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Testing of different passive sampler types for monitoring pesticides in Swedish aqueous environment

Test av olika typer av passiva provtagare samt utveckling av fätmetoder och analysmetoder för svenska förhållanden

Halland (Photo: Lutz Ahrens)

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Contents

1. Summary

Passive sampling is a promising tool for monitoring of pesticides in water with minimal infrastructure and low contaminant concentrations. Passive sampling is based on an in-situ deployment of devices/sorbent capable of accumulating contaminants freely dissolved in water. Such accumulation occurs via diffusion, typically over periods of days to weeks, and can be described by the compound specific sampling rate, which is the equivalent volume of water accumulated by the sampler per unit of time. Passive samplers have the advantages that they (i) are relatively inexpensive, easy to use, and do not require electricity to operate, (ii) measure time-integrated concentrations, and (iii) accumulate large volumes of water resulting in low limits of detection. In this study, passive samplers are characterized for over 100 individual pesticides in the water phase. The extraction method was optimized and the uptake capacity for three different passive sampler types were investigated including (i) polar organic chemical integrative sampler (POCIS)-A (Oasis hydrophilic–lipophilic balance (HLB) sorbent), (ii) POCIS-B (triphasic sorbent admixture (Isolute ENV+ and Ambersorb 1500)), and (iii) silicone rubber sheets (SR). Overall, the results of this study will improve our understanding of the concept, challenges, and application of passive sampling for future monitoring strategies of pesticides in the Swedish environment.

2. Introduction

Conventional methods for monitoring pesticides in the aquatic environment mainly rely on grab and mechanical sampling. However, this method may not fully account for temporal variations in concentrations due to fluctuations in flow, precipitation, or episodic inputs (e.g., combined sewer overflows or sewage lagoon release) (Kreuger 1998; Carlson et al. 2013). Another disadvantage of the classical monitoring strategies is the low water volume typically used for analysis resulting in relatively high detection limits (Gunold et al. 2008).

In the past few years, passive sampling has been identified as a promising alternative tool, allowing for continuous monitoring of an aquatic system over extended period of time and determining time-weighted average (TWA) concentrations of pesticides in water with minimal infrastructure and low contaminant concentrations (Alvarez et al. 2004). To derive TWA concentrations during field experiments, sampling uptake rates of analyte in the samplers (R_S) are required. However, R_S data are scarce for a large number of pesticides.

In the current study we characterize three different passive sampler types including Oasis hydrophilic–lipophilic balance (HLB) polar organic chemical integrative sampler (POCIS A), triphasic sorbent admixture (Isolute ENV+ and Ambersorb 1500) (POCIS B), and silicone rubber (SR), for measuring pesticides in the water phase. The specific objectives of this study include (i) to review the literature for monitoring of pesticides in water using passive sampling, (ii) to

optimize the extraction method, and (iii) to perform a kinetic uptake study for over 100 individual pesticides using three different passive sampler types.

3. Literature review

3.1 Principles

Passive sampling is based on free flow of analyte molecules from the sampled medium to a collecting medium in a sampling device, as a result of a difference in chemical potentials of the analyte between the two media (Vrana et al. 2005).

The uptake profile of the chemical to the passive sampler medium (PSM) can be divided into three sections. Initially, the uptake of analytes is nearly linear and the rate of desorption from the receiving phase to water is negligible. The linear uptake continues approximately until half-saturation of the receiving phase is obtained and then becomes curvilinear. Finally, as exposure time increases, the net uptake declines and approaches equilibrium partitioning with the medium, i.e., the uptake and release rates will be equal (**Figure 1**).

