A two-component mass balance model for calibration of solid-phase microextraction fibers for pyrethroids in seawater

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Abstract

Determination of the analyte-specific distribution coefficient between the aqueous and sorbing phases is required for estimation of the aqueous-phase concentration of the analyte of interest using polymeric materials. Poly(dimethylsiloxane)-coated solid-phase microextration (PDMS-SPME) fiber-water partition coefficients (K_fs) for eight common-use pyrethroids were determined using a two-compartment mass balance model and parameters determined in experimental seawater microcosms. Mass balance, epimerization, and aqueous-phase degradation (i.e., hydrolysis) were characterized using gas chromatography-negative chemical ionization mass spectrometry to facilitate K_f estimation. Of the eight pyrethroids, only bifenthrin exhibited increasing sorption on the SPME fiber over the entire time-series exposure, indicating that its K_f value could be estimated through a stable-compound model. The remaining pyrethroids were found to be unstable (half-life <22 days), underscoring the importance of accounting for degradation in estimating K_f. The two-compartment model explained the experimental time-series data for bifenthrin (R^2 >0.98) and the remaining unstable pyrethroids (R^2 >0.7), leading to estimated values of log K_f between 5.7 to 6.4 after correcting for residual dissolved organic carbon (DOC) in the experimental seawater. These K_f values can be used to determine freely dissolved pyrethroid concentrations in the pg/L range using PDMS-SPME in fresh or seawater matrices under equilibrium conditions in laboratory or field applications.

Introduction

Passive samplers, such as semi-permeable membrane devices (SPMDs; Huckins *et al*. 1990), low density polyethylene (PE; Booij *et al*. 2002, Adams *et al*. 2007), polyoxymethylene (POM; Hawthorne *et al*. 2009), and solid-phase microextraction (SPME; Arthur and Pawliszyn 1990) fibers, have been used to pre-concentrate hydrophobic organic compounds (HOCs) at ultra-low concentrations for monitoring, assessment of bioavailability, fate and toxicity, and toxicity identification evaluation (TIE; Bayen *et al*. 2009, Rubio and Perez-Bendito 2009, Harwood *et al*. 2012). SPME-based samplers which combine sampling, isolation, and enrichment with the ability to directly inject the loaded polymer coated fiber into chromatographic instrumentation are among the more promising alternatives to conventional, off-line sampling, extraction, and analysis methodology (Zeng *et al*. 2004, Ouyang and Pawliszyn 2007, Maruya *et al*. 2009). Fibers coated with polydimethylsiloxane (PDMS) have been employed to sample HOCs in sediment porewater *ex situ* (Hawthorne *et al*. 2005) and more recently *in situ* (Maruya *et al*. 2009, Lu *et al*. 2011) and assuming either non-equilibrium (kinetic) or equilibrium conditions. *A priori* knowledge of the fiber-water partition coefficient (K_f) is needed to estimate aqueous-phase HOC concentration (Zeng *et al*. 2004, Maruya *et al*. 2009). These compound specific values are typically determined in laboratory calibration experiments.

Synthetic pyrethroids are active ingredients in commercial and household pesticide formulations that are potentially toxic to non-target aquatic organisms (Weston *et al*. 2004). Among the most commonly used pyrethroids, bifenthrin and permethrin lack a cyano-group ("type I"), while those with a cyano-group on the α-carbon (e.g., cyfluthrin and cypermethrin) are known as "type II" (Supplemental Information (SI) Figure SI-1 available at ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2012AnnualReport/ar12_07SI.pdf). Due to the asymmetric carbon atoms on the pyrethroid structural skeleton, 1 to 2 pairs of isomers are possible, each of which may contain 2 to 4 pairs of enantiomers. Epimerization at the α-carbon position for type II pyrethroids has been previously observed in the aqueous phase (Leicht *et al*. 1996, Mastovska and Lehotay 2004, Liu *et al*. 2005, Qin and Gan 2007, You and Lydy 2007, Li *et al*. 2009). With a log K_{ow} range of 5 to 7, pyrethroids are readily sorbed by particulates and exhibit very low aqueous concentrations. In coastal environments, pyrethroids mobilized by runoff are eventually transported to estuaries and into oceanic waters of pH ~8 (Anderson *et al*. 2010, Lao *et al*. 2010). Evidence that some pyrethroids degrade rapidly under alkaline conditions (Laskowski 2002) suggests that they would be rapidly hydrolyzed in seawater, despite reports of persistence and toxicity in estuarine sediments (Holmes *et al*. 2008, Lao *et al*. 2010).

Previously, PDMS-SPME fibers were used to quantify pyrethroid concentrations in freshwater assuming they were stable in the aqueous phase (i.e., transformation during calibration was assumed to be negligible). Thus, currently available K_f values based on a one-compartment model do not account for loss processes such as hydrolysis (Hunter *et al*. 2009). In order to accurately determine the dissolved-aqueous or "bioavailable" concentrations of pyrethroids using SPME in situ, however, a calibration procedure that addresses aqueous stability in seawater (or porewater of estuarine/marine sediments) is needed for more accurate determination of K_f. Furthermore, epimerization of type II pyrethroids may present additional complications to consider for proper calibration.

