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Development of polyurethane-based passive samplers for ambient monitoring of urban-use insecticides in water☆

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ABSTRACT

Widespread use of insecticides for the control of urban pests such as ants, termites, and spiders has resulted in contamination and toxicity in urban aquatic ecosystems in different regions of the world. Passive samplers are a convenient and integrative tool for *in situ* monitoring of trace contaminants in surface water. However, the performance of a passive sampler depends closely on its affinity for the target analytes, making passive samplers highly specific to the types of contaminants being monitored. The goal of this study was to develop a passive sampler compatible with a wide range of insecticides, including the strongly hydrophobic pyrethroids and the weakly hydrophobic fipronil and organophosphates. Of six candidate polymeric thin films, polyurethane film (PU) was identified to be the best at enriching the test compounds. The inclusion of stable isotope labeled analogs as performance reference compounds (PRCs) further allowed the use of PU film for pyrethroids under non-equilibrium conditions. The PU sampler was tested in a large aquarium with circulatory water flow, and also deployed at multiple sites in surface streams in southern California. The concentrations of pesticides derived from the PU sampler ranged from 0.5 to 18.5 ng/L, which were generally lower than the total chemical concentration measured by grab samples, suggesting that suspended particles and dissolved organic matter in water rendered them less available. The influence of suspended particles and dissolved organic matter on bioavailability was more pronounced for pyrethroids than for fipronils. The results show that the developed PU film sampler, when coupled with PRCs, may be used for rapid and sensitive *in-situ* monitoring of a wide range of insecticides in surface water.

1. Introduction

Pesticides are an extremely diverse group of man-made chemicals. Many studies show that pesticide use in agriculture contributes to non-point source pollution to surface water via runoff and ground water contamination through leaching (Aravinna et al., 2017; Houbraken et al., 2017; Reichenberger et al., 2007). In recent years, an increasing number of studies also suggest that pesticide use, especially the use of insecticides for structural pest control around homes, results in contamination of surface aquatic systems in urban regions (Gan et al., 2012; Jorgenson et al., 2013; Maruya et al., 2016). Monitoring of urban-use insecticides in ambient water represents an ongoing challenge because of the distinct physicochemical properties of these compounds. In the past, most monitoring programs relied on collecting discrete grab water samples at a given time point, which provides data specific only to the location or time point being sampled and may not at all reflect the actual state of contamination (Fedorova et al., 2013; Kaserzon et al., 2012). Consequently, alternative sampling methods, including passive samplers, have been developed for integrative sampling (Assoumani et al., 2013; DiFilippo and Eganhouse, 2010). Among passive samplers, thin film-based samplers are considered to be more suitable for field applications than, e.g., thin fibers, due to their durability, flexibility, and relatively large sorbent volumes (Adams et al., 2007; Allan et al., 2013; Qin et al., 2010; Reitsma et al., 2013).

Passive samplers generally employ a sorbent material allowing the partition of target analytes from water to the sorbent phase (Cui et al., 2013b). At equilibrium, the concentration in water (C_{water}) is

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derived from the concentration in passive sampler ($C_{sampler}$) through the use of a polymer-water partition coefficient ($K_{sampler-water}$). Therefore, the sensitivity of a passive sampler depends closely on its ability to enrich the target analytes from water, largely limiting a given passive sampler's usefulness to analytes of similar properties (e.g., hydrophobicity or K_{ow}). For instance, polyethylene film (PE) or silicone rubber sheet is suited for strongly hydrophobic compounds such as PAHs, PCBs and DDT, while polyacrylate-coated film or polyvinyl film is more compatible with weakly hydrophobic compounds (Lao et al., 2016; Lohmann, 2012; Muir and Lohmann, 2013; Rusina et al., 2010). The need to match specific passive samplers with target analytes is a significant bottleneck to their more widespread implementation.

The overall aim of this study was to develop a passive sampler for simultaneous monitoring of a large number of urban-use insecticides in surface water. The target compounds include eight synthetic pyrethroids, two organophosphates, and fipronil and its three biologically active metabolites. Pyrethroids and fipronil are popular current-use insecticides in regions such as California, while organophosphate insecticides diazinon and chlorpyrifos were heavily used in the recent past (Maruya et al., 2016; Smalling et al., 2013; Weston and Lydy, 2012; Weston et al., 2015). The occurrence of these insecticides in surface water has been linked to acute and chronic aquatic toxicities, especially to invertebrates (Amweg et al., 2006; Bartlett et al., 2016; Brogan and Relyea, 2017; Maul et al., 2008; Ural and Sağlam, 2005; van Wijngaarden et al., 2009). These compounds also differ greatly in their physicochemical properties, with log K_{ow} ranging from 3.81 for diazinon to 7.00 for lambda-cyhalothrin (Brogan and Relyea, 2017; Laskowski, 2002). The developed sampler was shown to be capable of detecting trace levels of these insecticides in surface streams in southern California under ambient conditions.

