Polyethylene Passive Samplers for Quantifying Dissolved Hydrophobic Organic Contaminants in Aquatic Environments

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Outline

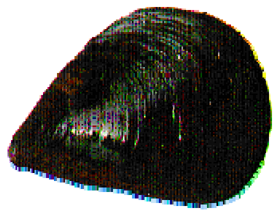
- Introduction & Motivation
- Hydrophobic Organic Contaminants & Regulatory Concern
- Partitioning and Time to Equilibrium
- PED Field Measurements: Boston Harbor
- PED & SPME Laboratory Measurements
- Pyrethroids
- Conclusions

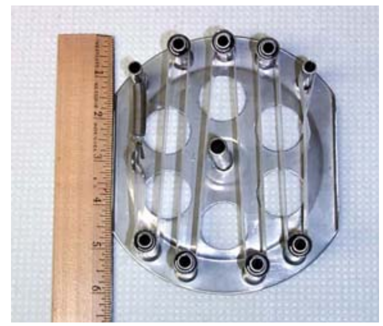
Introduction & Motivation: Dissolved Phase & Passive Samplers

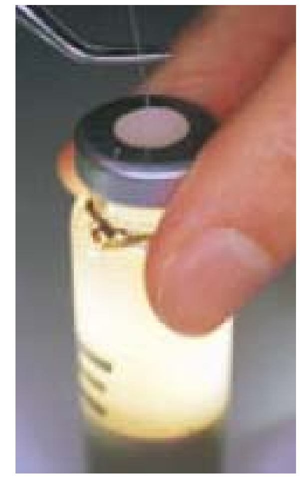
Freely Dissolved Phase

- This freely dissolved fraction is of interest as it is the bioavailable fraction (does not include DOM-bound fraction)

- **Low concentrations make it difficult to measure chemicals!**







Passive Samplers

- Mussel Watch

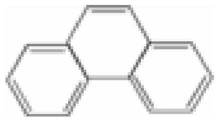
- Semipermeable Membrane Devices (SPMDs)

- Solid Phase Microextraction (SPMEs)

- **Polyethylene Devices (PEDs):** Passive samplers used to measure the activity or fugacity of HOCs in the environment based on the partitioning of HOCs between polyethylene & water.

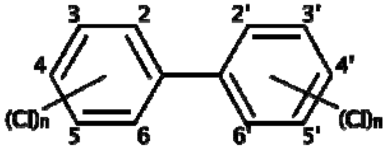
Hydrophobic Organic Contaminants (HOCs)

Polycyclic Aromatic Hydrocarbons (PAHs)



- sources:
  - combustion of fossil fuels and wood (non-point source)
  - oil spills (point source)

- toxic, carcinogenic, & mutagenic



Polychlorinated Biphenyls (PCBs)

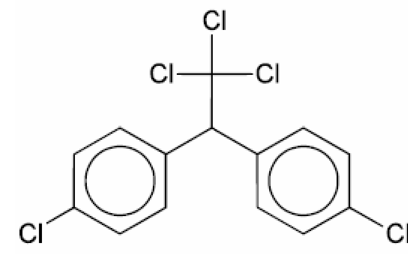
- manufactured in the U.S. between 1929 & 1979 as insulating fluids in transformers and capacitors (tradename: Arochlor)

- estimated that General Electric released between 200,000 to 1.3 million pounds of PCBs into the Hudson River between the 1940's and 1977 (EPA, 2000)

- toxic (neurological, developmental, reproductive problems) and carcinogenic

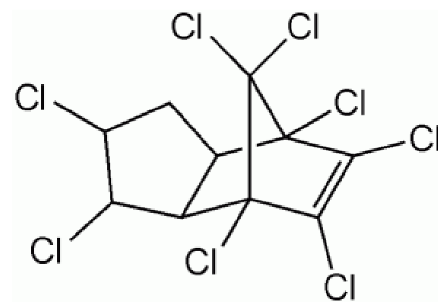
Hydrophobic Organic Contaminants (HOCs)

Dichloro-Diphenyl-Trichloroethane (DDT) and Metabolites (DDE, DDD)



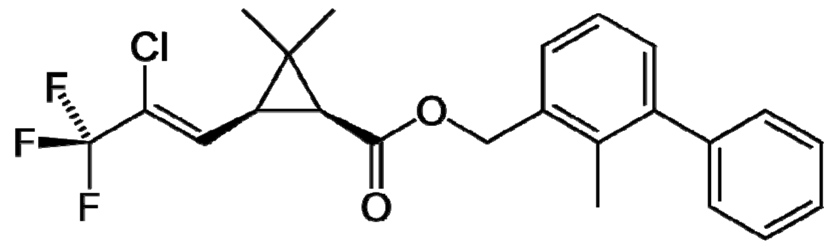
- insecticide used during WWII and after
- banned in the US in 1972—now world-wide (with exception for vector control—India & China)
- estimated that Montrose Chemical released (via Joint Power Pollution Control Plant) 1700 tons of DDT from the late 1950s to early 1970s on Palos Verdes shelf
- toxic, thinning of eggshells

Chlorinated Pesticides



- chlordane and heptachlor
- insecticide banned in U.S. in 1988

Hydrophobic Organic Contaminants (HOCs)



bifenthrin

Pyrethroids

- current-use synthetic insecticides
- uses for agricultural crops, nurseries, urban structures and landscaping, home/garden
- In 2004, 1.4 million lbs sold in California (Spurlock & Lee, 2008)
- acute toxicity to aquatic organisms (LC_{50} = 0.4 μg/L; *Daphnia magna*)

