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Characterization of five passive sampling devices for monitoring of pesticides in water

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ABSTRACT

Five different passive sampler devices were characterized under laboratory conditions for measurement of 124 legacy and current used pesticides in water. In addition, passive sampler derived time-weighted average (TWA) concentrations were compared to time-integrated active sampling in the field. Sampling rates (R_S) and passive sampler-water partition coefficients (K_{PW}) were calculated for individual pesticides using silicone rubber (SR), polar organic chemical integrative sampler (POCIS)-A, POCIS-B, Chemcatcher® SDB-RPS and Chemcatcher® C_{18}. The median R_S ($L\,day^{-1}$) decreased as follows: SR (0.86) > POCIS-B (0.22) > POCIS-A (0.18) > Chemcatcher® SDB-RPS (0.05) > Chemcatcher® C_{18} (0.02), while the median $\log K_{PW}$ ($L\,kg^{-1}$) decreased as follows: POCIS-B (4.78) > POCIS-A (4.56) > Chemcatcher® SDB-RPS (3.17) > SR (3.14) > Chemcatcher® C_{18} (2.71). The uptake of the selected compounds depended on their physicochemical properties, i.e. SR showed a better uptake for more hydrophobic compounds (log octanol–water partition coefficient (K_{OW}) > 5.3), whereas POCIS-A, POCIS-B and Chemcatcher® SDB-RPS were more suitable for hydrophilic compounds ($\log K_{OW} < 0.70$). Overall, the comparison between passive sampler and time-integrated active sampler concentrations showed a good agreement and the tested passive samplers were suitable for capturing compounds with a wide range of K_{OW}'s in water.

1. Introduction

The continuous emissions of pesticides to the aquatic environment are posing a risk to wildlife and human health [1]. 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) [2,3]. Another disadvantage of classical monitoring strategies is the low water volume typically used for analysis resulting in relatively high detection limits [4]. Passive sampling has been identified as a promising alternative tool; allowing continuous monitoring of an aquatic system over an extended period of time and determining time-weighted average (TWA) water concentrations of pesticides with minimal infrastructure and low contaminant concentrations [5,6]. Passive sampling is based on an *in situ* deployment of devices/sorbent capable of accumulating contaminants freely dissolved in water.

Passive samplers have been applied for pesticides in fresh water [7,8], cave streams [9], marine waters [10], groundwater [11] and wastewater [12]. Passive samplers have been mainly used for monitoring purposes [13,14], but they are also applicable for toxicology testing [15,16], non-target analysis [17] and serve as an alternative to sediment- and biomonitoring [18]. To predict TWA water concentrations of contaminants, passive samplers need to be calibrated under controlled conditions and known exposure concentrations [14]. The uptake of the contaminant depends on the passive sampler-water partition coefficients (K_{PW}), which in turn depends on the passive sampler material, sampler design, physicochemical properties of the contaminant and environmental conditions (e.g., water turbulence, temperature) [13,14,19]. A range of passive samplers are used for monitoring pesticides in water, however, previous studies seldom characterized different types of passive samplers for a broad range of contaminants simultaneously [13,20].

The aim of this study was to characterize five different types of passive samplers, including silicone rubber (SR), polar organic chemical integrative sampler (POCIS)-A, POCIS-B, Chemcatcher® SDB-RPS and Chemcatcher® C_{18}, for a broad range of legacy and current used pesticides in water. The specific objectives included (i) to optimize and validate an analytical method for 124 individual

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pesticides using five different types of passive samplers, (ii) to assess the sampling rates (R_S) and K_{PW} for the pesticides in a laboratory uptake study, (iii) to correlate the uptake of individual pesticides with their physicochemical properties, and (iv) to compare the pesticide concentrations derived by the passive samplers to time-integrated active sampling in the field.

2. Experimental

2.1. Chemicals and reagents

In total 124 legacy and currently used pesticides were investigated including herbicides, insecticides and fungicides (see Table 1 for a list of pesticides). All analytical grade standards were obtained from Teknolab AB (Kungsbacka, Sweden, for details see Table 1 and ref. [21]). Internal standards (ISs) fenoprop (2,4,5-TP), clothianidin-D_3, ethion and terbuthylazine-D_5 were purchased from Teknolab AB (Kungsbacka, Sweden). For chemical analysis, gradient grade methanol (MeOH), acetonitrile (ACN), formic acid (FA), acetone (ACE), ethyl acetate (EA) and petroleum ether (PE) were purchased from Sigma-Aldrich (Steinheim, Switzerland). 2-Propanol, acetic acid (HAc), cyclohexane (CH), dichloromethane (DCM) and 25% ammonia solution were purchased from Merck (Darmstadt, Germany). Ultrapure water was produced by a Milli-Q Advantage Ultrapure Water purification System (Millipore, Billercia, MA) and filtered through a 0.22 μm Millipak Express membrane. Stock standard solutions were prepared in gradient grade ACN or MeOH, and stored at −18 °C. Fresh working standards and calibration solutions were prepared by appropriate dilution of the stock solutions as required. Prior to use, all laboratory glassware was cleaned with hot water and ethanol, cleaned in a dishwasher, and heated in an oven at 400 °C for 8 h.

2.2. Sampler design and preparation

Five different passive sampling devices, including SR (Altec Products, Bude, England), POCIS-A and POCIS-B (EST, St. Joseph, MO, USA), Chemcatcher® SDB-RPS, and Chemcatcher® C_{18} (Supelco, St Paul, MN, USA), were chosen in this study based on the characteristics of commercially available phases and suitability for a wide range of compounds (Table 2). SR sheets (600 mm × 600 mm) were cut into stripes of 2.5 mm × 600 mm and 2.5 mm × 314 mm and were held together using stainless steel connectors to obtain a total sampler stripe size of 2.5 mm × 914 mm. The SRs were pre-cleaned by Soxhlet extraction for 96 h using EA, dried under gentle nitrogen gas, and mounted on stainless steel spider sample holders (EST, St. Joseph, MO, USA). For POCIS-A, 220 mg of Oasis HLB bulk sorbent and for POCIS-B 220 mg Isolute ENV+ and Ambersorb 1500 sorbent mixture was placed between two polyethersulfone (PES) membranes (EST, St. Joseph, MO, USA). The Chemcatcher® SDB-RPS and Chemcatcher® C_{18} were also placed between two PES membranes. Both POCIS and Chemcatcher® were mounted on stainless steel sample holders (EST, St. Joseph, MO, USA).

2.3. Laboratory uptake experiments

The uptake study was conducted in three rectangular glass containers (each ∼95 L) filled with water from River Fyris, Uppsala, Sweden (DOC = 17 mg L^{-1}). Tank (1) SR (n = 16), tank (2) POCIS-A (n = 16), POCIS-B (n = 16), and tank (3) Chemcatcher® SDB-RPS (n = 16), Chemcatcher® C_{18} (n = 16). All experiments were performed at a constant water temperature (∼20 °C) and under turbulent water conditions (∼10 cm s^{-1}) using two electric pumps attached to the wall on each side. To minimize the effect of photodegradation, the experiments were performed in the dark. Each glass container was initially fortified with a pesticide standard mixture containing 124 pesticides ($c \approx 400$ ng L^{-1} for individual pesticides in the water tank). To determine the sampling rates of the pesticides, the passive samplers were successively removed from the tanks in duplicates at time intervals of 5, 11, 20, and 26 days. In addition, the concentrations of the pesticides in each tank were monitored by collecting 100 mL water samples at day 0, 5, 11, 20, and 26. For quality control, blank samples were exposed to room air for 1 h at day 0 and then stored and treated as real samples. All passive samples were extracted directly after sampling. All extracts as well as the 100 mL water samples collected from the tanks were stored at −18 °C until further analysis.

