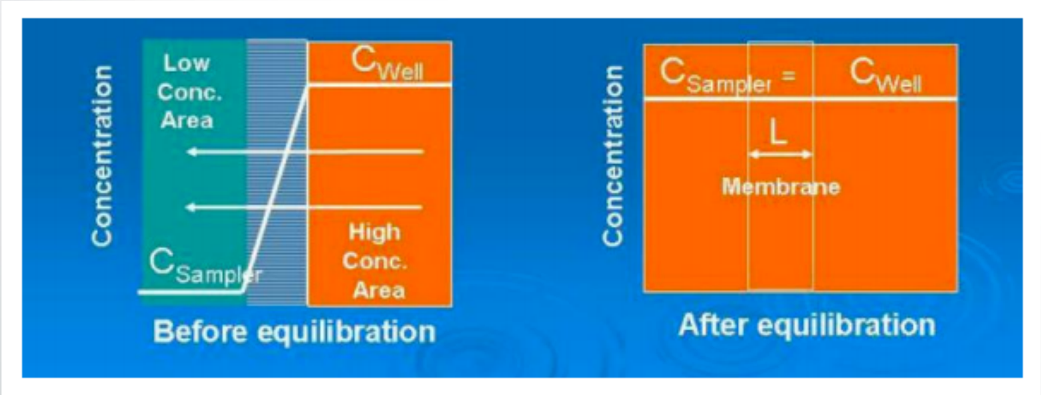
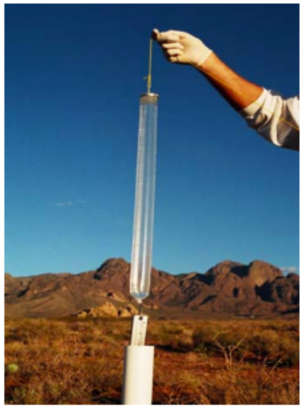
US Interagency Technical & Regulatory Council (ITRC) Guidance Documents for Using Passive Samplers for Groundwater





Example Groundwater Passive Samplers (grab samplers)



Hydrasleeve

SNAP Sampler

Diffusion (Equilibrium) Sampler Examples

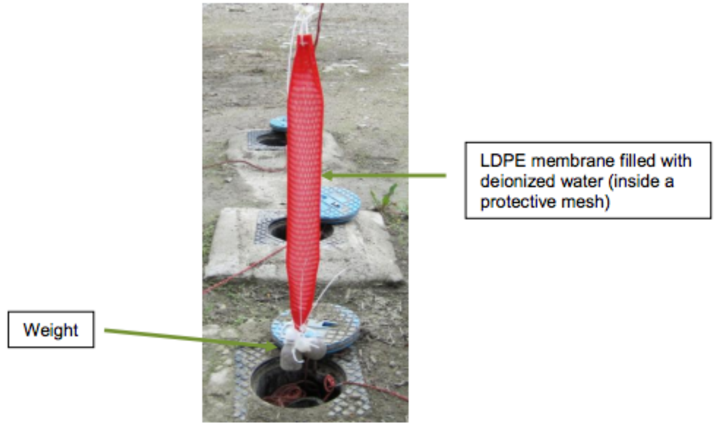


Figure 6: Polyethylene Diffusion Bag (PDB)

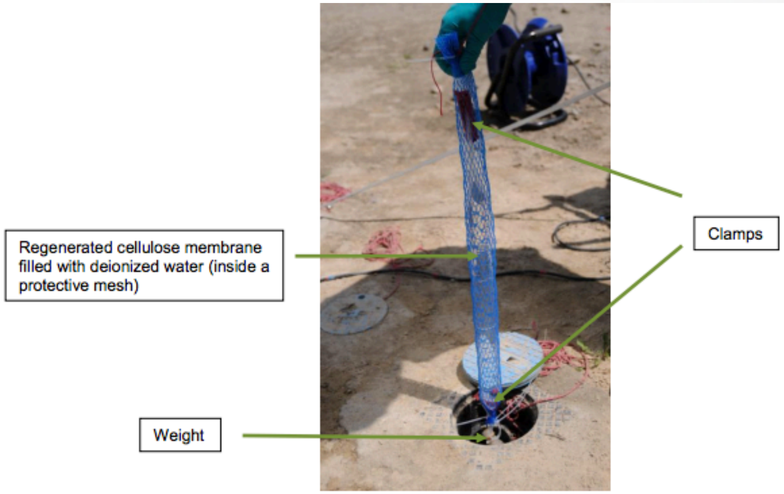
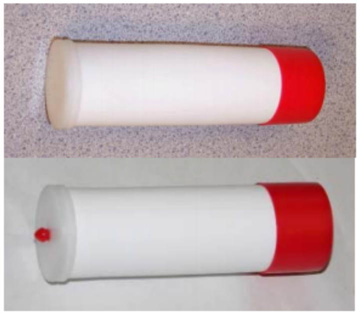


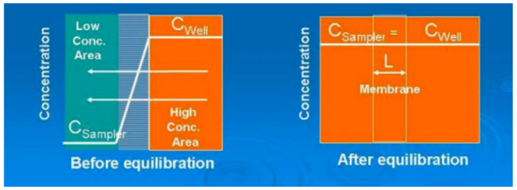
Figure 7: Regenerated cellulose dialysis membrane



Porous PE

Examples of Other PSDs for Surface Water, Groundwater, Sediment & Soil

- LDPE: low-density polyethylene
- nsPSD: non-selective PSD using OASIS HLB in a 10um HPLC solvent frit
- LF nsPSD: large format nsPSD, proprietary sorbent and 200 um mesh
- CIPS: composite integrated passive sampler (patent pending)
- POCIS: polar organic chemical integrative sampler (OASIS HLB)
- SPMD: semi-permeable membrane device



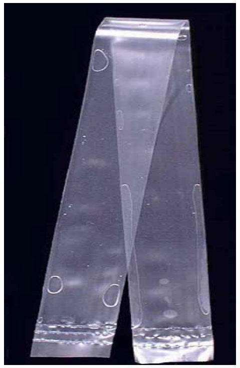

nsPSD


POCIS

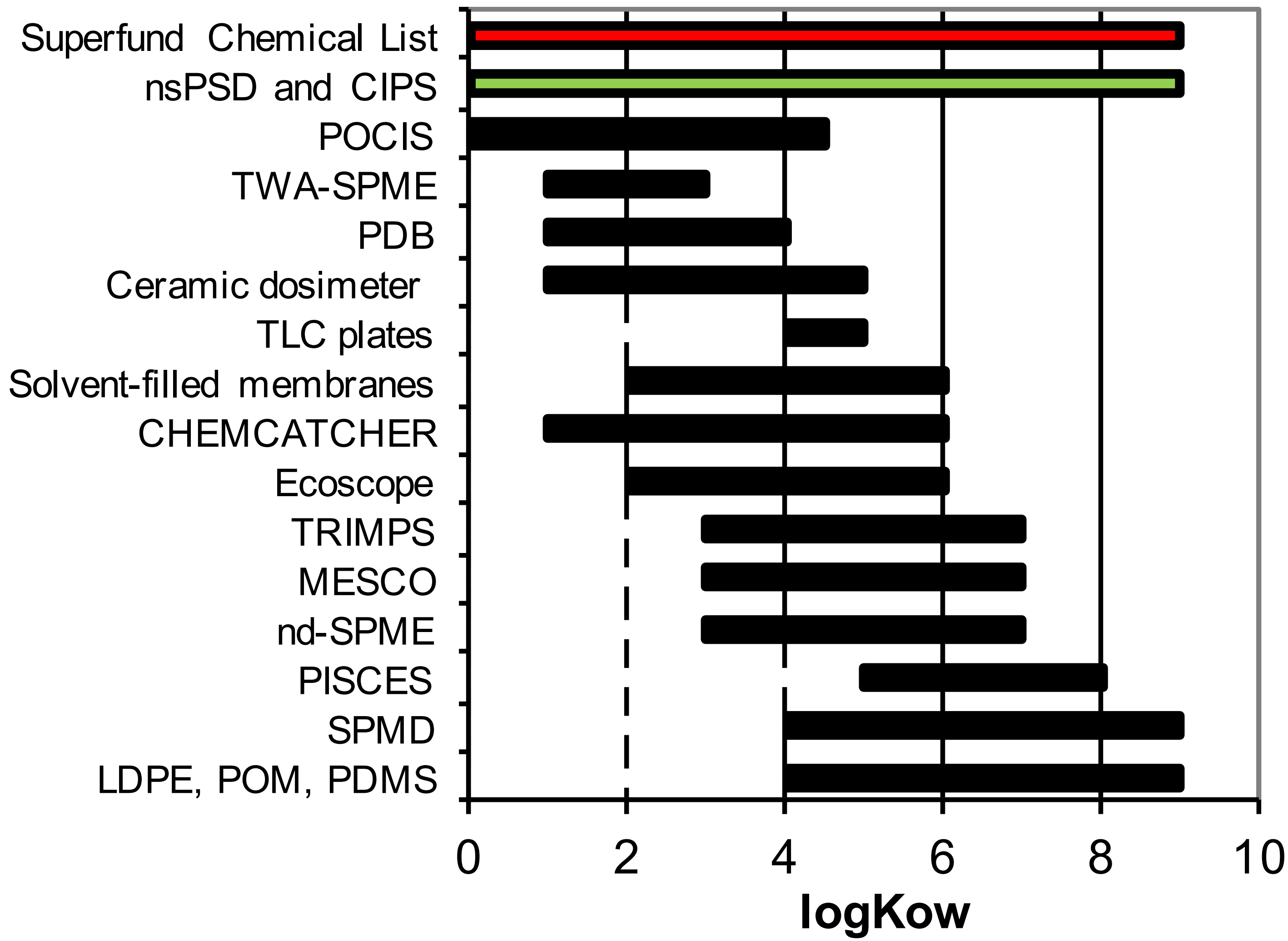

LDPE PSD


LF nsPSD


CIPS


SPMD

Overall Goal: Advance design/use of PSDs to be more universal, quantitative, and used in site/risk assessment



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Laboratory Calibration:

Uptake rates $k_u = (N_t - N_o) / t$ (eq 1)

k_u: uptake rate (ng/d)
N_t: amount accumulated in PSD at time, t, (ng)
N_0: amount initially in PSD (ng)
t: time of deployment (d)

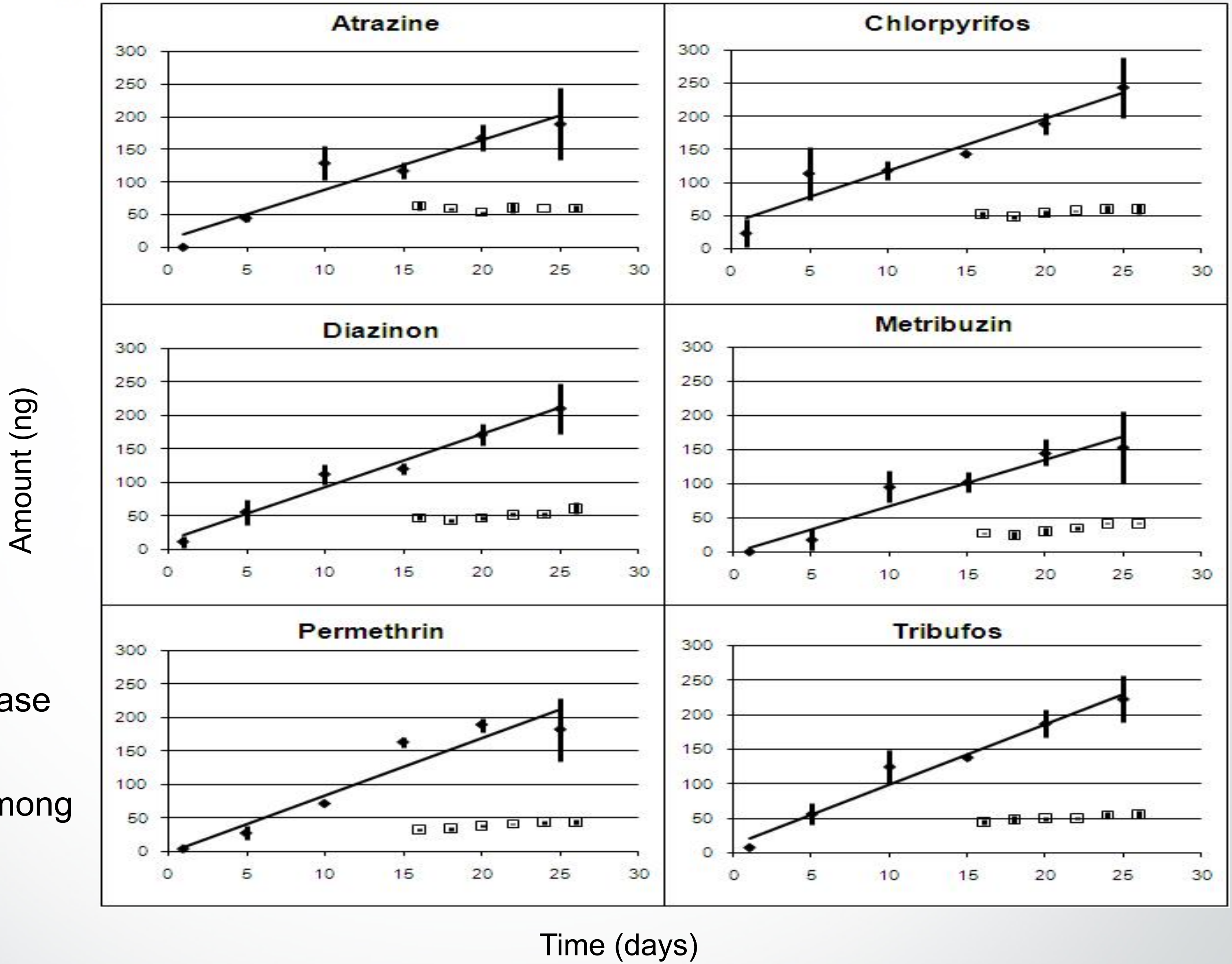
Sampling rates $R_s = k_u / C_{w,fd}$ (eq 2)

