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

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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 fipronil. 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.

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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 integrating 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
derived from the concentration in passive sampler ($C_{\text{passive}}$) through the use of a polymer-water partition coefficient ($K_{\text{samplers-water}}$). 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 $K_{\text{ow}}$). 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 biochemically 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; Smalleg 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 (Anweg et al., 2006; Barrlett 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 $K_{\text{ow}}$ 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 (fenpropatrin, lambda-cyhalothrin, bifenthrin, permethrin, cyfluthrin, cypermethrin, esfenvalerate and deltamethrin), two organophosphates (diazinon and chlorpyrifos), and fipronil and its three biochemically active metabolites (desulfynyl 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), fenpropatrin (100%) from Valant (Valent Creek, CA), and deltamethrin (99.6%) from Bayer Crop Science (Research Triangle Park, NC). Fipronil (98.9%), desulfynyl fipronil (97.8%), fipronil sulfide (98.3%) 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-d5 (99%) and phenoxo-13C6-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), poloxymethylene (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

| Chemicals            | Water solubility (μg/mL) | Log $K_{\text{ow}}$ | MS/MS ions (m/z) | Retention time (min) |
|----------------------|--------------------------|---------------------|------------------|----------------------|
| Diazinon             | 40⁰                      | 3.81⁰               | 304 > 179        | 8.8                  |
| Desulfynyl 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                 |
| Fenpropatrin         | 1.03 × 10⁻²              | 6.00                | 181 > 152        | 18.1                 |
| Lambda-cyhalothrin   | 5.00 × 10⁻³              | 7.00                | 181 > 152        | 19.6                 |
| Bifenthrin           | 1.4 × 10⁻⁶              | 6.40                | 181 > 166        | 17.7                 |
| cis-Bifenthrin       | 1.0 × 10⁻⁶              | 6.10                | 183 > 153        | 21.3                 |
| 13C6-cis-Permethrin  | 5.50 × 10⁻³              | 5.97                | 189 > 174        | 21.1                 |
| Cyfluthrin           | 2.3 × 10⁻³              | 6.54                | 163 > 127        | 22.5                 |
| Cypermethrin         | 4.0 × 10⁻⁴              | 5.97                | 163 > 127        | 22.7                 |
| PCB-209              | 6.0 × 10⁻⁴              | 5.62                | 499 > 428        | 23.4                 |
| Esfenvalerate        | 2.0 × 10⁻⁴              | 4.53                | 181 > 152        | 25.9                 |

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

Noted: The data of water solubility and log $K_{\text{ow}}$ 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).
combined extract was evaporated to 1 mL under vacuum before instrumental analysis.

2.3. Measurement of sampler-water partition coefficients

The above film selection test resulted in the identification of polyurethane film (PU) as the best film for the various insecticides. Subsequent method development, optimization and application experiments were therefore carried out using the PU film. To determine \( K_{\text{sampler-water}} \), PU film was cut to pieces of 1.5 \( \times \) 20 mm, and cleaned by water, methanol and hexane. After air-drying, one piece of PU film was placed in a 1 L water containing each pesticide at 1 \( \mu \text{g}/\text{L} \) pesticides. The solution was continuously mixed using a magnetic stirring bar. To compensate for any potential loss of pesticide adsorption to glass surfaces, the solution was renewed every 3 or 4 d. Triplicate samples were periodically removed for analysis over a 43-d time period. The \( K_{\text{sampler-water}} \) was estimated by fitting all \( C_{\text{sampler}} \) and \( C_{\text{water}} \) values to a first-order kinetic equation (Ai, 1997):

\[
y = y_0 \left(1 - e^{-k_{\text{abs}}t}\right)
\]

where \( y \) and \( y_0 \) are \( C_{\text{sampler}}/C_{\text{water}} \) values at time \( t \) and at equilibrium, respectively, with \( y_0 \) equal to \( K_{\text{sampler-water}} \), and \( k_{\text{abs}} \) is the absorption rate constant.

2.4. Use of performance reference compounds (PRCs) for pyrethroids

Partition of pyrethroids into the PU film was found to be very slow, and an apparent equilibrium was not reached after 43 d of equilibration. Stable isotope labeled bifenthrin (d5-bifenthrin) and permethrin (13C6-permethrin) were used as performance reference compounds (PRCs) for calibration, so that a PU sampler may be used under non-equilibrium conditions. The PRC-preloaded PU strips (5 \( \times \) 20 mm) were suspended in 250 mL of each pesticide at 10 \( \mu \text{g}/\text{L} \) for each compound. After continuous mixing for 48 h, the PRC-impregnated PU strips were retrieved and rinsed with water. A subset of 3 preloaded strips was randomly selected to determine the initial amount of PRCs preloaded onto the film.