The objective of this study was to determine PDMS-SPME K_f values for eight common-use pyrethroids (and isomers thereof) using a two-compartment mass balance model that accounts for transformation (i.e., distinguishes between "stable" and "unstable" pyrethroids) in seawater. Mass balance, degradation rate, epimerization, and time-dependent pyrethroid concentration profiles were characterized in spiked seawater time-series experiments to facilitate modeling. SPME sorbents and exposure conditions were selected to achieve the lowest possible detectability of dissolved phase pyrethroids. After correction for residual dissolved organic carbon (DOC) associated with seawater, the resulting calibration parameters (including K_fs) were subsequently employed to determine the freely dissolved concentrations of target pyrethroids in laboratory microcosms containing field-collected estuarine sediments.

Theory

For calibration, SPME fibers are exposed to water spiked with the compound of interest in a closed system (e.g., a covered glass flask) without chemical supplementation after commencement of the experiment. For a compound that has a sufficiently long aqueous phase half-life to maintain net uptake by the passive sampler, the concentration-time profile can be described by a two-compartment mass balance model in which uptake and elimination of the "stable" compound by the passive sampler is assumed to follow first-order kinetics (Vaes *et al*. 1996 a,b; Bayen *et al*. 2009):

$$\frac{dC_f}{dt} = k_1 C_w - k_2 C_f \qquad \text{Eq. 1}$$

$$C_w = \frac{n_w}{V_w} = \frac{n^0 - n_f}{V_w} = C_w^0 - \frac{C_f \times V_f}{V_w} \qquad \text{Eq. 2}$$

where C_f is the concentration (ng/L) on the SPME fiber; C_w and C_w^0 are the final and initial aqueous concentrations (ng/L), respectively; k_1 and k_2 are the uptake and elimination rate constants, respectively; V_f and V_w are the fiber coating and aqueous phase volumes, respectively; n_w and n_f are the masses of the compound in the aqueous phase and on the fiber, respectively; n^0 is the initial mass of the compound in the aqueous phase; and t is the time of SPME fiber exposure.

Assuming a clean fiber initially (C_f^0), solving for C_f gives

$$C_f = \frac{k_1 \times C_w^0}{B}(1 - e^{-Bt}) \qquad \text{Eq. 3}$$

with

$$B = k_2 + \frac{k_1 \times V_f}{V_w} \quad \text{Eq. 4}$$

The elimination-rate constant k_2 can then be calculated from Eq. 4, and the partition coefficient (K_f) is defined as

$$K_f = \frac{k_1}{k_2} \quad \text{Eq. 5}$$

For a compound whose aqueous phase half-life is too short to support net uptake by the passive sampler, a two-compartment mass balance model with simultaneous degradation in the aqueous phase represents the uptake and elimination of the "unstable" compound by the SPME fiber (Figure 1). This model is described by linear differential equations for the concentration in water and on the SPME fiber (Wagner 1976, Holz and Fahr 2001, Berezhkovskiy 2004):

$$\frac{dC_w}{dt} = -(k_1 + b)C_w + k_2 C_f \quad \text{Eq. 6}$$

$$\frac{dC_f}{dt} = k_1 C_w - k_2 C_f \quad \text{Eq. 7}$$

where b is the aqueous phase hydrolysis-rate constant; the aqueous phase and fiber concentrations (C_w and C_f) are then derived as follows

$$C_w = \frac{C_w^0}{\alpha - \beta}\left[(k_2 - \beta)e^{-\beta t} - (k_2 - \alpha)e^{-\alpha t}\right] \quad \text{Eq. 8}$$

$$C_f = \frac{k_1 C_w^0}{\alpha - \beta}\left[e^{-\beta t} - e^{-\alpha t}\right] \quad \text{Eq. 9}$$

where α and β are hybrid-rate constants for uptake by and elimination from the fiber,

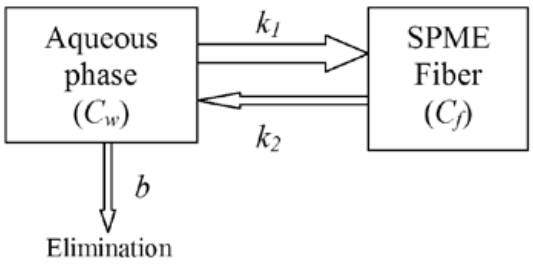

Figure 1. Two-compartment mass balance model for the uptake and elimination of target chemicals by a sorptive passive sampler (e.g., SPME fiber) with simultaneous loss in the aqueous phase.

respectively; both are functions of all system-rate constants (i.e., k_1, k_2 and b). Further, Eq. 9 can be fitted to experimental time-series data of C_f to obtain k_1, α, and β.

