Video Article

Characterization and Application of Passive Samplers for Monitoring of Pesticides in Water

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Abstract

Five different water passive samplers were calibrated under laboratory conditions for measurement of 124 legacy and current used pesticides. This study provides a protocol for the passive sampler preparation, calibration, extraction method and instrumental analysis. Sampling rates (R_S) and passive sampler-water partition coefficients (K_{PW}) were calculated for silicone rubber, polar organic chemical integrative sampler POCIS-A, POCIS-B, SDB-RPS and C_{18} disk. The uptake of the selected compounds depended on their physicochemical properties, *i.e.*, silicone rubber showed a better uptake for more hydrophobic compounds (log octanol-water partition coefficient (K_{OW}) > 5.3), whereas POCIS-A, POCIS-B and SDB-RPS disk were more suitable for hydrophilic compounds (log K_{OW} < 0.70).

Video Link

The video component of this article can be found at https://www.jove.com/video/54053/

Introduction

Pesticides are continuously introduced to the aquatic environment and may pose a risk to aquatic organisms[1]. Monitoring of pesticides in the aqueous environment is typically performed using grab sampling, however, this sampling technique does not fully account for temporal variations in concentrations due to fluctuations in flow or episodic inputs (*e.g.*, precipitation, combined sewer overflows, sewage lagoon release)[2,3]. Thus, monitoring methods need to be improved for a better estimation of environmental risks associated with pesticides. Passive sampling allows continuous monitoring over an extended period of time with minimal infrastructure and low contaminant concentrations[4,5].

Passive samplers have been shown to be a valuable tool for the monitoring in groundwater[6], fresh water[7-10], wastewater[11] and marine waters[12]. Besides monitoring purposes[13,14], passive samplers have also been used for non-target analysis[15], toxicology testing[16,17], and as an alternative to sediment- and biomonitoring[18]. Passive samplers accumulate chemicals continuously from water and provide time weighted average (TWA) concentrations[14]. The uptake of the contaminant depends on the sampling rate (R_S) and passive sampler-water partition coefficient (K_{PW}), which depends on the passive sampler design, sampler material, physicochemical properties of the contaminant, and environmental conditions (*e.g.*, water turbulence, temperature)[13,14,19,20].

The detailed video aims to show how to calibrate and apply passive samplers for pesticides in water. The specific objectives included *i)* to perform preparation, extraction and instrumental analysis for 124 individual pesticides using five different types of passive samplers, including silicone rubber, polar organic chemical integrative sampler (POCIS)-A, POCIS-B, SDB-RPS and C_{18} disk, *ii)* to assess R_S and K_{PW} for the pesticides in a laboratory uptake study, and *iii)* to demonstrate how to select the appropriate passive sampler of the target compound of interest and how to calculate TWA concentrations for the respective passive sampler.

Reference standards and passive sampler devices

Target compounds included 124 legacy and currently used pesticides including herbicides, insecticides and fungicides (**Table 1**). Internal standard mixture (IS mixture) included fenoprop (2,4,5-TP), clothianidin-D_3, ethion and terbuthylazine-D_5. Other used chemicals included methanol (MeOH), acetonitrile (ACN), acetone (ACE), dichloromethane (DCM), cyclohexane (CH), ethyl acetate (EA), petroleum ether (PE), 2-propanol, 25% ammonia solution, acetic acid (HAc) and formic acid (FA). Five different passive sampling devices were characterized, including silicone rubber, POCIS-A and POCIS-B, SDB-RPS, and C_{18} disk[1,21].

Table 1. Passive sampler sampling rate (R'_S, L day^{-1}), sampler-water partition coefficients (K'_{PW}, L kg^{-1}) and equations (Eq.) used for the calculation of concentrations in field samples for individual pesticides[a]. (Reprinted from Journal of Chromatography A, 1405, Lutz Ahrens, Atlasi

Daneshvar, Anna E. Lau, Jenny Kreuger, Characterization of five passive sampling devices for monitoring of pesticides in water, 1-11, Copyright (2015), with permission from Elsevier.)[22] Please click here to download this file.