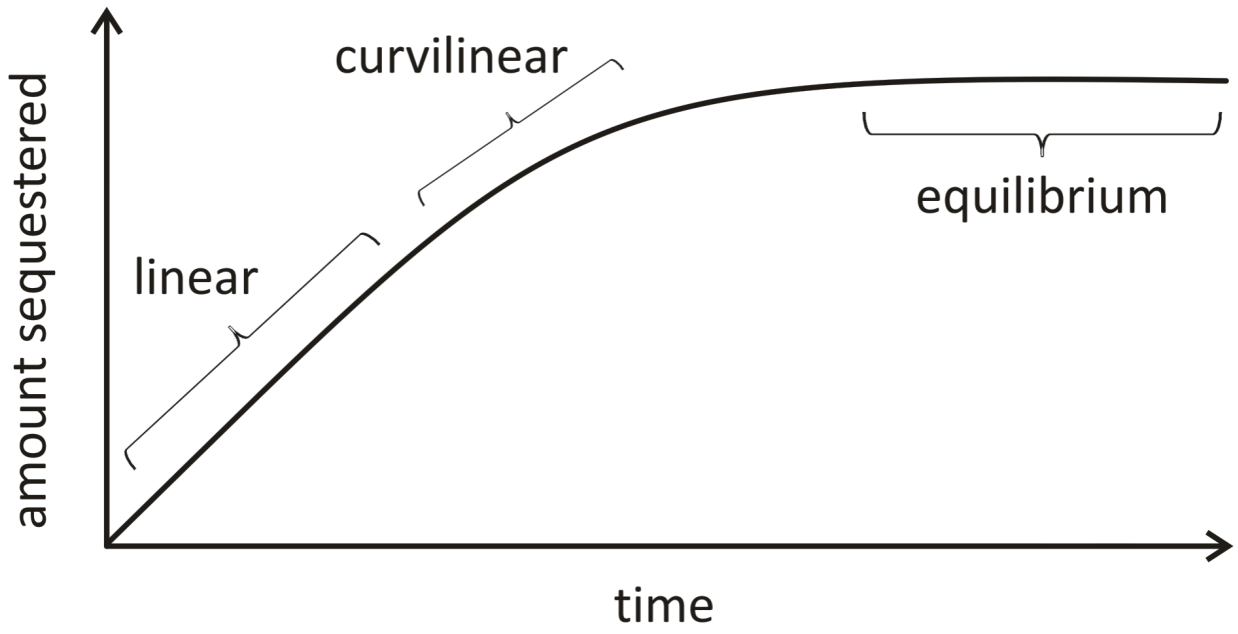

Figure 1. Uptake curve for the sequestered amount of target compounds in passive samplers.

The exchange kinetic between passive sampler and water phase can be described by the following first-order reaction:

$$c_s(t) = c_w \frac{k_1}{k_2} (1 - e^{-k_2 t}) \quad (1)$$

where c_s is the concentration of analyte in the sampler after exposure time t, c_w is the TWA concentration of the analyte in the water phase, and k_1 and k_2 are uptake and release rate constants, respectively.

3.2 Passive sampler types

There are basically two types of passive samplers, equilibrium sampler and integrative sampler.

3.2.1 Equilibrium passive sampler

In this type of sampler, the exposure time is sufficiently long (days to weeks) to establish the equilibrium between the water and receiving phase and to reach stable concentrations after a known response time (response time needs to be shorter than any fluctuation in the environment medium) (Vrana et al. 2005). In this situation, Eq. 1 reduces to:

$$c_s\,(t) = c_w\,\frac{k_1}{k_2} \tag{2}$$

3.2.2 Integrative passive sampler

This type of sampler provides TWA concentrations of chemical over deployment periods ranging from weeks to months. Integrative passive sampler allows to capture fluctuating concentrations. For accurate sampling, the exposure duration should fall within a phase before a state of equilibrium is reached.

The integrative passive sampler works in the linear or integrative phase of uptake where the sorbent is assumed to act as an infinite sink for contaminants and the desorption rate of analyte is negligible compared to the uptake rate. Therefore, Eq. 1 reduces and is rearranged to (Kingston et al. 2000; Vrana et al. 2005):

$$c_w = \frac{M_s\,c_s}{R_s\,t} \tag{3}$$

where c_w is the TWA concentration of the analyte in the water phase, M_s is the mass of sorbet, and R_s is the sampling rate (the volume of water cleared in a unit of time for a given molecule).

To calculate c_w of pollutants in the aquatic environment from Eq. 3, the sampler needs to be calibrated before deployment for the target analyte by determining R_s in controlled laboratory condition.