Assuming hydrolysis obeys first-order kinetics, the parameter b in Eq. 6 can be determined in an independent time-series experiment:

$$\ln\left(\frac{C_0}{C}\right) = bt \quad \text{Eq. 10}$$

and k_2 is calculated as follows:

$$k_2 = \frac{\alpha\beta}{b} \quad \text{Eq. 11}$$

and K_f is determined as before using Eq. 5. The parameters B, α, and β are independent of C_w^0 and C_f, whereas k_1, C_w^0 , and C_f are related by

$$\frac{k_1'}{k_1''} = \frac{C_w^{0''}}{C_w^{0'}} = \frac{C_f'}{C_f''} \quad \text{Eq. 12}$$

where ′ and ′′ denote two scenarios, e.g., for differing DOC concentrations. Thus, Eq. 12 can be used to correct for DOC in estimating K_f (see Supporting Information for details).

Under steady-state conditions, the aqueous concentration is assumed constant (i.e., $C_w \approx C_w^0 \approx C_w^\infty$; Mayer *et al*. 2000, Xie *et al*. 2009, Hawker 2010). Under non-depletive conditions, the aqueous concentration and passive-sampling profile can be represented as

$$C_w^0 = C_w^\infty = \frac{C_f}{K_f(1 - e^{-k_2 t})} \quad \text{Eq. 13}$$

and at apparent equilibrium

$$C_w = \frac{n_f}{K_f V_f} \quad \text{Eq. 14}$$

The models described above address both kinetic and equilibrium passive sampling regimes. For short-term ("kinetic phase") applications, the time series profile is linear and the governing relationship in Eq. 13 reduces to $C_w = C_f/(k_2 K_f t) = C_f/(k_1 t)$. In this scenario, k_1 and k_2 are useful parameters in addition to K_f. For long-term ("equilibrium") exposure, the magnitude of C_w is inversely proportional to V_f (Eq. 14) which in turn is proportional to the square of the

SPME fiber coating thickness, indicating that the "detectability" of this approach under equilibrium conditions is maximized by increasing the thickness of the sorptive coating.

Methods

Chemicals and Materials

Bifenthrin (98.8%), permethrin (97.0%), and cypermethrin (95.1%) were obtained from FMC (Princeton, PA, USA). Esfenvalerate (98%) was purchased from Chem Service (West Chester, PA, USA). Cyfluthrin (92%) and deltamethrin (99.4%) were obtained from Bayer CropScience (Stilwell, KS, USA). Lambda-cyhalothrin (98.7%) and fenpropathrin (99.7%) were supplied by Syngenta (Bracknell, Berks, UK) and Valent (Walnut Creek, CA, USA), respectively. Sodium azide was purchased from Mallinckrodt Baker (Phillipsburg, NJ, USA). All solvents were Optima grade purchased from Fisher Scientific (Fair Lawn, NJ, USA). New 100 μm (V_f = 0.612 μL) PDMS-coated SPME fibers purchased from Supelo (Bellefonte, PA, USA) were conditioned at 250°C for 0.5 hours, and kept in sealed glass vials in a freezer before use. Glass covered magnetic stirring bars (60 × 8 mm) were purchased from Big Science (Huntersville, NC, USA). Polytetrafluoroethylene (PTFE) sheets and aluminum foil were rinsed with deionized water, sonicated in methylene chloride, and dried at 100°C prior to use.

SPME Calibration Procedure

An aliquot of stock solution (20 mg/L) in hexane containing all eight target pyrethroids was transferred and exchanged to 2 ml acetone, and spiked into 100 ml seawater (sand filtered; DOC = 0.50 ±0.15 mg/L; salinity = 33.1%; conductivity = 50.0 μS; pH = 8.1) in a graduated cylinder. The spiked seawater was then diluted into two 20 L glass carboys containing 12 L seawater and sodium azide at 0.5 g/L. The final solution (24 L total; nominally 50 ng/L each pyrethroid) was homogenized using a glass rod and left to equilibrate for 1 hour.

Six 1.6-L glass Erlenmeyer flasks filled to the top with spiked seawater (at the final diluted concentration) and glass-covered stir bars were covered with PTFE sheet and aluminum foil and placed on magnetic stir plates. After 2 hours of stirring at 250 rpm, four SPME fibers were introduced through the PTFE/foil cover, and each fiber was extruded into the seawater. The contents of the exposure vessels were kept at room temperature (22 ±2°C) and shielded from ambient light with sheets of aluminum foil. Nine 1-L flasks containing spiked seawater and stir bars served as "no SPME" controls. At 1, 5, 12, 18, 28, and 60 d, a single flask was sacrificed and SPME fibers were removed, carefully wiped with a paper tissue to remove residual water, and stored at –20ºC in the dark until analysis. For 12, 18, and 28 days, duplicate control flasks were used. The pyrethroids remaining in seawater or sorbed to glassware were extracted with dichloromethane (DCM; 100 ml × 3 and 20 ml × 3, respectively). One liter of spiked seawater was extracted at day zero to obtain C_w^0. Prior to extraction, 25 ng of PCB 209 was spiked into each flask as a recovery surrogate. DCM extracts were solvent-exchanged into hexane, concentrated to 0.5 ml, and supplemented with PCB 205 as an internal standard. Seawater and empty flasks from the no-SPME control were also extracted to characterize the overall mass balance of spiked pyrethroids; aqueous phase concentrations were used to estimate hydrolysis-rate constants (*b*) and half-lives.