Protocol

1. Passive Sampler Design and Preparation

1. **Silicone rubber sheets**
    1. Cut the silicone rubber sheets (600 mm x 600 mm, 0.5 mm thick) into stripes of 2.5 mm x 600 mm and 2.5 mm x 314 mm using a stainless steel cutter and connect them using a stainless steel blind rivet (3.2 mm x 10 mm) with a rivet gun to obtain a total sampler stripe size of 2.5 mm x 914 mm (surface area = 457 cm^2, sorbent mass = 15.6 g, volume = 22.9 cm^3).

2. Place the silicone rubbers in an extraction chamber of a Soxhlet apparatus. Add 50 ml EA in the extraction chamber and add 250 ml EA and three boiling stones in a 500 ml round bottle flask.
    1. Connect the extraction chamber with the bottle flask and a condenser. Clean the silicone rubbers by Soxhlet extraction for 96 hr at approximately 80 °C, and dry them thereafter under gentle nitrogen gas.

3. Attach the silicone rubber stripe to a stainless steel spider sample holder by wrapping the silicone rubber stripe around the rods on the holder (**Figure 1**). Attach each end of the silicone rubber stripe to a rod on the holder using cable ties.

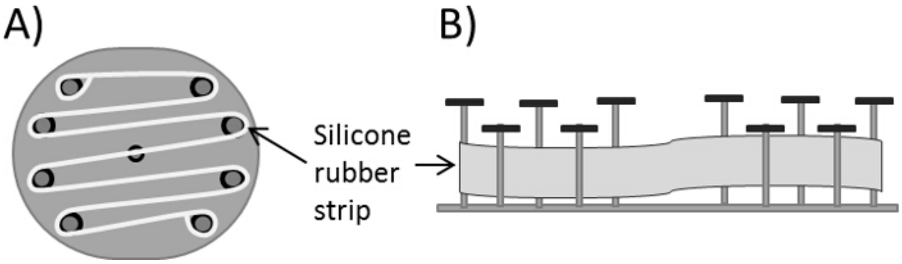

Figure 1. Schematic of silicone rubber. Passive sampler schematic for silicone rubber showing the attachment of the silicone rubber stripe to a stainless steel spider sample holder **A**) from the top and **B**) the side view. Please click here to view a larger version of this figure.

2. **POCIS-A and POCIS-B**
    1. For POCIS-A, place 220 mg of HLB bulk sorbent (surface area = 1.78 x 10^6 cm^2) between two 9.0 cm by 9.0 cm square polyethersulfone (PES) membranes (**Figure 2**).
    2. For POCIS-B, place 220 mg of a sorbent mixture (*i.e.*, hydroxylated polystyrene-divinylbenzene resin (80%) and a carbonaceous adsorbent dispersed on a styrene divinylbenzene copolymer (20%)) (surface area = 2.82 x 10^6 cm^2) between two PES membranes (**Figure 2**).
    3. Compress the sorbent and two PES between two stainless steel rings manually (inner Ø = 5.4 cm) and secure it on a stainless steel sample holder (**Figure 2**).

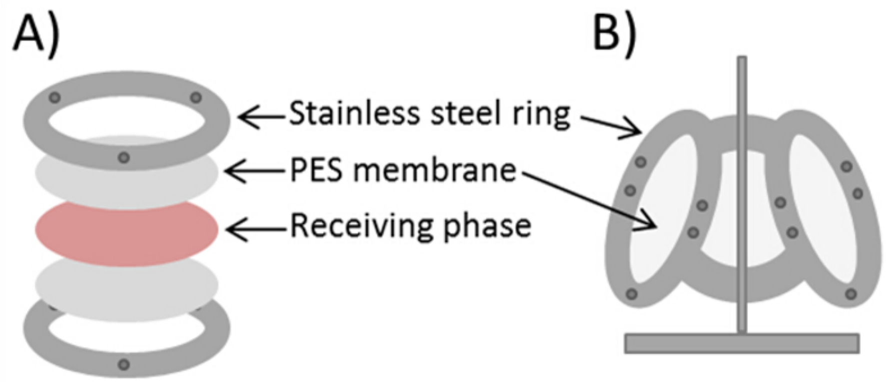

Figure 2. Schematic of passive sampler disks. Passive sampler schematic for POCIS A, POCIS B, SDB-RPS disk and C_{18} disk showing **A**) the assembling of the passive sampler using stainless steel rings, polyethersulfone (PES) membranes, and the receiving phase, and **B**) the assembling on a stainless steel sample holder. Please click here to view a larger version of this figure.