2.4. Sample extraction

2.4.1. SR

Prior to extraction, the SRs were dried under a stream of high purity nitrogen gas and spiked with an ISs mixture. Soxhlet extraction of the SR was performed separately using different solvent mixtures for pesticides analysed by gas chromatography–mass spectrometry (GC–MS, Agilent 5975C, Agilent Technologies, Palo Alto, CA, USA) and pesticides analysed by liquid chromatography–tandem mass spectrometry (LC–MS/MS, Agilent G 6460, Agilent Technologies, Palo Alto, CA, USA). For pesticides analysed by GC–MS, the solid–liquid extraction was carried out using 300 mL PE/ACE (50/50, v/v) for 19 h. The extracts were concentrated by rotary evaporation followed by gentle nitrogen blow-down to 1 mL and the solvent was exchanged to CH/ACE (90/10, v/v). For pesticides analysed by LC–MS/MS, the extraction was carried out using 300 mL MeOH for 19 h. The extracts were concentrated by rotary evaporation followed by gentle nitrogen blow-down to 1 mL and the solvent was exchanged to ACN.

2.4.2. POCIS

POCIS-A and POCIS-B passive samplers were extracted using solid-phase extraction (SPE) using separate extraction methods for pesticides analysed by GC–MS and LC–MS/MS. In this method, the POCIS sampler was carefully opened and the sorbent was transferred with 18 MΩ-cm Millipore water into a pre-cleaned empty polypropylene SPE cartridge (6 mL) containing two polyethylene (PE) frits (Supelco, St Paul, MN, USA). To remove all traces of water, the sorbent was dried by vacuum. The weight of the empty and packed SPE cartridge was recorded to control the weight of the sorbent material. Prior to elution, the sorbent was spiked with a mixture of ISs. For pesticides analysed by GC–MS, POCIS-A and POCIS-B sorbents were eluted using 5 mL EA. The extracts were then reduced to 1 mL by gentle nitrogen blow-down and the solvent was exchanged to CH/ACE (90/10, v/v). For pesticides analysed by LC–MS/MS, POCIS-A and POCIS-B cartridges were eluted using 1.5 mL MeOH followed by 8 mL DCM/MeOH (80/20, v/v). The extracts were reduced to 1 mL by gentle nitrogen blow-down and the solvent was exchanged to ACN.

2.5. Chemcatcher®

For the extraction of the Chemcatcher® SDB-RPS and Chemcatcher® C_{18}, individual disks were transferred to a glass beaker and dried under nitrogen gas. The disk was spiked with a mixture of ISs and sonicated two times, first with 5 mL of EA for 10 min and then with 3 mL of EA for 10 min. The two extracts were combined, transferred into a glass tube, concentrated to 2 mL by gentle nitrogen blow down, and split into two 1 mL fractions (for GC–MS and LC–MS/MS analysis, respectively). For pesticides analysed by GC–MS analysis, the extracts were concentrated to 0.5 mL by gentle nitrogen blow-down and the solvent was exchanged to CH/ACE (90/10, v/v). For pesticides analysed by LC–MS/MS, the

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]

Substance	CAS-nr.	Type[c]	log K_{OW}	SR			POCIS-A			POCIS-B		Chemcatcher® RPS		Chemcatcher® C_{18}		
				R_S	log K_{PW}	Eq.	R_S	log K_{PW}	Eq.	R_S	log K_{PW}	R_S	log K_{PW}	R_S	log K_{PW}	Eq.
Acetamiprid	135410-20-7	I	0.8	0.02	>1.4[e]	L	0.38	4.6	C	0.77	4.9	0.03	4.1	0.01	2.2	E
Aclonifen[b]	74070-46-5	H	4.4	0.54	3.5	E	0.003	2.7	L	0.02	>3.6[e]	NP	NP	NP	NP	NA
Alachlor[b]	15972-60-8	H	3.1	1.58	3.4	C	0.29	4.7	C	0.46	4.9	0.12	3.5	0.09	2.9	E
Alpha-cypermethrin	67375-30-8	I	5.5	0.72	NC	C	NP	NP	NA	NP	NP	NPW	NPW	NPW	NPW	NA
Amidosulfuron	120923-37-7	H	−1.6	0.0001	NC	E	0.11	3.5	L	0.06	3.3	0.01	1.9	0.001	NC	E
Atrazine[b]	1912-24-9	H	2.7	1.54	2.9	C	0.57	4.8	C	0.97	5.0	0.03	2.8	0.10	2.3	E
Desethylatrazine	6190-65-4	M	1.5	0.08	1.5	C	0.42	4.4	C	0.85	4.8	0.15	4.0	0.02	1.8	E
Desisopropylatrazine	1007-28-9	M	1.2	0.01	0.6	C	0.22	4.0	C	0.62	4.5	0.09	3.6	0.01	1.3	E
Azoxystrobin	131860-33-8	F	2.5	1.58	3.7	C	0.18	4.6	C	0.19	4.7	0.09	>4.0[e]	0.06	>3.6[e]	L
2,6-dichlorobenzamide (BAM)	2008-58-4	M	0.38	0.005	0.3	C	0.17	3.8	C	0.57	4.4	0.03	3.2	0.005	0.7	E
Benazolin	3813-05-06	H	1.3	0.19	>1.8[e]	NA	0.004	1.6	E	0.002	1.9	NP	NP	NP	NP	NA
Bentazone	25057-89-0	H	−0.46	0.04	>1.1[e]	NA	0.02	2.5	E	0.02	2.8	0.004	2.0	NP	NP	NA
Bifenox[b]	42576-02-3	H	3.6	0.95	NC	E	NC	NC	L	NC	NC	NPW	NPW	NPW	NPW	NA
Bifenox acid	53774-07-5	M	4.6	0.07	>1.5[e]	NA	0.15	3.9	C	0.03	3.2	0.001	>2.0[e]	NP	NP	NA
Bitertanol	55179-31-2	F	4.1	1.71	4.4	C	0.14	4.4	L	0.17	4.7	0.10	>4.1[e]	0.05	>3.7[e]	L
Boscalid	188425-85-6	F	3.0	NPW	NPW	NA	NPW	NPW	NA	NPW	NPW	0.01	NC	0.01	>2.4[e]	E
Carbendazim	10605-21-7	F, M	1.5	0.14	>1.8[e]	L	0.22	4.4	C	0.22	4.4	0.01	1.8	0.01	1.9	E
Carbofuran	1563-66-2	I, M	1.8	0.005	0.4	E	0.18	5.1	C	0.29	5.3	0.04	4.3	0.05	3.3	E
Carfentrazone-acid	128621-72-7	M	–[d]	NP	NP	NA	0.10	3.7	C	0.02	3.2	0.001	1.6	NP	NP	NA
Carfentrazone-ethyl	128639-02-1	H	3.4	0.02	NC	E	NC	NC	C	0.06	NC	NPW	NPW	NPW	NPW	NA
Chlorfenvinphos[b]	470-90-6	I	3.8	3.60	4.2	E	0.16	5.1	C	0.25	5.4	0.06	>3.8[e]	0.01	>3.1[e]	C
Chloridazon	1698-60-8	H	1.2	0.01	0.8	C	0.44	4.6	C	0.85	4.8	0.06	3.6	0.01	1.2	E
Chlorpyrifos[b]	2921-88-2	I	4.7	1.21	4.9	E	0.05	4.0	L	0.04	>4.1[e]	NPW	NPW	NC	NC	L
Clomazone	81777-89-1	H	2.5	2.00	3.5	C	0.39	4.8	C	0.62	5.0	0.13	>4.1[e]	0.06	>3.6[e]	L
Clopyralid	1702-17-6	H	−2.6	NP	NP	NA	NP	NP	NA	0.01	1.7	NP	NP	NP	NP	NA
Clothianidin	210880-92-5	I, M	0.91	NP	NP	NA	0.22	4.3	C	0.46	4.6	0.03	3.3	0.004	0.7	E
Cyanazine	21725-46-2	H	2.1	0.11	1.9	C	0.28	4.7	C	0.49	4.9	0.13	>4.0[e]	0.02	2.3	C
Cyazofamid	120116-88-3	F	3.2	0.01	1.4	C	0.07	5.3	C	0.11	5.5	NP	NP	NP	NP	NA
Cybutryne[b]	28159-98-0	B	–[d]	0.29	3.1	E	0.07	>4.4[e]	L	0.14	4.5	0.01	>2.9[e]	0.05	3.2	C
Cyflufenamid	180409-60-3	F	4.7	3.18	NC	E	0.003	>4.2[e]	L	0.12	>4.4[e]	0.02	>3.3[e]	0.01	>2.7[e]	L
Cyfluthrin	68359-37-5	I	6.0	0.70	NC	E	NP	NP	NA	NP	NP	NPW	NPW	NPW	NPW	NA
Cycloxydim	101205-02-1	H	1.4	0.003	0.5	E	0.26	5.1	C	0.23	5.1	NP	NP	NP	NP	NA
Cyprodinil	121552-61-2	F	4.0	0.14	2.8	E	0.16	4.0	L	0.07	>4.3[e]	NP	NP	0.01	>2.5[e]	L
2,4-D	94-75-7	H, M	−0.83	NP	NP	NA	0.03	2.7	E	0.005	2.4	NP	NP	NP	NP	NA
Deltamethrin	52918-63-5	I, M	4.6	0.48	NC	E	NPW	NPW	NA	NPW	NPW	NPW	NPW	NPW	NPW	NA
Difenoconazole	119446-68-3	F	4.2	1.75	5.1	E	0.06	3.9	L	0.01	4.3	0.06	>3.8[e]	0.04	>3.4[e]	L
Diflufenican	83164-33-4	H	4.2	0.29	3.5	E	0.14	4.5	L	0.01	>3.8[e]	0.04	>3.2[e]	0.04	>3.0[e]	L
Dichlorprop	120-36-5	H	2.3	NP	NP	NA	0.03	3.1	E	0.01	2.7	0.0004	1.1	NP	NP	NA
Dichlorvos[b]	62-73-7	I, M	1.9	NP	NP	NA	0.18	NC	E	0.05	NC	NPW	NPW	NPW	NPW	NA
Dimethoate	60-51-5	I, M	0.70	0.02	1.1	C	0.40	4.6	C	0.88	5.0	0.07	3.8	0.01	1.7	E
Diuron[b]	330-54-1	H	2.9	NP	NP	NA	0.18	4.7	C	0.28	4.9	NPW	NPW	NPW	NPW	NA
α-endosulfan[b]	959-98-8	I	3.1	2.34	NC	E	0.50	NC	L	0.59	NC	NPW	NPW	NC	NC	NA
β-endosulfan[b]	33213-65-9	I	3.1	1.86	NC	E	0.08	NC	E	0.21	NC	NPW	NPW	NC	NC	NA
Endosulfan sulfate	1031-07-8	M	3.7	1.24	4.1	E	0.12	4.5	C	0.09	>4.6[e]	0.11	>4.0[e]	0.11	>3.7[e]	L
Epoxiconazole	135319-73-2	F	3.3	2.22	4.2	E	0.17	4.6	C	0.28	4.8	0.06	3.5	0.04	2.7	E
Esfenvalerate	66230-04-4	I	6.2	0.38	3.4	C	NP	NP	NA	NP	NP	NPW	NPW	NPW	NPW	NA
Ethofumesate	26225-79-6	H	2.7	1.98	3.5	C	0.27	4.7	C	0.43	5.0	0.10	>4.0[e]	0.05	>3.5[e]	L
Fenitrothion	122-14-5	I	3.3	0.56	3.7	C	0.39	4.8	L	0.08	4.5	NPW	NPW	NPW	NPW	NA
Fenpropidin	67306-00-7	F	2.6	1.07	NC	E	0.21	5.5	L	0.28	5.8	NP	NP	0.03	3.5	L
Fenpropimorph	67564-91-4	F	4.5	NP	NP	NA	0.07	5.1	E	0.73	>5.7[e]	NP	NP	0.01	NC	L
Florasulam	145701-23-1	H	−1.2	NP	NP	NA	0.01	2.2	E	0.01	2.7	0.05	>3.1[e]	NP	NP	NA
Fluazinam	79622-59-6	F	4.0	NC	NC	NA	NPW	NPW	NA	NPW	NPW	NPW	NPW	NPW	NPW	NA