R_s: sampling rate (L/d)
k_u: uptake rate (ng/d)
$C_{w,fd}$: freely-dissolved concentration (ng/L)

Field Deployments:

Quantitative $C_{w,fd} = N_t / R_s t$ **(eq 3)**

Uptake Curves



♦ represents the amount in the uPSD
☐ represents the water concentration

All pesticides remained in the linear uptake phase (30-day)

Variability low among replicates

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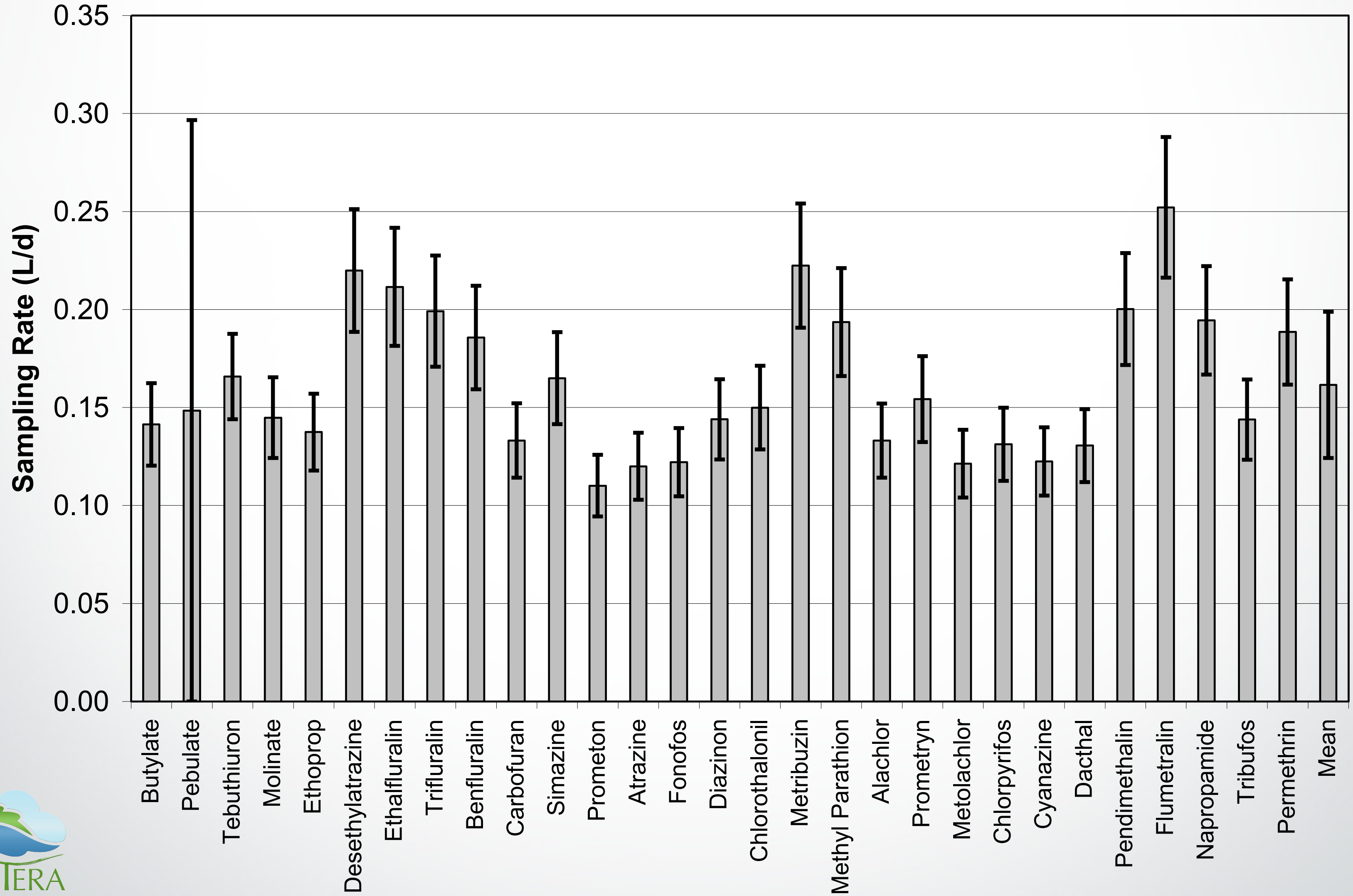
35 Current-use Pesticides

Chemical	log K_{ow}	Chemical	log K_{ow}	Chemical	log K_{ow}
Metribuzin	1.49	Fenamiphos	3.29	Trifluralin	5.31
Methidathion	1.58	Phorate	3.37	Benfluralin	5.31
Malathion	2.29	Alachlor	3.37	Fenpropathrin	5.62
Carbofuran	2.30	Chlorothalonil	3.66	Cyfluthrin	5.74
Carbaryl	2.35	Prometryn	3.73	Tribufos	5.75
Simazine	2.40	Diazinon	3.86	Deltamethrin	6.18
Phosmet	2.48	Disulfoton	3.86	Cypermethrin	6.38
Captan	2.74	Propiconazole	4.13	Esfenvalerate	6.76
Methyl Parathion	2.75	Terbufos	4.24	Cyhalothrin (lambda)	6.85
Atrazine	2.82	Chlorpyrifos	4.66	Permethrin	7.43
Ethoprop	3.14	Pendimethalin	4.82	Bifenthrin	8.15
Metolachlor	3.24	Ethalfluralin	5.23		

Log Kow Range: 1.49 – 8.15

Sampling Rates (R_s values in L/day: $C_w = N / R_s * t$)

conversion of 1st order uptake rate to more convenient units



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Field sampling for atrazine

Sampling:

- Surface waters collected at 13 sites downgradient from source in Yunnan, China
- nsPSD samples:
  - Triplicate
- Water samples:
  - Days 1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29

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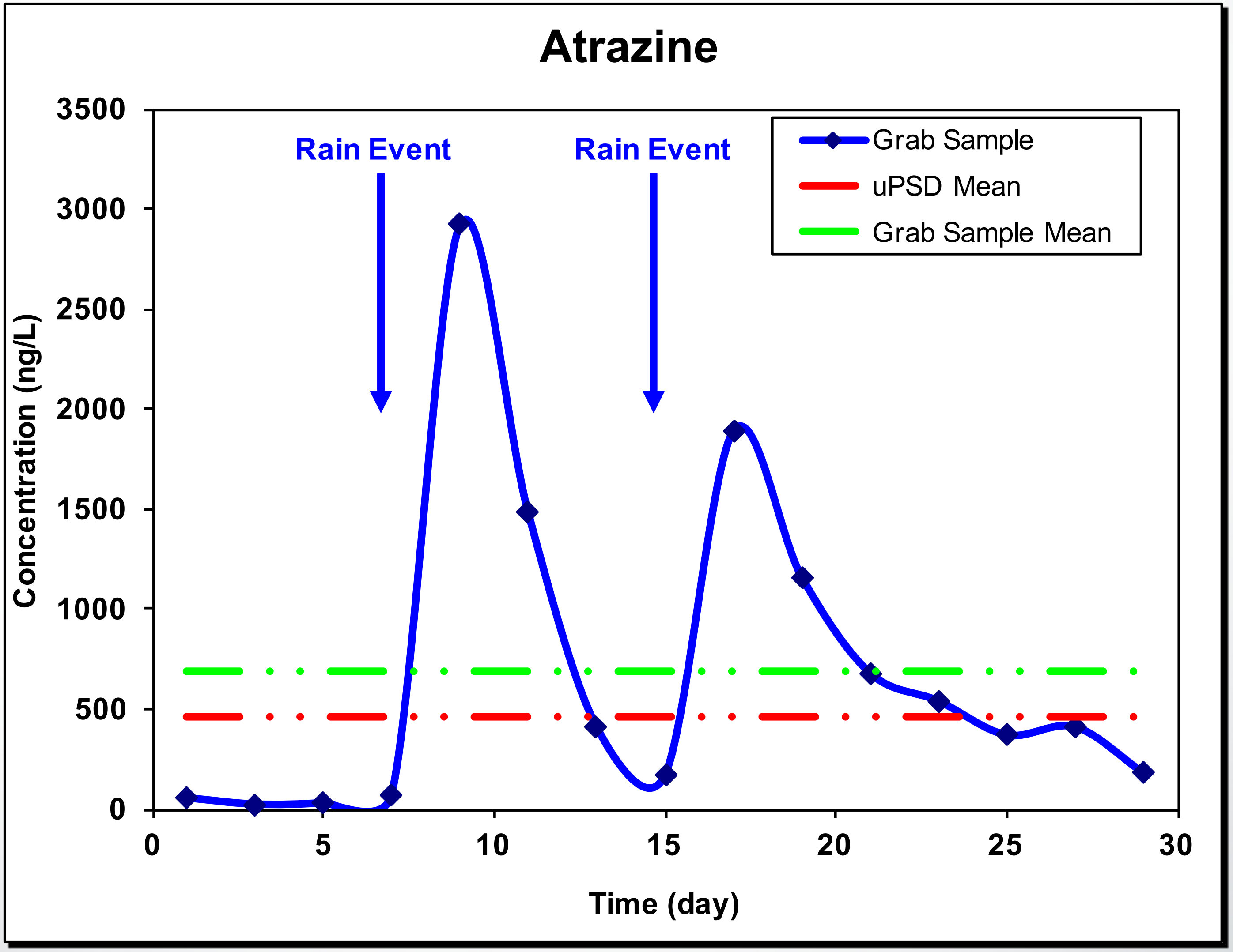
Field Data



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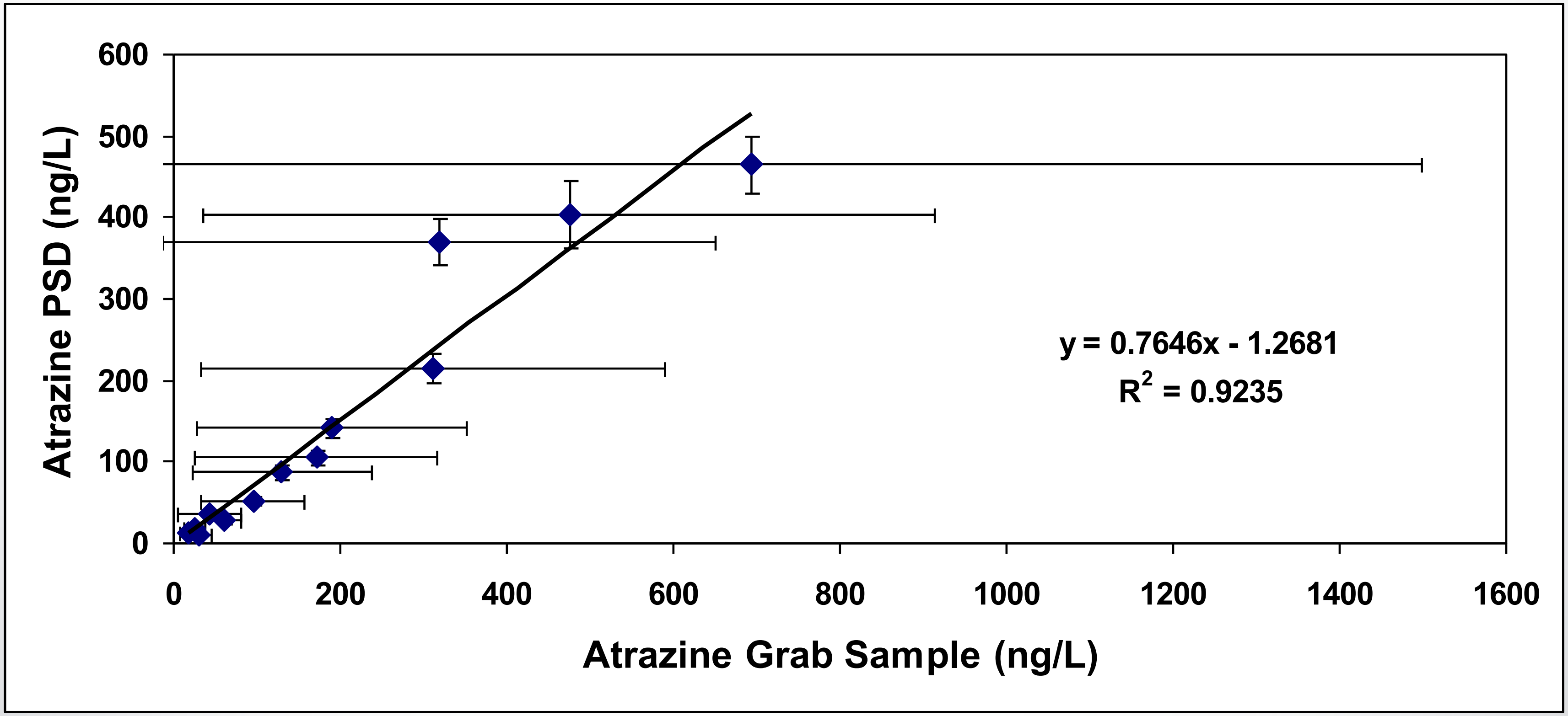
Field Data:

Grab samples collected every other day for 1 month at 13 sites, gradient from source. PSD estimate is ~75% of mean grab estimate.



