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Development of film-based passive samplers for *in situ* monitoring of trace levels of pyrethroids in sediment☆

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ABSTRACT

Residues of pyrethroid insecticides tend to accumulate in bed sediments due to their strong hydrophobicity. Rather than the total or bulk sediment concentration, it is the freely dissolved concentration (C_{free}) that drives toxicity to benthic invertebrates. In this study we developed thin film-based samplers for *in situ* ambient monitoring of pyrethroids at trace levels in sediment. Out of five common polymer materials, polyethylene (PE) and silicone rubber (SR), were identified to offer superior enrichment for pyrethroids from sediment. To circumvent the slow equilibrium process, ^{13}C-permethrin and bifenthrin-d_5 were preloaded onto the films as performance reference compounds (PRCs). The PRC-preloaded film samplers were deployed at five sites in Southern California under field conditions for 7 d and retrieved for analysis. The sediment porewater C_{free} of eight pyrethroids derived from PRC-PE films ranged from 173 to 903 ng/L, accounting for 18.2–36.1% of the corresponding total porewater concentrations. The PRC-SR film samplers yielded C_{free} values closely mimicking those from the PRC-PE samplers, cross-validating the two sampling devices. Additionally, a significant positive association was found between the observed mortality from toxicity tests using *Hyalella azteca* and the C_{free} of bifenthrin ($r = 0.628$, $p = 0.02$). A significant linear correlation ($R^2 = 0.99$) between C_{free} derived from *in situ* monitoring and that of *ex situ* measurement under equilibrium conditions was also observed. Results from this study demonstrated that the film-based samplers may be used for *in situ* ambient monitoring to detect biologically relevant contamination of pyrethroids in bed sediments, which may contribute to improved risk assessment for this class of widely used insecticides.

1. Introduction

Pyrethroids, a class of synthetic insecticides, are widely used in pest management in agriculture, landscape maintenance, and urban settings as replacements for organochlorine and organophosphate products (Denholm et al., 2002). It has been estimated that pyrethroids account for over 35% of the global insecticide market share (Global Pyrethroid Insecticide Market, 2017). Occurrence of their residues in urban streams (Albaseer et al., 2011; Hintzen et al., 2009; Weston et al., 2009), surface water (Woudneh and Oros, 2006; Xue et al., 2017), and estuary sediments (Amweg et al., 2006; Li et al., 2017; Weston et al., 2004) has attracted attention on their potential toxicity in aquatic ecosystems. With exceptionally high hydrophobicity (log K_{ow} 4.60–6.54), low water solubility (0.014–10.3 μg/L), and long hydrolysis half-life (>183 d at pH 7) (Table S1, Laskowski, 2002), pyrethroids tend to bind to suspended solid particles that subsequently deposit to the sediment bed, highlighting the need to consider their sediment toxicity.

Occurrence of pyrethroid residues in surface aquatic systems has stimulated considerable interest in their monitoring, particularly in regions such as the highly urbanized California (Amweg et al., 2006; Holmes et al., 2008; Li et al., 2017). Sediment contamination of pesticides and other chemicals is traditionally assessed by the so-called grab sampling approach, followed by exhaustive chemical extraction, before quantification (Booij et al., 2016; Kim et al., 2014). However, the resulting bulk sediment

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concentration (C_{total}) is often a poor indicator for potential biological effects because ample evidence suggested that it is the freely dissolved concentration (C_{free}) in the sediment porewater dictates the chemical activity that drives the actual toxicity of strongly hydrophobic chemicals (Di Toro et al., 1991; Lao et al., 2016; Maruya et al., 2015). Isolating porewater by centrifugation and analyzing the porewater after liquid-liquid extraction are the standard method for determining sediment porewater concentration (Bao and Zeng, 2011; Ter Laak et al., 2006). However, in addition to being time consuming and labor-intensive, even centrifugation at a very high-speed does not exclude dissolved organic matter (DOM) from the porewater. Sample collection, transportation, storage, and handling may also disturb the original equilibrium between sediment and porewater (Bao and Zeng, 2011).

Over the last two decades, solid-phase microextraction (SPME) has been developed to detect C_{free} directly in surface water and sediment for various compounds (Arthur and Pawliszyn, 1990; Chen and Pawliszyn, 2004), especially those which are highly hydrophobic. However, a SPME fiber is inherently small and does not provide sufficient sensitivity for *in situ* sampling under field conditions, which, along with its fragility, limits its practical application (Liu et al., 2013). Thin films, based on an equilibrium sampling principle similar to SPME, have found increasing use as passive samplers. These film sampling devices are inexpensive, durable, flexible, and thus particularly amendable for field deployment (Adams et al., 2007; Chang et al., 2014; Reitsma et al., 2013). Silicone rubber (SR) (Yates et al., 2011), low-density polyethylene (PE) (Tomaszewski and Luthy, 2008), and other polymer-based films have been tested in the detection of PAHs, PCBs, and DDT in sediment (Beckingham and Ghosh, 2013; Burgess et al., 2015). However, thin film samplers are under-developed for current-use pesticides, including pyrethroid insecticides.