Table 1 (*Continued*)

Substance	CAS-nr.	Type[c]	log K_{OW}	SR			POCIS-A			POCIS-B		Chemcatcher® RPS		Chemcatcher® C_{18}		
				R_S	log K_{PW}	Eq.	R_S	log K_{PW}	Eq.	R_S	log K_{PW}	R_S	log K_{PW}	R_S	log K_{PW}	Eq.
Fludioxonil	131341-86-1	F	4.1	0.97	3.2	C	0.08	4.4	C	0.11	4.6	0.004	>2.7[e]	0.003	>2.1[e]	E
Flupyrsulfuron-methyl	144740-54-5	H	1.2	NP	NP	NA	0.05	NC	E	0.04	NC	NPW	NPW	NPW	NPW	NA
Fluroxypyr	69377-81-7	H	2.0	NP	NP	NA	0.003	1.4	E	0.002	2.1	NP	NP	NP	NP	NA
Flurprimidol	56425-91-3	GR	3.3	1.64	3.7	C	0.28	4.7	C	0.43	4.9	0.12	>4.0[e]	0.07	>3.5[e]	L
Flurtamone	96525-23-4	H	3.2	1.09	3.1	C	0.27	4.7	C	0.45	4.9	0.09	>3.9[e]	0.01	2.3	E
Flusilazole	85509-19-9	F	3.9	2.50	4.3	E	0.11	4.5	C	0.18	4.7	0.08	>3.9[e]	0.02	2.9	C
Flutriafol	76674-21-0	F	2.3	0.89	2.7	C	0.44	4.7	C	0.61	4.9	0.07	>3.8[e]	0.09	3.1	E
Foramsulfuron	173159-57-4	H	−0.8	0.0001	NC	L	0.12	3.9	C	0.05	3.5	0.01	1.9	NP	NP	NA
Fuberidazole	3878-19-1	F	2.7	0.44	2.6	C	0.17	4.6	C	0.29	4.9	NC	NC	NPW	NPW	NA
α-hexachlorocyclohexane[b]	319-84-6	M	3.8	3.65	3.9	E	0.86	>5.3[e]	L	1.11	>5.4[e]	0.04	>3.8[e]	0.07	>3.4[e]	L
β-hexachlorocyclohexane[b]	319-85-7	M	3.8	0.83	2.8	E	0.50	>4.5[e]	L	0.73	>5.0[e]	0.10	>4.0[e]	0.04	>3.4[e]	L
γ-hexachlorocyclohexane[b]	58-89-9	I	3.8	2.78	3.2	E	0.45	>5.1[e]	L	0.76	>5.2[e]	0.09	>4.1[e]	0.08	>3.8[e]	L
δ-hexachlorocyclohexane[b]	319-86-8	M	3.8	1.43	3.8	E	0.39	>5.0[e]	L	0.57	>5.1[e]	0.02	NC	0.03	NC	L
Hexazinone	51235-04-2	H	1.2	0.04	>1.8[e]	C	0.44	4.6	C	0.82	4.8	0.05	>3.6[e]	0.01	2.0	E
Hexythiazox	78587-05-0	I	2.7	4.07	NC	E	0.46	4.8	L	0.12	5.1	0.01	>3.5[e]	0.02	>3.2[e]	C
Imazalil	35554-44-0	F	2.6	0.28	NC	E	0.01	3.4	L	0.01	3.5	0.01	1.5	0.02	3.1	L
Imidacloprid	138261-41-3	I	0.6	0.002	>0.7[e]	C	0.18	4.4	C	0.38	4.7	0.08	>3.8[e]	0.01	1.3	E
Iodosulfuron-methyl-Na	144550-36-7	H	1.6	NP	NP	NA	0.49	>4.7[e]	C	0.04	3.4	0.03	3.3	NP	NP	NA
Iprodione	36734-19-7	F	3.1	0.42	2.3	E	0.62	4.9	E	0.78	5.1	0.10	NC	0.01	NC	L
Isoproturon[b]	34123-59-6	H	2.5	0.65	2.6	C	0.37	4.8	C	0.63	5.0	0.14	>4.4[e]	0.05	3.1	E
Lambda-cyhalothrin	91465-08-6	I	6.9	0.73	4.0	C	NP	NP	NA	NP	NP	NPW	NPW	NPW	NPW	NA
Linuron	330-55-2	H	3.0	1.54	3.1	C	0.12	4.7	C	0.19	5.0	0.01	3.0	0.01	2.5	E
Mandipropamid	374726-62-2	F	2.1	1.88	4.1	C	0.06	4.2	L	0.03	4.4	0.01	>3.2[e]	0.01	>3.0[e]	L
MCPA	94-74-6	H, M	−0.8	NP	NP	NA	0.01	2.7	E	0.01	2.5	NP	NP	NP	NP	NA
Mecoprop	16484-77-8	H	0.02	NP	NP	NA	0.04	2.9	E	0.01	2.6	0.0004	>1.5[e]	NP	NP	NA
Mesosulfuron-methyl	208465-21-8	H	−0.5	NP	NP	NA	0.06	3.5	C	0.01	3.1	0.01	>2.8[e]	NP	NP	NA
Methabenzthiazuron	18691-97-9	H	2.6	1.64	3.1	C	0.28	4.8	C	0.40	4.9	0.02	2.9	0.03	2.4	E
Metalaxyl	57837-19-1	F	1.7	0.58	2.5	C	0.45	4.7	C	0.74	4.8	0.06	>3.8[e]	0.03	>3.3[e]	C
Metamitron	41394-05-2	H	0.9	0.01	0.8	C	0.36	4.6	C	0.71	4.9	0.05	3.8	0.01	1.5	E
Metazachlor	67129-08-2	H	2.5	1.36	3.0	C	0.50	4.8	C	0.81	4.9	0.11	>4.0[e]	0.05	>3.5[e]	C
Methiocarb	2032-65-7	I	3.2	NC	NC	L	0.08	NC	L	0.10	NC	NPW	NPW	NPW	NPW	NA
Metolachlor	51218-45-2	H	3.1	1.29	3.4	C	0.22	4.6	C	0.34	4.8	0.11	>4.0[e]	0.07	>3.6[e]	C
Metrafenone	220899-03-6	F	4.3	2.44	4.7	E	0.06	4.5	L	0.09	4.6	0.07	>3.8[e]	0.05	>3.2[e]	L
Metribuzin	21087-64-9	H	1.7	0.18	1.9	C	0.57	4.7	C	1.00	5.0	0.11	>4.0[e]	0.06	2.4	E
Metsulfuron-methyl	74223-64-6	H, M	−1.7	0.0001	NC	C	0.07	3.5	C	0.06	3.6	0.004	2.2	0.0004	NC	E
Penconazole	66246-88-6	F	3.7	2.49	4.2	E	0.17	4.6	C	0.29	4.9	0.09	>4.0[e]	0.07	>3.6[e]	C