3.3 Performance reference compounds (PRCs)

For a given compound, R_s is often affected by different factors such as receiving phase material, physicochemical properties of the target analytes, water temperature, water velocity, and

biofouling (Vrana and Schüürmann 2002; Stephens et al. 2005; Booij et al. 2006; Vrana et al. 2006; Gunold et al. 2008). Therefore, to compensate for the effect of environmental variables, performance reference compounds (PRCs), analytically non-interfering compounds, can be added to passive samplers prior to deployment. The rate of PRC loss during the exposure can be used to estimate in situ sampling rates of the analytes of interest (Morin et al. 2012). In the first step, the elimination rate constant of the PRC is calculated according to Eq. 4.

$$\frac{C_s}{C_{s0}} = e^{-k_e t} \quad (4)$$

where c_{s0} is the initial concentration of the PRC in the sorbent before its exposure and k_e is the elimination rate constant of the PRC.

In the second step, the sampling rate is corrected as follows:

$$R_{s(corr)} = \left(\frac{k_{ePRC(field)}}{k_{ePRC(lab)}}\right) \times R_{s(lab)} \quad (5)$$

where $R_{s(corr)}$ is the corrected sampling rate, $k_{ePRC(field)}$ is the elimination constant of the PRC measured in filed, $k_{ePRC(lab)}$ is the elimination constant of PRC measured in the laboratory, and $R_{s(lab)}$ is the laboratory sampling rate.

3.4 Overview of passive sampling devices

Although there are many different types of integrative passive sampler, they all have a barrier between the sampled medium and receiving phase, which defines the selectivity of the sampler and restrict certain classes of analytes (Vrana et al. 2005). An overview on application and limitation of commonly used passive samplers with a potential for use in environmental monitoring programmes are summarized in **Table 1**.

Table 1: Overview of passive sampling devices for organic pollutants

Sampler	Sampler media	Target analytes	Advantages	Drawbacks	Reference
POCIS A	Oasis hydrophilic–lipophilic balance (HLB) sorbent enclosed in a polyethersulphone membrane	Herbicides and pharmaceuticals	High sensitivity, sampler capacity can be adjusted by proper sorbent materials, membrane has low susceptibility to biofouling, and calibration data available for many chemicals	The use of PRCs is limited	Alvarez et al. 2004
POCIS B	Triphasic sorbent admixture (Isolute ENV+ and Ambersorb 1500) enclosed in a polyethersulphone membrane				
SR	Silicone rubber	Hydrophobic organic compounds	Simple construction, low, simple sample processing, and calibration data available for many analyte classes	Lower sampling capacity than SPMDs	Booij et al. 2002
LDPE	Low-density polyethylene				
Chemcatcher	A housing made of inert plastic, containing a disk of solid receiving phase bound in a porous polymer, and a disk of diffusion-modulating membrane	Polar and non-polar organic compounds	Selectivity of the sampler can be adjusted by proper combination of membrane and Empore disks. Calibration data are available for many chemicals		Kingstone et al. 2000
SPMD	Flat tube of LDPE filled with triolein	Hydrophobic semi-volatile organic compounds	Widely used and commercially available, well-established procedures, high sensitivity, and calibration data available for many analyte classes	Complicated sample clean-up, susceptible to biofouling	Huckins et al. 1993
SPME	A fibre coated with a liquid (polymer), a solid (sorbent), or a combination of both	Hydrophobic chemicals, including PAHs, PCBs, organochlorine pesticides	Negligible depletion extraction and a cheap disposable device	Low sensitivity	Heringa and Hermens 2003
PDB	Dialysis membrane or a low-density polyethylene bag filled with distilled water	Polar organic compounds	Relatively cheap and rapid sample recovery	Not suitable for sampling semi-volatile organic compounds	Vroblesky et al. 1997

3.5 Application of passive samplers for pesticides

Passive samplers have been applied to a wide range of micropollutants (e.g., pesticides, pharmaceuticals, industrial chemicals, and hormones) in fresh water systems (Muñoz et al. 2010), cave streams (Fox et al. 2010), coastal aquifer (Metcalfe et al. 2011), groundwater (Dougherty et al. 2010), and wastewater treatment systems (MacLeod and Wong 2010).