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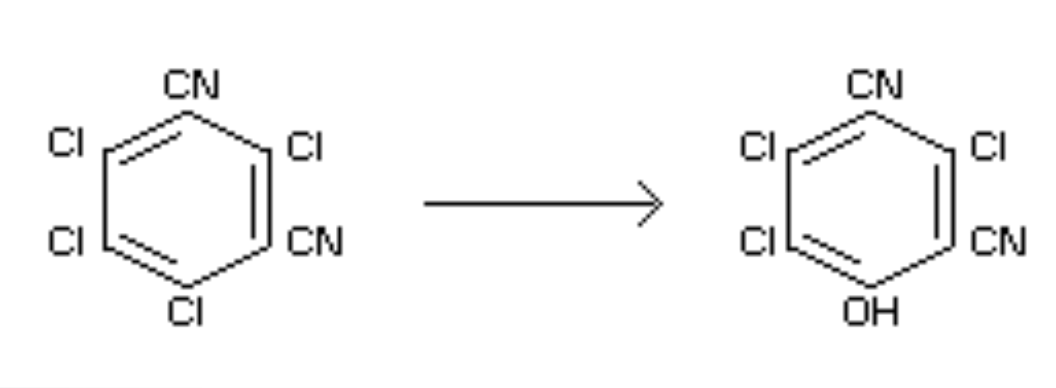
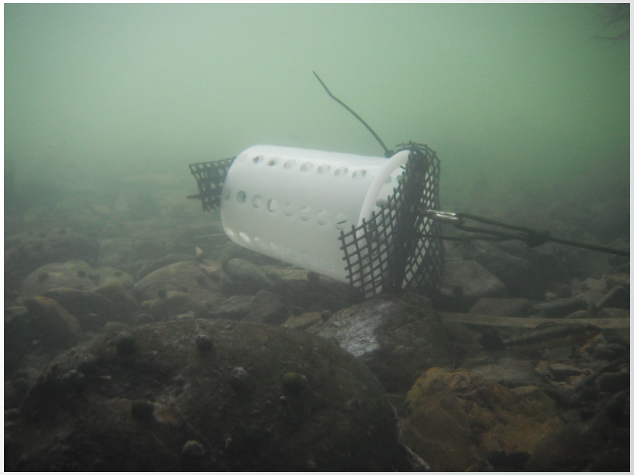
Chlorothalonil and 4OH-CHT as a Case Study





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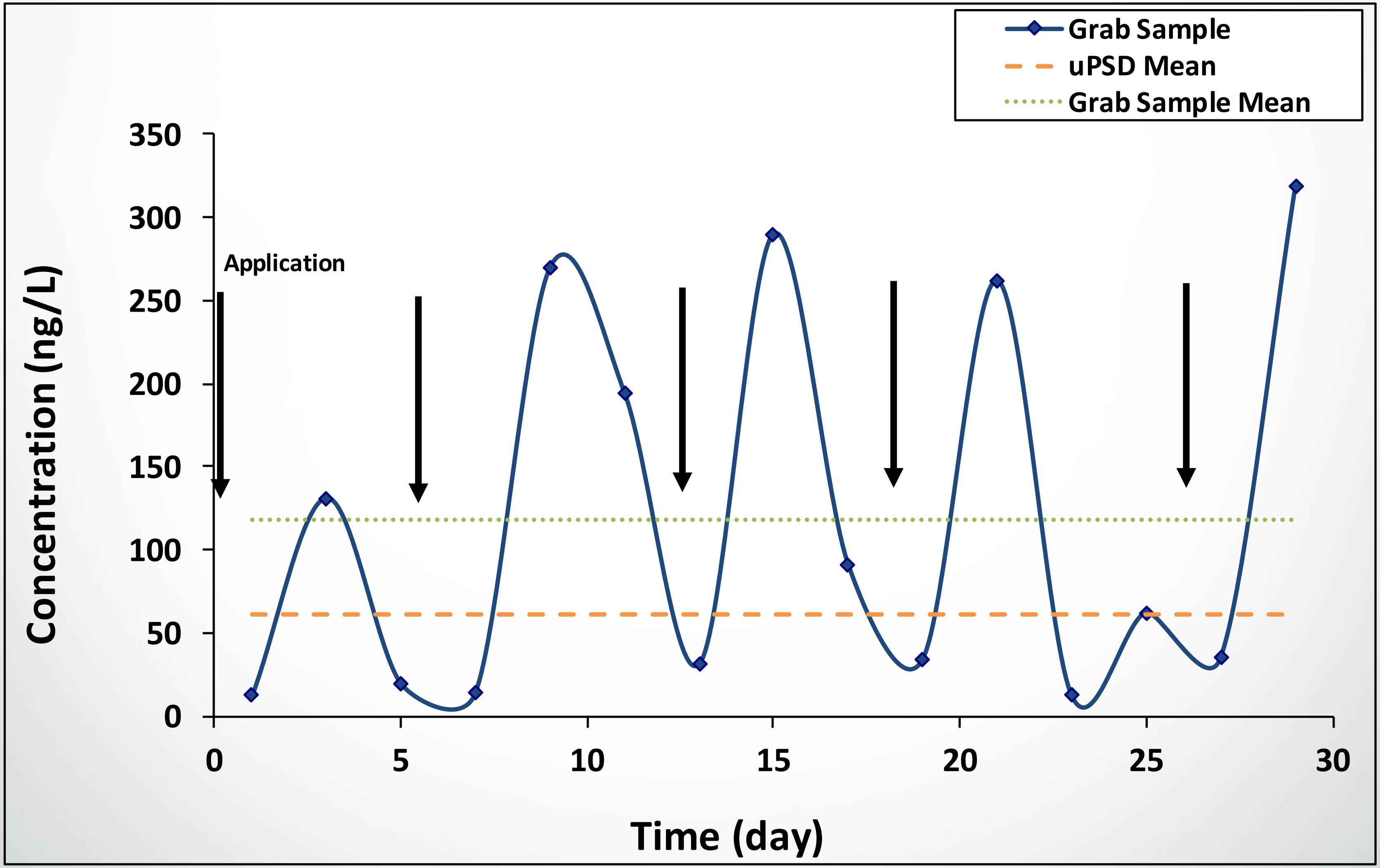
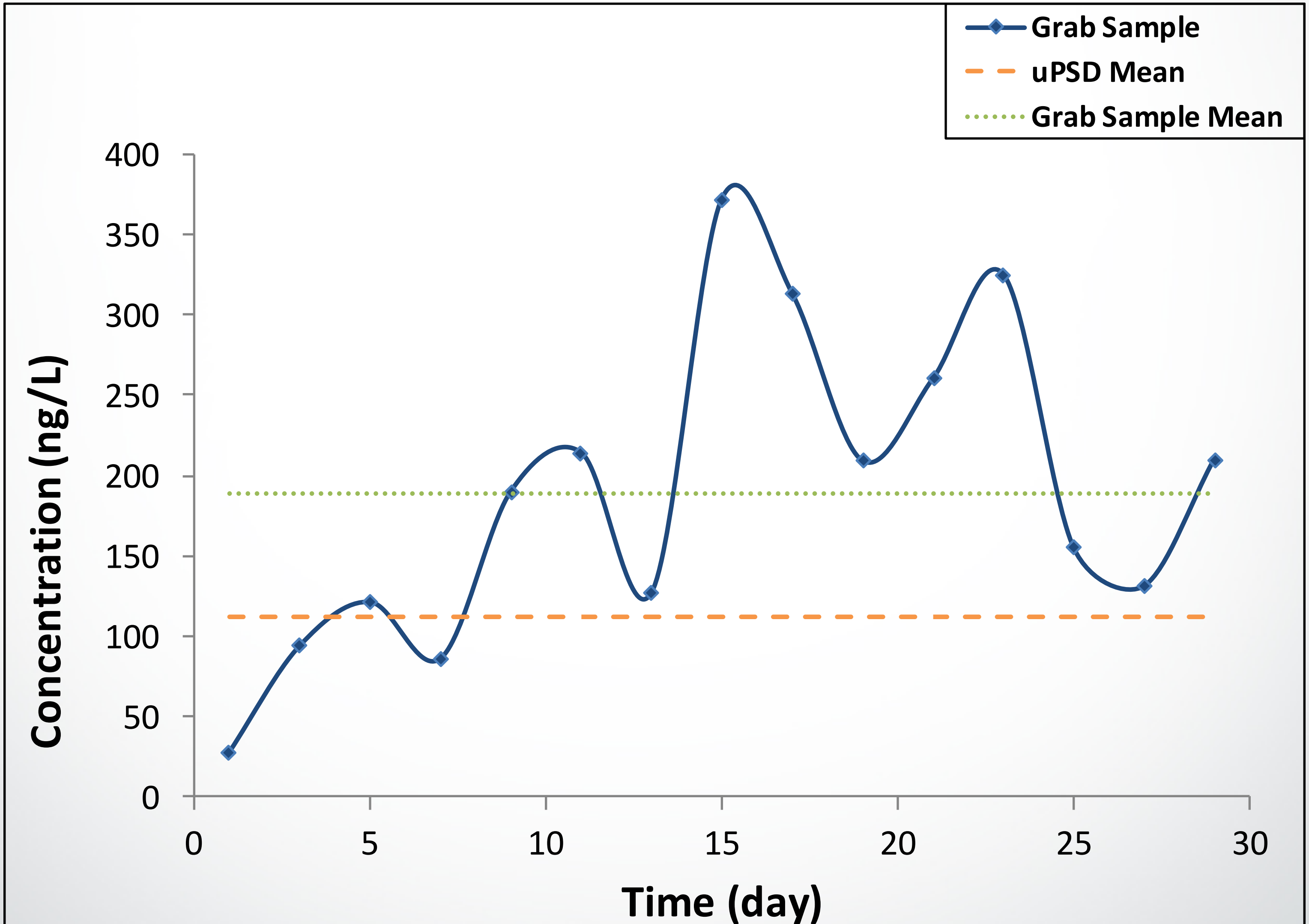
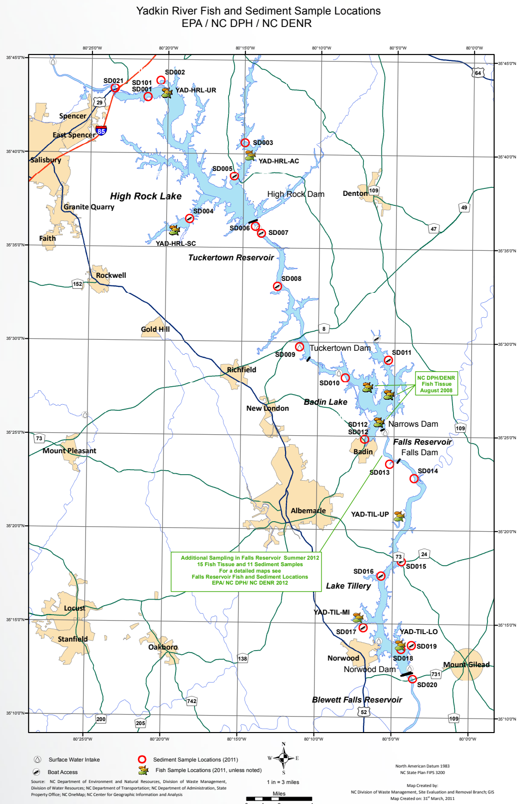
Chlorothalonil in retention pond at golf course

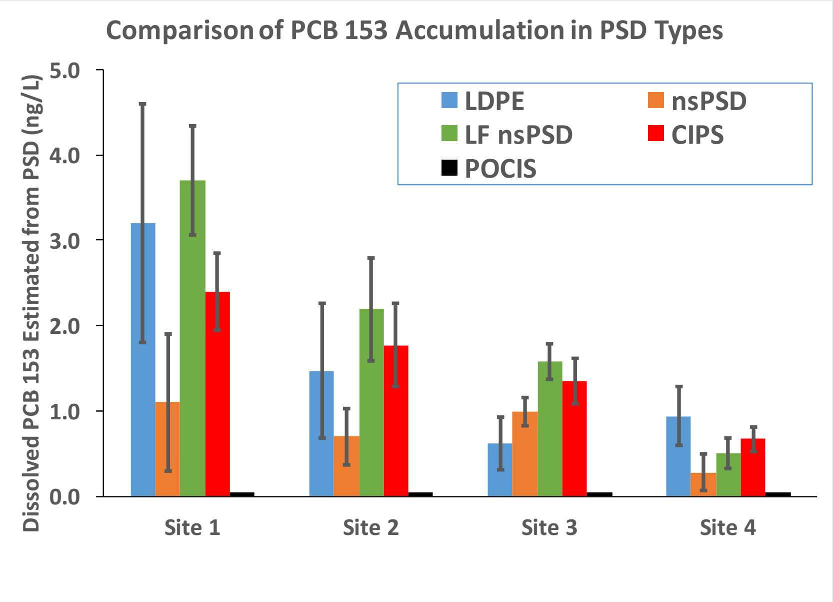


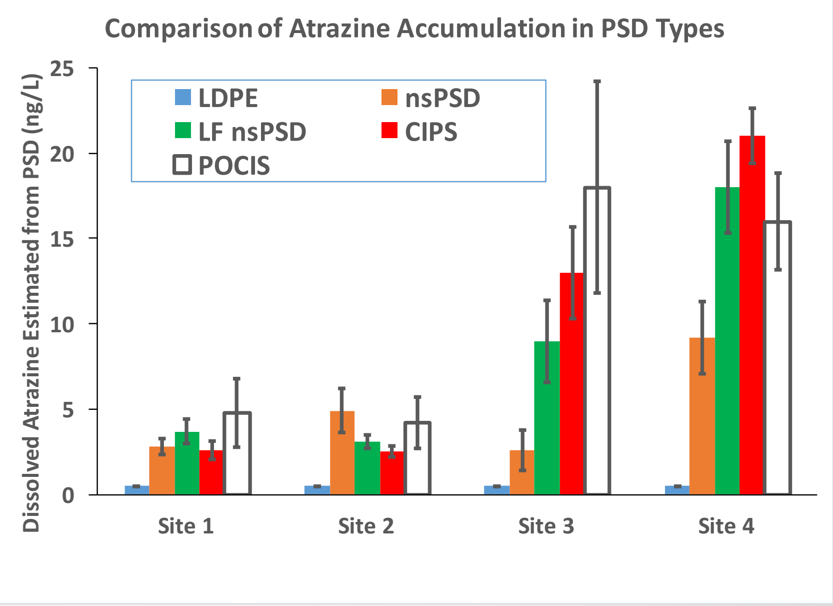
4OH-CHT in retention pond at golf course