Regulatory & Environmental Concerns

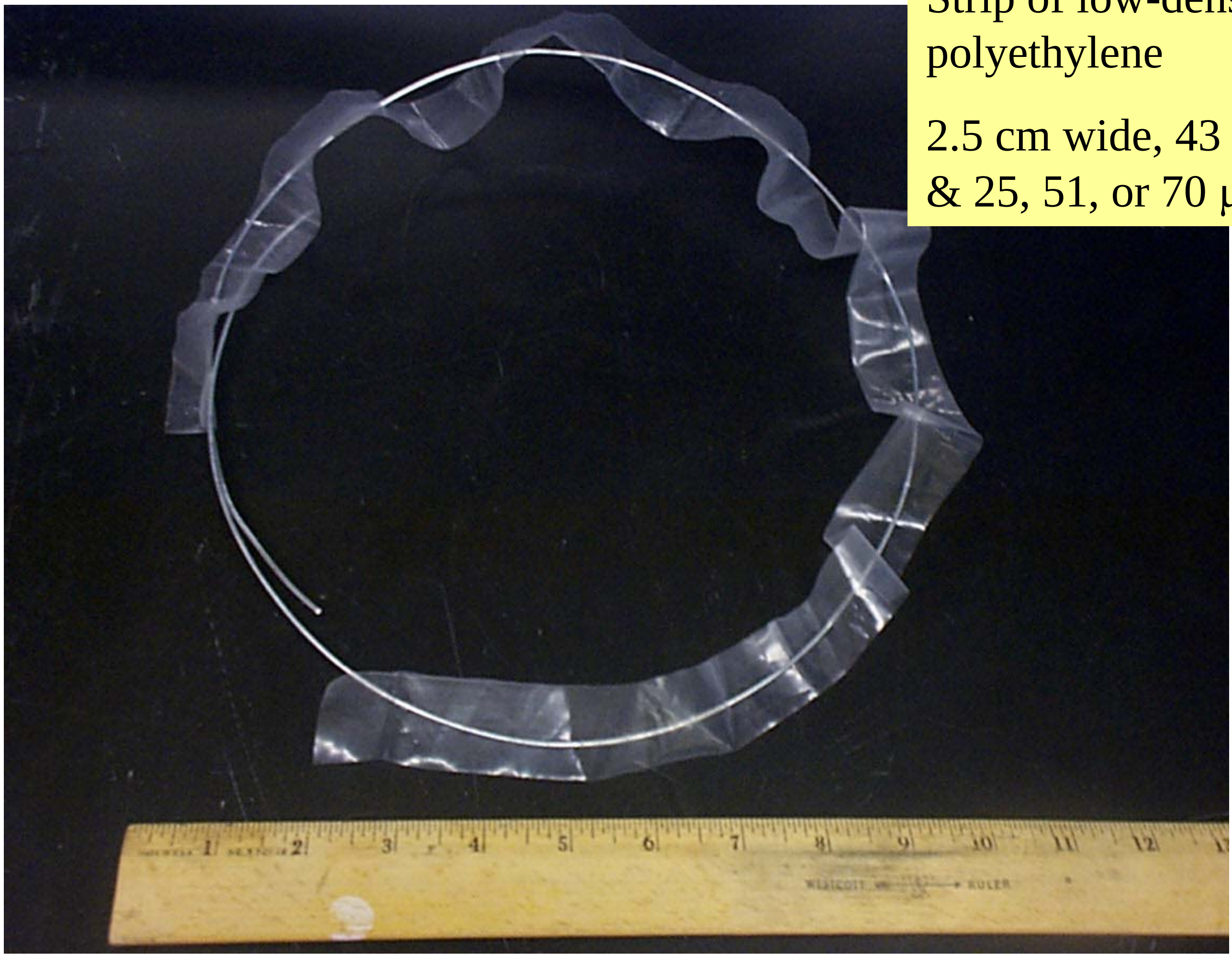
- PAHs, PCBs, DDT, chlordane are all contaminants of concern
  - California's 303(d) List of Impaired Water Bodies
  - Total Maximum Daily Loads

- Pyrethroids emerging contaminants of concern

- Ballona Creek Estuary TMDL recommends improved water quality methods
  - Current MDLs are 0.05 μg/L to 0.1 μg/L for PAHs, PCBs, and pesticide
  - PEDs allow for MDLs ranging from 0.04 pg/L (PCB 180) to 0.015 ng/L (phenanthrene)

- Contaminants in the freely dissolved fraction are the bioavailable fraction are most closely correlated to chemical toxicity

PEDs: Polyethylene Devices



Strip of low-density polyethylene

2.5 cm wide, 43 cm long, & 25, 51, or 70 μm thick

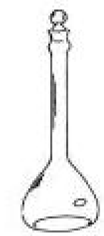
PEDs: Parameters needed for use

Equilibrium Partitioning

$$K_{PEW} = \frac{C_{PE}}{C_W}$$

For pyrene,

K_{PEW} = 100,000 (mol/kg$_{PE}$)/(mol/L$_w$) so



100,000 mols/ 1 kg plastic

1 mol/ 1 L water

where K_{PEW} is the equilibrium polyethylene-water partitioning coefficient,

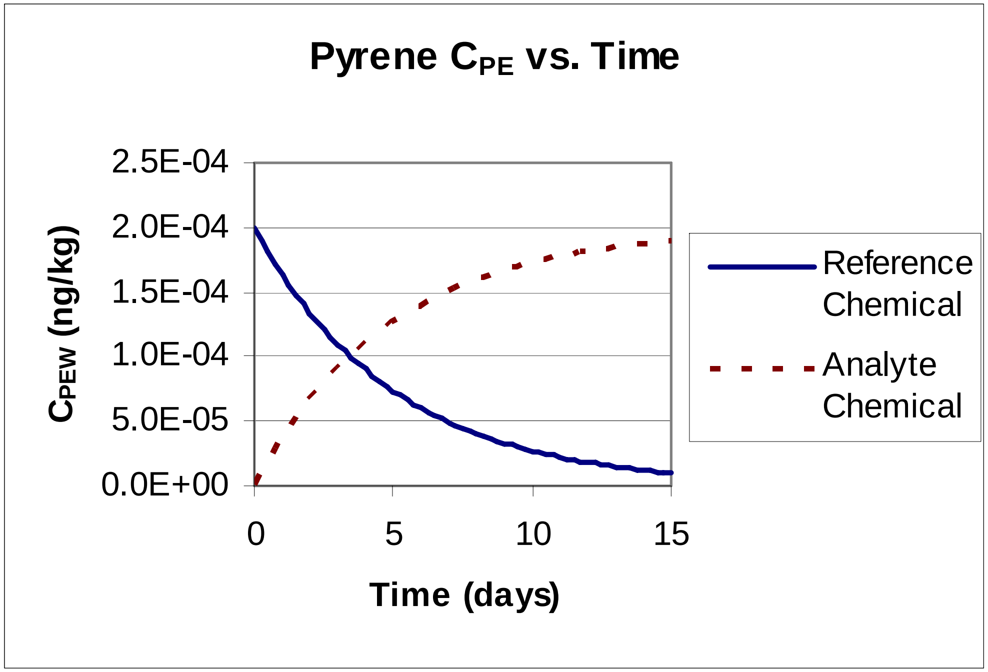
C_{PE} is the chemical concentration in the polyethylene, and

C_W is the chemical concentration in the water.