Pendimethalin	40487-42-1	H	5.2	4.71	NC	E	0.001	>4.3[e]	L	0.04	4.6	0.003	NC	0.01	NC	L
Permethrin	52645-53-1	I	6.1	0.59	NC	E	NP	NP	NA	NP	NP	NPW	NPW	NPW	NPW	NA
Phenmedipham	13684-63-4	H	3.6	NPW	NPW	NA	NPW	NPW	NA	NPW	NPW	NPW	NPW	NPW	NPW	NA
Picloram	1918-02-1	H	−1.9	NPW	NPW	NA	NC	NC	E	NC	NC	NPW	NPW	NPW	NPW	NA
Picoxystrobin	117428-22-5	F	3.6	2.11	4.4	E	0.08	4.6	C	0.07	4.9	0.13	>3.9[e]	0.01	>3.0[e]	L
Pirimicarb	23103-98-2	I	1.7	0.96	2.9	C	0.37	4.7	C	0.62	5.0	0.09	>4.0[e]	0.05	>3.4[e]	C
Prochloraz	67747-09-5	F	3.5	0.74	3.8	E	0.01	3.7	C	0.19	NC	0.04	>3.4[e]	0.03	>3.3[e]	L
Propamocarb	25606-41-1	F	0.8	0.18	>2.6[e]	C	0.17	4.2	C	0.37	4.8	0.03	>2.9[e]	0.003	1.9	E
Propiconazole	60207-90-1	F	3.7	2.27	3.3	E	0.16	4.4	C	0.29	4.6	0.09	>3.9	0.02	>3.2[e]	C
Propoxycarbazone-Na	181274-15-7	H	−1.6	NP	NP	NA	0.05	NC	E	0.01	NC	0.002	NC	NP	NP	NA
Propyzamide	23950-58-5	H	3.3	1.46	3.1	C	0.30	>4.8[e]	C	0.48	5.0	0.12	>4.1[e]	0.03	>3.4[e]	C
Prosulfocarb	52888-80-9	H	4.5	0.52	NC	E	0.13	4.4	L	0.01	3.4	NP	NP	NC	NC	L
Prothioconazole-desthio	120983-64-4	M	–[d]	1.85	3.6	C	0.29	4.7	C	0.44	4.9	0.09	>3.9[e]	0.06	>3.5[e]	L
Pyraclostrobin	175013-18-0	F	4.0	2.02	5.2	E	0.03	3.2	L	0.03	>3.7[e]	0.001	>1.5[e]	0.002	>1.7[e]	NA
Pyroxulam	422556-08-9	H	−1.0	0.0002	NC	E	0.13	3.9	C	0.09	3.8	0.01	2.7	0.001	NC	E
Quinmerac	90717-03-6	H	−0.4	0.001	NC	C	0.004	>1.9[e]	L	0.08	3.1	0.01	2.8	0.004	1.4	E

Quinoxyfen[b]	124495-18-7	F	4.7	0.52	2.8	E	0.004	2.7	L	0.02	3.4	NP	NP	NP	NP	NA
Rimsulfuron	122931-48-0	H	−1.5	NP	NP	NA	NP	NP	NA	0.01	4.9	0.01	NC	NP	NP	NA
Silthiofam	175217-20-6	F	3.7	1.79	3.6	C	0.29	4.7	C	0.48	4.9	0.11	>4.1[e]	0.07	>3.7[e]	C
Simazine[b]	122-34-9	H	2.3	0.23	1.8	C	0.48	4.7	C	0.85	4.9	0.05	>3.7[e]	0.05	2.2	E
Spiroxamine	118134-30-8	F	2.9	2.48	4.8	E	0.28	5.4	L	0.25	5.7	0.002	1.8	0.04	>3.3[e]	C
Sulfosulfuron	141776-32-1	H	−0.77	0.0001	NC	C	0.19	4.2	L	0.04	3.6	0.01	1.9	0.001	NC	E
Tau-fluvalinate	102851-06-9	I	7.0	0.30	NC	NA	NP	NP	NA	NP	NP	NPW	NPW	NPW	NPW	NA
Terbutryn[b]	886-50-0	H, M	3.7	0.32	3.7	E	2.12	4.4	L	0.25	>4.7[e]	0.02	2.5	0.02	>3.0[e]	C
Terbuthylazine	5915-41-3	H	3.2	2.54	3.6	C	0.45	4.8	C	0.72	5.0	0.11	>4.1[e]	0.07	>3.6[e]	C
Desethyl-terbuthylazine	30125-63-4	M	2.3	1.06	2.3	E	0.97	4.7	C	1.62	4.9	0.12	>4.2[e]	0.02	>3.2[e]	C
Thiacloprid	111988-49-9	I	1.3	0.03	>1.7[e]	C	0.39	4.8	C	0.69	5.0	0.12	4.3	0.01	2.7	E
Thiamethoxam	153719-23-4	I	−0.13	0.0003	NC	C	0.25	4.3	C	0.62	4.8	0.06	3.5	0.005	0.7	E
Thifensulfuron-methyl	79277-27-3	H	−1.7	NP	NP	NA	0.02	2.8	E	0.01	2.8	0.002	>2.2[e]	NP	NP	E
Thiophanate-methyl	23564-05-8	F	1.5	NP	NP	NA	NC	NC	E	NC	NC	NP	NP	NP	NP	NA
Tolclofos-methyl	57018-04-9	F	4.6	1.69	4.6	E	1.37	5.1	L	0.01	4.1	NPW	NPW	NPW	NPW	NA
Tolylfluanid	731-27-1	F	3.9	NPW	NPW	NA	NPW	NPW	NA	NPW	NPW	NPW	NPW	NPW	NPW	NA
Tribenuron-methyl	101200-48-0	H	0.8	NP	NP	NA	0.05	3.5	C	0.03	3.4	0.02	3.0	0.002	0.3	E
Trifloxystrobin	141517-21-7	F	4.5	3.23	5.3	E	0.43	>4.8[e]	L	0.98	>5.2[e]	0.01	NC	0.005	NC	NA
Trifluralin[b]	1582-09-8	H	5.3	NC	NC	E	NC	NC	L	NP	NP	NC	NC	NC	NC	NA
Triflusulfuron-methyl	126535-15-7	H	0.96	NP	NP	NA	0.16	4.3	L	0.04	3.8	0.02	3.1	0.002	NC	E
Trinexapac-acid	104273-73-6	M	0.26	NPW	NPW	NA	NPW	NPW	NA	NPW	NPW	NPW	NPW	NPW	NPW	NA
Trinexapac-ethyl	95266-40-3	GR	−0.29	0.0002	NC	L	0.03	3.7	C	0.09	3.6	0.02	2.9	0.002	1.5	E
Triticonazole	131983-72-7	F	3.3	0.99	3.2	C	0.23	4.6	C	0.41	4.8	0.08	>3.9[e]	0.05	>3.5[e]	C