3. **SDB-RPS disk and C_{18} disk**
    1. Place the SDB-RPS (surface area = 35 cm^2, sorbent mass = 0.34 g, volume = 1.7 cm^3) and C_{18} disks (surface area = 35 cm^2, sorbent mass = 0.58 g, volume = 1.7 cm^3) between two PES membranes (**Figure 2**). Compress the disks and two PES between two stainless steel rings manually (inner Ø = 5.4 cm) and secure it on a stainless steel sample holder (**Figure 2**).

2. Laboratory Uptake Experiments

NOTE: The Laboratory uptake experiments were performed to quantitatively characterize the uptake kinetics for 124 individual pesticides for five different passive sampler devices under controlled conditions.

1. Conduct the uptake study in rectangular glass containers (each ~95 L): Tank 1) silicone rubber (*n* = 16), tank 2) POCIS-A (*n* = 16), POCIS-B (*n* = 16), and tank 3) SDB-RPS disk (*n* = 16), C_{18} disk (*n* = 16). Fill natural water into the three tanks.
2. Perform all experiments at a constant water temperature (~20 °C) and under turbulent water conditions (~10 cm sec^{-1}) using two electric pumps attached to the wall on each side. Perform the experiments in the dark to minimize the effect of photodegradation.
3. Spike each glass container with a pesticide standard mixture containing 124 pesticides using a glass syringe ($c \approx 400$ ng L^{-1} for individual pesticides in the water tank). Take out the passive samplers manually from the tanks, at time intervals of 5, 11, 20, and 26 days, to determine the sampling rates of the pesticides.
4. Monitor the concentrations of the pesticides in each tank by collecting 100 ml water samples at day 0, 5, 11, 20, and 26. The analysis of the water samples is performed as described elsewhere[21].
    1. For quality control, expose blank samples to room air for 1 hr at day 0 and then store and treat them as real samples. Store all extracts as well as the 100 ml water samples collected from the tanks at -18 °C until further analysis.