Pyrethroid Concentrations in Sediment Porewater

A time-series experiment was conducted for 120 days using two field-contaminated sediment samples with detectable pyrethroids collected in October 2008 from the Ballona Creek estuary, an urban waterway in Los Angeles County, CA (Lao *et al*. 2010). A 350 ml aliquot of sieved and homogenized sample in triplicate for each of the sediments was transferred into a 1 L borosilicate glass graduated cylinder wrapped in aluminum foil. Four SPME porewater samplers previously developed by the Southern California Coastal Water Research Project (Maruya *et al*. 2009) were placed into each sediment chamber, and then each chamber was capped with PTFE sheets, aluminum foil, and rubber bands to minimize water evaporation. The SPME fibers were collected at 14, 28, 60 and 120 d and kept at -20°C in dark until analysis. Dissolved organic carbon (DOC) was determined in an aliquot of sediment porewater that was isolated by centrifugation, filtered and acid-decarbonized using a Shimadzu TOC-VCSH Total Organic Carbon analyzers (Columbia, MD, USA).
Instrumental Analysis

An Agilent 7890 GC (Wilmington, DE, USA) with 5975C mass selective detector (MSD) and

a DB-XLB capillary column (30 m × 0.25 mm × 0.25 µm) was used to analyze target pyrethroids. Ultrahigh purity helium (>99.999%) was the carrier gas at a flow rate of 1.9 ml/minute. The GC oven was programmed as follows: 90°C (1-minute hold); ramp to 150°C at 5°C/minute; ramp to 260°C at 3°C/minute; ramp to 320°C at 20°C/minute (5-minute hold). The splitless injection volume was 1 µL at 280°C. The MSD was operated in the negative chemical ionization (NCI) mode with a 40% methane flow rate. The transfer line, ion source, and quadrupole were maintained at 320, 150, 150 °C, respectively. Target pyrethroids were detected in the selected ion monitoring (SIM) mode and quantified via a multi-point internal standard (PCB 205) calibration curve. SPME fibers were manually injected using the splitless mode for six minutes at the specified injector temperature, and desorbed masses of target compounds were calculated using a multi-point external standard curve. Isomers that could be resolved by the protocol were quantified individually as described previously (Lao *et al*. 2010).

Quality Assurance/Quality Control

A comprehensive, performance-based quality assurance/quality control approach that included analysis of procedural blanks, matrix spikes for all eight target pyrethroids, and surrogate recoveries for individual sample extracts was adopted. For the time-series calibration experiment, the mean standard deviation for concentration of all target pyrethroids was 28 ±4.8% (n = 4 fibers). No detectable pyrethroids were found in procedural blanks consisting of solvent, sodium sulfate, or seawater. The mean recoveries of target pyrethroids spiked in triplicate water blanks at 2.5 and 100 ng/L were 67 ±11% and 78 ±12%, respectively. The mean recovery of PCB 209 was 97 ±8% (n = 29) for SPME calibration samples including seawater and glassware extractions with and without fibers. Results were not corrected for surrogate recovery. The SPME detection limit for target pyrethroids ranged from 0.0001 to 0.017 ng/L (minimum S/N of 3). Regression and statistical analyses were performed using SigmaPlot and SigmaStat (SPSS Inc., Chicago, IL, USA), respectively.

Results and Discussion

Experimental System Mass Balance

The time-dependent mass distribution for bifenthrin and deltamethrin among the aqueous phase, experimental surfaces (glass flask, stir bar) and SPME fibers is shown in Figure 2, where loss is defined as the difference between the spiked amount (as 100%) and the sum of the measured components. Similar to bifenthrin and deltamethrin, all type II pyrethroids exhibited loss when dissolved in seawater of, in some cases, greater than 90%. This was in contrast to losses in the 40 to 60% range for bifenthrin (type I). On the SPME fiber, only bifenthrin exhibited a consistent increase in sorbed mass within the calibration time period. In contrast, the SPME-sorbed mass for all other pyrethroids (e.g., deltamethrin) increased initially for a few days before decreasing over the remaining exposure time. Near the end of the time series, some pyrethroids (e.g., cypermethrin, cyfluthrin and λ-cyhalothrin; data not shown) were almost completely depleted from the