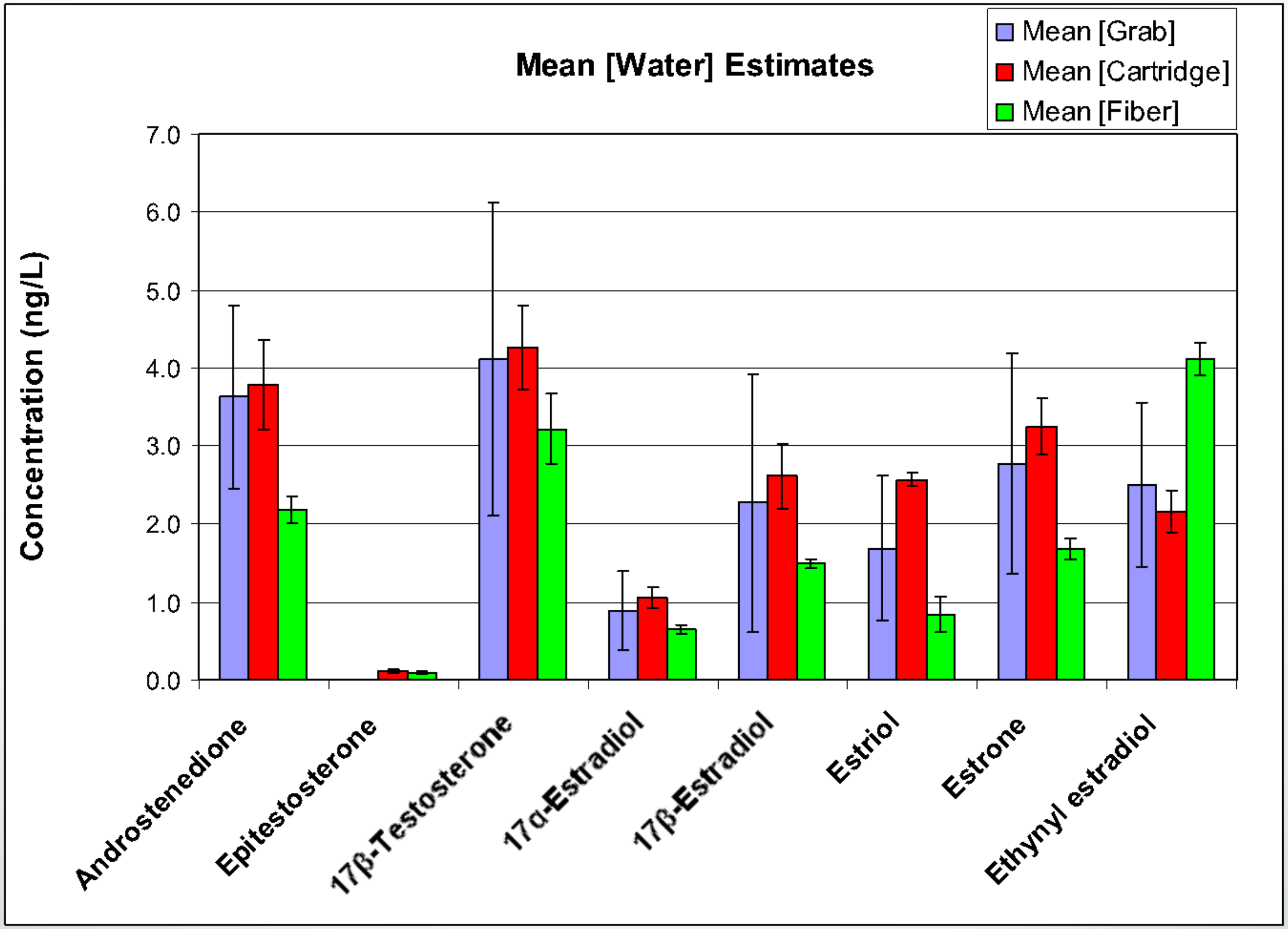

Yadkin River Fish and Sediment Sample Locations
EPA / NC DPH / NC DENR
High Rock Lake
High Rock Dam
Tuckertown Reservoir
Tuckertown Dam
Badin Lake
Narrows Dam
Falls Reservoir
Falls Dam
Lake Tillery
Norwood Dam
Blewett Falls Reservoir
Spencer
East Spencer
Salisbury
Granite Quarry
Faith
Rockwell
Gold Hill
Richfield
New London
Denton
Mount Pleasant
Badin
Albemarle
Locust
Stanfield
Oakboro
Norwood
Mount Gilead


nsPSD
POCIS
LDPE PSD
LF nsPSD
CIPS

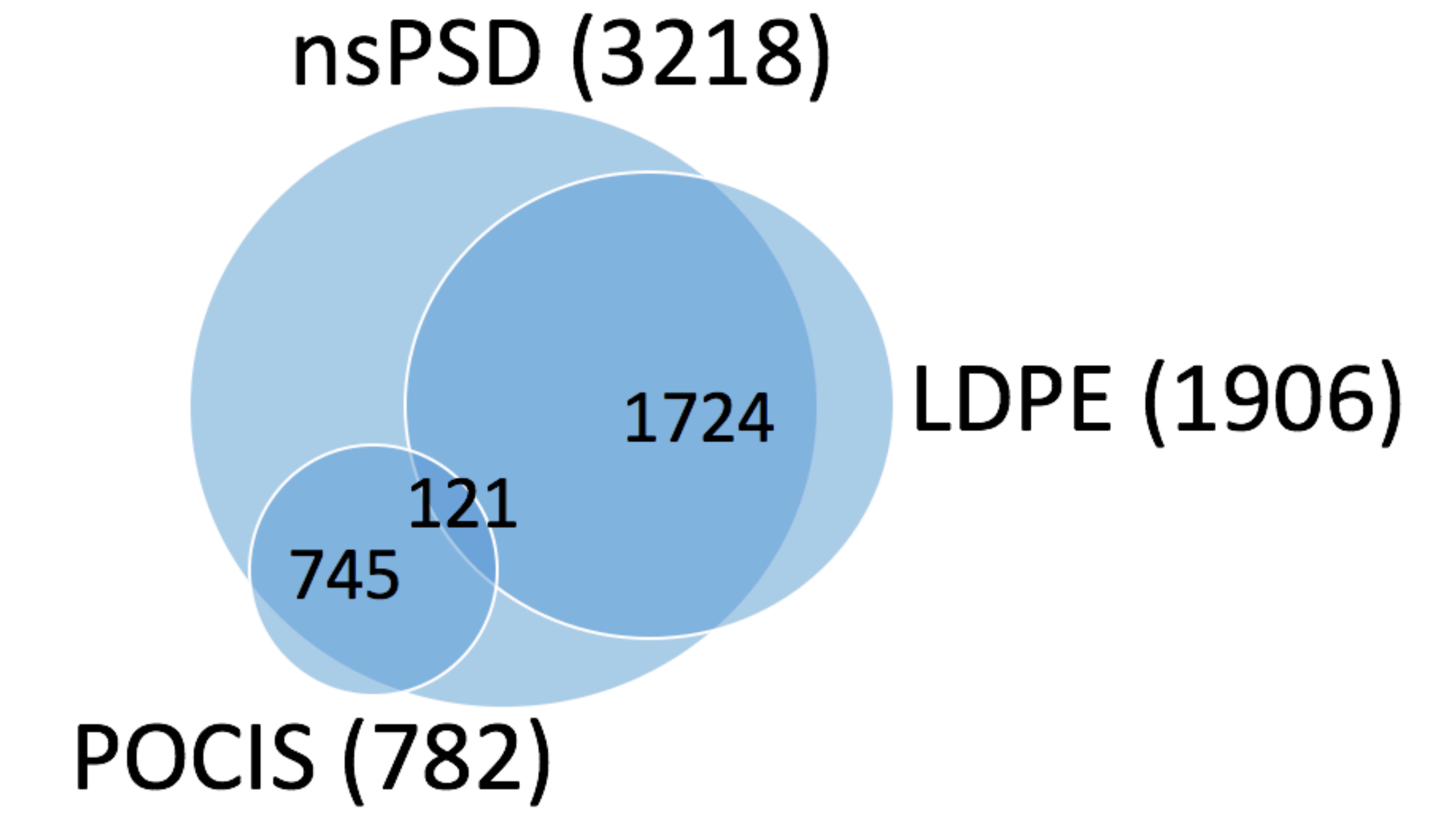

Comparison of PCB 153 Accumulation in PSD Types
Dissolved PCB 153 Estimated from PSD (ng/L)
5.0
4.0
3.0
2.0
1.0
0.0
LDPE
nsPSD
LF nsPSD
CIPS
POCIS
Site 1
Site 2
Site 3
Site 4


Comparison of Atrazine Accumulation in PSD Types
Dissolved Atrazine Estimated from PSD (ng/L)
25
20
15
10
5
0
LDPE
nsPSD
LF nsPSD
CIPS
POCIS
Site 1
Site 2
Site 3
Site 4

Groundwater under land application of municipal wastewater: Hormones



Non-target analysis by GCxGC TOF (Leco Pegasus 4D) shows that the nsPSD almost captures the sum of LDPE and POCIS (molecular features)



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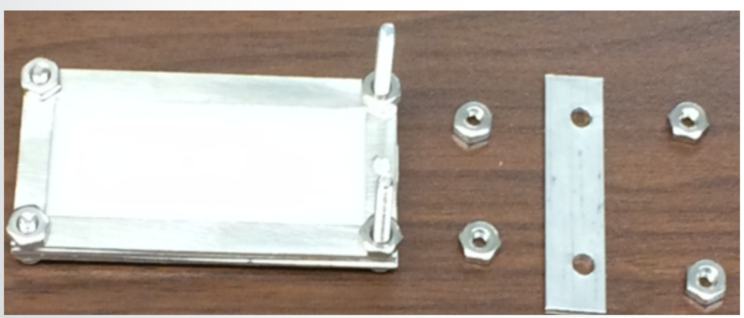
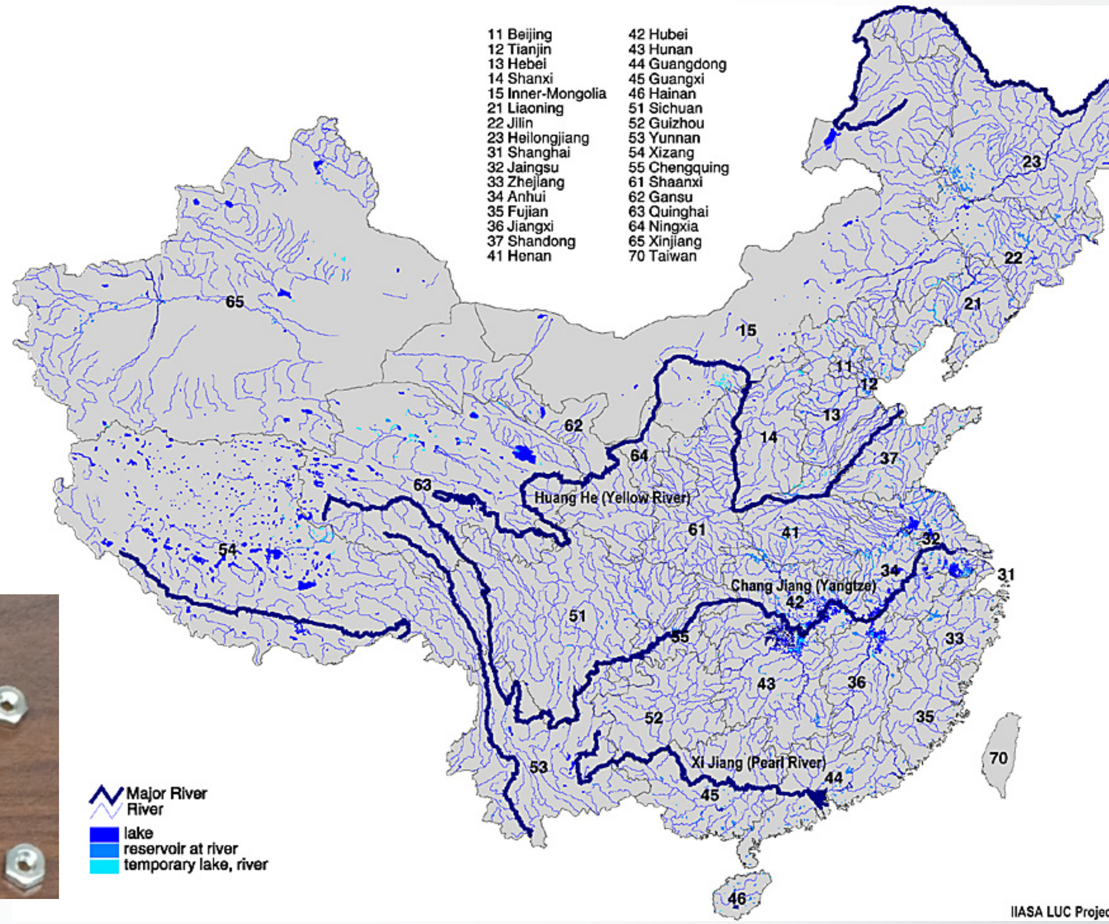
Projects in Asia