3. Sample Extraction

1. **Silicone rubber**
    1. Prior to extraction, dry the silicone rubber stripe under a stream of high purity nitrogen gas.
    2. For gas chromatography-mass spectrometry (GC-MS) analysis, carry out the solid-liquid extraction using Soxhlet extraction[22].
        1. Place the silicone rubber into the Soxhlet extractor. Add 250 ml PE/ACE (50/50, v/v) and 3 boiling stones into the round bottle flask.
        2. Spike the silicone rubber with 100 µl of an IS mixture ($c = 5$ ng ml^{-1}) using a glass syringe. Add 50 ml PE/ACE (50/50, v/v) into the Soxhlet extractor. Switch on the heater and run the Soxhlet extraction for 19 hr and then switch off the heater.
        3. Concentrate the extracts by rotary evaporation followed by gentle nitrogen blow-down to 1 ml. Exchange the solvent to CH/ACE (90/10, v/v) by adding three times 1 ml CH/ACE (90/10, v/v) during the nitrogen blow-down to 1 ml.
    3. For liquid chromatography−tandem mass spectrometry (LC-MS/MS) analysis, carry out the extraction using Soxhlet extraction[22].
        1. Place the silicone rubber into the Soxhlet extractor. Add 250 ml MeOH and 3 boiling stones into the round bottle flask and 50 ml MeOH into the Soxhlet extractor. Spike the silicone rubber with 100 µl of an IS mixture ($c = 5$ ng ml^{-1}) using a glass syringe.
        2. Switch on the heater and run the Soxhlet extraction for 19 hr and then switch off the heater. Concentrate the extracts by rotary evaporation followed by gentle nitrogen blow-down to 1 ml. Exchange the solvent to ACN by adding 1 ml ACN during the nitrogen blow-down to 1 ml.
2. **POCIS-A and POCIS-B**
    1. Open the POCIS sampler carefully and transfer the sorbent with ultrapure water using a funnel into a pre-cleaned empty polypropylene solid phase extraction (SPE) cartridge (6 ml) containing two polyethylene (PE) frits. Dry the sorbent by vacuum to remove water. Record the weight of the empty and packed SPE cartridge to control the weight of the sorbent material. Please note that different cartridges are used for GC-MS and LC-MS/MS analysis.
    2. Prior to elution, spike the sorbent with 100 µl of an IS mixture ($c = 5$ ng ml^{-1}) using a glass syringe. Elute POCIS-A and POCIS-B sorbents using 5 ml EA for GC-MS[22].
        1. Concentrate the extracts to 1 ml by gentle nitrogen blow-down. Exchange the solvent to CH/ACE (90/10, v/v) by adding three times 1 ml CH/ACE (90/10, v/v) during the nitrogen blow-down to 1 ml.
    3. Elute POCIS-A and POCIS-B cartridges using 1.5 ml MeOH followed by 8 ml DCM/MeOH (80/20, v/v) for LC-MS/MS analysis[22]. Concentrate the extracts to 1 ml by gentle nitrogen blow-down. Exchange the solvent to ACN by adding 1 ml ACN during the nitrogen blow-down to 1 ml.
3. **SDB-RPS and C_{18} disk**
    1. Transfer individual disks of SDB-RPS and C_{18} disk into a glass beaker and dry them under nitrogen gas. Spike the disks with 100 µl of an IS mixture ($c = 5$ ng ml^{-1}) using a glass syringe and sonicate them two times in a glass beaker at room temperature, first with 5 ml of EA for 10 min and then with 3 ml of EA for 10 min.
    2. Transfer both extracts into one glass tube, concentrate them to 2 ml by gentle nitrogen blow down, and split them into two 1 ml fractions (for GC-MS and LC-MS/MS analysis, respectively).
    3. Concentrate the extracts to 0.5 ml by gentle nitrogen blow-down and exchange the solvent to CH/ACE (90/10, v/v) for GC-MS analysis[22]. Concentrate the extracts to 0.5 ml by gentle nitrogen blow-down and exchange the solvent to ACN for LC-MS/MS analysis[22].

4. Water Samples

1. Spike 20 ml water sample with 100 µl of an IS mixture ($c = 5$ ng ml^{-1}) using a glass syringe, add 3 ml of DCM, vortex for 3 min, and decant into a phase separator for GC-MS analysis [22].

    1. After the two phases are separated, percolate the DCM phase into a glass tube. Repeat the extraction using 3 ml DCM, and rinse the tube with 2 ml DCM. Finally, concentrate the extracts to 0.5 ml by gentle nitrogen blow-down and exchange the solvent to CH/ACE (90/10, v/v).

2. Analyze the water samples using large volume injection, similar to the method described elsewhere by LC-MS/MS [21].

5. Instrumental Analysis

1. GC-MS analysis
    1. Perform the instrumental analysis of the CH/ACE extracts using GC-MS systems in electron ionization (EI) and negative chemical ionization (NCI) mode, respectively[22].
    2. For the GC-MS method using EI, inject aliquots of 1 µl with splitless injection method on a HP-5MS UI column (30 m, 0.25 mm inner diameter, 0.25 µm film).
    3. For the GC-MS method using CI, inject aliquots of 3 µl on a HP-5MS UI column (30 m, 0.25 mm inner diameter, 0.25 µm film).

2. HPLC-MS/MS analysis
    1. Perform the instrumental analysis of the ACN extracts using HPLC-MS/MS interfaced with an electrospray ionization source in negative ((-)ESI) and positive-ion mode ((+)ESI)[22].
    2. For (+)ESI, dilute 100 µl of the ACN extracts with 900 µl ultrapure water adjusted to pH 5 using FA .
    3. For (-)ESI, dilute 100 µl of the ACN extracts with 900 µl solution of 1% FA in ultrapure water.
    4. For (+)ESI, use a binary gradient consisting of 2-propanol/methanol/10 mM ammonium formate (6/2/92, v/v/v) and MeOH at a flow rate of 0.3 ml min^{-1}.
    5. For (-)ESI, use a binary gradient consisting of ACN/ultrapure water 0.1% HAc and ACN + 0.1% HAc at a flow rate of 0.3 ml min^{-1}.
    6. Inject all samples using a large volume injection of 500 µl using two online SPE columns (both 20 x 2 mm id and 20-25 µm particle size), and an analytical column (C_{18}, 100 x 3 mm, 3.5 µm)[21].