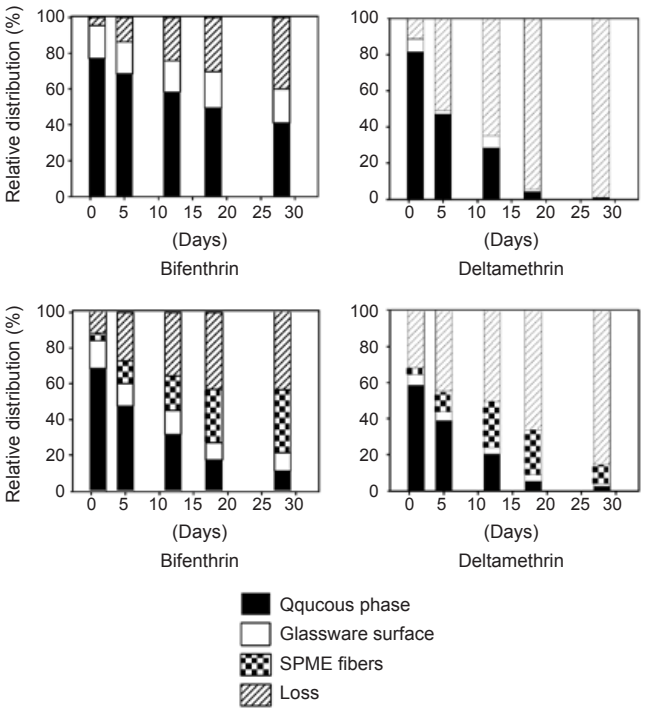

Figure 2. Percent total mass of bifenthrin and deltamethrin in the bulk aqueous phase, SPME fibers, and experimental (glassware) surfaces including stir bars in "no SPME" controls (top) and in calibration vessels containing SPME fibers (bottom). Loss is defined as the difference between spiked pyrethroid mass and the sum of the measured experimental components.

aqueous and fiber phases. These results demonstrated that bifenthrin was sufficiently stable in the aqueous phase to be modeled as using the stable compound model (Eqs. 1 and 2), while the other pyrethroids required the use of the unstable compound model (Eqs. 6 and 7).

Determination of Model Parameters

The initial aqueous phase concentration, C_w^0, applied in the models (e.g., Eq. 3 or Eq. 9) for each isomer was measured by liquid-liquid extraction (Table 1). The measurement of bifenthrin, fenpropathrin, and (*cis*- and *trans*-) permethrin was straightforward. However, estimation of C_w^0 for the type II pyrethroids (λ-cyhalothrin, esfenvalerate and deltamethrin) needed to account for epimerization at the α-carbon position because large amounts of non-spiked isomers (Table 1) were detected in the aqueous phase by SPME fiber (Leicht *et al*. 1996, Mastovska and Lehotay 2004, Liu *et al*. 2005, Qin and Gan 2007, You and Lydy 2007, Li *et al*. 2009). As indicated by isomer to parent concentration ratios, the epimerization quickly reached steady-state in seawater by the end of day one (Figure SI-2). The C_w^0 value for each individual isomer was then readily estimated using the average isomer-concentration ratio for days 1 through 18, i.e., λ-cyhalothrin (0.79 ±0.02), esfenvalerate (1.26 ±0.04), and deltamethrin (0.96 ±0.03). Epimerization was also expected for cyfluthrin and cypermethrin, but reversible interconversion between the co-spiked isomers caused no apparent change in their isomer ratios. Thus, the isomer-specific C_w^0 for cyfluthrin and cypermethrin was estimated using the day-0 spiking solution (Liu *et al*. 2005).

Table 1. Enantiomer configuration and initial aqueous phase concentration (C_w^0) of target pyrethroids and their isomers in seawater calibration experiments.

Pyrethroid	Enantiomer Configuration	C_W^0 (ng/L)
Bifenthrin	*Cis-(1R, 3R)* *Cis-(1S, 3S)*	41.8
Fenpropathrin	*R* and *S*	42.5
Cis-permethrin	*Cis-(1R, 3R)* *Cis-(1S, 3S)*	16.6
Trans-permethrin	*Trans-(1R, 3S)* *Trans-(1S, 3R)*	24.6
λ-Cyhalothrin isomer*	*Cis-(1S, 3S)-αS* *Cis-(1R, 3R)-αR*	18.7
λ-Cyhalothrin	*Cis-(1R, 3R)-αS* *Cis-(1S, 3S)-αR*	23.7
Esfenvalerate isomer*	*(2S, αR)* *(2R, αS)*	21.6
Esfenvalerate	*(2S, αS)* *(2R, αR)*	17.1
Deltamethrin isomer*	*Cis-(1R, 3R)-αR*	17.3
Deltamethrin	*Cis-(1R, 3R)-αS*	18
Cyfluthrin		39.0 [a]
Cypermethrin		40.0 [b]
Isomer I	*Cis-(1S, 3S)-αS* *Cis-(1R, 3R)-αR*	9.99 [a] 10.0 [b]
Isomer III	*Trans-(1S, 3R)-αS* *Trans-(1R, 3S)-αR*	9.33 [a] 9.19 [b]
Isomer II	*Cis-(1R, 3R)-αS* *Cis-(1S, 3S)-αR*	9.37 [a] 9.81 [b]
Isomer IV	*Trans-(1R, 3S)-αS* *Trans-(1S, 3R)-αR*	9.02 [a] 9.29 [b]

* non-spiked isomer
[a] Cyfluthrin
[b] Cypermethrin

In preliminary experiments, no epimerization was observed in acetone spiked with target pyrethroids or in instrument calibration solutions in hexane. Thus, epimerization in aprotic solvents such as acetone, DCM and hexane used in this study was not observed. The isomer to parent concentration ratios for λ-cyhalothrin, esfenvalerate and deltamethrin rapidly stabilized in seawater in both SPME and no-SPME control flasks by Day 1, in contrast to an apparent lag for the SPME fiber phase (Figure SI-2). This suggests epimerization in the seawater phase, obviating the need to consider decomposition on the coating phase in the two-component model.