Lancang-Mekong River
Yangtze River
Nujiang River
Red River (Hong Ha)
Pearl River (Zhujiang)
Rayong oil spill (2013)
Other wetland and remediation projects





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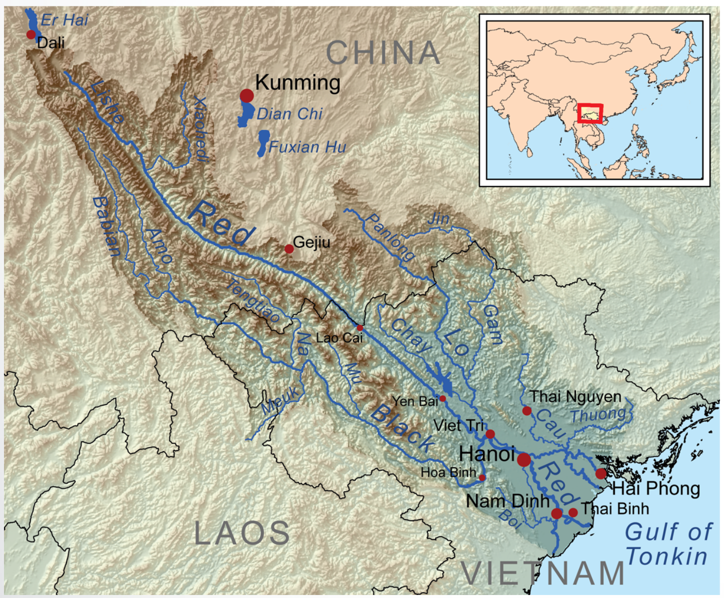
Organic Pollutants in Red River, China and Vietnam

Study is designed to understand the sources and fate of pesticides, petroleum hydrocarbons, and industrial chemicals along the Red River



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US EPA Guidance Document for Using Passive Samplers at Superfund Sites

(sediment only at this time)


EPA United States Environmental Protection Agency

Office of Superfund Remediation and Technology Innovation and Office of Research and Development

Sediment Assessment and Monitoring Sheet (SAMS) # 3

Guidelines for Using Passive Samplers to Monitor Organic Contaminants at Superfund Sediment Sites

December 2012

OSWER Directive 9200.1-110 FS

Simplified model of the partitioning processes that control the bioavailability of PAH

P: Parent PAH

M: PAH metabolites (oxy-PAH)

K_{PSW} and K_{MSW}: PSD-water partition coefficients of P and M

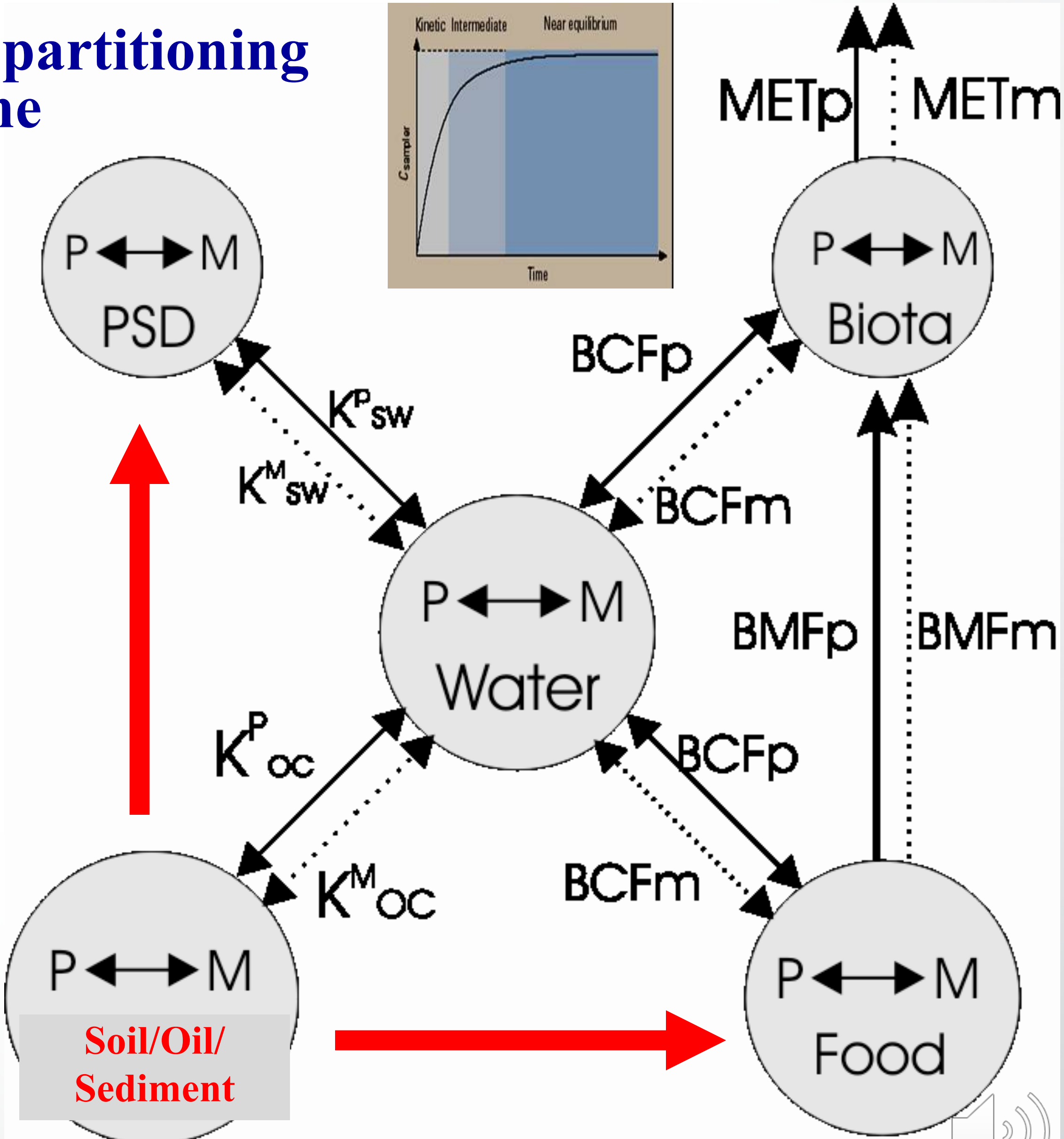
K_{POC} and K_{MOC}: oil or other organic carbon sorption coefficients of P and M

BCF: bioconcentration factor

BMF: biomagnification factor

MET: metabolic clearance

K_{POM} and $K_{D\ (sediment)}$ determined via POM in equilibria with water and sediment using two-phase equilibria model (EqP)



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Adjusting for Relative Bioavailability (RBA)

$$RBA = \frac{\text{Measured } C_{biota} \text{ exposed to source (soil, sediment, oil)}}{\text{Predicted } C_{biota} \text{ from two-phase EqP model}}$$

(default, $K_D = C_{soil} / C_w = f_{OC} K_{OC} = f_{OC} K_{OW}$)

Or

$$RBA = \frac{\text{Predicted absorption using POM method}}{\text{Predicted } C_{biota} \text{ from two-phase EqP model}}$$

(default, $K_D = C_{soil} / C_w = f_{OC} K_{OC} = f_{OC} K_{OW}$)

RBA can be used to adjust Hazard Quotient and Risk-Based Benchmarks for both Human and Ecological Health

$$HQ = C_{measured} \times RBA / C_{benchmark}$$

HQ (or risk) ↓ when RBA < 1.0

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Impetus for this study

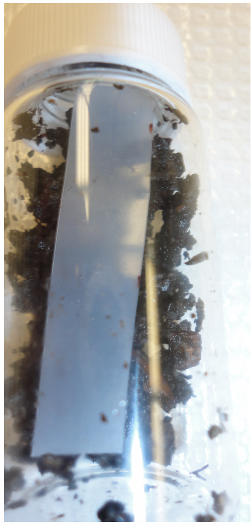
- Default assumption is PAH bioavailability in soil/sediment is 100% (RBA =1.0), but there is mounting evidence that PAH can have low bioavailability under certain conditions (e.g., weathering of oil, soot/charcoal) so that RBA < 1.0
- Several promising methods to measure RBA in soil/sediment (using slurries with uptake into SPME, PDMS, LDPE, POM)

- However, we have some critical knowledge/methodology gaps to fill to increase our confidence in using RBA in risk assessments
  - Lack of standardized and validated methods for estimating RBA (without using animals)
  - Limited site implementation/verification
  - Limited number of PACs studied: focus on BaP, with some work on other carcinogenic PAH and the EPA 16 or EPA 34 PAH

Measuring freely dissolved PAH using POM and SPME

SPME

POM



PDMS

Polymer and soil-water slurry were allowed to reach equilibrium

Objectives of this study

1. Extend the POM partitioning methodology to
   a) include many more PACs by measuring K_{POM} for 58 PACs (54 more are pending)
   b) Measure K_D values for these PACs between water and fresh or weathered oil

   where, $K_D = C_{sediment} / C_{water}$ and $C_{water} = C_{POM} / K_{POM}$

2. Apply this POM methodology to predict RBA of 58 PACs in oil-contaminated sediments and compare to measured RBA in aquatic biota (oysters) exposed to these sediments

Method of measuring K_{POM}

→

For K_{POM} the PAH conc. varied
Static renewal
Now using flow-thru

→

Shake (or slow stir) for 3, 7, 10, 15, 20, and 30 days at 25°C

↓

Extract POM and water, measure PAH by GCMS SIM. Measured PAH was within 10% of nominal PAH

←

Estimate K_{POM} from linear partition model

$$K_{POM} = C_{POM} / C_{Water}$$

Polycyclic Aromatic Compounds (PACs)

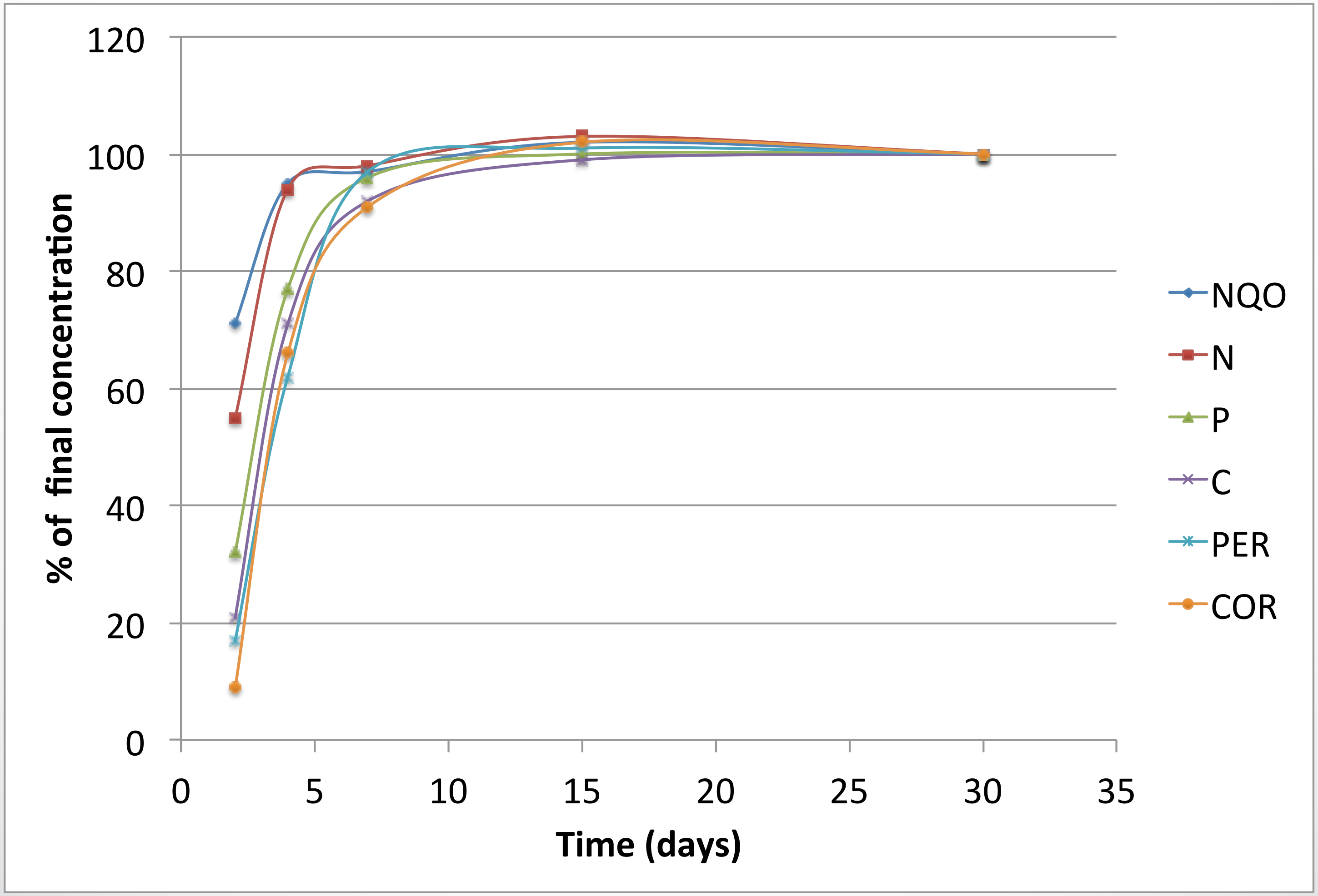
naphthalene	N	anthracene	AN
biphenyl	BIP	2-methylanthracene	2MAN
dibenzofuran	DBF	fluoranthene	FL
C1-naphthalenes	N1	pyrene	PY
C2-naphthalenes	N2	C1-fluoranthenes/pyrenes	FP1
C3-naphthalenes	N3	C2-fluoranthenes/pyrenes	FP2
C4-naphthalenes	N4	C3-fluoranthenes/pyrenes	FP3
1-methylnaphthalene	1MN	benz[a]anthracene	BaA
2-methylnaphthalene	2MN	retene	Re
2,6-dimethylnaphthalene	DMN	chrysene	C
2,3,5-trimethylnaphthalene	TMN	C1-chrysenes	C1
acenaphthylene	Acy	C2-chrysenes	C2
acenaphthene	Ace	C3-chrysenes	C3
fluorene	F	C4-chrysenes	C4
C1-fluorenes	F1	benzo[b]fluoranthene	BbF
C2-fluorenes	F2	benzo[k]fluoranthene	BkF
C3-fluorenes	F3	benzo[a]pyrene	BaP
1-methylfluorene	1MF	benzo[e]pyrene	BeP
dibenzothiophene	D	perylene	PER
C1-dibenzothiophenes	D1	indeno[1,2,3-c,d]pyrene	IDP
C2-dibenzothiophenes	D2	dibenz[a,h]anthracene	DBA
C3-dibenzothiophenes	D3	benzo[g,h,i]perylene	BgP
C4-dibenzothiophenes	D4	coronene	COR
phenanthrene	P		
C1-phenanthrenes/anthracenes	P1	1,4-naphthoquinone	NQO
C2-phenanthrenes/anthracenes	P2	9-fluorenone	FO
C3-phenanthrenes/anthracenes	P3	9,10-anthraquinone	AQO
C4-phenanthrenes/anthracenes	P4	benzofluorenone	BFO
1-methylphenanthrene	1MP		
2-methylphenanthrene	2MP		
3-methylphenanthrene	3MP		

This list extends PAHs well beyond the 16 EPA Priority Pollutant PAHs to include alkyl homologues and individual alkyl PAH that dominate PAH distribution in both fresh and weathered crude oil and also includes some related heterocyclic compounds.