[a] NP = Not accumulated in the passive sampler; NC = not calculable; NPW = not detected in the passive sampler and water; NA = not available; L = linear model; C = curvilinear model; E = equilibrium model.

[b] Priority substances in the EU Water Framework Directive.

[c] B = Biocide, F = fungicide, GR = growth regulator, H = herbicide, I = insecticide, M = metabolite.

[d] Not available.

[e] Pesticide concentration not equilibrated in the passive sampler, values should be handled as estimates.

Table 2
Overview of the five passive sampling devices.

Passive sampler	Characteristics	Surface area (a_p, cm^2)	Sorbent mass (m_p, g)	Volume (V_p, cm^3)
SR	Silicone rubber stripes (25 mm × 914 mm, 0.5 mm thick)	457	15.6	22.9
POCIS-A	220 mg Oasis hydrophilic–lipophilic balance (HLB) sorbent (particle Ø 29.4 μm, surface area ~808 $m^2\ g^{-1}$)[a]	1.78×10^6	0.22	–[c]
POCIS-B	220 mg sorbent mixture of 80% Isolute ENV+ (particle Ø 117 μm, surface area ~1000 $m^2\ g^{-1}$)[a] and 20% dispersion of Ambersorb 1500 (particle Ø 225 μm, surface area ~1200 $m^2\ g^{-1}$)[b] and S-X3 bio-beads	2.82×10^6	0.22	–[c]
Chemcatcher® SDB-RPS	Styrene-divinyl benzene reversed phase polymer (SDB-RPS) Empore™ disk (Ø 47 mm)	35	0.34	1.7
Chemcatcher® C_{18}	C_{18} Empore™ disk (Ø 47 mm)	35	0.58	1.7

[a] Manufacturer–supplied information.
[b] See ref [21].
[c] Not available.

extracts were reduced to 0.5 mL by gentle nitrogen blow-down and the solvent was exchanged to ACN.

2.6. Water samples

Water samples taken from the laboratory uptake experiments were analysed for pesticides using validated methods described elsewhere [21]. For pesticides analysed by GC–MS analysis, water samples were processed using liquid–liquid extraction (LLE) using 20 mL water samples spiked with a mixture of ISs in an Eppendorf tube. For the LLE, 3 mL of DCM was added, vortexed for 3 min, and decanted into a phase separator (Isolute, Biotage, Uppsala, Sweden). After the two phases were separated, the DCM phase was percolated into a glass tube, the extraction process was repeated with 3 mL DCM, and the Eppendorf tube was rinsed with 2 mL DCM. Finally, the extracts were concentrated to 0.5 mL by gentle nitrogen blow-down and the solvent was exchanged to CH/ACE (90/10, v/v). For pesticides analysed by LC–MS/MS, the water samples were analysed using large volume injection, similar to the method described elsewhere [21].

2.7. Instrumental analysis

The instrumental analysis of the CH/ACE extracts was performed using GC–MS using electron ionization (EI) and negative chemical ionization (NCI), respectively. For the GC–MS method using EI, aliquots of 1 μL were injected with splitless injection method on a HP-5MS UI column (30 m, 0.25 mm inner diameter, 0.25 μm film, J&W Scientific, Folsom, CA, USA). For the GC–MS method using CI, aliquots of 3 μL were injected on a HP-5MS UI column (30 m, 0.25 mm inner diameter, 0.25 μm film, J&W Scientific, Folsom, CA, USA).

The instrumental analysis of the ACN extracts was performed using HPLC-MS/MS interfaced with an electrospray ionization source in negative ((−)ESI) and positive-ion mode ((+)ESI). For (+)ESI, 100 μL of the ACN extracts were diluted with 900 μL Millipore water adjusted to pH 5, and for (−)ESI 100 μL of the ACN extracts were diluted with 900 μL solution of 1% FA in Millipore water. The samples were injected using a large volume injection of 500 μL, enriched on an online SPE column (Strata C_{18}-E followed by a Strata X, both 20 mm × 2 mm i.d. and 20–25 μm particle size, Phenomenex, Torrance, CA), and then transferred on an analytical column (Zorbax Eclipse Plus C_{18}, 100 mm × 3 mm, 3.5 μm, Agilent Technologies, Palo Alto, CA, USA) (for details see ref [21]). For the compounds analyzed in positive mode, 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} was used. For the compounds analyzed in negative mode, a binary gradient consisting of ACN/Milli-Q 0.1% HAc and ACN + 0.1% HAc at a flow rate of 0.3 mL min^{-1} was used.

Considering non-normal distribution of our data, tested by a Shapiro–Wilk test, we used 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). The statistical test was performed in *R* version 3.1.0.

2.8. Theory on passive sampling

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 of the chemical will be equal.

The volume of water that has been sampled after a given exposure period is defined as the equivalent water volume (V_{eq}, L) for a passive sampler.

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

where N^t is the accumulated amount of target compounds in the passive sampler after t days of exposure (ng) and c_w is the concentration in the water phase using grab and time integrated active sampling (ng L^{-1}). The sampling rate (R_S, L day^{-1}) is derived from the linear uptake phase of the uptake profile, by taking the slope of V_{eq} versus deployment time. The K_{PW} (L kg^{-1}) for individual pesticides were calculated using Eq. (2).

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

where m_p is the sorbent mass per sampler (ng).

In the linear uptake phase, the sorbent is assumed to act as an infinite sink for contaminants and the desorption rate of the analyte is negligible compared to the uptake rate. Eq. (3) can be used to calculate the TWA concentration of the analyte in water derived by the passive sampler (c_{TWA}, ng L^{-1}).