PEDs: Parameters needed for use

Time to equilibrium (i.e., $k_{exchange}$)

$$C_{W\infty} = \frac{C_{PEt}}{(1 - e^{-k_e t}) \cdot K_{PEW}}$$



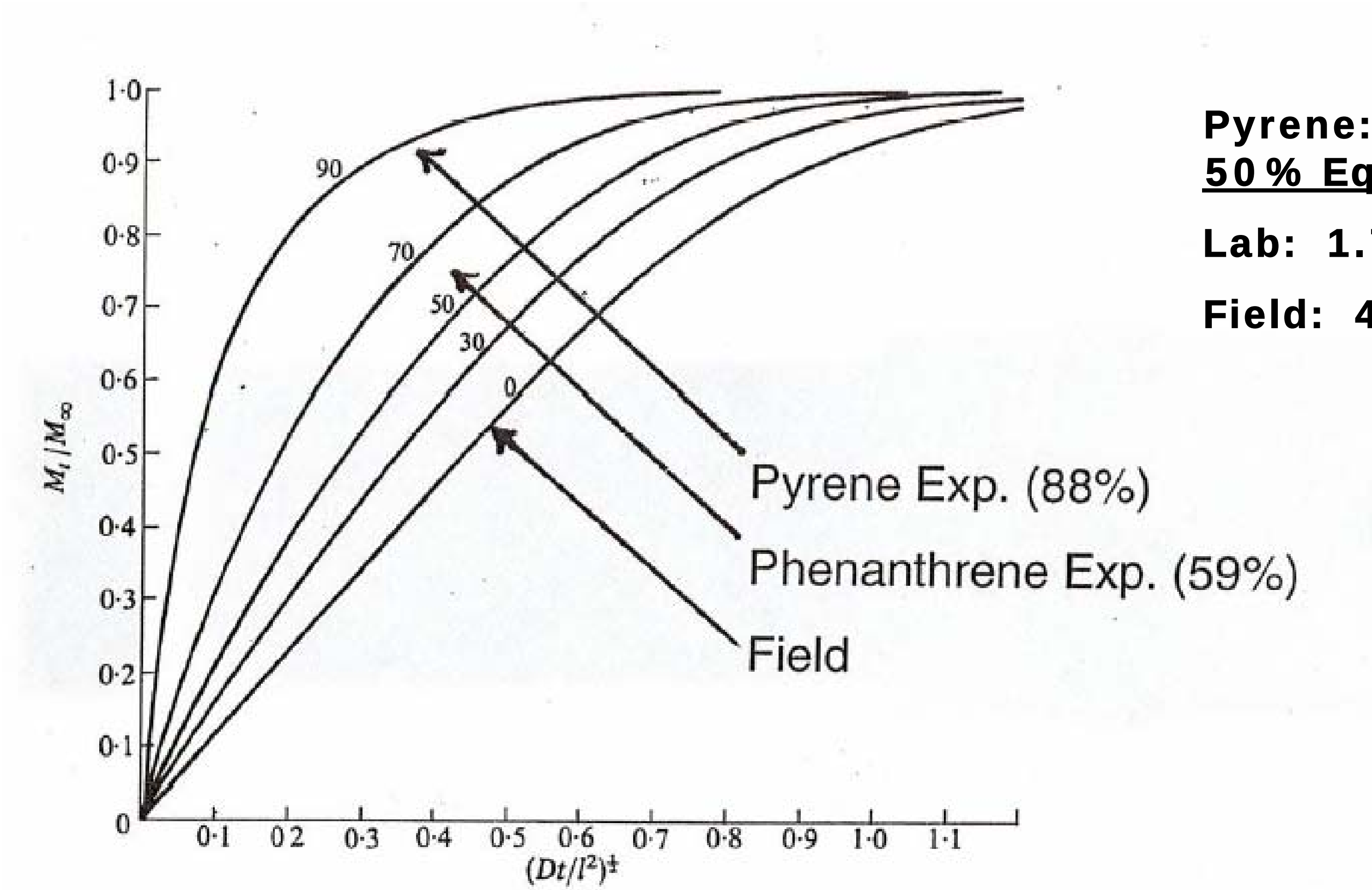
where $C_{W\infty}$ is the chemical concentration in the water at equilibrium,

C_{PEt} is the chemical concentration in the polyethylene at time t,

k_e is the exchange rate coefficient and

K_{PEW} is the equilibrium polyethylene-water partitioning coefficient

Time to Equilibrium Dependent on Percentage of Solute Finally Taken up by Sampler



Pyrene: Time for **<u>50% Equilibrium</u>**

Lab: 1.7 hrs

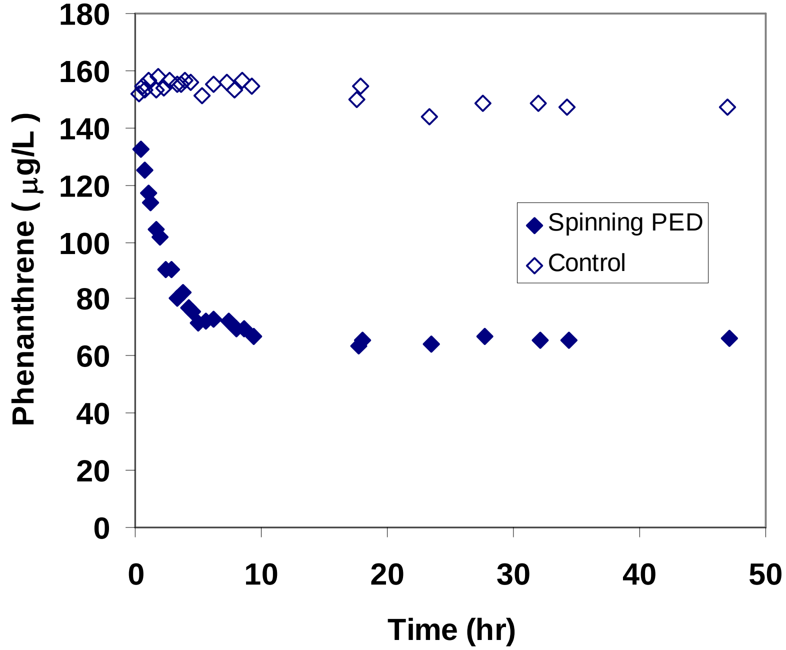
Field: 43 hrs

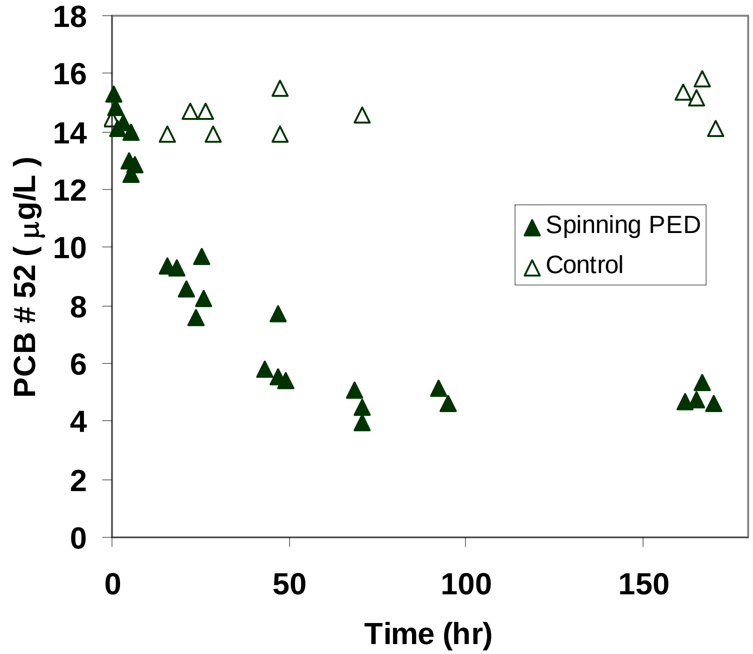
Uptake by a plane sheet from a stirred solution where