Calibration using PRCs works under the assumption that kinetics of absorption of target analytes from water onto the film is similar to desorption of PRCs from the film into water, that is, absorption of target analytes and desorption of PRCs obey isotropy. A batch equilibration experiment was carried out to validate the isotropic exchange between pyrethroid absorption onto the PU film and desorption of d5-bifenthrin and 13C6-permethrin from the film. Absorption of pyrethroids onto the PU film may be described as (Ai, 1997):

\[
n = n_0 \left(1 - e^{-k_{\text{abs}}t}\right)
\]

where \( n \) and \( n_0 \) are the amounts of pyrethroids absorbed onto the PU film at time \( t \) and at equilibrium, respectively, and \( k_{\text{abs}} \) is the absorption rate constant. Desorption of PRCs from the PU film may be described as (Chen and Pawliszyn, 2004; Zhou et al., 2007):

\[
q = q_0 e^{-k_{\text{des}}t}
\]

where \( q_0 \) and \( q \) are the initial amount of PRCs preloaded on the PU film and the amount remaining on the film at time \( t \), respectively, and \( k_{\text{des}} \) is the desorption rate constant. If isotropy holds, Eqs. (2) and (3) may be combined as:

\[
\frac{n}{n_0} + \frac{q}{q_0} = 1
\]

Therefore, if the sum of \( n/n_0 \) and \( q/q_0 \) is 1 at any sampling interval (under non-equilibrium condition), \( n_0 \) may be obtained using Eq. (4) after \( q \) and \( n \) are determined for the PU film, which can then be used to calculate \( C_{\text{sampler}} \) that is, \( C_{\text{sampler}} = n_0/M_{\text{sampler}} \).

The isotropy validation experiment was conducted as follows: one piece (1.5 mm \( \times \) 20 mm) of PRC-preloaded PU film was placed in a glass vial containing 25 mL of each pyrethroid at 10 \( \mu \text{g}/\text{L} \). The solution was mixed at 120 rpm on a horizontal shaker, and triplicate samples were removed after 1, 2.5, 4, 6, 8, 16, 24, 30, 48, 96, 144, 192, or 288 h for extraction and analysis of non-labeled and isotope labeled pyrethroids, as described above.

2.5. Laboratory simulation experiment

The sampler performance was tested by measuring \( C_{\text{free}} \) of pesticides in a large glass tank under simulated conditions. An acetone solution (2.5 mL) containing pesticides (100 \( \mu \text{g}/\text{mL} \)) was spiked into a 280 L glass aquarium containing 250 L of water to arrive at an initial nominal concentration of 1 \( \mu \text{g}/\text{L} \) for each pesticide. The PRC-preloaded PU strips (5 \( \times \) 50 mm) were suspended in the middle of the aquarium using a steel wire. A pump was used to circulate the water at a constant velocity. Three PU samplers were retrieved at 2, 4, or 8 d after the deployment and three water samples (0.5 L) were simultaneously collected at each sampling interval. The PU samplers were extracted and analyzed for the target pesticides as described above. The water samples were simultaneously extracted and analyzed to derive the total chemical concentration.

2.6. Field applications

The performance of PU samplers was further tested under field conditions. The PRC-preloaded PU strips (5 \( \times \) 50 mm) were secured with fishing hooks in parallel in a stainless steel mesh cage (Fig. S1; Supplementary Material), and the cages were deployed at multiple points (sites WC1, WC3, SC2, and SC3) in small surface streams.
draining urban neighborhoods in Orange County, California in May 2015 (Fig. S2). The PU samplers were retrieved after 4 d. Grab water samples (1 L) were simultaneously collected at the sample locations before the deployment and at the time the PU samplers were retrieved. The retrieved PU samplers and grab water samples were transported on ice to the laboratory and stored at 4 °C before analysis.