6. Theory on Passive Sampling

NOTE: The uptake profile of the chemical to the passive sampler medium (PSM) is divided into three sections: Linear, curvilinear and equilibrium (**Figure 3**).

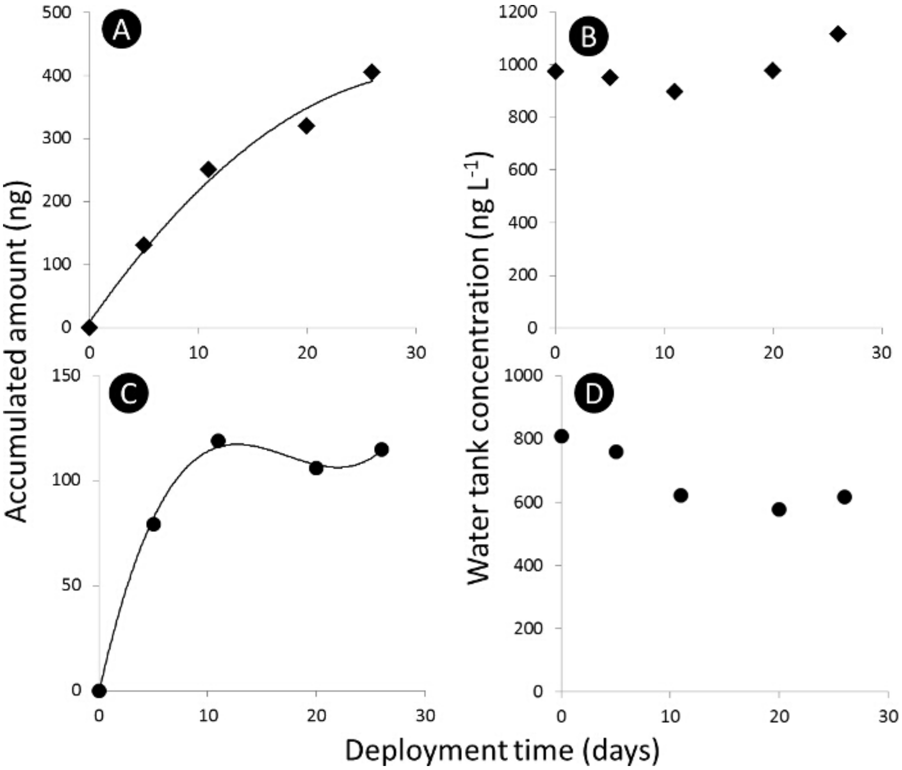

Figure 3. Passive sampler uptake curve. A) and **C**) uptake curve for the accumulated amount of acetamiprid and dimethoate, respectively, in the passive samplers (N_t) in ng absolute, and **B**) and **D**) water tank concentration of acetamiprid and dimethoate, respectively, in ng L^{-1}. Please click here to view a larger version of this figure.

1. Calculate the equivalent water volume (V_{eq} L) for a passive sampler by dividing the accumulated amount of target compounds in the passive sampler after *t* days of exposure (N^t, ng) by the concentration in the water phase using grab and time integrated active sampling (c_w, ng L^{-1}).

$V_{eq} = \frac{N^t}{c_w}$ (1)

2. Derive the sampling rate (R_S, L day^{-1}) from the linear uptake phase of the uptake profile, by taking the slope of V_{eq} versus deployment time.
3. Calculate the K_{PW} (L kg^{-1}) for individual pesticides using Eq. 2.

   $K_{PW} = \frac{N^t}{c_w m_p}$ (2)

   where m_p is the sorbent mass per sampler (ng).
4. In the linear uptake phase, calculate the TWA concentration of the analyte in water derived by the passive sampler (c_{TWA}, ng L^{-1}) using Eq. 3.

   $c_{TWA} = \frac{N^t}{R_S t}$ (3)

   where R_S is the sampling rate (L day^{-1}), and *t* is the deployment time (days).
5. In the curvilinear phase, calculate c_{TWA} using Eq. 4.

