Development of passive samplers for *in situ* measurement of pyrethroid insecticides in surface water ☆

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ABSTRACT

Pyrethroid insecticides are widely used in urban environments, and their occurrence has been recently associated with aquatic toxicity in urban surface streams. Synthetic pyrethroids are strongly hydrophobic compounds, highlighting the importance of the freely dissolved concentration (C_{free}), rather than the total chemical concentration, for better prediction of potential effects in aquatic ecosystems. The goal of this study was to develop a simple, robust and field-applicable passive sampling methodology that may be used for *in situ* monitoring of trace levels of pyrethroids in surface water. Among a range of polymer films, polyethylene film (PE) was found to be the most efficient at absorbing pyrethroids from water. To circumvent the long equilibrium time, ^{13}C-permethrin and bifenthrin-d_5 were preloaded on the PE sampler as performance reference compounds (PRC). Desorption of isotope-labeled PRCs was found to be isotropic to the absorption of target analytes. The optimized method was first tested in large circulating tanks simulating various environmental conditions. The derived C_{free} values were consistently smaller than the total aqueous concentration in salt water or water containing humic acids. The PE samplers were further deployed at multiple field sites for 7 d in Southern California and analysis demonstrated good monitoring reproducibility and sensitivity under ambient environmental conditions. The developed passive sampler approach is ideal for application for *in situ* sampling under field conditions, and the use of PRCs allows sampling with short and flexible time intervals.

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1. Introduction

Pyrethroids are widely used in urban settings for structural pest control around homes, leading to their appearance in urban surface waterways in many regions of the world (Hladik and Kuivila, 2009; Chang et al., 2010; Feo et al., 2010; Bereswill et al., 2013; Gilbreath and McKee, 2015). A number of studies showed that pyrethroids occurred in urban streams, often at total concentrations potentially acute toxic to native invertebrates (Amweg et al., 2005; Hintzen et al., 2009; Weston and Lydy, 2010; Weston et al., 2011; Delgado-Moreno et al., 2011). Such findings have greatly prompted efforts for surface water monitoring of pyrethroids, especially in regions such as California (Woudneh and Oros, 2006; Weston and Lydy, 2010; Ensminger et al., 2013). However, even though contamination of surface water with man-made chemicals is a universal concern, their monitoring remains a technical challenge (Namieśnik et al., 2005). In most cases, grab samples are withdrawn from surface water. However, grab samples represent only discrete individual points in time and space (Kim et al., 2014). Transportation and storage of large-volume liquid samples add uncertainties to the measurement (Lee et al., 2002). For chemicals such as pyrethroids, surface water monitoring is further complicated by the fact that they are strongly hydrophobic and are readily sorbed to suspended solids and dissolved organic matter (DOM), while it is the freely dissolved concentration (C_{free}) that drives the aquatic toxicity (Muir et al., 1994; Heringa et al., 2004; Semple et al., 2004; Budd et al., 2007; Palmquist et al., 2011; Jiang et al., 2012; Cui et al., 2013; Greenberg et al., 2014; Delgado-Moreno et al., 2015; Maruya et al., 2015). Therefore, a highly desirable method should

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selectively monitor C_{free} of pyrethroids in surface water in a time or space integrated manner, and could easily be deployed *in situ*.

In previous studies, solid-phase microextraction (SPME) has been explored for measuring C_{free} of pyrethroids in surface water (Barrionuevo and Lancas, 2002; Casas et al., 2006; Li et al., 2009; Feo et al., 2010; Harwood et al., 2012). Results consistently showed that presence of suspended solids or DOM, even at low levels, greatly decreased C_{free} and inhibited bioavailability or toxicity to aquatic invertebrates (Muir et al., 1994; Yang et al., 2006, 2007; Palmquist et al., 2011). While ideal in laboratory bench applications, SPME fiber is inherently small and fragile, limiting its potential for robust field applications. Operating on similar principles, thin polymeric films have increased sensitivity compared with SPME, due to their larger polymer volumes and contact areas. Thin film samplers have been developed and used on a range of hydrophobic contaminants, including PAHs, PCBs, and PBDEs (Adams et al., 2007; Hawthorne et al., 2009; Qin et al., 2010; Reitsma et al., 2013; Allan et al., 2013; Bao et al., 2013; Beckingham and Ghosh, 2013; Chang et al., 2014; Burgess et al., 2015). However, so far few studies have considered their application potential for pesticides such as pyrethroids.

The goal of this study was to develop a robust and sensitive film passive sampler that may be used for *in situ* monitoring of pyrethroids in surface water at trace levels. Different polymer-based films were first screened to select the optimum sorbent for enriching pyrethroids from water. Accumulation kinetics and film-water partition coefficients were subsequently derived for 8 commercially important pyrethroid compounds. To circumvent the long time needed for attaining equilibrium, stable isotope labeled analogues were used as performance reference compounds (PRCs) for calibration. The optimized sampler was further tested under both laboratory simulated and ambient field conditions.