2.7. Instrumental analysis

The identification and quantification of pesticides were performed on a Varian 3800 GC coupled with a Varian 1200 triple quadrupole mass spectrometer (GC-MS/MS; Varian, Sunnyvale, CA). An aliquot of 1 or 2 µL of the final extract was injected at 240 °C in the pulsed splitless mode at 45 psi with the purge valve closed for 1.0 min. A DB-5MS capillary column (30 m × 0.25 mm × 0.25 µm, Agilent, Wilmington, DE) was used for separation and high purity helium (99.999%) was used as the carrier gas at a flow rate of 1.0 mL/min. The oven temperature was set at 80 °C for 1.0 min, increased to 160 °C at 25 °C/min, and then increased to 300 °C at 5 °C/min and held at 300 °C for 7 min. The MS/MS was operated in electron ionization (EI) mode at 70 eV with multiple reaction monitoring (MRM), and the MRM transitions of ions monitored are listed in Table 1. The transfer line, ionization source, and manifold temperatures were set at 300, 250, and 40 °C, respectively.

2.8. Quality assurance and quality control

All experiments were conducted in triplicates and the results were expressed as mean ± standard deviation. External surrogate (PCB-209) was introduced into all samples before extraction to check for carry-over of analytes between samples. To control for contamination arising from experimental procedures, a midpoint calibration curve was 0.99 or above. Difference between treatments was determined by one-way analysis of variance (ANOVA) using Origin 8.6 (OriginLab; Northampton, MA), unless stated otherwise.

3. Results and discussion

3.1. Evaluation of film types for broad analyte compatibility

Six types of thin films, i.e., polyethersulfone, polycarbonate, polyoxymethylene, polydimethylsiloxane, polyurethane (PU), and polyvinyl chloride, were chosen as candidates to test their enrichment potential for eight pyrethroids, two organophosphates, and four fipronils in water. All of the six thin films have been previously used on specific groups of organic compounds (DiFilippo and Eganhouse, 2010; Fedorova et al., 2013; Genuáldi et al., 2010; Gibbs et al., 2017; Kohoutek et al., 2010; Lissalde et al., 2014; Posada-Ureta et al., 2016; Shetty et al., 2014). The polyethersulfone and polycarbonate films were found to physically disintegrate after 1 d of mixing, so they were excluded from further testing. Additionally, no detectable amounts of pesticides were found on the polyvinyl chloride film likely due to the polar property of the film. As shown in Fig. 1, the polydimethylsiloxane film enriched pyrethroids, but not fipronils. The PU film showed high affinity for both pyrethroids and fipronils, and the enrichment was generally greater than the polyoxymethylene film. Therefore, the PU film was selected as the film type best suited for monitoring the suite of insecticides considered in this study.

3.2. Sampler-to-water partition coefficient (K_{sampling-water})

The coefficient $K_{sampling-water}$ is essential for deriving $C_{free}$ of analytes when using a passive sampler (Hunter et al., 2009; Mayer et al., 2000; Poerschmann et al., 1997). After identification of the best film, the uptake kinetics of pesticides from water to the PU film was determined. The $K_{sampling-water}$ was estimated by fitting all $C_{sampling}/C_{water}$ values to Eq. (1). The results of regression analysis are shown in Table 2. The fit was good for the majority of target analytes ($r^2 > 0.70$), except for diazinon ($r^2 = 0.38$), cyfluthrin ($r^2 = 0.51$), and cypermethrin ($r^2 = 0.49$). There was a clear increasing trend for all pesticides in their accumulation on the PU film (Fig. 2). However, except for diazinon, fipronil, and desulfinyl fipronil, the other pesticides did not appear to have reached equilibrium between the PU strip and water even after 43 d of equilibration.

The highest $K_{sampling-water}$ value was found for deltamethrin (5.72), followed by, in a decreasing order, chlorpyrifos (5.07), fenpropatrin (5.02), fipronil sulfone (4.96), and fipronil sulfinde (4.86).

### Table 2

| Chemicals          | Log $K_{sampling-water}$ (RT) | $K_{abs}$ | $r^2$ |
|--------------------|-------------------------------|-----------|------|
| Diazinon           | 2.89                          | 1.21                                | 0.38 |
| Desulfuryl fipronil| 4.46                          | 0.127                              | 0.92 |
| Chlorpyrifos       | 5.07                          | 0.0312                             | 0.94 |
| Fipronil sulfide   | 4.86                          | 0.0564                              | 0.89 |
| Fipronil           | 3.68                          | 0.321                               | 0.89 |
| Fipronil sulfone   | 4.96                          | 0.0281                              | 0.82 |
| Fenpropatrin       | 5.02                          | 0.0929                              | 0.76 |
| Lambda-cyhalothrin | 4.72                          | 0.101                               | 0.80 |
| Bifenthrin         | 4.23                          | 0.165                               | 0.89 |
| Permethrin         | 4.17                          | 0.239                               | 0.74 |
| Cyfluthrin         | 3.89                          | 0.301                               | 0.51 |
| Cypermethrin       | 3.95                          | 0.500                               | 0.49 |
| Esfenvalerate      | 4.48                          | 0.0920                              | 0.92 |
| Deltamethrin       | 5.72                          | 0.0767                              | 0.97 |