D is the diffusion coefficient, *t* is time, and *l* is one-half of the sheet thickness

Numbers on curves indicate the percentage of solute finally taken up by the sheet (Crank, 1975)

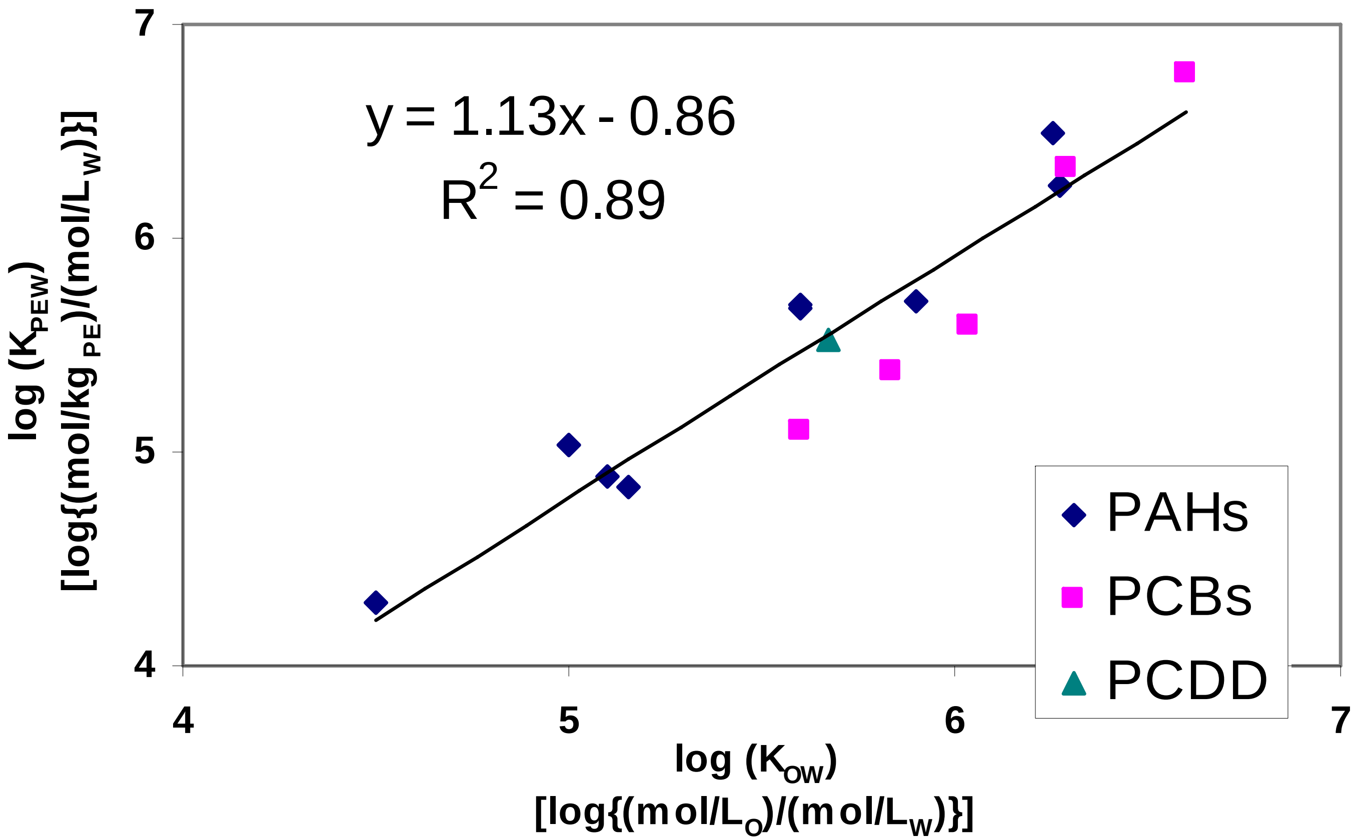
PEDs: Time for Equilibrium in Closed Lab Experiment





(Adams et al, 2007)

