Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supporting Information for:

Characterisation and comparison of the uptake of ionizable and polar pesticides, pharmaceuticals and personal care products by aquatic passive samplers

Sarit L. Kaserzon[a] *, Darryl W. Hawker[b], Karen Kennedy[a], Michael Bartkow[c], Steve Carter[d], Kees Booij[e] and Jochen F. Mueller[a]

[a]*The University of Queensland, The National Research Centre for Environmental Toxicology (Entox), 39 Kessels Rd., Coopers Plains QLD 4108, Australia*

[b]*Griffith University, School of Environment, Nathan QLD 4111, Australia*

[c]*SEQWater, PO Box 16146, City East QLD 4002, Australia*

[d]*Queensland Health Forensic and Scientific Services, Coopers Plains QLD 4108, Australia*

[e]*NIOZ Royal Netherlands Institute for Sea Research, P.O. Box 59, 1790 AB Texel, The Netherlands*

* Corresponding Author. Tel.: +61 (0)7 32749060. Fax: +61 (0)7 32749003, E-mail address: k.sarit@uq.edu.au

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Text S1. HPLC/tandem mass spectrometry analysis details for pesticides and PPCPs.

Each sample extract was analysed separately in both positive and negative ion multiple reaction monitoring mode (MRM). Separation was achieved using a 3 μm 150 × 2 mm Luna C_{18} (2) column (Phenomenex, Torrance, CA) run at 45 ^{o}C, and a flow rate of 0.35 mL min^{-1} with a linear gradient (A = 1% acetonitrile/ 99% HPLC grade water, B = 95% acetonitrile/ 5% HPLC grade water both containing 0.1% formic acid). The linear gradient (%B) for positive ion monitoring mode was 0 min 8%, 3.5 min 35%, 11 min 100%, 14 min 100%, 14.1 min, 8% and 17.4 min 8%. The linear gradient (%B) for negative ion monitoring mode was 0 min 15%, 10.3 min 100%, 13.3 min 100%, 13.4 min 15% and 16.4 min 15%). Analyte concentrations were determined using the internal standard method and a four-point calibration using standard concentrations from 5 to 100 μg L^{-1}. Compound identification was based on comparing retention times and transition intensity ratios between the sample and an appropriate standard from the same run. Compound identity was confirmed if the two transitions were present, retention time was within 0.15 minutes of the standard and the relative intensity of the confirmation transition was within 30% of the expected value.

Text S2. QA/QC

Replicate grab samples were collected on the first day (t = 0; n = 6) and on days 1, 3, 10, 17 and 26 (n = 2) of exposure (Table S1). The t = 0 grab samples were stored (4 °C). Grab samples were processed in five batches. Each batch contained at least one duplicate (non-zero exposure time) and one of the t = 0 replicates. The coefficient of variation in the analysis of the t = 0 replicates was ≤ 30 % with the exception of Triclosan at 37% (Table S3). Controls (80 mL of ultra pure water) were processed alongside grab samples (n = 4) (Table S2). Tap water used to fill the tank system was also analysed for background levels of target POCs (n = 1).

Fabrication controls (i.e. non-exposed) POCIS and Chemcatchers^{TM} (*n* = 2 for each sampler configuration) were employed alongside the exposed samplers during the preparation, deployment, extraction and analysis of these samplers (Table S4).

Relatively low concentrations (0.1 – 1.2 ng L^{-1}) of caffeine, DEET, triclosan, ametryn and prometryn were detected in two or more water blanks (total n = 4). No chemicals were detected in the tap water used for the calibration system. Caffeine (≤ 20 ng $sampler^{-1}$) and DEET (≤ 4 ng $sampler^{-1}$) were also detected in all passive sampler blanks (n = 2). Triclosan was detected in all Chemcatcher^{TM} blanks (≤ 3 ng $sampler^{-1}$), but not in modified POCIS. Ametryn, dicamba, flumeturon, picloram, prometryn and terbutryn were all detected in only one type of passive sampler (n = 1) with levels of ≤ 3 ng $sampler^{-1}$. No blank subtraction was performed on data from exposed samplers.