* The $K_{sampling-water}$ values were measured at room temperature (RT).
Diazinon, fipronil, and cyfluthrin had lower log \( K_{\text{sampler-water}} \) values (Table 2). The results suggested that a very long time would be needed for pyrethroids to reach equilibrium in the PU film, precluding the use of PU film under equilibrium conditions and justifying the need to incorporate PRCs for the practical use of PU samplers for ambient monitoring.

3.3. Isotropy validation

Following the PRC preloading procedures used in this study, 4.02 ± 1.73 and 4.21 ± 0.73 μg/g of \(^{13}\)C_6-bifenthrin and \(^{13}\)C_6-permethrin were loaded onto the PU film, respectively. Deuterated analogue \(^2\)D-bifenthrin was used as PRC for bifenthrin and \(^{13}\)C_6-permethrin was used as PRC for the other pyrethroids due to structural similarity. The absorption of the non-labeled pyrethroids (n/n\_0) from the spiked water was found to generally mirror the desorption of the labeled PRCs (q/q\_0) from the PU film to the bathing water (Fig. 3). The sum of n/n\_0 and q/q\_0 was generally in the range of 0.8–1.2 and was not statistically different from 1 for most of the time points (p > 0.05, One-Sample t-Test). This suggests isotropy between absorption of pyrethroids onto the sampler and desorption of the isotope labeled analogues from the PU film into water. In a previous study, good isotropy was also observed for pyrethroids between polydimethylsiloxane fiber and water (Cui et al., 2013a). The results suggested that the PU sampler, if coupled with PRCs, may be used under non-equilibrium conditions for detecting \( C_{\text{free}} \) of pyrethroids in water. This is advantageous because a short, flexible sampling interval makes the use of passive samplers much more feasible for ambient monitoring.

The uptake of diazinon, chlorpyrifos, and fipronils appeared to have reached a steady state in 96 h, as no further increases were evident thereafter (Fig. 3i). Therefore, 96 h (4 d) was set as the sampling time interval for all target pesticides considered in this study. The \( C_{\text{free}} \) values of organophosphates and fipronils were calculated directly from \( C_{\text{sampler}} \) at the time of sampling, while \( C_{\text{free}} \) values of pyrethroids were estimated from Eq. (5) by using the desorption fraction of PRCs.

3.4. Validation of passive sampler under simulated conditions

The performance of PU thin-film sampler was first evaluated on the target pesticides under simulated conditions in a large glass tank. The total chemical concentrations (\( C_w \)) measured following solvent extraction were in the low μg/L range (Table 3) and remained relatively constant over time (p > 0.05, one-way ANOVA), suggesting that sorption onto the PU sampler did not appreciably deplete the chemical pool in the system. A slight increase in the concentrations of pesticides derived from the PU thin-film passive sampler (\( C_{\text{free}} \)), which will be calculated from \( C_0(K_{\text{sampler-water}}) \), was observed (Hunter et al., 2009; Mayer et al., 2000; Poerschmann et al., 1997). As can be seen in Table 3, the \( C_w \) values at 4 d were in agreement with those found for \( C_{\text{free}} \). This is due to the glass aquarium contains no suspended particles or dissolved organic matter, and thus analysis of water should give concentration similar to \( C_{\text{free}} \). This result further validates that the assumption that isotope labeled analogues may be used as PRCs to calibrate PU sampling so the PU thin-film passive sampler may be used under non-equilibrium conditions with flexible sampling time for the measurement of \( C_{\text{free}} \) of pesticides in water (Cui et al., 2013a, b; Bao et al., 2015; Jia et al., 2014).