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

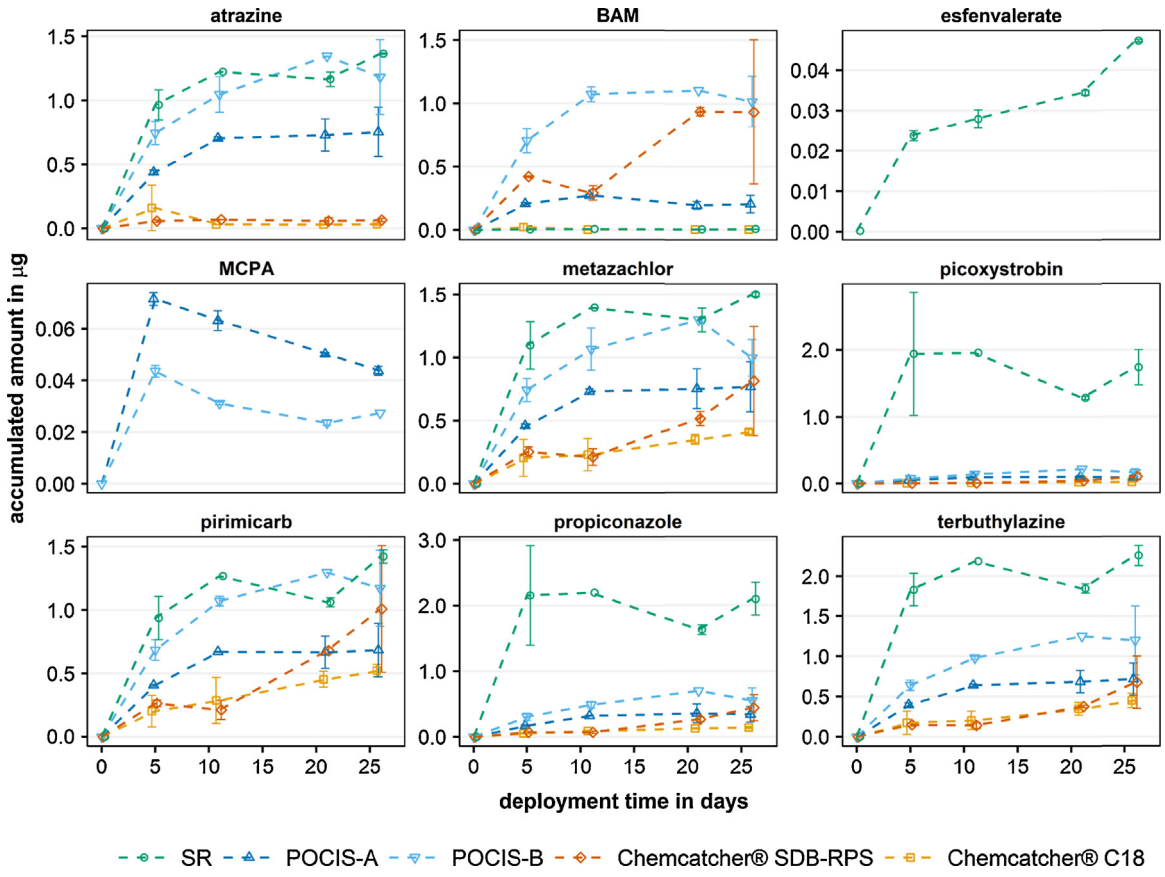

Fig. 1. Uptake profiles of selected pesticides in water (µg absolute) for silicone rubber (SR), polar organic chemical integrative sampler (POCIS)-A, POCIS-B, Chemcatcher® SDB-RPS, and Chemcatcher® C_{18} at time intervals of 0, 5, 11, 20, and 26 days.

where R_S is the sampling rate (L day^{-1}), and t is the deployment time (days).

In the curvilinear phase, Eq. (4) can be used to calculate c_{TWA}.

$$c_{TWA} = \frac{N^t}{K_{PW} m_p (1 - e^{-(R_S/K_{PW} m_p)t})} \quad (4)$$

In the equilibrium phase, where the exposure time is sufficiently long to establish equilibrium between the water and receiving phase, Eq. (4) can be used to calculate c_{TWA}.

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

3. Results and discussion

3.1. Quality assurance and quality control

The limits of detection (LOD), limits of quantification (LOQ), linearity, recovery and repeatability are given in Tables S1–S5 in the Supplementary Information (SI). The linearity of the calibration curves were $r^2 > 0.99$. A few pesticides were detected in the blank samples at low concentration level (Tables S1–S5 in the SI). The LODs were calculated from the blanks (average of blanks + 3 × standard deviation (σ)) or the lowest calibration point if no blank was detected. The average LODs are 8.0 pg absolute injected on column for SR, 1.7 pg absolute for POCIS-A, 1.6 pg absolute for POCIS-B, 3.0 pg absolute for Chemcatcher® SDB-RPS, and 1.6 pg absolute for Chemcatcher® C_{18} (for details see Tables S1–S5 in the SI). Average method recoveries were 68%, 110%, 92%, 89% and 70% for SR, POCIS-A, POCIS-B, Chemcatcher® SDB-RPS and Chemcatcher® C_{18}, respectively and the average standard deviations for individual pesticides were 5%, 10%, 11%, 13% and 14% for SR, POCIS-A, POCIS-B, Chemcatcher® SDB-RPS and Chemcatcher® C_{18}, respectively (Tables S1–S5 in the SI). The average repeatability for individual pesticides ($n = 10$) were 19%, 20%, 16%, 33% and 36% for SR, POCIS-A, POCIS-B, Chemcatcher® SDB-RPS and Chemcatcher® C_{18}, respectively.

3.2. Passive Sampler Sampling Rates and Sampler-Water Partition Coefficients for SR, POCIS-A, POCIS-B, Chemcatcher® SDB-RPS and Chemcatcher® C_{18}

The uptake profiles of individual pesticides over the deployment time are given in Fig. 1 and Figure S1 in the SI. Most pesticides had a short linear uptake curve (5–10 days) and equilibrated after 26 days, i.e. for SR (89 of the 124 target compounds), POCIS-A (97 of 124), POCIS-B (99 of 124), Chemcatcher® SDB-RPS (32 of 124) and Chemcatcher® C_{18} (36 of 124). 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. Eight of the target compounds were neither detected in the water phase nor in the passive sampler (i.e. amisulbrom, desmedipham, heptachlor, heptachlor-epoxide, indoxacarb, phenmedipham, tolylfluanid and trinexapac-acid). This could be due to sorption to the glass wall of the water tank or degradation due to short half-life in water.

The median R_S (L day^{-1}) were 0.86 (SR), 0.22 (POCIS-B), 0.18 (POCIS-A), 0.05 (Chemcatcher® SDB-RPS) and 0.02 (Chemcatcher® C_{18}). The high R_S for SR can be explained by the higher sorbent mass (m_p) of SR ($m_p = 15.6$ g) compared to the other passive samplers ($m_p = 0.22$–0.58 g). The sorbent mass normalized median R_S (L g^{-1} day^{-1}) were 0.06 (SR), 1.00 (POCIS-B), 0.82 (POCIS-A),