2. Materials and methods

2.1. Chemicals and materials

Eight pyrethroids (fenpropathrin, lambda-cyhalothrin, bifenthrin, permethrin, cyfluthrin, cypermethrin, esfenvalerate, and deltamethrin), representing most of the commercially important pyrethroid products, were used as target analytes in the method development and validation experiments. All pyrethroids had a purity of $\geq 97.0\%$ and were obtained from FMC (Princeton, PA), Bayer CropScience (Kansas City, KS), Syngenta (Greensboro, NC) and Valent (Mahomet, IL). Two isotope labeled pyrethroids, bifenthrin-d_5 (99%) and phenoxy-$^{13}C_6$-*cis*-permethrin (99%), were purchased from Toronto Research Chemicals (North York, Ontario, Canada), and Cambridge Isotope Laboratories (Andover, MA), respectively. All solvents and other chemicals used in the study were gas chromatography (GC) or analytical grade.

For this study, four different polymer-based films were tested: low-density polyethylene (PE) film (25 μm thickness, BBB Accredited Business, Cleveland, OH), polyurethane (PU) film (400 μm thickness, American Polyfilm, Branford, CT), polyoxymethylene (POM) film (100 μm thickness, Specialty Silicone Products, New York, NY), and polymethylmethacrylate (PMMA) film (40 μm thickness, Polymer Source, Quebec, Canada). The four thin films were cut into small pieces of pre-determined areas before use. The film samples were all cleaned by sonication in hexane for 1 h prior to use.

2.2. Film selection for pyrethroid sampling

The different types of films were compared for their ability to absorb pyrethroids from water under the same conditions and to select the film displaying the maximal analyte enrichment. A stock solution containing all 8 pyrethroids was made in acetone at 100 mg/L for each compound. A working solution of 100 μg/L for each compound was prepared by adding 1.0 mL of the stock solution to 1000 mL deionized water. One strip of each film was placed in 25 mL of the working solution in a 40-mL glass vial, and the vials were shaken at 120 rpm for 48 h on a horizontal shaker. Three replicates were used for each film type. At the end of 48 h mixing, both water (25 mL) and film were analyzed for pyrethroid concentrations after solvent extraction using the methods described below.

2.3. Absorption kinetics of pyrethroids on PE film

The above experiment identified polyethylene (PE) as the best film type for absorbing pyrethroids, and subsequent method development experiments were carried out using PE film as the sorbent material in the passive sampler. Absorption kinetics of pyrethroids on the PE film was measured in DI water to determine the time required for reaching equilibrium between the film and water, and to obtain the film-water partition coefficient ($K_{\text{film-water}}$). Briefly, a PE film strip (5×20 mm) was placed in a 40-mL glass vial with 25 mL water containing 100 μg/L of each pyrethroid, and then mixed at 120 rpm on a horizontal shaker. After 0, 1, 3, 5, 8, 16, 24, 48, 96, 144, 192, 240, 288, 384, 432, 576 or 720 h of mixing, triplicate samples were removed for analysis. Both PE film and water were analyzed after solvent extraction.

The film-water partition coefficient $K_{\text{film-water}}$, the ratio of a pyrethroid on the film over that in water ($C_{\text{film}}/C_{\text{water}}$) at equilibrium, was estimated by fitting $C_{\text{film}}/C_{\text{water}}$ values at different time intervals to a first-order kinetics equation:

$$C_{\text{film}} \Big/ C_{\text{water}} = K_{\text{film-water}} \left(1 - e^{-k_{abs}^t} \right) \qquad (1)$$

where k_{abs} is the absorption rate constant. At equilibrium, C_{free} in the water could be derived from C_{film} through the use of $K_{\text{film-water}}$:

$$C_{\text{free}} = \frac{C_{\text{film}}}{K_{\text{film-water}}} \qquad (2)$$

2.4. Isotropy validation experiments

To circumvent the long time needed for achieving partition equilibrium between the PE film and water for pyrethroids, performance reference compounds (PRCs) were incorporated for calibration. The use of PRCs for calibration operates on the assumption of symmetry or isotropy between desorption of PRCs from the sampler and absorption of target analytes onto the sampler. A subsequent experiment was thus carried out to validate the isotropy. Stable isotope-labeled bifenthrin and *cis*-permethrin were used as PRCs in this study. To preload bifenthrin-d_5 and phenoxy-$^{13}C_6$-*cis*-permethrin onto the PE film, multiple PE film strips (5×20 mm) were placed in 300 mL water/acetone (8:2, v/v) solution containing 10 μg/L of each labeled compound, and the solution was mixed on a shaker at 120 rpm. After 48 h, the PRC-loaded PE films were collected and a subset was used for analysis of PRCs on the film to obtain the preloaded PRC amount (q_0) and determine the consistency of PRC loading.

When in contact with water, desorption of a PRC from the PE film may be described as (Chen and Pawliszyn, 2004):

$$q = q_0 e^{-k_{des}^t} \qquad (3)$$

where q_0 is the preloaded amount, q is the amount of the PRC