2. Materials and methods

2.1. Chemicals

Eight pyrethroids (fenpropathrin, lambda-cyhalothrin, bifenthrin, permethrin, cyfluthrin, cypermethrin, esfenvalerate and deltamethrin), two organophosphates (diazinon and chlorpyrifos), and fipronil and its three biologically active metabolites (desulfinyl fipronil, fipronil sulfide and fipronil sulfone, referred as fipronils hereafter), were examined in this study (Table 1). Standards of diazinon (purity 99.3%), chlorpyrifos (99.5%), lambda-cyhalothrin (99.5%), bifenthrin (99%), cyfluthrin (>98%), and esfenvalerate (>98%), were purchased from Chem Service (West Chester, PA). Permethrin (97%) and cypermethrin (>98%) were obtained from FMC (Princeton, NJ), fenpropathrin (100%) from Valent (Walnut Creek, CA), and deltamethrin (99.6%) from Bayer Crop Science (Research Triangle Park, NC). Fipronil (98.9%), desulfinyl fipronil (97.8%), fipronil sulfide (98.8%) and fipronil sulfone (99.7%) were obtained from the U.S. Environmental Protection Agency's National Pesticide Standard Repository (Fort Meade, MD). Isotope labeled standards (*rac-cis*)-Z-bifenthrin-d_5 (99%) and phenoxy $^{13}C_6$-cis-permethrin (99%) were purchased from Toronto Research Chemicals (Toronto, Ontario, Canada) and Cambridge Isotope Laboratories (Andover, MA), respectively. Organic solvents, including dichloromethane, methanol, acetone and hexane, were of HPLC grade and purchased from Fisher Scientific (Pittsburgh, PA). All glassware and anhydrous sodium sulfate (10–60 mesh; Fisher Scientific) were baked at 400 °C for 4 h before use to prevent cross-contamination.

2.2. Selection of thin films

Through literature survey, six types of thin films were initially considered as candidate sorbents for passive samplers and their enrichment capacities for the selected insecticides were evaluated in water to determine the film best suited for all compounds. The films included polyethersulfone (25 μm in thickness, Goodfellow, Coraopolis, PA), polycarbonate (20 μm, Goodfellow), polyoxymethylene (76 μm, CS Hyde, Lake Villa, IL), polydimethylsiloxane (127 μm, Specialty Silicone Products, Ballston Spa, NY), polyurethane (381 μm, Acrotech, Lake City, MN), and polyvinyl chloride (50 μm, Goodfellow). The films were cut to strips of 2 × 2 cm and cleaned in water, methanol and then hexane, and air-dried. The film strips were subsequently placed in a 100 mL water containing each insecticide at 1 μg/L. After 24 h of mixing, the film strips were retrieved, dried with a tissue, cut to small pieces, and extracted with 20 mL of acetone/hexane (1:1, v:v) by shaking for 30 min. The extract was transferred to a 250-mL round bottom flask. The same extraction procedure was repeated for a total of three times and the

Table 1
Selected physicochemical properties and ions monitored for target chemicals.

Chemicals	Water solubility (μg/mL)	Log K_{ow}	MS/MS ions (m/z)	Retention time (min)
Diazinon	40[a]	3.81[b]	304 > 179	8.8
Desulfinyl fipronil	0.4	4.63	388 > 333	9.8
Chlorpyrifos	0.73	5.00	314 > 258	11.0
Fipronil sulfide	0.2	4.77	351 > 255	11.6
Fipronil	1.6	4.01	368 > 213	11.9
Fipronil sulfone	1.0	3.68	383 > 255	13.5
Fenpropathrin	1.03×10^{-2}	6.00	181 > 152	18.1
Lambda-cyhalothrin	5.0×10^{-3}	7.00	181 > 152	19.6
Bifenthrin	1.4×10^{-5}	6.40	181 > 166	17.7
d_5-Bifenthrin			186 > 171	17.7
Permethrin	5.50×10^{-3}	6.10	183 > 153	21.3
$^{13}C_6$-Permethrin			189 > 174	21.1
Cyfluthrin	2.3×10^{-3}	5.97	163 > 127	22.5
Cypermethrin	4.0×10^{-3}	6.54	163 > 127	22.7
PCB-209			499 > 428	23.4
Esfenvalerate	6.0×10^{-3}	5.62	167 > 125	24.9
Deltamethrin	2.0×10^{-4}	4.53	181 > 152	25.9

Noted: The data of water solubility and log K_{ow} for pyrethroids, fipronil and its three degradates, and chlorpyrifos were cited from (Laskowski, 2002) and (Walse et al., 2004), respectively.
[a] Data cited from (Sharom et al., 1980).
[b] Data cited from (Brogan and Relyea, 2017).