For example, silicon rubber (SR) passive sampling was used for the preliminary identification of 47 pesticides and 22 herbicides in fresh water systems in Scotland and United Kingdom (UK) (Emelogu et al. 2013). The results demonstrated the potential of the passive sampler for detection and semi-quantification of a large number of compounds, reflecting the lower limits of detection obtained by this device over conventional water sampling methods.

Although passive sampling methods already serves as a versatile, economic, and robust tool to monitor temporal and spatial concentrations, there are experimental, compound-specific, and environmental factors that can affect the sampling rate (R_s). Thus, published sampling rates should not be treated as definitive numbers.

4. Material and methods

4.1 Materials and chemicals

Methanol (MeOH), acetone (ACE), acetonitrile (ACN), dichloromethane (DCM), and cyclohexane (CHE) purchased from Merck (SupraSolv, Darmstadt, Germany). Ethyl acetate (EtAC), and petroleum ether (Peth) were purchased from Fluka Analytical/Sigma-Aldrich (pesticide residue analysis).

Passive sampler canisters, Spider carriers, and POCIS holders were purchased from Environmental Sampling Technologies (EST), Inc. (St. Joseph, MO, USA). The polyethersulfone (PES) membranes Oasis hydrophilic–lipophilic balance (HLB) sorbent (for POCIS A), and Triphasic sorbent admixture (Isolute ENV+ and Ambersorb 1500) (for POCIS B) were purchased from EST. Empty 6 mL polypropylene SPE tubes with polyethylene (PE) frits were purchased from Supelco. SR sheets (thickness 0.5 mm, 600 mm x 600 mm) were purchased from Altec.

All analytical standards and internal standards were obtained from Teknolab AB (Kungsbacka, Sweden). Two different working standard and internal standard solutions were prepared: (i) for pesticides analyzed by liquid chromatography−tandem mass spectrometry (LC-MS/MS, Agilent G 6410), and (ii) for pesticides analyzed by gas chromatography–mass spectrometry (GC-MS, Agilent 5975C) (for details see Jansson and Kreuger, 2010).

4.2 Extraction and recovery experiments

4.2.1 POCIS

Empty polypropylene SPE tubes (6 mL) with polyethylene (PE) frits were packed with 200 mg of either Oacis HLB bulk sorbent (POCIS A) or Triphasic sorbent admixture (POCIS B). Before extraction, the sorbent was spiked with pesticide standard mixture and internal standard solutions. The extraction method for pesticides analysed by LC-MS/MS and GC-MS was tested separately.

For the pesticides analysed by LC-MS/MS, POCIS A and B cartridges were spiked with a pesticide standard mixture. Different solvents/solvent mixtures were tested to investigate the performance of the extraction method:

- MeOH
- ACN
- MeOH followed by MeOH/EtAc (50/50, v/v)
- MeOH followed by MeOH/DCM (20/80, v/v)
- ACE followed by ACN

For the pesticides analysed by GC-MS, POCIS A and B cartridges were spiked with a pesticide standard mixture. The extraction method was tested by using different solvents/solvent mixtures:

- EtAc
- ACE
- DCM

The extracts were concentrated by gentle nitrogen blow down to 1 mL. The solvent was exchanged to ACN for LC-MS/MS analysis and CHE and ACE (90/10, v/v) for GC-MS analysis.

4.2.2 SR

The SR sheets (600 x 600 mm) were cut into sampler stripes of 2.5 mm x 600 mm and 2.5 mm x 314 mm and were held together using stainless steel connectors to obtain a total sampler stripe size of 2.5 mm x 914 mm. The SRs were pre-cleaned by Soxhlet extraction for 96 hours using EtAc and then dried under gentle nitrogen gas. The extraction was carried out using Soxhlet apparatus with different solvents/solvent mixtures for about 16 hours. The pesticide standard mixtures and internal standard solutions were spiked before extraction. The extraction method for pesticides analysed by LC-MS/MS and GC-MS was tested separately.