We have added 54 more PACs

- Benzothiophenes
- Naphthobenzothiophenes
- Decalins
- higher MW (302) PACs
- 30 more polar PACs (acridines, carbazoles, other O- and N-PACs)

PAH reach equilibrium with 75 um POM in ~10 days



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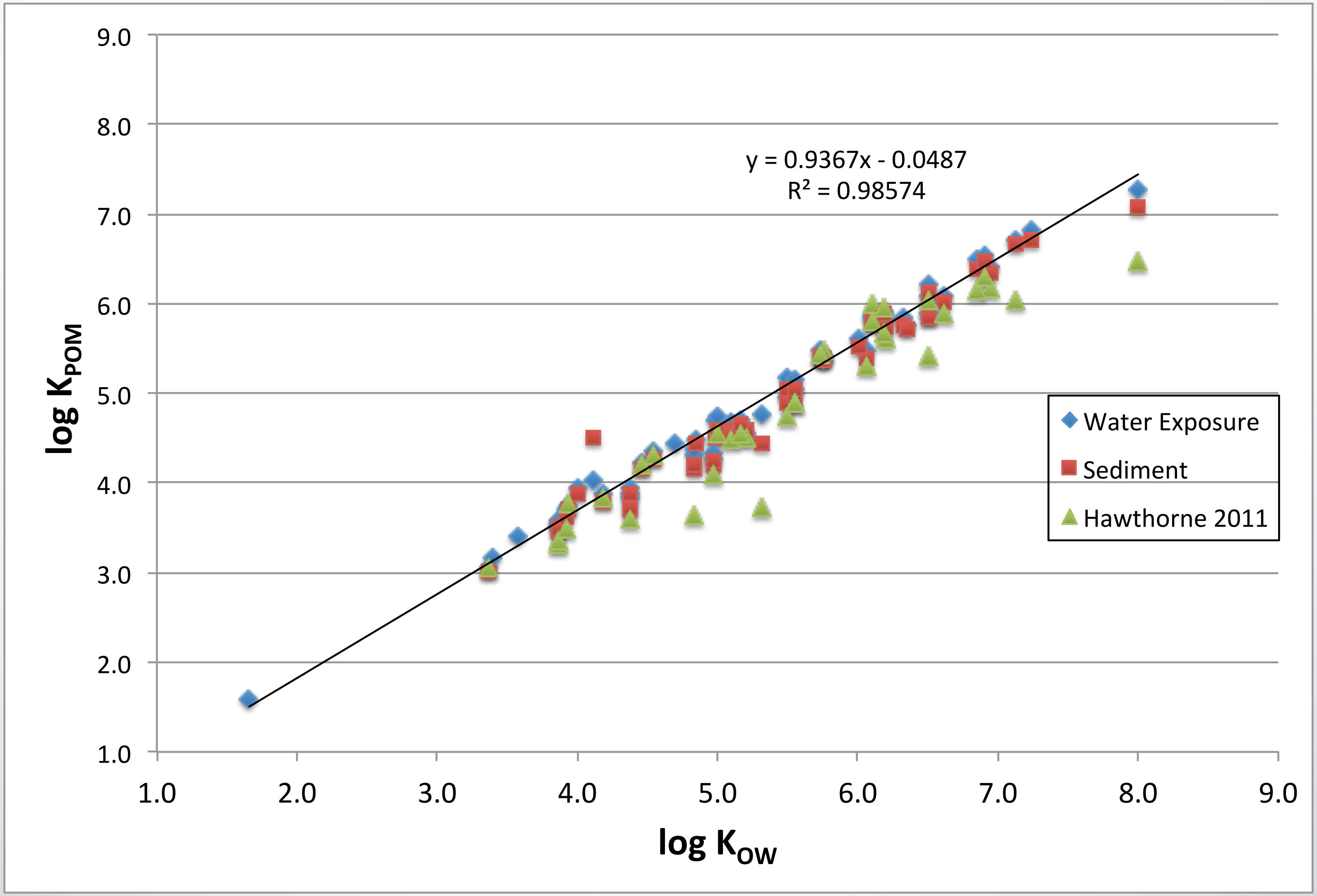
Log K_{OW} is a reasonable predictor of log K_{POM}



Measuring K_D (K_{oil}) of PACs from oiled sediment

For K_{POM} the PAH conc. varied
For K_{OIL} the oil:water ratio varied and used a bottom-draining WAF flask

Shake (or slow stir) for 3, 7, 10, 15, 20, and 30 days at 25°C

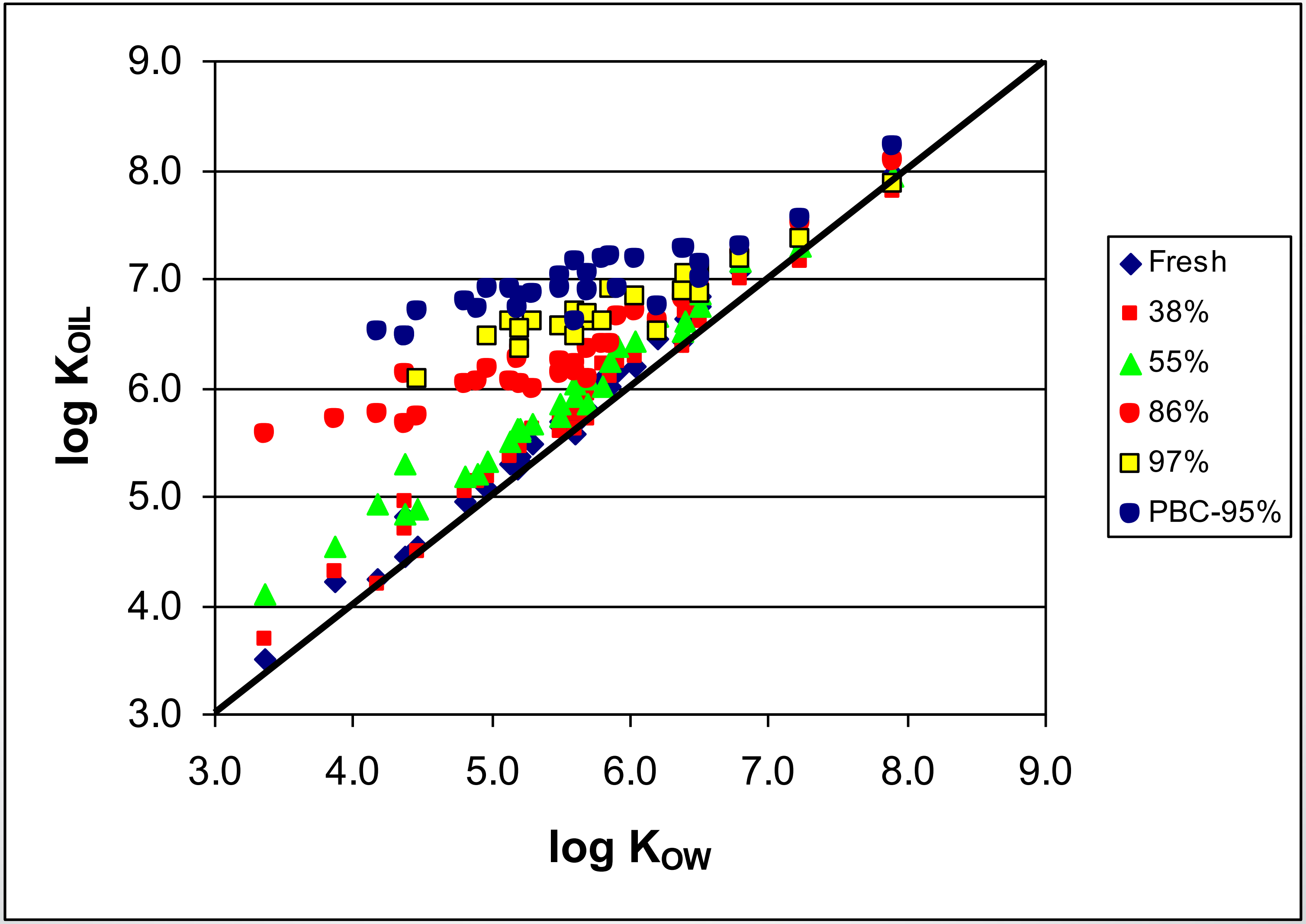
Extract POM and water, measure PAH by GCMS SIM. Measured PAH was within 10% of nominal PAH

Estimate K_D from linear partition model

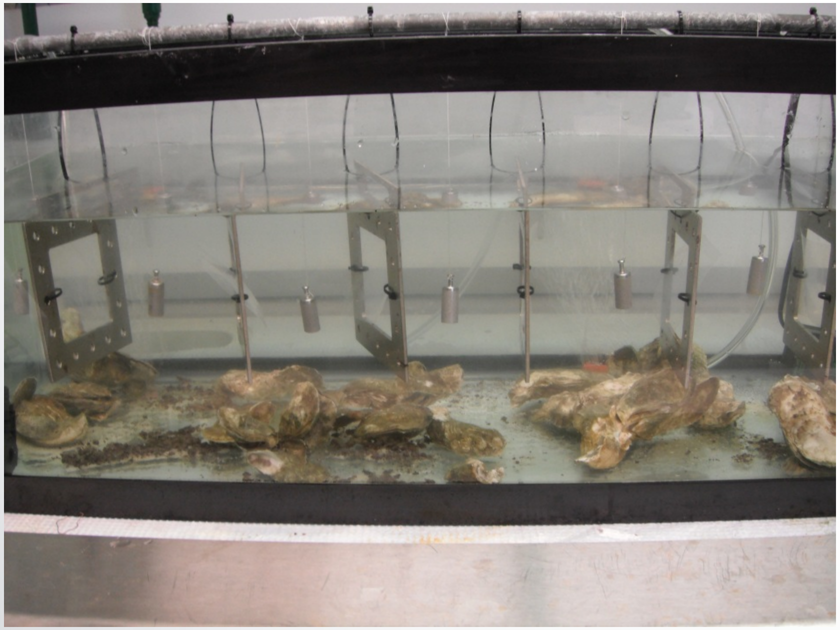
$$K_D = C_{sediment} / C_{water}$$

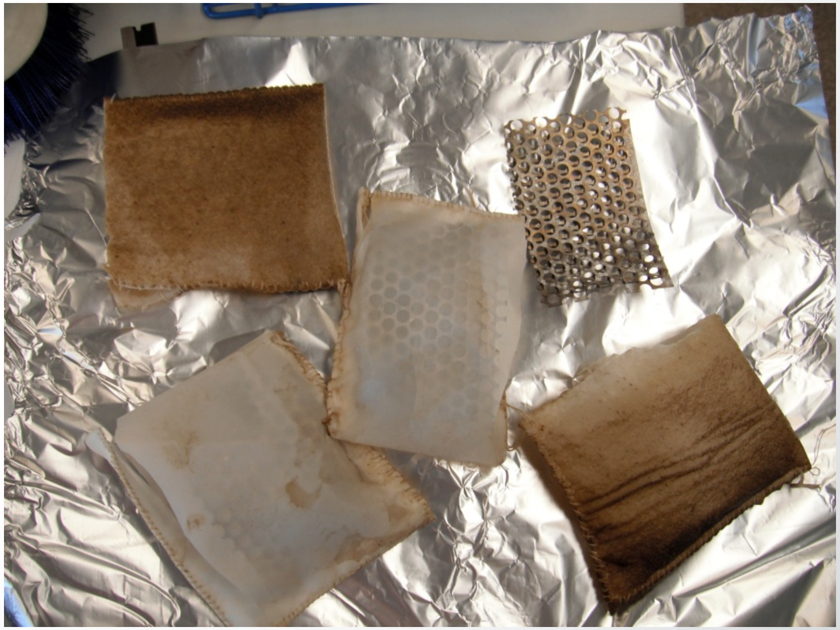
$$C_{water} = C_{POM} / K_{POM}$$

Effect of Weathering of SLC Oil on K_D (K_{oil})



Ex-situ measurement of PAC bioavailability (RBA) from oil using oysters and POM exposed to oil-contaminated sediment





