Calibrating Polyethylene Devices (PEDs) to Quantify Organic Pollutant Concentrations and Loadings in Impaired Urban Waterways

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Abstract:

Technologies to measure ultratrace dissolved concentrations of hydrophobic organic chemicals (HOCs) in aquatic environments are limited, inefficient, and costly. Polyethylene devices (PEDs), passive samplers in which HOCs partition from water into polyethylene, represent a new approach for measuring ng/L or lower concentrations, data that are critical for assessing the validity of total maximum daily loads (TMDLs) currently under development for impaired urban waterways. This study focuses on determining polyethylene-water partitioning coefficients (K_{PEW}s) for TMDL-regulated HOCs, including DDTs, chlordanes PCBs and PAHs. K_{PEW} for 16 model HOCs determined in lab batch experiments was correlated with hydrophobicity (log K_{PEW} = 0.97 log K_{OW} – 0.14, R^2 = 0.92; p = 0.04). To correct for nonequilibrium conditions, PED exchange rates (k_e) will be measured by pre-loading reference HOCs (*e.g.* perdeuterated PAHs) into PEDs and following their desorption into the aqueous phase of an infinite bath (90 L) spiked with native HOCs. The large volume provides for fractional uptakes into the PEDs less than 0.095 for all except the most hydrophobic HOCs in study. Using the parameters characterized in this study, PEDs can be used to measure dissolved HOC concentrations in impaired urban waterways throughout Southern California, including Ballona Creek and Santa Monica Bay.

Why Quantify Organic Pollutants?

- Total Maximum Daily Loads (TMDLs)
  - Clean Water Act mandated
  - Set for individual water body for each pollutant depending on the use of the water body (e.g. recreation, drinking water, aquatic habitat)
- Ballona Creek requires TMDLs for organics
- Limit further contamination
- Low level dissolved HOCs difficult to quantify
- We want to quantify TMDL-regulated HOCs for Ballona Creek

What are PEDs?

- Polyethylene devices
- Strips of low-density polyethylene, ~ 2 feet long and 2 inches wide and woven onto a copper wire
- Passively absorb HOCs (e.g. PAHs, PCBs, DDTs)
- Pros/Cons
  - Very cheap and easy to construct
  - Have a high capacity for HOC absorption, even at low dissolved concentrations
  - Some post-processing
  - Minor biofouling (correction method explained with exchange rate)

Study Objectives

- Identify HOCs of concern for Ballona Creek (TMDLs)
- Determine compound specific K_{PEW}, k_e
- Compare with SPME (Solid-phase microextraction)
- Quantify aqueous phase HOCs in Ballona Creek, an ultra-urban, highly modified and channelized waterway in Los Angeles County, CA

How PEDs Work

- Partitioning Coefficient (K_{PEW})

  Ratio of concentration of chemical in PED to concentration in water at equilibrium

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

- Exchange Rate (k_e)

  Needed to correct for non-equilibrium conditions

  Rate of absorption and desorption of HOC within PED

$$k_e = \ln\left(\frac{C_{PE0,r}}{C_{PEt,r}}\right) \cdot t^{-1}$$

Assuming that the sorption and desorption rates are equivalent

$$C_{PE\infty} = \frac{\left(C_{PEt} - C_{PE0} \cdot e^{-k_e t}\right)}{\left(1 - e^{-k_e t}\right)}$$

Substitute this into K_{PEW} equation

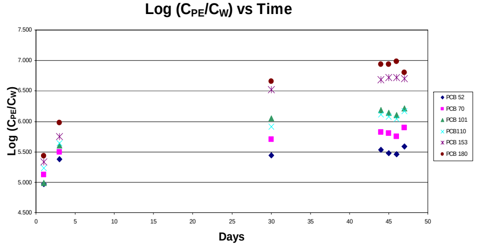
$$C_{W\infty} = \frac{C_{PEt}}{\left(1 - e^{-k_e t}\right) \cdot K_{PEW}}$$

Partitioning Coefficient (K_{PEW})

K_{PEW} Experiment

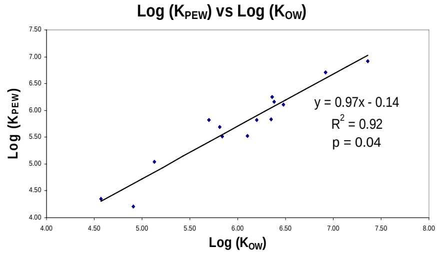
- PEDs were exposed to water spiked with 16 model HOCs.
- The concentration of each HOC was kept below 10% saturation.
- A PED (~0.6mg) was added to a round bottom flask with HOCs and continuously stirred.
- An RBF was stopped on day 1, 3, 10, 30, 44, 45, 46, and 47.
- PED and water extracts were analyzed by GC-MS.
- QA/QC included a control, a blank, and extraction efficiency (recovery surrogates).
- Round Bottom Flasks were housed in paper bags to prevent photo degradation.

Are we at equilibrium?



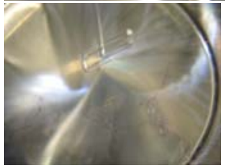
The simplest way to determine if you have equilibrium constants is to graph them versus time. The 6 PCBs studied (52, 70, 101, 110, 153, and 189) are shown. The log (C_{PE}/C_W) for days 44, 45, 46, and 47 are K_{PEW}s – the uptake curve has flattened out at this point, indicating that equilibrium has been achieved.

Correlating to K_{OW}



K_{PEW}s measured in the laboratory were averaged (days 44, 45, 46, 47) and were found to correlate with octanol-water partition constants. Using this graph, we can estimate a K_{PEW} for any HOC present in the field for which a K_{OW} is known.

Exchange Rate Kinetics (k_e)



Ongoing Work: Exchange Rate (k_e) Experiment

- PEDs were preloaded
  - With reference compounds
  - 80/20 methanol/ water mixture
- PEDs were cut
  - ½ extracted
  - Other ½ placed in 90-L stock pot with water and HOCs
- Triplicate PEDs were removed on day 2, 7, 14, 30, and 45.
- PED and water extracts were analyzed by GC-MS
- QA/QC included blanks, triplicates, and recovery surrogates

Why Use Large Volume Stock Pot?

- Large volume mimics infinite bath – allowing for minimal HOC uptake into PED (<10%)
- Uptake < 10% for 12/16 HOCs – allows field times to equilibrium to be determined for these 12
- Calculate k_e for preloaded reference compounds
- Use k_e to predict HOC concentrations in water (stock pot)
- Use known HOC concentrations in water to validate k_e predictions

Future Work

Complete k_e experiment – current results are pending

Deploy PEDs and SPMEs in Ballona Creek (Summer 2007)

- Measure dissolved HOC concentrations
- Compare PED and SPME in the field
- Estimate dry weather dissolved phase loadings (to assess TMDL waste load allocations)

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