PEDs: Measured K_{PEW}s as a function of K_{OW}

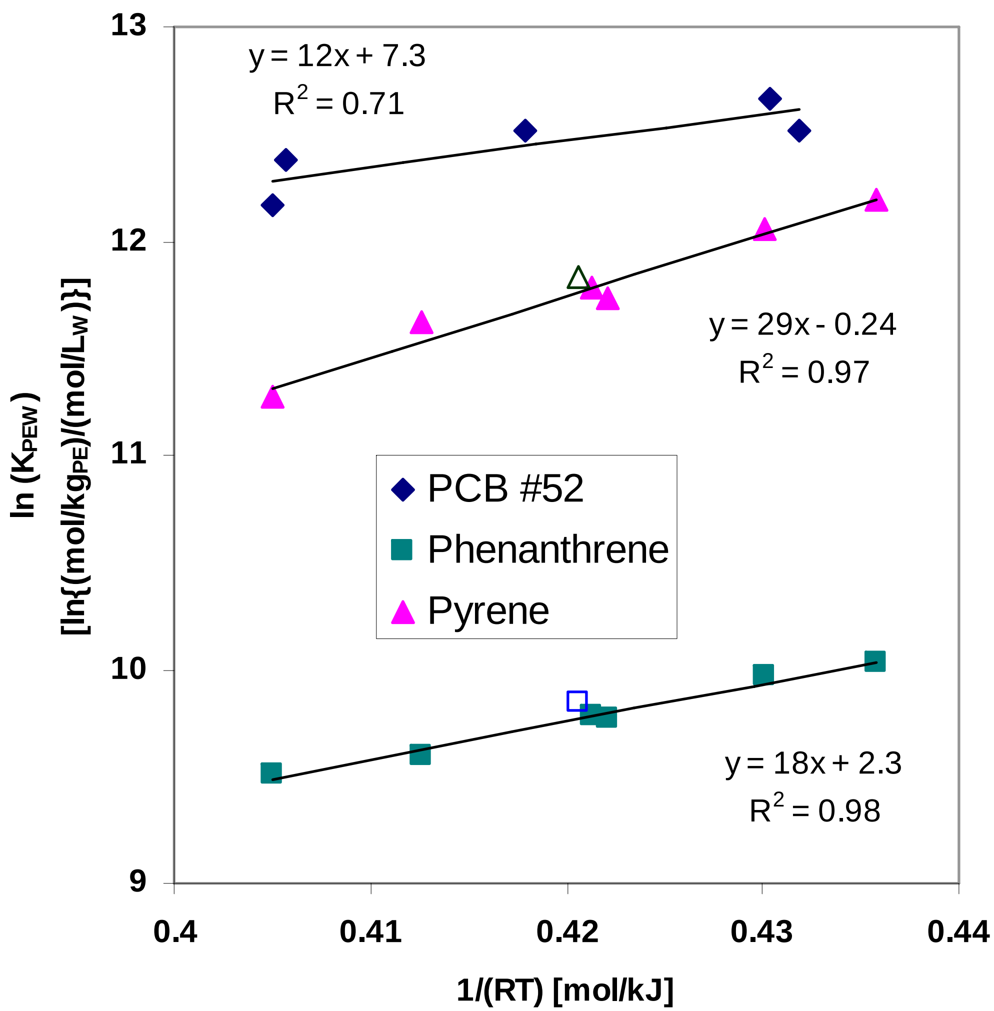


(Adams et al, 2007)

PEDs: Temperature and Salinity Corrections

- Excess Enthalpy of Solution, H_s^e can be used to correct for temperature differences

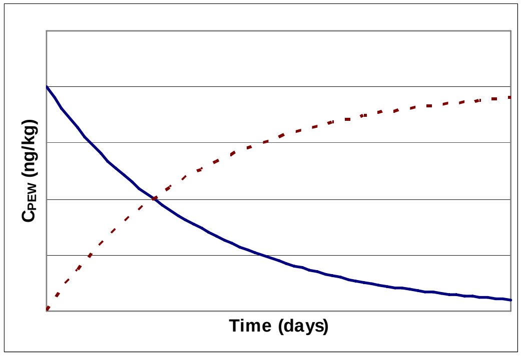
- Setchenow constant, K_s can be used to correct for salinity effects (open triangle and square)



(Adams et al., 2007)

Spiked vs. PE-Deduced Dissolved Concentrations in Seawater

- Seawater samples with known HOC concentration
- Pre-added deuterated reference compounds added
- Sampling for 2 days (non- equilibrium)
- k-exchange used to correct for time to equilibrium

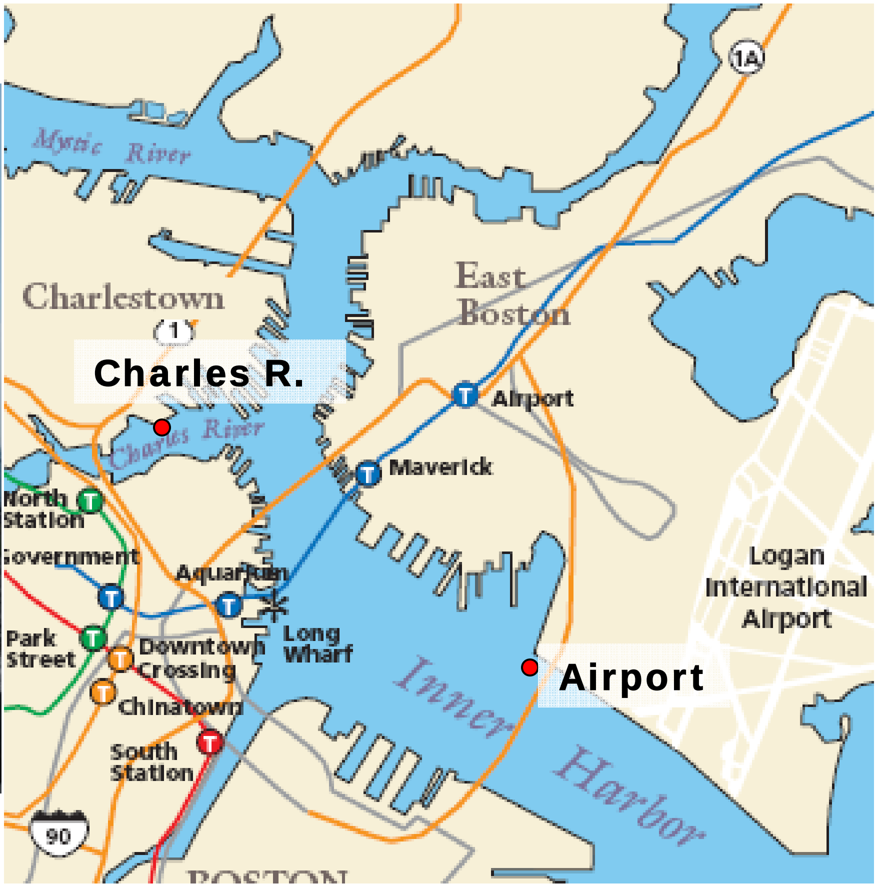


Test	HOC	Spiking concentration (ng/L)	PED-measured concentration (ng/L)
Spring	Phenanthrene	450 ± 50	410 ± 70
	Fluoranthene	500 ± 60	450 ± 140
Summer	Phenanthrene	450 ± 50	340 ± 120
	Fluoranthene	500 ± 60	730 ± 260

(Adams et al., 2007)

Boston Harbor Field Measurements

- Two Sites: Near Charles River and Airport
- 15 days in December (2 & 3°C; 33 psu; POC = 0.2 mg/L)
- Total Water: (One point in time) vs. PED (Time-averaged)



Boston Harbor Dissolved Concentrations: Total Water Extracts vs. PEDs

Chemical	Location	Total water extracts (ng/L)	Estimated dissolved fraction	PED extracts (ng/L)
phenanthrene	Airport	8	0.99	10
	near Charles River	10	0.99	10
pyrene	Airport	7	0.98	5
	near Charles River	8	0.98	2
PCB # 52	Airport	< 0.03	0.93	0.07
	near Charles River	< 0.02	0.94	0.06

Ongoing Research

PED & SPME Laboratory and Field Sampling (Sayre et al., in prep)

- **Quantifying** PAHs, PCBs, and chlorinated pesticides (e.g., DDT, chlordane) in laboratory and field

Pyrethroids in Ballona Creek Estuary (Lao et al., 2008)

- Using PEDs to measure 8 pyrethroids in Ballona Creek Estuary

PED and SPME Estimated Method Detection Limits

Partition Coefficients for Analytes of Interest with Estimated Method Detection Limits

Chemical	Log K_{OW} ($Lw/L_{octonol}$)	Log K_f (100 μm) (Lw/L_{fiber})	Log K_{PEW}[f] (51 μm) (Lw/kg_{PE})	Method Detection Limit (ng/L)	
				SPME	PE
Phenanthrene	4.52[a]	3.90[c]	4.33	5.1	0.015
Pyrene	5.00[a]	4.86[d]	5.02	0.56	0.003
Benzo[a]pyrene	6.35[a]	5.82[c]	6.61	0.06	0.0001
PCB 52	6.17[b]	5.52[c]	5.51	0.12	0.001
PCB101	6.65 [b]	5.61[e]	6.16	0.10	0.0002
PCB153	7.09 [b]	6.45 [c]	6.71	0.014	0.0001
PCB180	7.21 [b]	6.54 [c]	6.91	0.012	0.00004
cis-Chlordane	6.22	5.37 [c]	5.53	0.17	0.0009
DDE	6.96	5.68 [c]	6.25	0.028	0.0002

(Sayre et al., in prep)

[a]Sangster, 1989; [b]Ruelle, 2000; [c]Maruya et al, 2009; [d]Doong & Chong, 2000; [e]Zeng et al., 2005; [f]Sayre et al, in prep.