Hydrolysis-rate constants (*b*) and the half-lives of pyrethroids (Table 2) and their isomers (Table SI-1) were estimated by measuring their aqueous phase concentration in no-SPME control flasks using Eq. 10. Bifenthrin was resistant to hydrolysis and had the longest half-life among the pyrethroids. *Trans*-permethrin hydrolyzed faster than the *cis*- isomer. The isomers of cyfluthrin and cypermethrin exhibited relatively short half-lives, with the *cis*-isomers degrading at a slightly slower rate than the *trans*-isomers. Previous studies have confirmed that pyrethroid hydrolysis becomes more rapid from neutral to alkaline aqueous media (Camilleri 1984; Takahashi *et al*. 1985a,b). Although some inconsistencies were observed the half-lives

Table 2. Hydrolysis-rate constants (b), correlation coefficients (R^2) in the estimation, and half-lives ($T_{0.5}$) of target pyrethroids in seawater.

	b (d^{-1})	R^2	$T_{0.5}$ (d)		
			pH 8.1[a]	pH 7[b]	pH 9[b]
Bifenthrin	0.02	0.988	35.0 ± 0.08	Stable	Stable
Cis-permethrin	0.029	0.981	24.3 ± 0.2	Stable	242
Trans-permethrin	0.082	0.988	8.50 ± 1.2	Stable	242
Cyfluthrin	0.156	0.958	4.44 ±1.7	183	1.84
Cypermethrin	0.142	0.964	4.87 ± 1.2	274	1.9
Deltamethrin	0.076	0.957	9.17 ± 0.1	Stable	2.15
Esfenvalerate	0.091	0.954	7.60 ± 0.2	Stable	Stable
Fenpropathrin	0.03	0.985	22.8 ± 1.1	555	14.4
λ-Cyhalothrin	0.168	0.957	4.13 ±0.8	Stable	8.66

[a] The present study

[b] Data from (Laskowski 2002)

measured at a typical seawater pH of 8.1 in this study generally lie within the values given by Laskowski (2002), which lends credence to the hypothesis that these pyrethroids are unstable under slightly alkaline conditions due to hydrolysis (Camilleri 1984). Other loss processes (e.g., sorption to glassware) were accounted for in mass balance determinations (Figure 2).

Estimation of K_f

SPME fiber concentrations of bifenthrin (C_f) versus time (t) fitted well ($R^2 = 0.99$) to the two compartment model (Eq. 3) for stable compounds using (Figure 3). After determination of k_2 (Eq. 4), the K_f value was calculated from Eq. 5 (Table SI-2). For a v_w of 1.6 L, the value of B (0.059) was almost two times larger than k_2 (0.034). If k_2 was directly estimated using Eq. 3, the resultant K_f value was 57% of that estimated using the two-compartment model, underscoring the importance of accurately determining k_2 (Vaes *et al*. 1996b, Xie *et al*. 2009).

For "unstable" pyrethroids, the variable concentrations in the aqueous and SPME phases were modeled using Eqs. 6 and 7. By fitting C_f versus t with known C_w^0 (Eq. 9), k_1, α, and β were obtained. Theoretically, α and β could be resolved by fitting C_w versus t (Eq. 8); however, the uncertainty in these estimates increases as the uncertainty in measured C_w increases, and the concentrations near the end of the time series became too low for reliable detection. The k_2 values were calculated using Eq. 11 because b values had been determined in the parallel control experiment; K_f values were subsequently calculated using Eq. 5 (Table SI-2). The correlation coefficient (R^2) for six of the eight targeted pyrethroids exceeded 0.85, indicating a good fit to the proposed model (Table 3), e.g., as shown for *cis*-permethrin and cyfluthrin (Figure 3). Isomer-specific K_f values were also estimated (Table SI-2), which have value for measurement of isomer-enriched formulations (e.g., beta-cypermethrin). In addition, isomer-specific

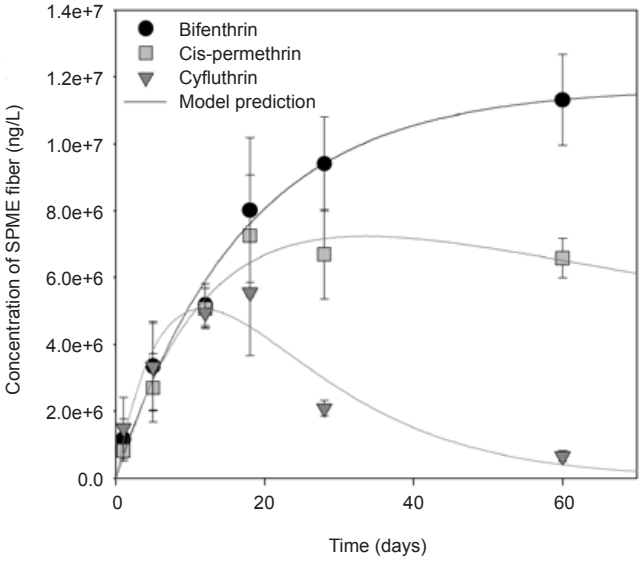

Figure 3. Experimental uptake kinetics for bifenthrin, *cis*-permethrin and cyfluthrin by SPME fibers coated with 100 µm polydimethylsiloxane (PDMS). Error bars represent one standard deviation (n = 4). Solid lines represent net uptake by SPME fibers as predicted by a two-compartment mass balance model.