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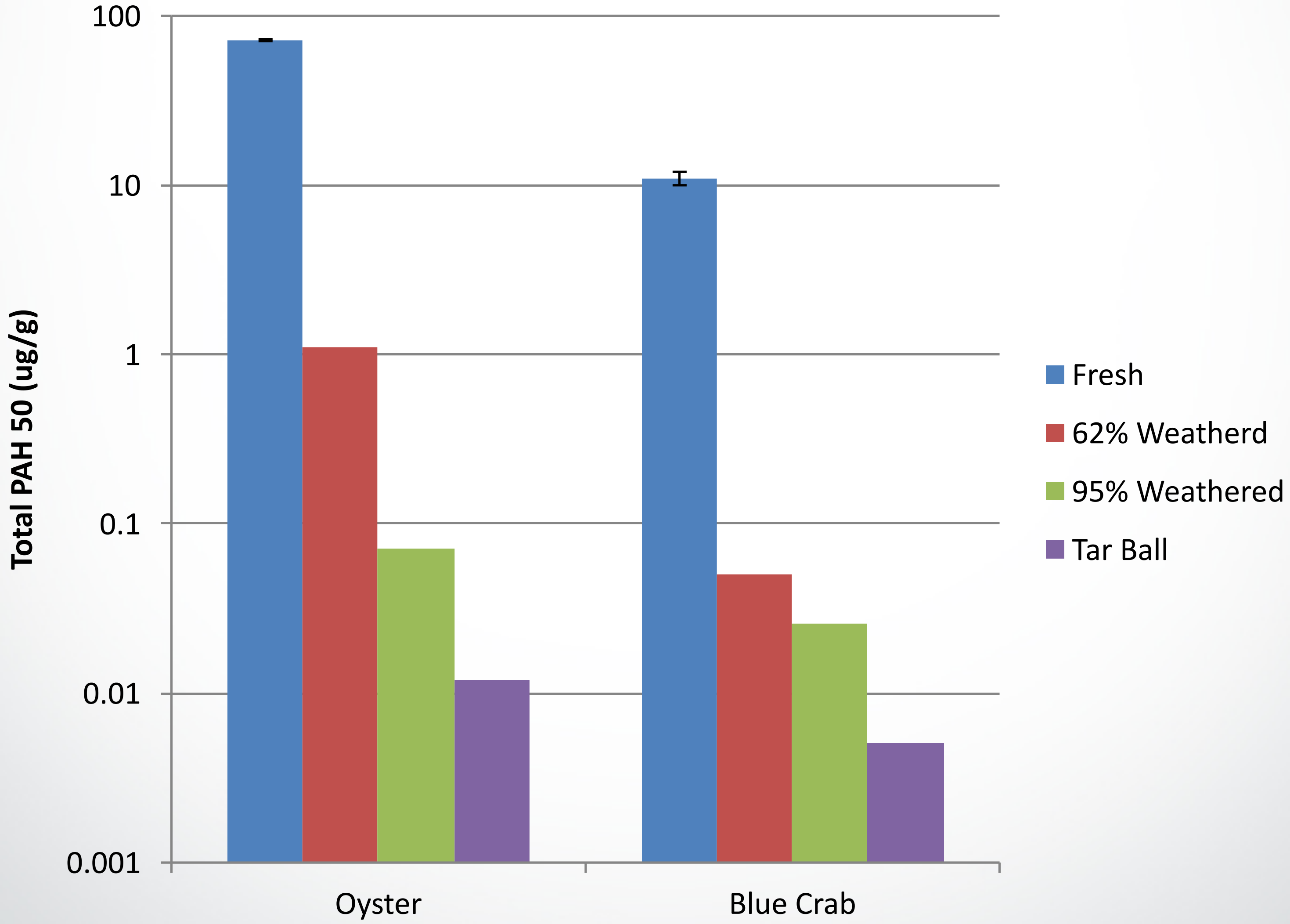
PAH Decreases in Biota When Oil Weathers (28-day exposure to WAF)



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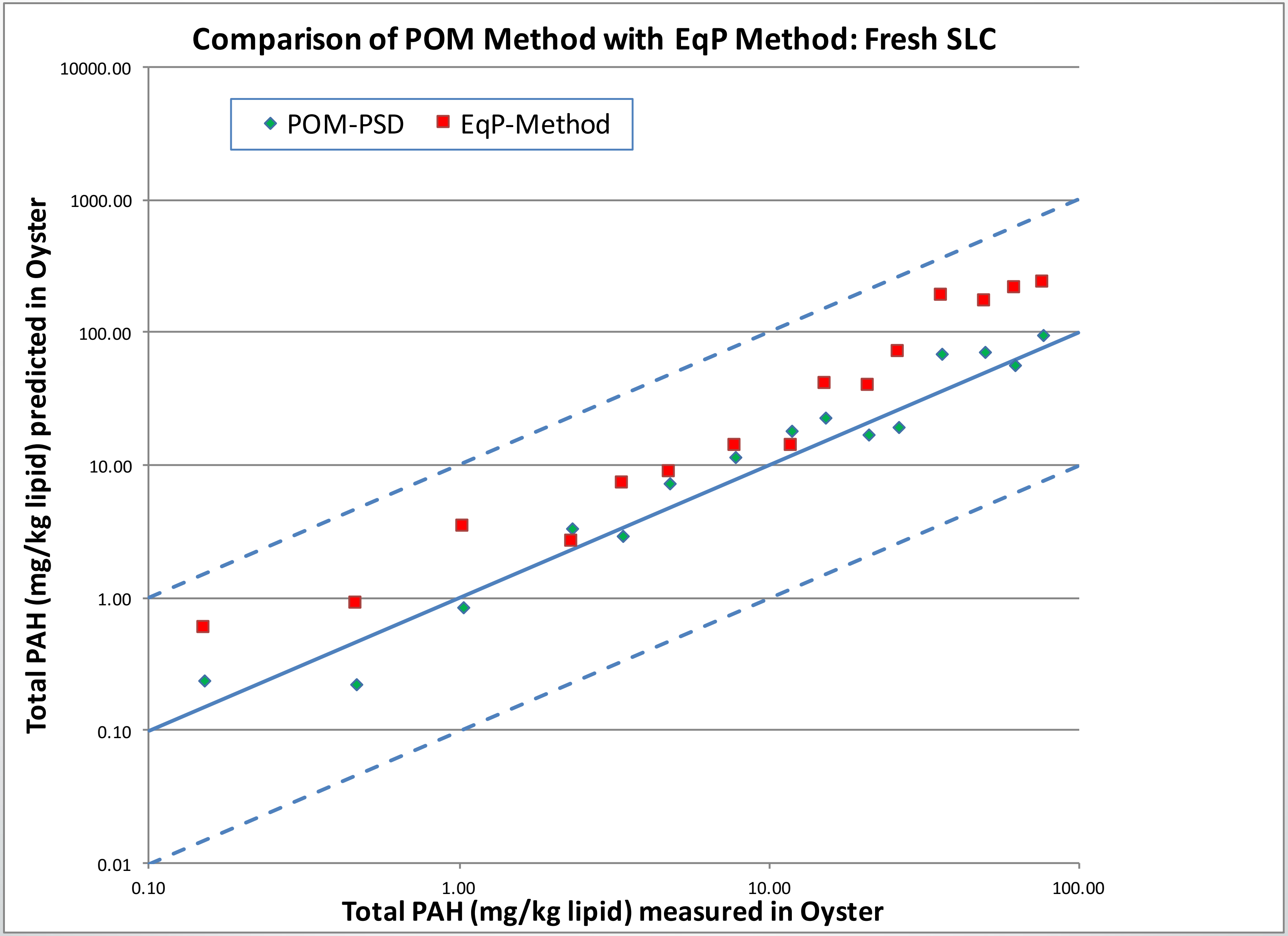
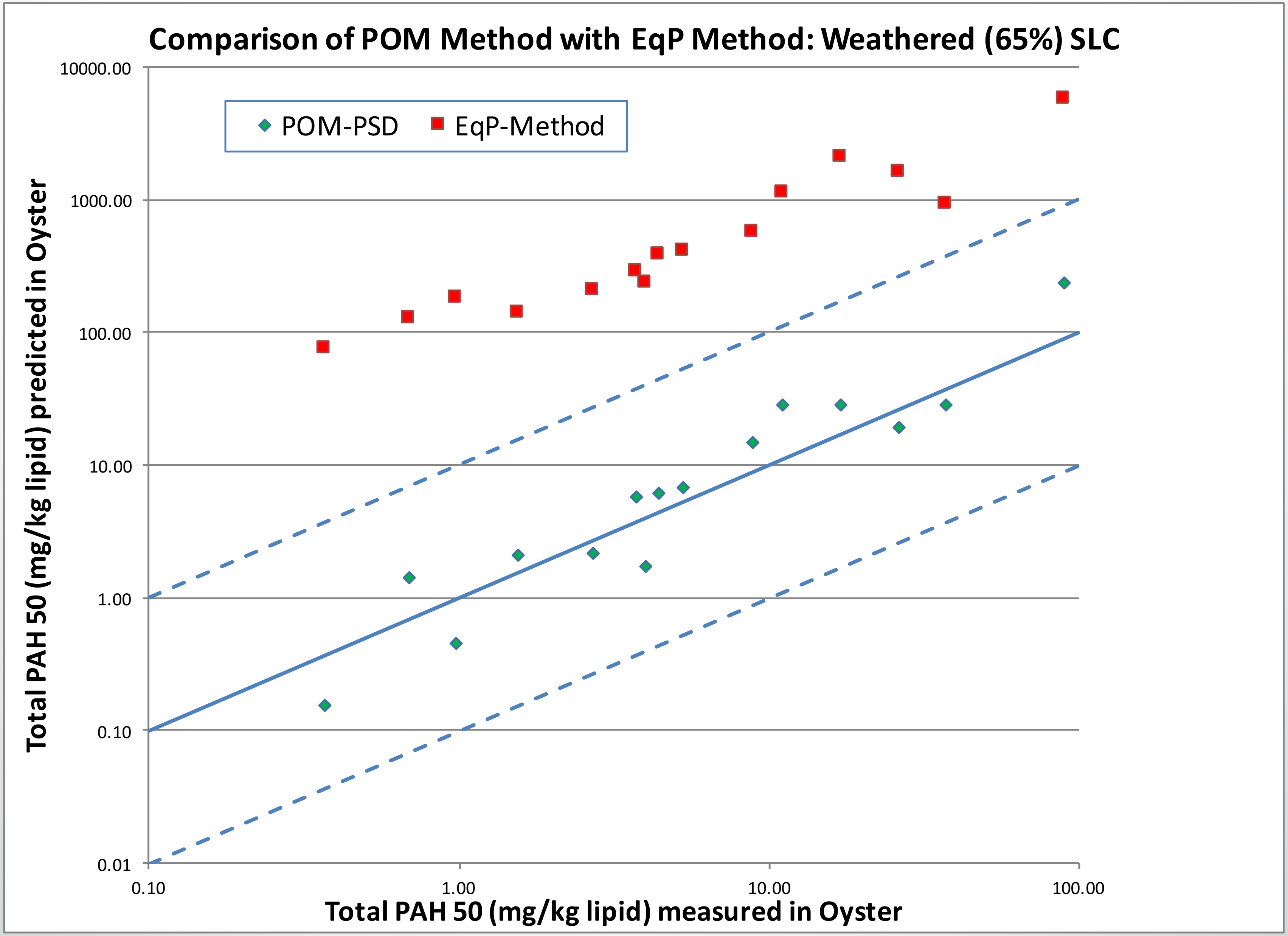
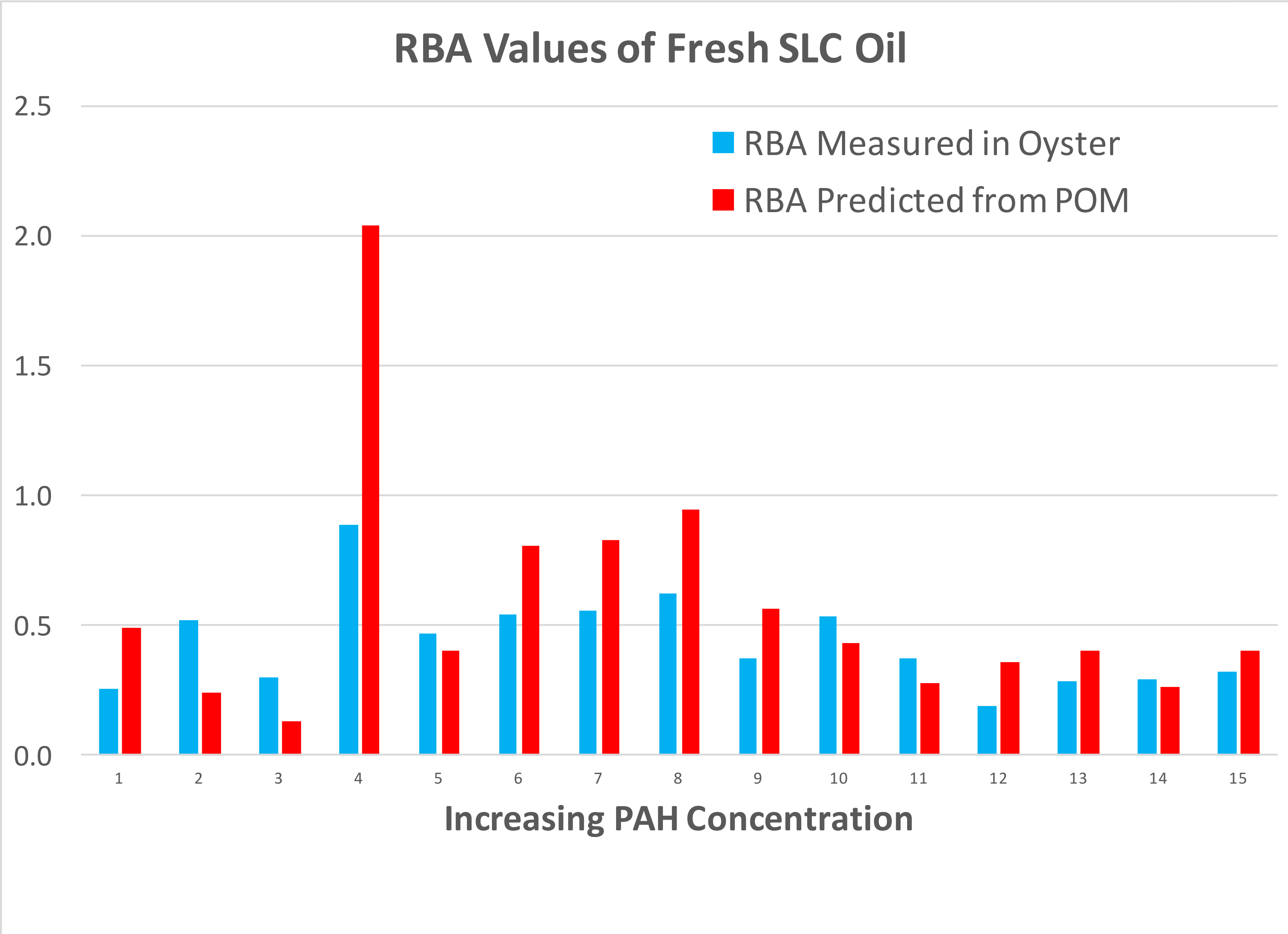
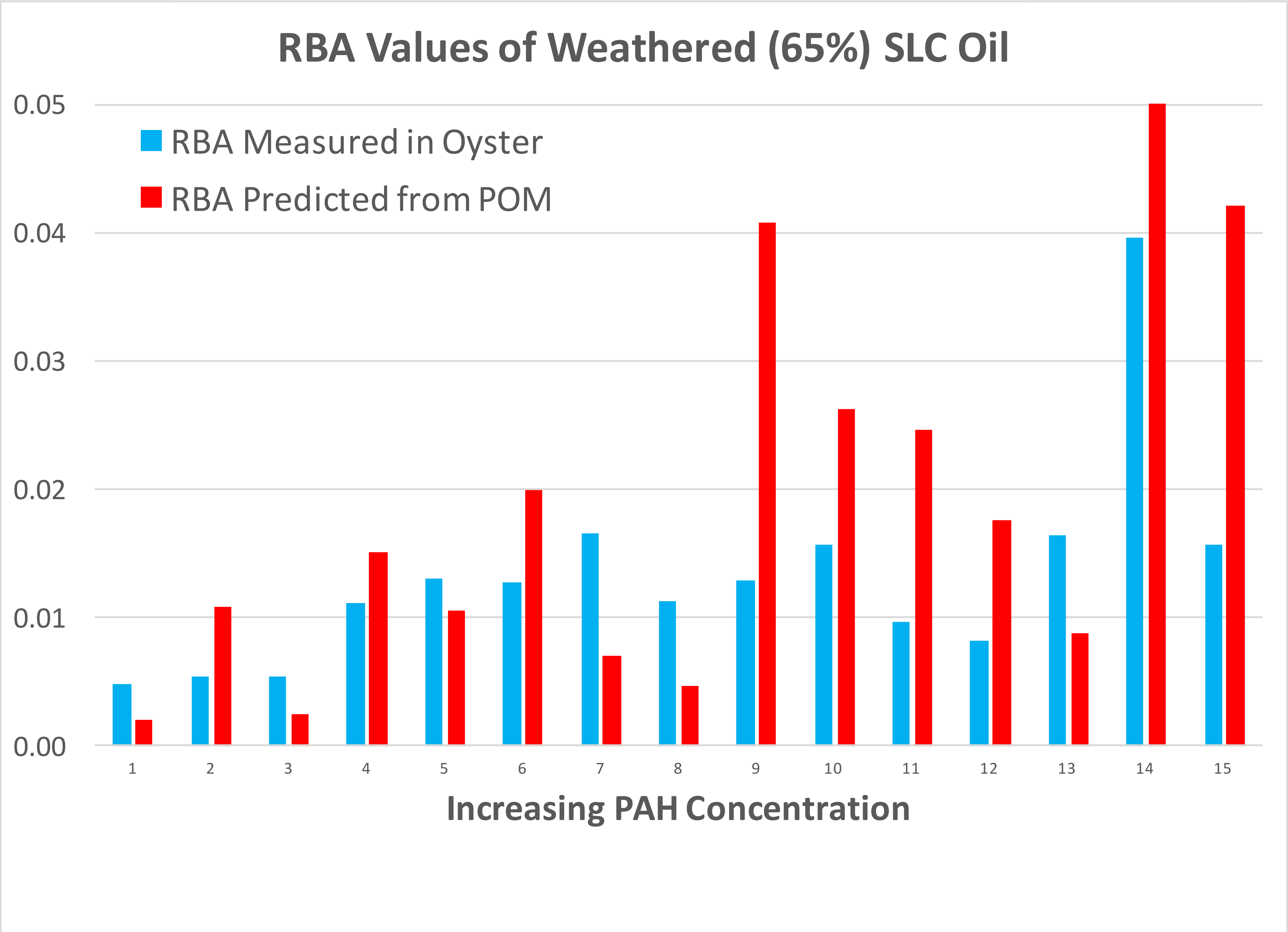