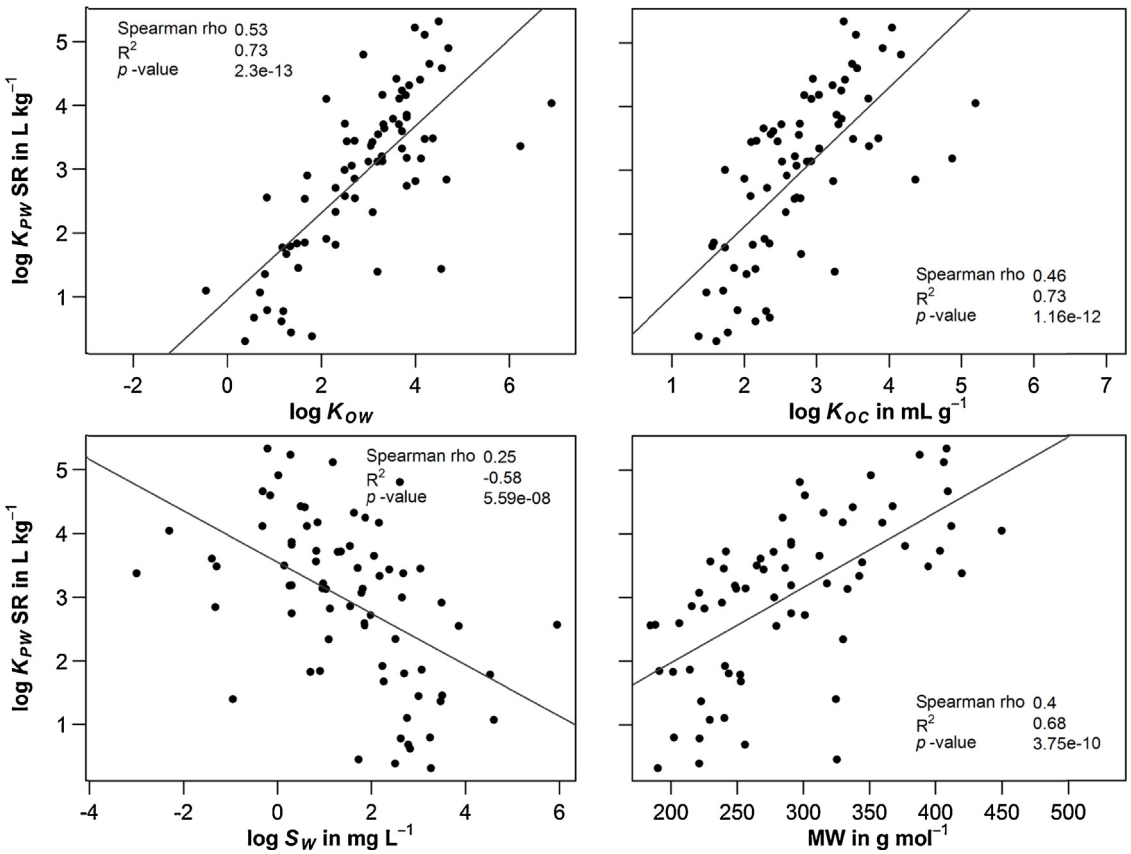

Fig. 2. Regression analysis between sampler-water partition coefficients (K_{PW}) for silicone rubber (SR) and octanol–water partition coefficient (K_{OW}), carbon–water partition coefficient (K_{OC}), water solubility (S_W), and molecular weight (MW).

0.15 (Chemcatcher® SDB-RPS) and 0.03 (Chemcatcher® C_{18}). The median log K_{PW} ($L\,kg^{-1}$) were 4.78 for POCIS-B, 4.56 for POCIS-A, 3.17 for Chemcatcher® SDB-RPS, 3.14 for SR and 2.71 for Chemcatcher® C_{18}. Differences can be explained by different surface areas (a_p) which were higher for POCIS-A and POCIS-B ($a_p = 1.78 \times 10^6\,cm^2$ and $2.82 \times 10^6\,cm^2$, respectively) compared to SR ($a_p = 457\,cm^2$), Chemcatcher® SDB-RPS and Chemcatcher® C_{18} ($a_p = 35\,cm^2$ for both). For POCIS-B, median R_S values for 33 pesticides were higher ($0.48\,L\,day^{-1}$) compared to the value presented by Alvarez et al. (median $R_S = 0.22\,L\,day^{-1}$, $n = 33$) [23]. In contrast, the median R_S for 8 pesticides using POCIS-B was lower ($0.48\,L\,day^{-1}$) compared to the previously reported data ($0.63\,L\,day^{-1}$) by Bartelt-Hunt et al. [24]. For POCIS-A, similar median R_S values were obtained for 7 pesticides in this study ($0.42\,L\,day^{-1}$) compared to Belles et al. using fast stirred exposure ($0.31\,L\,day^{-1}$), whereas the median R_S was lower using slow stirred exposure ($0.15\,L\,day^{-1}$) [25]. Furthermore, similar median R_S values for POCIS-A were found in this study ($0.22\,L\,day^{-1}$) compared to Morin et al. investigating 56 organic chemicals (alkylphenols and phenols, hormones, pesticides, pharmaceuticals, UV filter) using a flow-through calibration system ($0.19\,L\,day^{-1}$) [26], and Lissalde et al. investigating 33 pesticides using a static renewal

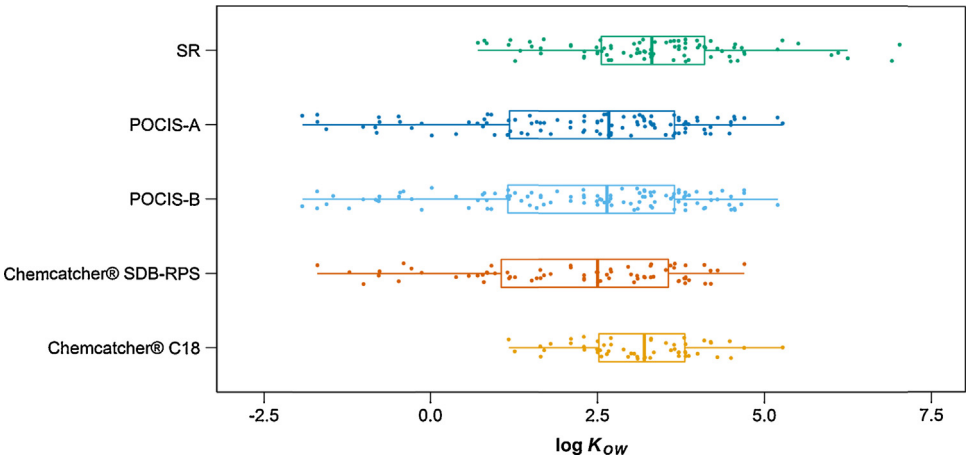

Fig. 3. Box–Whisker–Plots for individual pesticides taken up by silicone rubber (SR) ($n = 86$), polar organic chemical integrative sampler (POCIS)-A ($n = 106$), POCIS-B ($n = 110$), Chemcatcher® SDB-RPS ($n = 65$), and Chemcatcher® C_{18} ($n = 54$) in correlation to their octanol–water partition coefficient (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.