Table 3. Fiber water partition coefficients (logK_f) for the study pyrethroids after correction for dissolved organic carbon (DOC), with corresponding model fit and analyte-specific parameters from the two-compartment mass balance model.

	log K_{ow}	R^2	k_1 (1/d)	k_2 (1/d)	logK_f	Δ logK_f
Bifenthrin	6.40[a]	0.9855	20413	0.028	5.87±0.10	0.18
Cis-permethrin	6.5[b]	0.9687	64930	0.024	6.43±0.10	0.12
Trans-permethrin		0.9371	61031	0.029	6.33±0.10	0.11
Cyfluthrin	5.97[a]	0.876	40041	0.048	5.93±0.12	0.12
Cypermethrin	6.54[a]	0.8523	42192	0.044	5.99±0.12	0.1
Deltamethrin	6.1[c]	0.7965	51983	0.068	5.89±0.13	0.19
Esfenvalerate	6.24[d]	0.7434	74938	0.035	6.33±0.13	0.18
Fenpropathrin	6.00[a]	0.9634	57121	0.105	5.73±0.10	0.1
λ-Cyhalothrin	7.00[a]	0.7328	32574	0.025	6.12±0.11	0.14

[a] Data from (Laskowski 2002)

[b] from (Schimme et al. 1983)

[c] from (ATSDR 2003)

[d] from (European-Commission 2000)

K_fs are important for determining isomer to parent concentration ratios, which can aid in determining the relative occurrence and fate of such isomers in the environment (House *et al*. 2000; Allan *et al*. 2005). Half-lives of the uptake phase ($T_{0.5\alpha}$) and elimination phase ($T_{0.5\beta}$), as well as the time to reach maximum concentration (T_{max}) on the fiber, were also calculated (Table SI-3).

The K_f estimates were corrected for sorption of pyrethroids by DOC, reducing the freely dissolved concentration (C_w^{fo}) even though DOC concentration was low in the experimental seawater (~0.5 mg/L). Two correction methods were performed with details provided in Supporting Information. The first approach reduced C_w^0 its value to to the freely dissolved concentration (C_w^{fo}) in the model regression when values of K_{DOC} were available. The second method (no K_{DOC} value available) adjusted K_f by DOC mass. The near unity K_f ratio (1.06 ±0.17) between the first and second correction demonstrated that they produced essentially identical results (P = 0.83), suggesting that the simpler (second) approach is viable (Table SI-4). The average corrected k_1 values for both approaches increased 35 ±11% for all pyrethroids. With the exception of bifenthrin, the k_2 values did not change because α and β did not vary with C_w^0 and C_f (Table 3); for bifenthrin, k_2 declined 19% after correction. The final K_f values represent the average of the two corrections, increasing by 38 ±11% (or 0.14 ±0.03 logarithmic units) on average over the non DOC-corrected values.

The k_2 and octanol-water partition coefficient (log K_{ow}) listed in Table 3 showed an inverse linear relationship (log k_2 = -0.490 log K_{ow} + 1.719, R^2 = 0.539). Although not statistically significant, the general trend between log K_f and log K_{ow} was increasing (log K_f = 0.341 log K_{ow} + 3.897, R^2 = 0.205), whereas log k_1 vs. log K_{ow} did not show a clear trend (log k_1 = -0.151 log K_{ow} + 5.630, R^2 = 0.079). This indicates that the mass transfer for pyrethroids was limited by diffusion across the aqueous boundary layer between the PDMS coating and the bulk aqueous phase (Vaes *et al*. 1996a, Bayen *et al*. 2009).

For *in situ* applications, the hydrodynamic conditions encountered can be expected to be both different and variable than those created in the SPME calibration time series and field collected sediment exposure experiments described in this study. The incorporation of performance reference compounds (PRCs) into passive sorptive materials (e.g., SPME fibers in this case) allows for evaluation and correction for incomplete attainment of equilibrium, however, it is unrealistic to use PRCs for every target compound (Booij *et al*. 2002). Alternatively, the *in situ* k_2 value (k_2^{fB}) could be estimated for a target analyte using the exposure adjustment factor (EAF) method (Huckins *et al*. 2002, Ouyang *et al*. 2009) as follows:

$$k_2^{fB} = \frac{k_2^{lB} \times k_2^{fA}}{k_2^{lA}} \qquad \text{Eq. 15}$$

where k_2^{lA}, and k_2^{lB} are k_2 values of compounds (A and B) measured in a laboratory calibration; k_2^{fA} is the k_2 of compound A determined from *in situ* exposure. Therefore, one of the advantages of using the calibration models is to provide useful k_2 values.