   $c_{TWA} = \frac{N^t}{K_{PW} m_p \left(1 - e^{-\left(\frac{R_S}{K_{PW} m_p}\right)t}\right)}$ (4)
6. In the equilibrium phase, calculate c_{TWA} using Eq. 5.

   $c_{TWA} = \frac{N^t}{K_{PW} m_p}$ (5)

7. Statistical Data Analysis

1. Test non-normal distribution of the data using a Shapiro-Wilk test[23]. Use non-parametric Spearman's rank correlation for K_{PW} and R_S *vs* physicochemical properties of the tested pesticides (Spearman's rho ranging from -1 to 1)[24].

Representative Results

Five different passive sampler techniques were compared for the uptake of 124 legacy and current used pesticides including silicone rubber (**Figure 1**), and POCIS A, POCIS B, SDB-RPS and C_{18} disk (**Figure 2**). The performance of the extraction method and instrumental analysis was optimized. The outcome of the laboratory uptake experiments can be used to calculate the R'_S and *log* K'_{PW} values (**Table 1**) based on the uptake profile for individual pesticides (**Figure 3**). The results showed that silicone rubber is more suitable for hydrophobic compounds (log octanol-water partition coefficient (K'_{OW}) > 5.3), whereas more polar compounds (log K'_{OW} < 0.70) were better taken up by POCIS A, POCIS B and SDB-RPS disk (**Figure 4**). R'_S (L day^{-1}), K'_{PW} (L kg^{-1}) and equations (Eq.) can be used for the calculation of concentrations in field samples for individual pesticides (**Table 1**)[22].

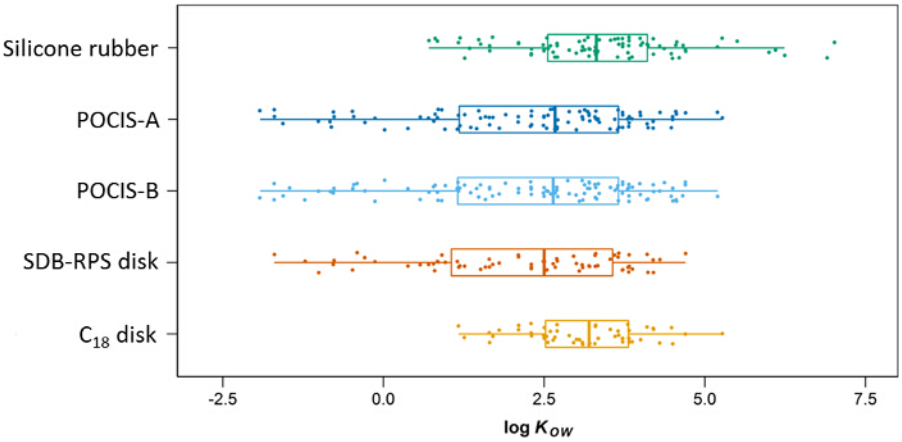

Figure 4. K_{OW} *vs* passive sampler type. Box-Whisker-Plots for individual pesticides taken up by silicone rubber (*n* = 86), polar organic chemical integrative sampler (POCIS)-A (*n* = 106), POCIS-B (*n* = 110), SDB-RPS disk (*n* = 65), and C_{18} disk (*n* = 54) in relation to their octanol-water partition coefficient (K_{OW}). Note: Pesticides were only included if the mean pesticide concentration in the passive sampler was greater than 0.1% compared to the mean pesticide concentration in the water. (Modified from Journal of Chromatography A, 1405, Lutz Ahrens, Atlasi Daneshvar, Anna E. Lau, Jenny Kreuger, Characterization of five passive sampling devices for monitoring of pesticides in water, 1-11, Copyright (2015), with permission from Elsevier.)[22] Please click here to view a larger version of this figure.