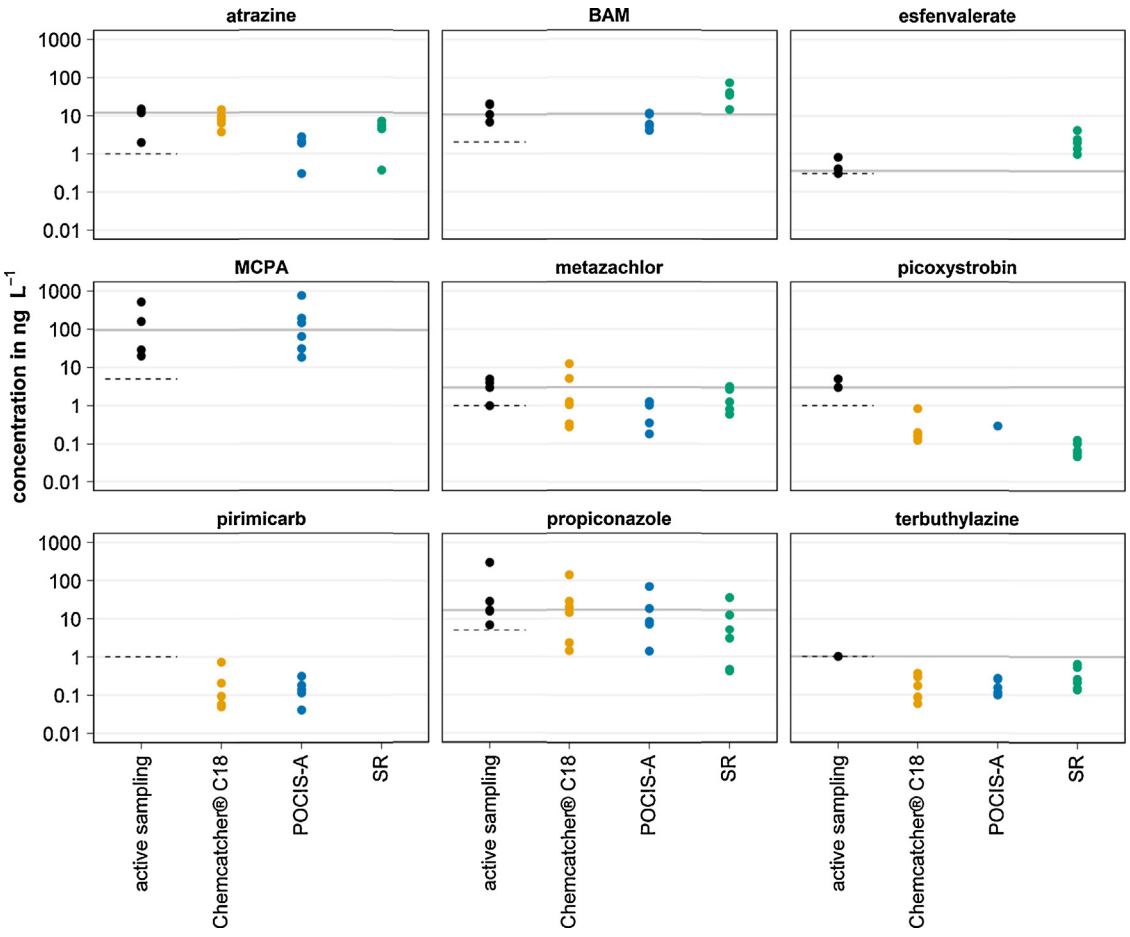

Fig. 4. Concentration levels of selected pesticides in water for active sampling, silicone rubber (SR), polar organic chemical integrative sampler (POCIS)-A, and Chemcatcher® C_{18} deployed for 7 days for 6 sampling periods at Halland in southern part of Sweden in July/August 2013. Note: The dashed line represents limits of detection (LOD) for active sampling and the solid line represents the median concentration for active sampling.

calibration system (0.19 L day^{-1}) [27]. Similar log K_{PW} and R_S values have been reported for Chemcatcher® SDB-RPS and Chemcatcher® C_{18} [28–30]. However, Chemcatcher® SDB-RPS showed a longer kinetic sampling period which might be due to a higher sorbent mass/surface area ratio, which was also observed in a previous study [28,31]. 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 [32].

3.3. The influence of pesticide physicochemical properties on their uptake by passive samplers

The K_{PW} for individual pesticides was correlated with the octanol–water partition coefficient (K_{OW}), carbon–water partition coefficient (K_{OC}), water solubility (S_W) and molecular weight (MW) for each passive sampler type. The log K_{PW} of SR showed a significant positive correlation with log K_{OW}, log K_{OC} and MW (Spearman's rho = 0.53 and 0.46, respectively; $p < 0.0001$, Fig. 2), while a significant negative correlation was observed between the log K_{PW} of SR and log S_W (Spearman's rho = 0.25 and 0.40, respectively, $p < 0.0001$, Fig. 2). A significant positive correlation was also observed between log K_{PW} of Chemcatcher® C_{18} and log K_{OW} (Spearman's rho = 0.48, $p < 0.0001$, Figure S2 in the SI). However, no significant correlation was found for the log K_{PW} of the other tested passive samplers (i.e. POCIS-A, POCIS-B, Chemcatcher® SDB-RPS and Chemcatcher® C_{18}) and the physicochemical properties of the tested pesticides. For the log R_S values, a significant positive correlation was only found between log R_S and log K_{OW} of SR (Spearman's rho = 0.56, $p < 0.0001$, Figure S2 in the SI). In previous studies, a positive linear relationship between R_S values and log K_{OW} has been reported for pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) using POCIS-A [33,34], whereas other studies have reported a curvilinear relationship for pharmaceuticals using POCIS-A [35]. In contrast, no clear trend has been found between R_S values and physicochemical properties for pharmaceuticals and their metabolites using POCIS-A [36] and for EDCs using POCIS-A and POCIS-B [37].

The K_{OW} has been shown to be a good parameter to predict the suitability of the passive sampler for specific target compounds [14,26]. 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 SR (K_{OW} = 0.70–7.0), POCIS A (−1.9 to 5.3), POCIS B (−1.9 to 5.2), Chemcatcher® SDB-RPS (−1.2 to 4.7) and Chemcatcher® C_{18} (1.3–5.3) (Fig. 3). Our results showed that SR 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 Chemcatcher® SDB-RPS (Fig. 3).

3.4. Derived water concentration of pesticides

The performance of SR, POCIS A and Chemcatcher® C_{18} was investigated at the river Halland in an agricultural area in southern Sweden. SR and POCIS A were selected for the field application because they showed the best performance in the laboratory

uptake study and additionally Chemcatcher® C_{18} was selected to cover different passive sampler types. The TWA concentrations for individual pesticides were calculated using Eqs. (3)–(5) depending on if the concentrations accumulated in the passive samplers were in the linear, curvilinear, or equilibrium phase, respectively, after a deployment time of 7 days. Overall, the comparison between passive sampler and time-integrated active sampler concentrations showed a good agreement (Fig. 4). In total, 36 individual pesticides were detected using weekly automatic time-integrated (active) sampling at Halland over a period of six weeks, while 42, 42 and 24 individual pesticides were detected using the passive samplers SR, POCIS-A and Chemcatcher® C_{18}, respectively (Table S6 in the SI). The active sampler detected 4 pesticides which were not detected by the passive samplers (i.e. alpha-cypermethrin, clopyralid, fluazinam and phenmedipham), whereas the passive samplers detected in total 29 pesticides which were not detected by the active sampler. Passive samplers are discussed to be used as a regulatory monitoring tool, for example, to monitor prioritory substances in the European Union Water Framework Directive (WFD) [38]. In this study, out of 18 prioritory substances, 3 were detected using active sampling (i.e. alpha-cypermethrin, atrazine and isoproturon), whereas 6 (i.e. aclonifen, alpha-HCH, atrazine, chlorpyrifos, isoproturon and simazine), 6 (i.e. atrazine, chlorpyrifos, cybutryne, diuron, isoproturon and simazine), and 3 (i.e. atrazine, isoproturon and simazine) were detected using the passive samplers SR, POCIS-A and Chemcatcher® C_{18}, respectively. The application of passive samplers as a monitoring tool for the WFD is restrained due to the fact that the environmental quality standards (EQS) in the WFD is based on the whole water concentration of the chemical (dissolved + particulate phase) whereas passive samplers determine only the freely dissolved concentrations [39]. Differences in the pesticide concentrations obtained from the active sampler and passive samplers can be explained by uncertainties involved in the calculation of the freely dissolved concentration using passive sampling, environmental variables (e.g., water temperature) and general analytical errors that contribute to uncertainties and the different sampling techniques [14,40].

4. Conclusion

The five passive sampler types tested in this study were suitable for measuring a wide range of different pesticides including 18 priority substances based on the EU WFD in the water phase. The comparison of the different passive sampler types showed the highest R_S ($L\,day^{-1}$) for SR (median = 0.86) and lowest for Chemcatcher® SDB-RPS (0.05) and Chemcatcher® C_{18} (0.02) indicating that SR is suitable for short-term monitoring of pesticides. On the other hand, POCIS-B and POCIS-A have the highest sorption capacity with a median $\log K_{PW}$ of 4.78 $L\,kg^{-1}$ and 4.56 $L\,kg^{-1}$. The sorption capacity ($\log K_{PW}$) was compound specific and showed a significant positive correlation with $\log K_{OW}$, $\log K_{OC}$ and MW ($p < 0.0001$) for SR and $\log K_{OW}$ ($p < 0.0001$) for Chemcatcher® C_{18}. In general, results revealed good agreement between sampler and time-integrated active sampler concentrations. However, active sampler monitoring methods have the advantage to provide generally (depending on the extraction method used) a better accuracy of the concentration levels in the water phase, while passive samplers are the ideal tool for screening of pesticides and the purpose of temporal-spatial trend studies. For field application, several factors need to be considered when selecting the appropriate passive sampler type: Firstly, the uptake of pesticides to the passive sampler is compound-specific (e.g., SR shows a better uptake for the more hydrophobic compounds (high K_{OW}), whereas POCIS-A and POCIS-B are better for more hydrophilic compounds (low K_{OW}). Secondly, passive samplers need to be practical and cost-effective for monitoring applications. Finally, the passive sampler should be selected according to the aim of the study, for example, target and non-target screening studies require passive samplers applicable for a wide variety of pesticides, and the passive sampler design might be different for toxicity tests by passive dosing.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chroma.2015.05.044

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