For the pesticides analysed by LC-MS/MS, the Soxhlet extraction was carried out using 300 mL MeOH, and 300 mL ACN/MeOH (2/1, v/v), respectively. For the pesticides analysed by GC-MS,

the Soxhlet extraction was carried out using 300 mL CHE/ACE (40/60, v/v) and 300 mL Peth/ACE (50/50, v/v), respectively.

The extracts were concentrated by rotary evaporation followed by gentle nitrogen blowdown to 1 mL. The solvent was exchanged to ACN for LC-MS/MS analysis and CHE and ACE (90/10, v/v) for GC-MS analysis.

Depending on the recovery results, the suitable solvents were selected and applied for the extraction of pesticides in the uptake experiments.

4.3 Uptake experiments

4.3.1 Sampler preparation

Both POCISs and SRs were mounted on stainless steel sample holders. Before deployment, SRs were stored in a closed dark glass container spiked with solution of PRCs (equilibrated for 24 h).

4.3.2 Experimental design

The uptake experiments were conducted in two rectangular glass containers (each about 95 L), one for POCIS A POCIS B, and one for SRs, filled with water from River Fyris. Each tank was connected to an electronic pump for simulating turbulent conditions in water. To prevent algae growth and degradation of pesticides, the sides of each tank were covered in aluminum foil. Each glass container was initially fortified with a pesticide standard mixture.

To determine the sampling rates of the pesticides by the POCISs and SRs, the samplers were successively removed from the tanks in duplicate at time intervals of 5, 11, 20, and 26 days. In addition, blank samples were collected on day 0 and extracted in the same way as the normal samples. The concentrations of the pesticides in each tank were monitored by collecting 100 mL water sample at day 0, 5, 10, 21, and 26. The whole volume of the grab samples was negligible compared to the large volume of the tank (about 95 L).

Prior to extraction, each POCIS sampler was opened above a funnel and the sorbent was washed into the empty polypropylene SPE tubes (10 mL) with a PE frit using 18 MΩ-cm Milli-Q water (Millipore). To remove all traces of water, the cartridges were dried by vacuum. Finally internal standards were added to the cartridges and the pesticides were extracted and analyzed using the same procedure as described in 4.2.1.

Prior to extraction, each SR was dried under a stream of high purity nitrogen followed by addition of internal standards. The pesticides were extracted and analyzed using the same procedure as described in 4.2.2.

5. Results and Discussion

5.1 Recovery tests

The recovery was investigated using different solvents/solvent mixtures (see 4.2). For the pesticides analysed by LC-MS/MS, the highest recoveries were observed using MeOH/DCM (20/80, v/v) for POCIS A and POCIS B, and MeOH for SR passive samplers. For the pesticides analysed by GC-MS, the highest recoveries were observed using EA, ACE, and Peth/ACE (50/50, v/v) for POCIS A, POCIS B, and SR, respectively. Method recovery values for POCIS A, POCIS B, and SR using the optimized solvents/solvent mixtures are given in **Figure 2**. Average recoveries were 105 ± 16%, 91 ± 38%, and 72 ± 35% for POCIS A, POCIS B and SR passive samplers, respectively. In general, highest recoveries were found for POCIS A whereas lower recoveries were found for SR.