Discussion

For quality control, as standard procedure, laboratory blanks, limits of detection (LOD), recoveries, and repeatability were examined[23]. A few pesticides were detected in the blank samples at low concentration levels. LODs were set as the value of the lowest point on the calibration curve which meets the criteria of a signal to noise ratio of 3. The average LODs were 8.0 pg absolute injected on column for silicone rubber, 1.7 pg absolute for POCIS-A, 1.6 pg absolute for POCIS-B, 3.0 pg absolute for SDB-RPS disk, and 1.6 pg absolute for C_{18} disk. All concentrations were corrected by the spiked IS mixture. Average method recoveries based on spiked passive samples of the native pesticides (*n* = 3) were 68%, 110%, 92%, 89% and 70% for silicone rubber, POCIS-A, POCIS-B, SDB-RPS disk and C_{18} disk, respectively. The average repeatability for individual pesticides (n = 10) were 19%, 20%, 16%, 33% and 36% for silicone rubber, POCIS-A, POCIS-B, SDB-RPS disk and C_{18} disk, respectively.

Most pesticides had a short linear uptake curve (5 to 10 days) and equilibrated after 26 days, *i.e.*, 89 of the 124 for silicone rubber, 97 of 124 for POCIS-A, 99 of 124 for POCIS-B, 32 of 124 for SDB-RPS disk and 36 of 124 for C_{18} disk. Therefore, for most pesticides a log K'_{PW} could be calculated (**Table 1**). If a pesticide did not equilibrate, a log K'_{PW} was assumed to be higher than the calculated log K'_{PW} for the equilibration phase. The median R'_S (L day^{-1}) were 0.86 for silicone rubber, 0.22 for POCIS-B, 0.18 for POCIS-A, 0.05 for SDB-RPS disk and 0.02 for C_{18} disk. The high R'_S for silicone rubber can be explained by the higher sorbent mass (m_p) of silicone rubber (m_p = 15.6 g) compared to the other passive samplers (m_p = 0.22-0.58 g). The median log K_{PW} (L kg^{-1}) were 4.78 for POCIS-B, 4.56 for POCIS-A, 3.17 for SDB-RPS disk, 3.14 for silicone rubber and 2.71 for C_{18} disk. Differences can be explained by different surface areas (a_p) which were higher for POCIS-A and POCIS-B (a_p = 1.78 × 10^6 cm^2 and 2.82 × 10^6 cm^2, respectively) compared to silicone rubber (a_p = 457 cm^2), SDB-RPS disk and C_{18} disk (a_p = 35 cm^2 for both). It is important to note that the R'_S can vary between different calibration methods and the type of passive sampler, thus there is a need to define standardized protocols for calibration procedures[25].

This study was performed using static depletion which has the advantage to have a simple set-up with many replicates but concentration depletion over time needs to be considered. Future uptake studies should be performed using flow-through exposure tanks with constant exposure concentrations or *in-situ* under realistic field deployment conditions[19]. Natural water was used in the laboratory calibration experiments, however, the DOC can have an influence on the determination of sampling rates.[19] Furthermore, the usage of performance and reference compounds (PRCs), which are spiked to the passive samplers before deployment, can be used to calculate *in-situ* uptake rates and allow for more accurate estimates of TWA concentrations.[26]

The log K_{PW} of silicone rubber and C_{18} disk showed a significant positive correlation with log K_{OW} (Spearman's rho = 0.53 and 0.48, respectively; $p < 0.0001$). For the log R_S values, a significant positive correlation was only found between log R_S and log K_{OW} of silicone rubber (Spearman's rho = 0.56, $p < 0.0001$). In general, the K_{OW} has been shown to be a good parameter to predict the suitability of the passive sampler for specific target compounds[14,27]. A variety of different pesticides were investigated in this study with a log K_{OW} ranging from -2.6 to 7.0. In general, the five tested passive samplers were capable to accumulate pesticides with a wide range of different K_{OW} for silicone rubber (K_{OW} = 0.70 - 7.0), POCIS A (-1.9 - 5.3), POCIS B (-1.9 - 5.2), SDB-RPS disk (-1.2 - 4.7) and C_{18} disk (1.3 - 5.3) (**Figure 4**). Our results showed that silicone rubber is more suitable for hydrophobic compounds (log K_{OW} > 5.3), whereas more polar compounds (log K_{OW} < 0.70) were better taken up by POCIS A, POCIS B and SDB-RPS disk (**Figure 4**).

Disclosures

The authors have nothing to disclose.

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