3.5. Field applications

The PU sampler was further tested under field conditions. The PRC-preloaded samplers were deployed at four locations in urban streams draining residential areas in Orange County, California. Three PU film strips (5 x 50 mm) were attached to the inside of a small stainless steel mesh cage and placed in the water for 4 d before retrieval and analysis. Grab water samples were collected at the time of sample retrieval and analyzed for the total chemical concentrations. Fipronil and three metabolites (desulfinyl fipronil, fipronil sulfide and fipronil sulfone) were found in all water samples with a detection frequency of 100%. Fipronil sulfone and fipronil were the predominant derivatives and the concentrations were in the range of 46.7–1960 ng/L, where the total concentrations of these
Fig. 3. Isotropy between absorption (●) and desorption (■) of eight pyrethroids (a–h) and uptake kinetics of fipronil and its metabolites, diazinon and chlorpyrifos (i) on the samplers. The sum of absorption ratio \(n/n_0\) and desorption ratio \(q/q_0\) at each time interval is represented by ▲. The dash line means value of 1. Note: BFT = bifenthrin, d5-BFT = d5-bifenthrin, PMT = permethrin, 13C6-cis-PMT = 13C6-cis-permethrin, FPT = fenpropathrin, L-CYH = lambda-cyhalothrin, CYF = cyfluthrin, CYP = cypermethrin, ESF = esfenvalerate, DMT = deltamethrin, FIP = fipronil, FIP-DSF = desulfinyl fipronil, FIP-SFD = fipronil sulfide, FIP-SFN = fipronil sulfone, DZN = diazinon, Chlor = chlorpyrifos.

Table 3
Comparison between pesticide concentrations (ng/L) derived from the passive sampler \(C_{\text{free}}\) and water \(C_w\).

| Chemicals          | 2d             | 4d             | 8d             |
|--------------------|-----------------|-----------------|-----------------|
|                    | \(C_{\text{free}}\) | \(C_w\)         | \(C_{\text{free}}\) | \(C_w\)         | \(C_{\text{free}}\) | \(C_w\)         |
| Diazinon           | 2620 ± 243      | 1700 ± 161      | 2620 ± 747      | 1400 ± 63.2      | 2360 ± 810        | 1290 ± 149      |
| Desulfynil fipronil| 1050 ± 207      | 2080 ± 223      | 1320 ± 1000     | 1960 ± 220       | 2040 ± 1190       | 1870 ± 194      |
| Chloprypiros       | 245 ± 49.6      | 779 ± 98.0      | 257 ± 209       | 432 ± 47.0       | 311 ± 170        | 267 ± 26.6      |
| Fipronil sulfide   | 530 ± 95.3      | 2000 ± 315      | 724 ± 948       | 1940 ± 281       | 1260 ± 1170       | 1840 ± 184      |
| Fipronil           | 1670 ± 289      | 2320 ± 381      | 2420 ± 1190     | 2410 ± 337       | 3170 ± 1560       | 2400 ± 193      |
| Fipronil sulfone   | 417 ± 65.1      | 2020 ± 462      | 588 ± 976       | 2110 ± 385       | 1020 ± 1320       | 2050 ± 175      |
| Fenpropathrin      | 135 ± 18.4      | 455 ± 114       | 201 ± 167       | 383 ± 73.5       | 356 ± 140        | 225 ± 27.7      |
| Lambda-cyhalothrin | 64.3 ± 8.75     | 152 ± 59.7      | 100 ± 96.1      | 223 ± 54.4       | 210 ± 116        | 191 ± 26.4      |
| Bifenthrin         | 141 ± 18.4      | 114 ± 54.8      | 198 ± 83.5      | 198 ± 52.6       | 364 ± 98.6       | 169 ± 29.2      |
| Permethrin         | 368 ± 19.6      | 185 ± 44.4      | 604 ± 110       | 236 ± 48.3       | 1200 ± 108       | 173 ± 19.9      |
| Cyfluthrin         | 353 ± 88.5      | 180 ± 50.4      | 685 ± 107       | 230 ± 40.7       | 1280 ± 117       | 182 ± 16.4      |
| Cypermethrin       | 297 ± 77.6      | 174 ± 39.8      | 583 ± 110      | 227 ± 33.7       | 1100 ± 115       | 176 ± 12.8      |
| Esfenvalerate      | 102 ± 9.33      | 145 ± 19.9      | 169 ± 98.1      | 194 ± 28.2       | 308 ± 106        | 161 ± 10.1      |
| Deltamethrin       | 8.53 ± 1.87     | 172 ± 20.7      | 14.4 ± 106      | 211 ± 33.0       | 24.7 ± 82.2      | 159 ± 42.3      |
compounds were determined in whole water samples (Gan et al., 2012).