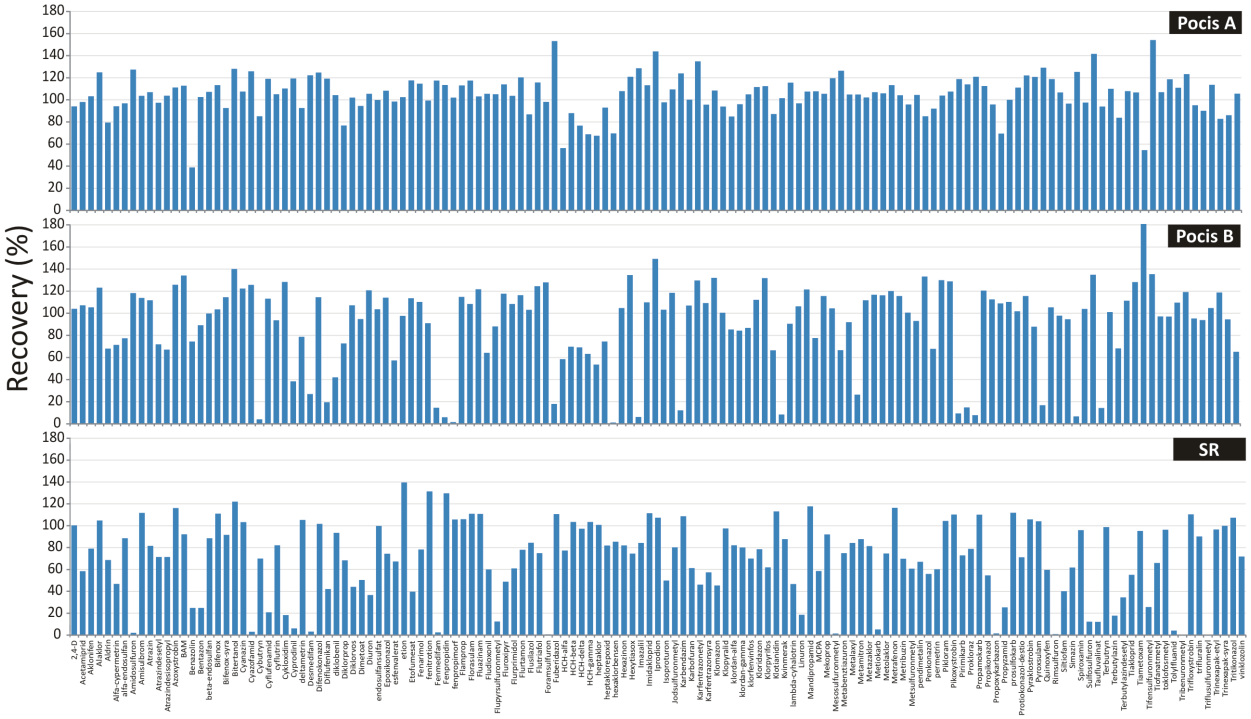

Figure 2. Recovery for individual pesticides using POCIS A (EtAc and MeOH/DCM, 20/80, v/v), POCIS B (ACE and MeOH/DCM, 20:80, v/v), silicone rubber (SR) (PE/Ac, 50/50, v/v and MeOH).

5.2 Uptake study

The uptake curves for individual pesticides after 5, 10, 15 and 21 days were investigated using POCIS A, POCIS B and SR. The uptake curves for selected pesticides are shown in **Figure 3**. In general, the three tested passive samplers were capable to measure almost all investigated target compounds. The not detection of the few pesticides (<5%) is probably caused by their degradation in water. However, these pesticides may not be detected in the regular monitoring programs.

For POCIS A and POCIS B, the investigated pesticides showed a relatively similar uptake behavior. The sequestered amount increased rapidly during the first 5 days and then the curve became curvilinear or reached equilibration. However, while most pesticides reached equilibrium for POCIS A, most pesticides sequestered by POCIS B were still in the curvilinear phase. This indicates that the maximum uptake capacity for POCIS B has not been reached.

For SR, there was a rapid uptake during the first 5 days, and then after 5 days most pesticides reached equilibrium. The sequestered amount for SR was by a factor of 2-10 higher compared to POCIS A and POCIS B.