Laboratory PED & SPME Comparisons

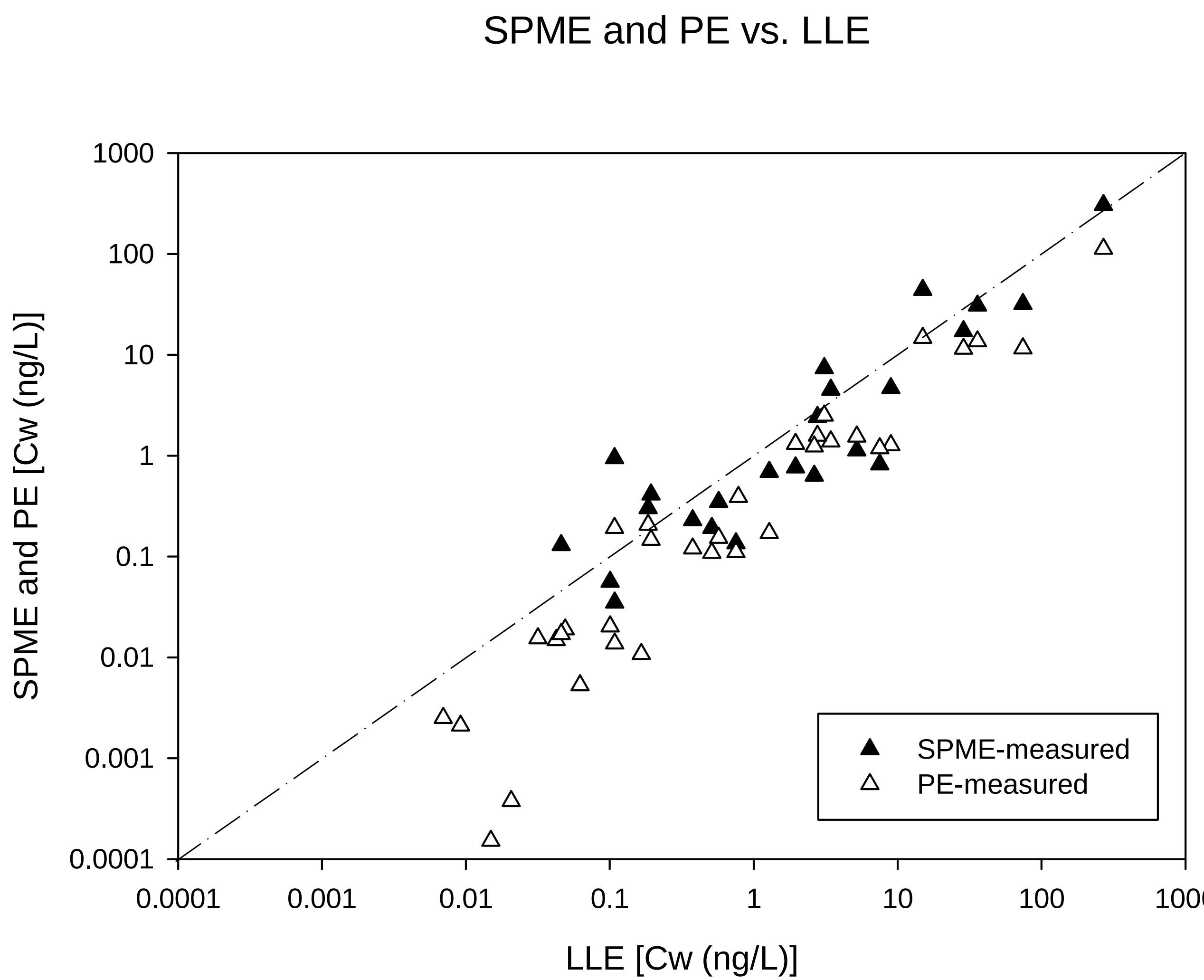
- Four 20-L carboys with PE and SPME in triplicate
- Dissolved concentrations over 4 orders of magnitude
- MDL for 2 g PE below that of SPME
- Two PE-measured concentrations at MDL diverged from LLE

SPME: slope = 0.91

(n = 24; R^2 = 0.81)

PE: slope = 1.1

(n = 34; R^2 = 0.90)



(Sayre et al., in prep)

Pyrethroids in Ballona Creek Estuary

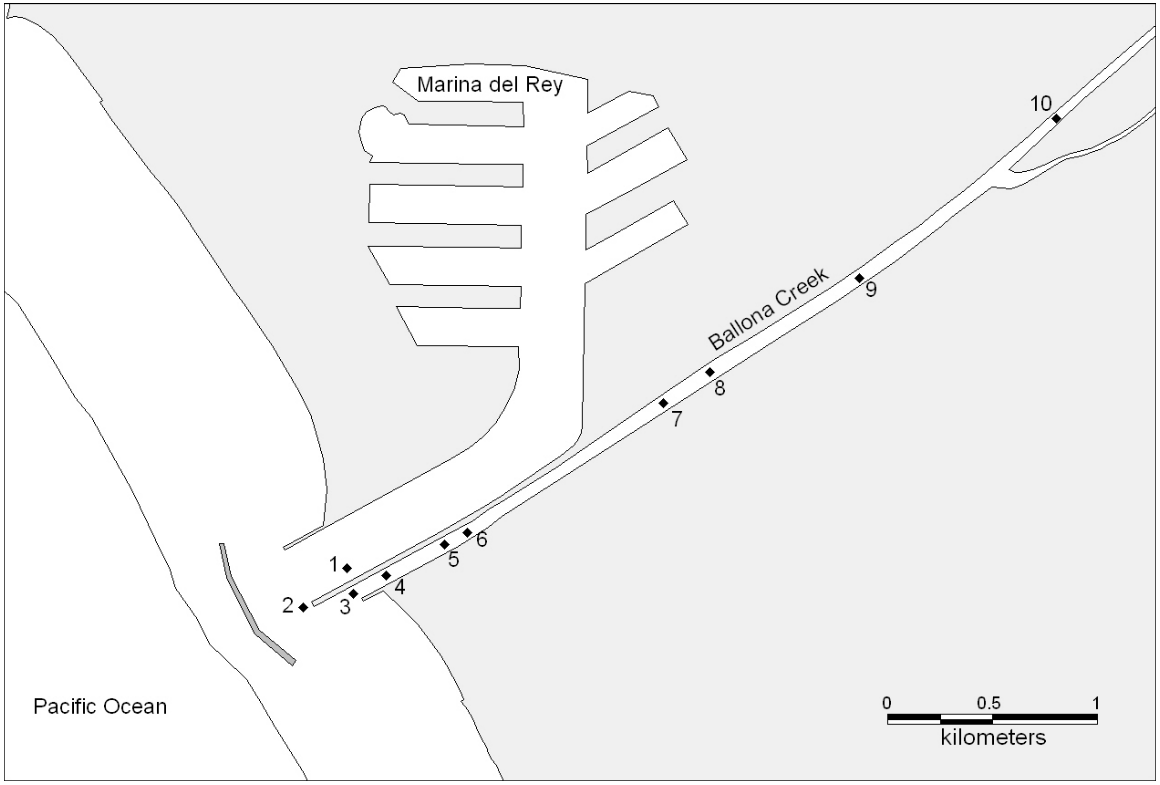
PEDs deployed in Ballona Creek Estuary to measure 8 target pyrethroids