In this study, we aimed to develop robust and ready-to-use samplers for all commercially important pyrethroid compounds for ambient sediment sampling. Different polymer based films were first evaluated to identify the film with the highest affinity for pyrethroids, and isotope-labeled standards were then introduced as performance reference compounds (PRCs) to allow the use of samplers under non-equilibrium conditions. The method performance for *in situ* use was demonstrated at multiple locations in Southern California, and validated against *ex situ* measurement. The thin-film passive samplers are capable of detecting pyrethroids at 1 ng/L (porewater), and may find wide use in regulatory and routine monitoring of pyrethroid residues in aquatic environments.

2. Materials and methods

2.1. Film selection for pyrethroids sorption

Low-density polyethylene (PE) film (25 μm thickness, Covalence, Minneapolis, MN), polymethylmethacrylate (PMMA) film (40 μm thickness, Polymer Source, Quebec, Canada), polyoxymethylene (POM) film (100 μm thickness, Specialty Silicone Products, New York, NY), polyurethane (PU) film (400 μm thicknesses, American Polyfilm, Branford, CT) and silicon rubber (SR) (500 μm thicknesses, GoodFellow, Coraopolis, PA) were obtained and used to compare their ability to absorb pyrethroids from sediment. The films were cut into pieces with applicable sizes, and cleaned by sonication in hexane (15 min, three times) before using. Bifenthrin, fenpropathrin, lambda-cyhalothrin, *cis*-permethrin, cyfluthrin, cypermethrin, esfenvalerate and deltamethrin, representing eight of the most used commercial pyrethroids, were included as the target analytes. Bifenthrin-d_5 (99%) and phenoxy-$^{13}C_6$-*cis*-permethrin (99%) were used as PRCs for calibrating all of the pyrethroids under non-equilibrium conditions. Sources and purities of these chemicals are provided in the Supplementary Information (SI).

The sediment was collected from Wood Creek in Orange County, CA, sieved through a 2-mm mesh and stored at 4 °C before use. The sediment was spiked with the 8 pyrethroid compounds at a concentration of 100 ng/g (dry weight, for each compound) in glass jars, and rotated on a roller for 24 h at 40 rpm for homogenization. The spiked sediment was then stored at 4 °C in the dark and rolled for 2 h once every week for the next 28 d to achieve phase equilibrium (Lao et al., 2016).

To evaluate the affinity of different films for the pyrethroids, one strip of each film (PE and PMMA, 20 × 5 mm; POM, PU and SR, 20 × 2 mm) was placed in 40 mL glass jars with 10 g of the spiked sediment and 5 mL sodium azide (200 mg/L) solution to inhibit microbial degradation during the exposure period. The sediment samples were then mixed at 120 rpm on a horizontal shaker for 48 h. Three replicates were used for each film type. At the end of the 48 h mixing, the films were retrieved, washed with deionized water and then air dried (Xue et al., 2017). Detailed procedures for the extraction of the film strips can be found in the SI.

2.2. Measurement of film-water partition coefficient (K_{fw})

The film-to-water partition coefficient K_{fw} is essential for deriving C_{free} from the analyte concentration on the film (Adams et al., 2007). The above experiments resulted in the identification of PE and SR films as the best two materials for absorbing pyrethroids in the sediment-water system. The K_{fw} values for the PE film (K_{PE}, or PE film-water partition coefficients) were determined in a previous study (Xue et al., 2017). A subsequent experiment was conducted to determine K_{fw} values for the SR film (K_{SR}, or SR film-water partition coefficients). Briefly, a SR film strip (20 × 2 mm) was placed in a 125-mL glass bottle with 100 mL water containing each pyrethroid at 100 μg/L, and then mixed at 120 rpm on a horizontal shaker. After 24, 72, 120, 168, 336, or 672 h of mixing, triplicate samples were removed for analysis. Both SR film (C_{SR}) and water (C_{water}) were analyzed for pyrethroids after solvent extraction. The K_{SR} was estimated by fitting all C_{SR} and C_{water} values to a first-order kinetic equation (Ai, 1997):

$$C_{SR}/C_{water} = K_{SR}\left(1 - e^{-k_{abs}t}\right) \quad (1)$$

where k_{abs} is the absorption rate constant.

2.3. Absorption kinetics of pyrethroids on PE and SR films

Both PE and SR films were exposed to the artificially contaminated sediment to determine the accumulation kinetics and the time to reach equilibrium under static and agitated conditions. Briefly, PE or SR film strips were placed in jars containing 50 g spiked sediment (dry weight) and 25 mL sodium azide solution (200 mg/L). For the static treatment, the sediment jars were kept at room temperature with a 16:8 h light/dark photoperiod. For the agitated treatment, the sample jars were mixed at 120 rpm on a horizontal shaker at room temperature with a 16:8 h light/dark photoperiod. After 24, 48, 96, 192, 288, 408, 552, and 720 h, triplicate film strips were removed, extracted and analyzed for pyrethroids. Additional details of the extraction steps are given in SI.

2.4. Isotropy validation experiment

The PRC calibration approach allows the use of passive samplers without requiring that equilibrium must be attained, thus greatly shortening the time needed for sampler deployment, particularly

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