To maintain constant aqueous phase concentrations of target HOCs during calibration, dynamic and flow-through systems have been used to compensate for analyte loss in experimental vessels. (Poerschmann *et al*. 2000, Shurmer and Pawliszyn 2000) For compounds that undergo transformation in the aqueous phase, such as the Type II (unstable) pyrethroids in this study, such compensation for long term exposures would be difficult to calibrate accurately, particularly for multiple compounds with different transformation rates. Alternatively, a short duration calibration experiment that enhances aqueous mass transfer via, e.g., fast stirring, has proven effective for water-stable chemicals (Ramos *et al*. 1998). This approach, however, is not amenable to incorporating hydrolysis, resulting in K_f values that may be underestimated (see also below). The two-component calibration model for unstable chemicals presented in this study can be applied for any sorptive coating thickness over a range of calibration times. Moreover, the slow stirring approach utilized herein avoids excessive evaporative loss, which is difficult to measure directly.

Estimated freshwater K_f values (Table SI-4) using the Setschenow equation (Ni and Yalkowsky 2003, Difilippo and Eganhouse 2010) were lower (0.18 ±0.01 logarithmic units) than in seawater (Dewulf *et al*. 1997). The freshwater K_f values reported in the present study were greater by as much as one log unit than previously reported estimates for permethrin, cyfluthrin, and esfenvalerate. Early measurements of log K_f values for pyrethroids with 7 and 30 µm PDMS fibers ranged between 3 and 4 (Bondarenko *et al*. 2007). You *et al*. reported a log K_f for permethrin of 5.59 ±0.04 using 10µm disposable PDMS fibers exposed for 21 d (You *et al*. 2007). Hunter *et al*. exposed 30 µm disposable PDMS fibers in 100 ml spiked water to measure K_f values of 5.46 ±0.3 (*cis*-permethrin), 5.37 ±0.3 (*trans*-permethrin), and 5.8±0.03 (esfenvalerate), calculated at 27, 18, and 10 d, respectively (Hunter *et al*. 2009). In the latter study, the K_f values reported for cyfluthrin and fenpropathrin at 5 and 7 d, respectively, were comparable (< 0.1 log units) with those estimated in the present study, whereas K_f values for bifenthrin and cypermethrin were greater (>0.25 log units). The inconsistencies between the present and the reported estimates somewhat could be attributed to neglect for correction of effects for pyrethroid unstable property and small water volume used in the calibration. Additionally, the higher estimated values of K_f for many pyrethroids (e.g., permethrin) in the present study suggests the potential to measure proportionally lower dissolved phase concentrations.

Sediment Porewater Measurements

Freely dissolved porewater concentrations of bifenthrin and deltamethrin in the two field collected Ballona estuary sediments estimated using Eq. 14 were found to be relatively stable from Day 14 through the end of the 120-day exposure (Table SI-5; Lao *et al*. 2010). The mean freely dissolved bifenthrin concentrations for sediments BCE1 and BCE 5 were 0.011 ±0.006 and 0.008 ±0.006 ng/L, respectively. For deltamethrin, the corresponding concentrations were 0.005 ±0.001 and 0.007 ±0.003 ng/L. Bifenthrin at concentrations of 6.20 ±2.89 and 6.26 ±1.45 ng/L for BCE1 and BCE 5, respectively, was the only detectable target pyrethroid in these porewater samples after liquid-liquid extraction. It follows that freely dissolved bifenthrin as measured by SPME was only a minor fraction of the total aqueous phase concentration as measured by liquid-liquid extraction. As reported previously (You *et al*. 2007, Hunter *et al*. 2009), association of bifenthrin with porewater DOC, measured at 17.0 ±2.2 (BCE1) and 31.1 ±1.2 (BCE5) mg/L, can account for the difference between the operationally defined and measured dissolved and total concentrations.

Previously, pyrethroids have been reported to be persistent in sediments, with half-lives >60 days (Lee *et al*. 2004, Gan *et al*. 2005, Qin *et al*. 2006). However, degradation in the aqueous phase as demonstrated herein may cause certain pyrethroids to be released from the sediment, creating a steady-state interphase transfer between sediment and the aqueous phase assuming sufficient mass of pyrethroid associated with the solid phase (Landrum 1989, Mayer *et al*. 2000, Booij *et al*. 2003, Xie *et al*. 2009). Consequently, aqueous phase pyrethroid concentrations could be envisioned as relatively stable during the time period required for passive sampling (i.e., days to weeks; Hawker 2010). Thus, passive samplers based on SPME that are pre-calibrated in the manner presented in this work

would be amenable for determining exceedingly low level (pg/L range) of time-averaged freely dissolved pyrethroid concentrations in both laboratory settings and *in situ* under relatively stable field conditions.

A two-compartment SPME calibration model was presented for pyrethroids that can be characterized as stable and unstable in seawater. This study utilized materials and conditions to maximize the detectability of these hydrophobic contaminants and underscores the importance of considering hydrolysis for effective ultra-trace measurement of unstable compounds in seawater matrices, including sediment porewater. The general principles described in this work can be readily applied for calibration of other compounds using passive samplers based on SPME, as well as other polymeric sorptive materials such as PE and POM.

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Supplemental Information

Supplemental Information is available at ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2012AnnualReport/ar12_07SI.pdf