PE deployed for 23 days (sites 1 -6)

In situ pump with XAD resin deployed at site 5 (4 days)

Estimated Method Detection Limits for target pyrethroids

	MDL ng/L
Bifenthrin	0.0003
Fenpropathrin	0.0028
Lamda-Cyhalothrin	0.0001
Cis-Permethrin	0.0161
Trans-Permethrin	0.0224
Cyfluthrin	0.0107
Cypermethrin	0.0027
Esfenvalerate	0.0150
Deltamethrin	0.0022
Average	0.0080

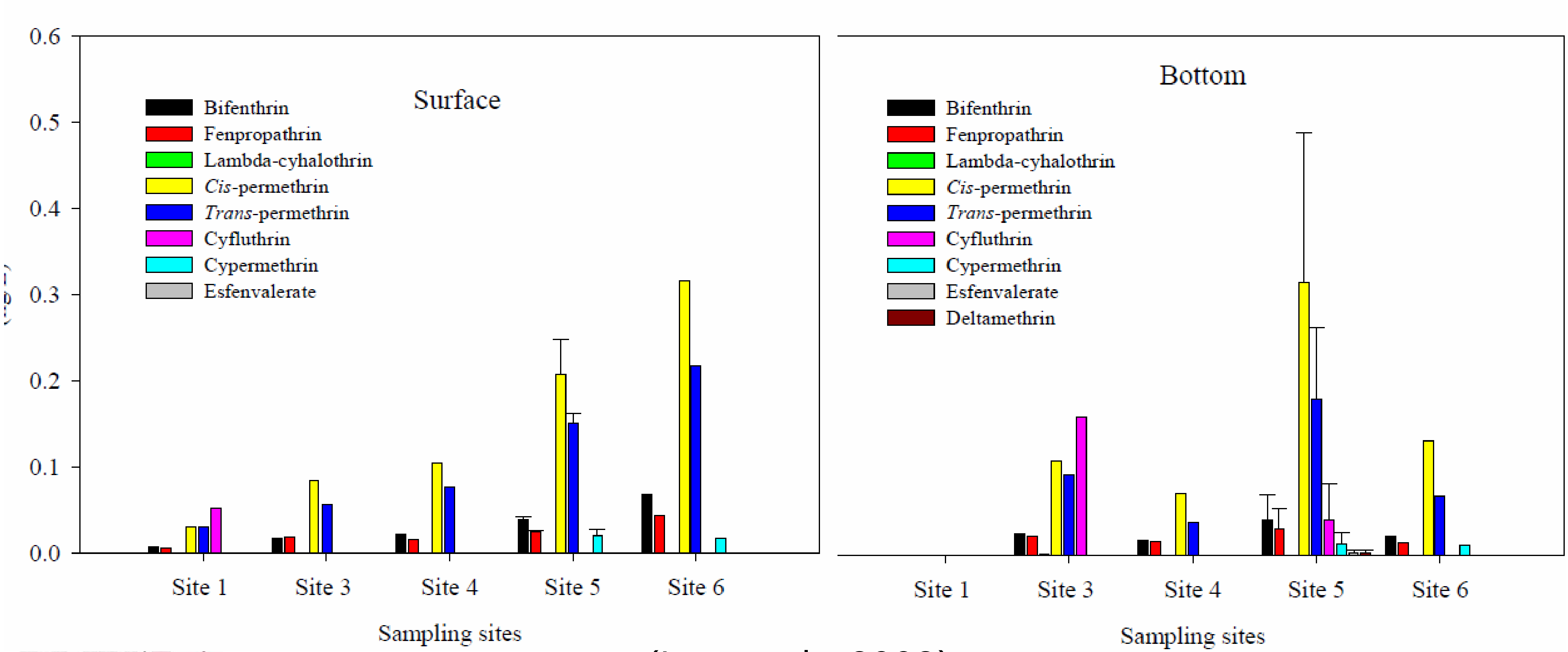


Sampling sites for PE Deployment in Ballona Creek Estuary (Sept.- Oct. 2007)

(Lao et al., 2008)

Pyrethroids in Ballona Creek Estuary

- Freely dissolved pyrethroids measured 0.5 m below water surface and 0.5 m above creek bottom
- Cis-permethrin ranging from 0.1 – 0.3 ng/L
- Bifenthrin ranging from 0.01 ng/L – 0.07 ng/L