As can be seen from Table 4, diazoin, chlorpyrifos and fenpropathrin were not detected in any of the water samples, while the other seven pyrethroids (lambda-cyhalothrin, bifenthrin, permethrin, cyfluthrin, cypermethrin, esfenvalerate, and deltamethrin) were found in all water samples with a detection frequency of 100%. The mean concentration of permethrin was 270 ng/L, which was 2–10 folds higher than those found for lambda-cyhalothrin (95.1 ng/L), deltamethrin (47.3 ng/L), bifenthrin (46.0 ng/L), cyfluthrin (29.7 ng/L), esfenvalerate (21.2 ng/L) and cypermethrin (18.4 ng/L). The pyrethroid concentrations in urban runoff outfalls in Orange County, California present in this study were 1–3 orders of magnitude higher than those found for coastal urban watersheds in southern California (permethrin: n.d.-1.7 ng/L) (Maruya et al., 2016), surface streams near San Francisco Bay, California (bifenthrin: n.d.-9.9 ng/L) (Weston et al., 2015) and urban runoff to the American River in northern California (bifenthrin: n.d.-106 ng/L, cyfluthrin: n.d.-26.6 ng/L, cypermethrin: n.d.-9.4 ng/L, permethrin: n.d.-111 ng/L) (Weston and Lydy, 2012). The elevated occurrence was likely due to heavier use of pyrethroid products in the southern California region due to warmer temperature and hence greater pest pressure.

In general, the concentrations of fenpropathrin and its three metabolites (desulfynyl fenpropathrin, fenpropathrin sulfide and fenpropathrin sulfone) derived from the PU thin-film sampler were slightly lower than those measured by the grab water samples, but the difference was not statistically significant (p > 0.05, one-way ANOVA, Table 4). This suggests that fenpropathrin and its metabolites are moderately hydrophobic, and the presence of suspended solids and dissolved organic matter did not appreciably decrease C_free compared to the total chemical concentration. Similarly, the pyrethroid concentrations determined by using PU thin-film sampler were slightly lower than those measured by the grab samples, while the concentrations agreed generally within one order of magnitude (p > 0.05, one-way ANOVA, Table 4). Comparatively, the matching in concentrations of pyrethroids determined by the two manners is fairly better than that for fenpropathrin, which may be due to pyrethroid data being PRCC-corrected while fenpropathrin data were calculated at equilibrium (no PRCC-correction) (Fernandez et al., 2012).

4. Application considerations

Pesticides including pyrethroids and fenpropathrin are commonly used in urban environments to control undesirable pests such as ants, termites, and spiders (Fernandez et al., 2012; Gan et al., 2012; Maruya et al., 2016; Weston and Lydy, 2012; Weston et al., 2015). Widespread use of such pesticides has caused their frequent occurrence in urban surface waters. Passive samplers (e.g. on the basis of thin-films) have been developed as novel tools for monitoring surface water contaminants. Due to discrepancy in physico-chemical nature (e.g. polarity) of chemicals, it is challenging to use one type of passive sampler to detect compounds with different properties. As shown in this study, the PU thin-film passive sampler was capable of simultaneously enriching and monitoring pyrethroids, organophosphates, and fenpropathrin in urban surface water. Comparatively, such thin-film samplers may be more suitable for field applications, due to their low-cost, durability, flexibility, and relatively large sorbent volume. The PU thin-film passive sampler therefore is promising to be used in ambient monitoring of a wide range of pesticides in surface water.

Loading of performance reference compounds (PRCs) in passive samplers enables non-equilibrium sampling, effectively removing the requirement for attaining equilibrium or steady state for highly hydophobic compounds such as pyrethroids (Cui et al., 2013b; Bao et al., 2013; Jia et al., 2014). The loading of PRCs may provide a great benefit due to the shortened and flexible deployment time, which is important since long-term deployment may lead to potential alterations of the sampler (e.g., biofouling, physical damages, or loss of sampling device) (Cui et al., 2013a; Jia et al., 2014). In the present study, isotope-labeled analogues (δ_13C-bifenthrin and δ_13C-permethrin) were used as PRCs for pyrethroids and the PRC calibration reduced the sampling time to only 4 d. It must be noted that many commercially-available standards labeled with δ_13C or deuterium are available for field applications on contaminants of diverse physicochemical properties, such as contemporary pesticides.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2017.09.002.
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