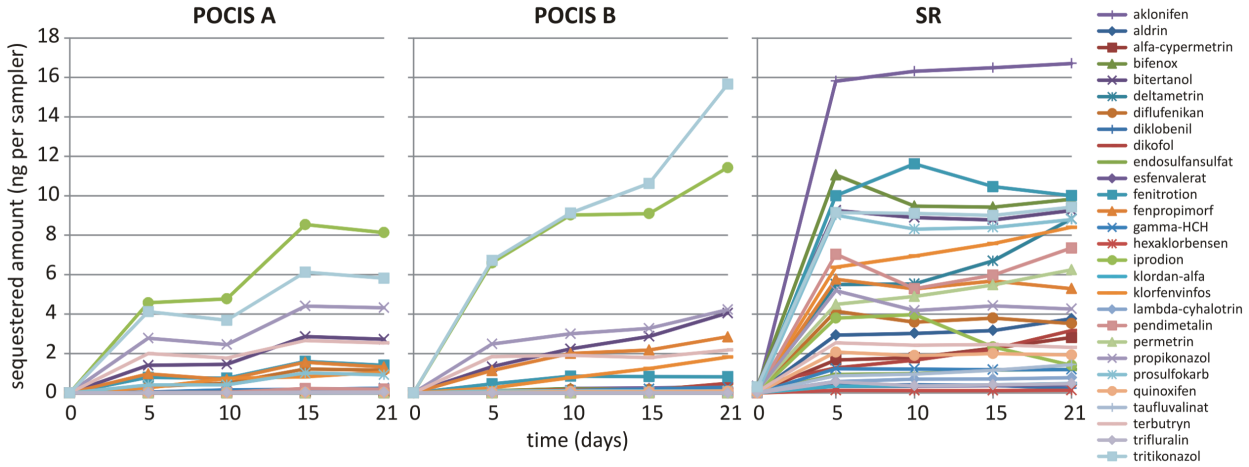

Figure 3. Uptake curves for selected pesticides in POCIS A, POCIS B and SR.

Over 100 individual pesticides were investigated in this study with a variety of different physicochemical properties. The *n*-octanol–water partition coefficient (K_{OW}) has been shown to be a good parameter to predict the suitability of the passive sampler for specific target compounds (Vrana et al. 2005). The log K_{OW} of our target compounds ranged between -2 to 7.6. Our results showed that POCIS A and POCIS B are suitable for pesticides with a log K_{OW} ranging from -2 to 6, whereas SR covers pesticides with a log K_{OW} range of 0 to 7.6 (**Figure 4**).

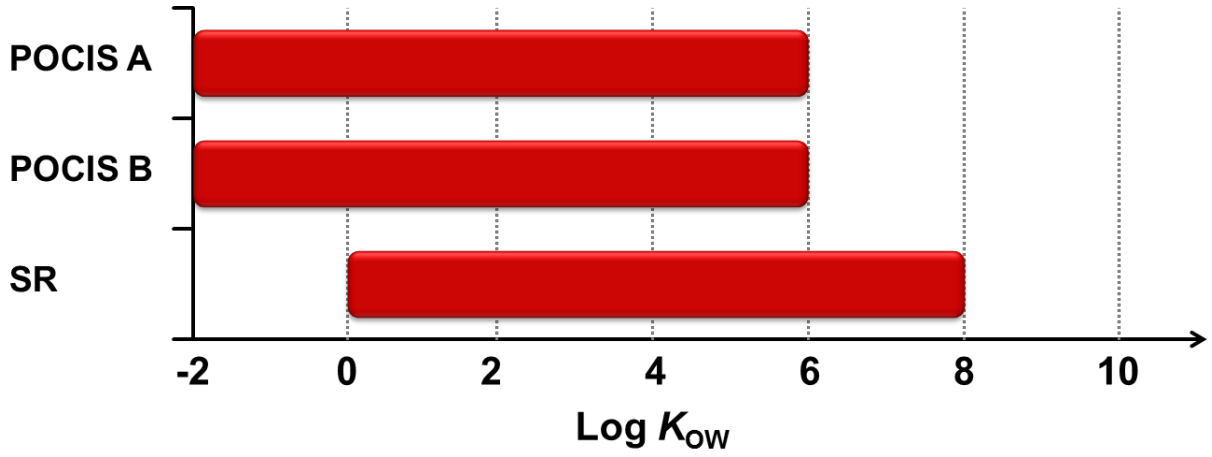

Figure 4. Application of the three tested passive samplers for pesticides depending on the n-octanol–water partition coefficient (K_{OW}).

5.3 Implications

The three different passive sampler types tested in this study are suitable for measuring pesticides in Swedish rivers. In general, the sequestered amount taken up by the SR was higher compared to POCIS A and POCIS B. However, POCIS A and POCIS B showed a better uptake performance for more polar compounds (log K_{OW} < 0), whereas more hydrophobic compounds (log K_{OW} > 6) were better taken up by SR. More work is required to compare the passive sampler results with active sampling in the field.

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