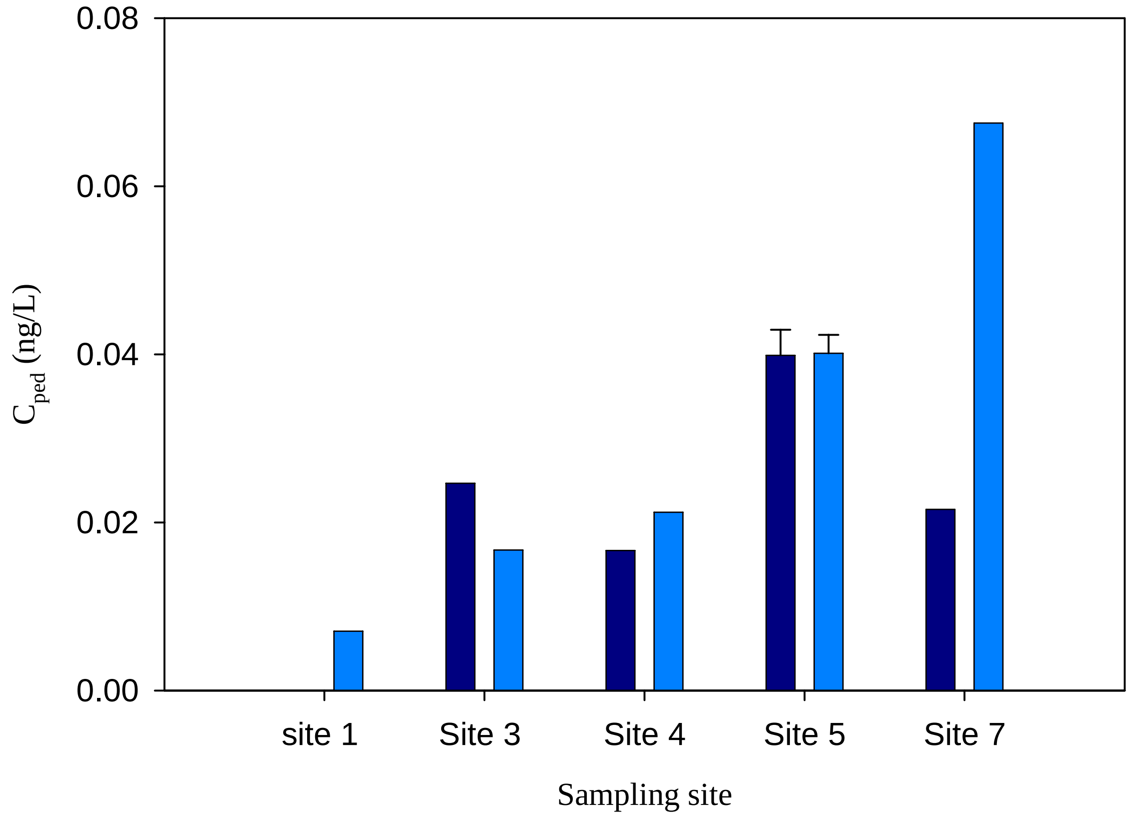


(Lao et al., 2008)

LMU|LA Loyola Marymount University

Pyrethroids in Ballona Creek Estuary

Dissolved bifenthrin concentrations increase with increasing distance from ocean



(Lao et al., 2008)

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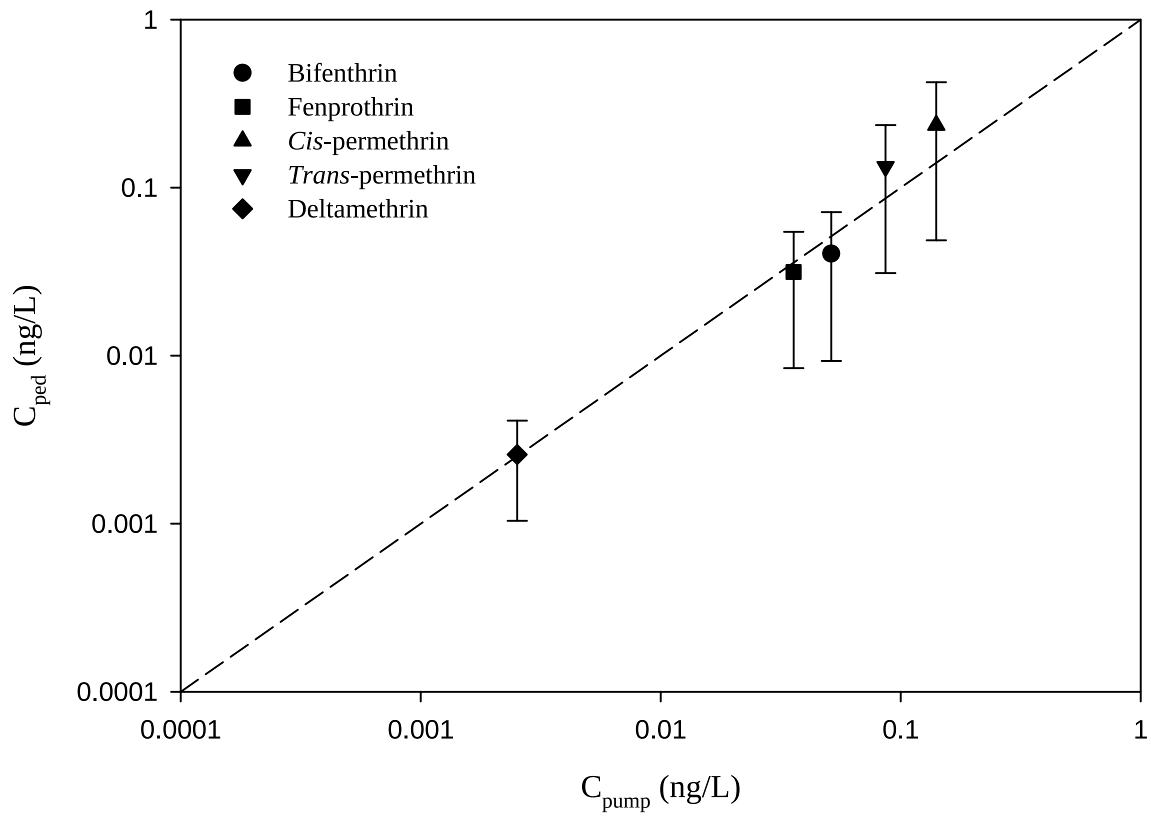
Pyrethroids in Ballona Creek Estuary

PED-measured vs. XAD-measured at Site 5 in Ballona Creek

- In situ pump 1.5 m from surface pumping 944 L used to measure dissolved conc.
- Strong correlation with PE-measured dissolved concentration



(Lao et al., 2008)

Conclusions

- PEDs are useful devices for the measurement of freely dissolved HOCs in the water column

- Time-averaged, in situ
- Simple extraction and clean-up procedure
- Equilibrium on order of days to weeks
- Reference compounds can be used to correct for non-equilbrium cases
- Temperature and salinity effects can be corrected
- Low detection limits (sub pg/L); increase in mass of PED will further lower DL
- Good agreement with LLE and SPME
- Field Measurements for pyrethroids at pg/L concentrations

Acknowledgments

Contributors

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Loretta Fernandez, MIT
John MacFarlane, MIT
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Adams, R.G., R. Lohmann, L.A. Fernandez, J.K. MacFarlane, and P.M. Gschwend. 2007. Polyethylene devices (PEDs): Passive samplers for measuring dissolved hydrophobic organic compounds in aquatic environments. *Environ. Sci. Technol.*, 41, 1317-1323.

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Sayre, J. M., R.G. Adams, W. Lao, K.A. Maruya. Comparing solid phase microextraction and polyethylene passive samplers for measuring ultra-low aqueous concentrations of regulated organic pollutants, *in preparation*