Comparison of POM Method with EqP Method: Weathered (65%) SLC
POM-PSD
EqP-Method
10000.00
1000.00
100.00
10.00
1.00
0.10
0.01
0.10
1.00
10.00
100.00
Total PAH 50 (mg/kg lipid) predicted in Oyster
Total PAH 50 (mg/kg lipid) measured in Oyster


RBA Values of Fresh SLC Oil
2.5
2.0
1.5
1.0
0.5
0.0
RBA Measured in Oyster
RBA Predicted from POM
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Increasing PAH Concentration

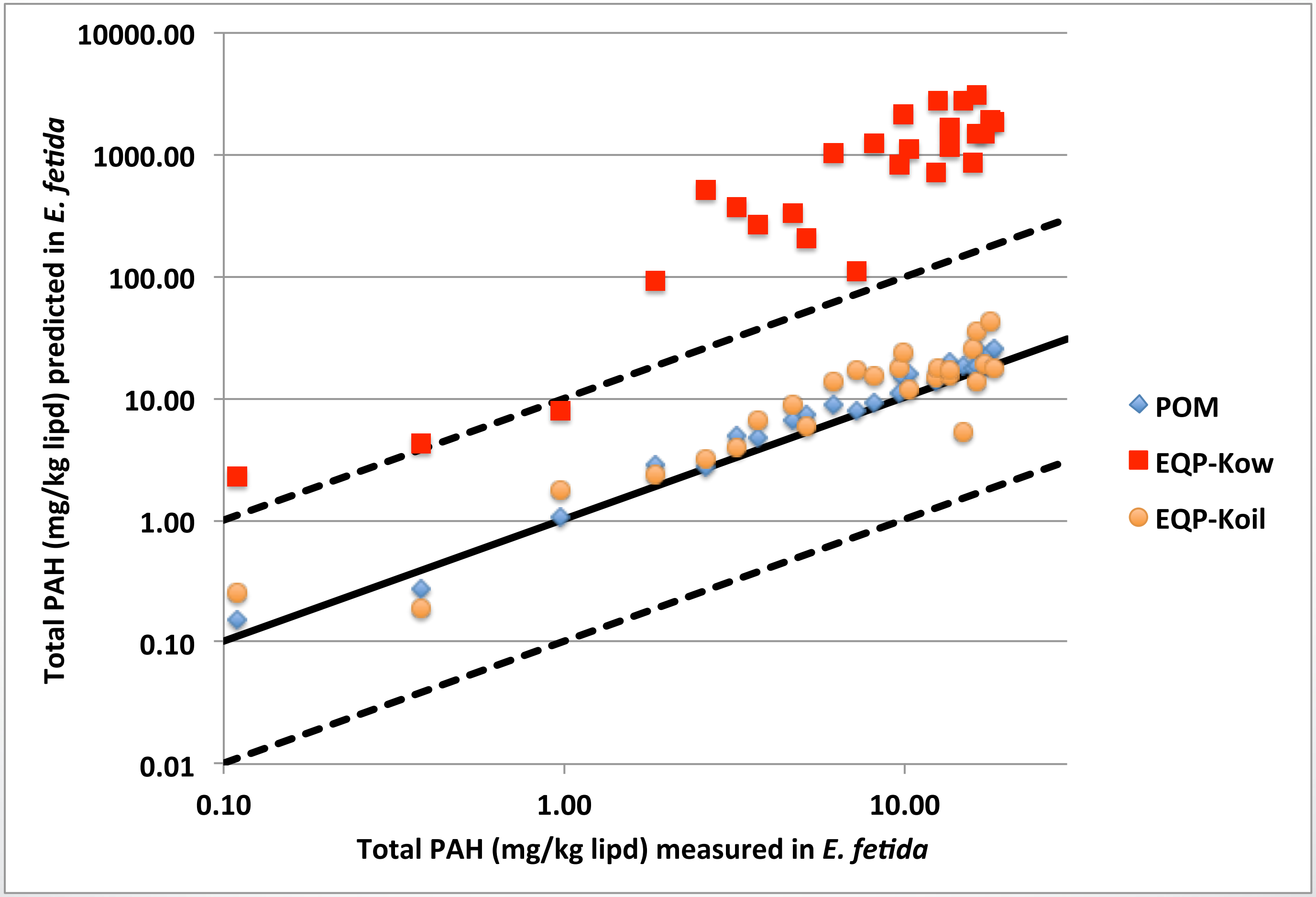

RBA Values of Weathered (65%) SLC Oil
RBA Measured in Oyster
RBA Predicted from POM
0.05
0.04
0.03
0.02
0.01
0.00
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Increasing PAH Concentration

Summary

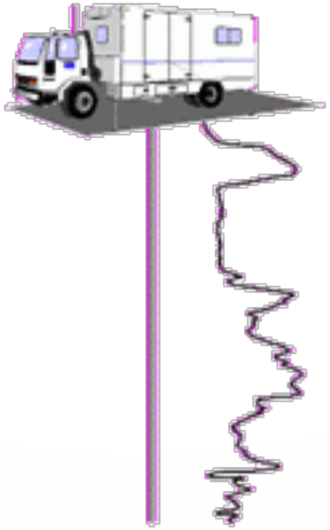
- Amount of PAH accumulated by oysters from fresh oil:
  - POM method provided excellent agreement with measured values, within about a factor of two
  - The default EqP method yielded higher values, but still within about a factor of five
- Amount of PAH accumulated by oysters from weathered oil:
  - POM method again provided excellent agreement with measured values, within about a factor of three
  - The default EqP method yielded much higher values, with most being about 100 times above that measured in the oysters
- RBA values ranged from ~ 0.2 – 1.2 in fresh oil
- RBA values ranged from <0.01 – 0.04 in weathered oil

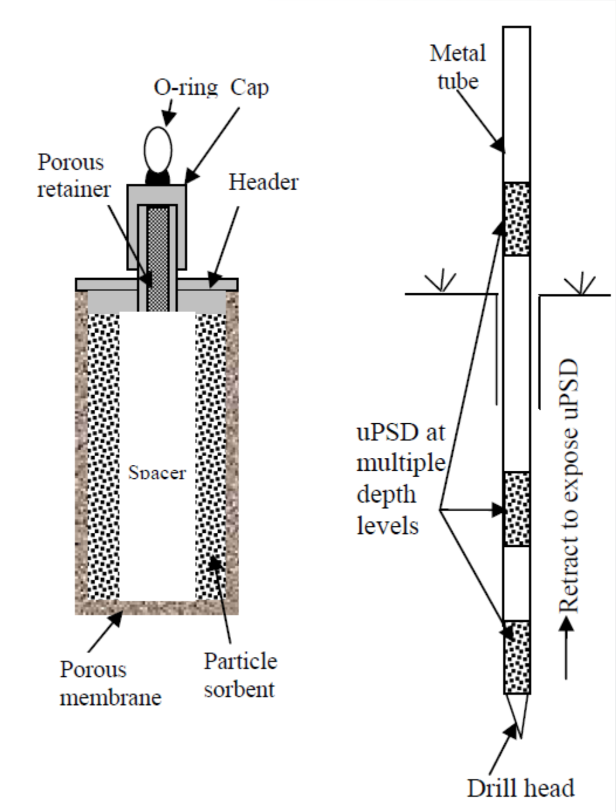
PAH soil toxicity and bioaccumulation tests with earthworms

Use of published BCFs or simple EQP theory based on K_{ow} values can greatly overestimate PAH accumulation in earthworms, but use of PSD provides excellent agreement with measured values.



Looking for partners interested in field testing this approach (in situ and ex situ)





Overall Summary

- Passive sampling is a practical, cost-effective means of estimating the time-weighted average (chronic) exposure to the bioavailable fraction of many chemicals in water, sediment and soil
- These values can be used directly in both ecological and human health risk equations to substitute for default assumptions of exposure to the total chemical obtained from “grab” sampling
- PSD data are acceptable in both the US and Europe, but further field verification is needed to gain wider acceptance and approval of official regulatory methods

Potential benefits of passive sampling

1. Potential cost savings
2. Time-weighted average (chronic) exposure
3. Higher detection sensitivity
4. Measure of relative bioavailability (RBA)
5. Reduction in use of test animals
6. Reduction in use solvents
7. Applicable to air, groundwater, surface water, soil, sediment
8. Regulatory acceptance is increasing – usually results in cost savings with either similar or more accurate RA

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Thank you!

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