Table S1. Mean analyte concentration in water (ng L^{-1}), S.D and normalised difference (%ND) from duplicate grab samples collected on days 1, 3, 10, 17 and 26 during the calibration study.

	Day 1			Day 3			Day 10			Day 17			Day 26		
	Average	*S.D*	ND%	*Average*	*S.D*	ND%	*Average*	*S.D*	ND%	*Average*	*S.D*	ND%	*Average*	*S.D*	ND%
Caffeine	355	49	20	280	14	7	320	14	6	290	57	28	250	28	16
Codein															
Carbamazepine	275	7	4	255	7	4	300	14	7	345	35	14	320	14	6
Dapsone	325	7	3	260	28	15	200	28	20	240	14	8	175	7	6
DEET	270	57	30	205	49	34	300	0	0	275	92	47	270	14	7
Hydrochlorothiazide	325	7	3	300	14	7	285	49	25	225	64	40	215	7	5
Triclosan	90	14	22	70	28	57	80	0	0	120	57	67	185	7	5
24 D	235	7	4	210	57	38	185	106	81	225	106	67	315	35	16
Ametryn	290	14	7	235	21	13	305	7	3	325	7	3	190	0	0
Bromacil	330	14	6	265	21	11	330	0	0	360	0	0	305	21	10
Dicamba	315	35	16	250	0	0	275	7	4	280	28	14	250	14	8
Diuron	360	28	11	255	21	12	330	14	6	370	14	5	285	7	4
Fluometuron	320	14	6	230	0	0	310	14	6	340	14	6	280	28	14
Haloxyfop	315	21	10	255	7	4	275	106	55	320	57	25	345	35	14
Picloram	220	14	9	185	21	16	205	49	34	195	49	36	215	7	5
Prometryn	290	14	7	205	35	24	300	28	13	305	35	16	190	14	11
Tebuthiuron	305	7	3	235	21	13	295	7	3	320	0	0	220	28	18
Terbutryn	245	7	4	200	28	20	270	14	7	280	42	21	180	14	11
Triclopyr	230	14	9	185	78	59	175	78	63	230	57	35	270	14	7

Table S2. Concentrations of chemicals (ng L^{-1}) in blank grab samples (*n* = 4).

	Average	*S.D*
Caffeine *	1	0
DEET	1.2	1
Triclosan	0.9	0.5
Ametryn *	0.1	0
Prometryn *	0.2	0

* *n* = 2

Table S3. Concentration of analytes (ng L^{-1}) in *t*=0 grab samples (*n*=6). Duplicate *t*=0 samples were extracted and analysed along with the first sample run. Thereafter, at least one one *t*=0 sample was extracted and analysed with each subsequent run.

Analyte	Concentrations in replicate (t=0) grab samples								
	t=0 (1)	***t=0 (2)***	***t=0 (3)***	***t=0 (4)***	***t=0 (5)***	***t=0 (6)***	***Average***	***S.D***	***%CV***
Caffeine	320	220	280	260	300	260	273	35	13
Codein									
Carbamazepine	300	270	290	290	350	350	308	34	11
Dapsone	250	300	270	310	190	120	240	73	30
DEET	220	250	190	220	300	300	247	45	18
Hydrochlorothiazide	370	330	280	280	290	230	297	48	16
Triclosan	70	70	90	140	130	170	112	41	37
2,4-D	190	190	160	190	180	190	183	12	7
Ametryn	210	250	250	300	370	220	267	60	22
Bromacil	250	290	270	380	410	340	323	64	20
Dicamba	330	300	260	260	310	240	283	35	12
Diuron	250	280	260	400	390	300	313	66	21
Fluometuron	240	260	230	330	390	290	290	61	21
Haloxyfop	220	210	250	320	270	130	233	64	27
Picloram	200	190	190	190	210	170	192	13	7
Prometryn	200	240	210	280	360	210	250	61	25
Tebuthiuron	210	230	230	300	360	260	265	56	21
Terbutryn	190	220	200	260	320	200	232	50	22
Triclopyr	140	170	170	230	280	160	192	53	27

Table S4. Amount of chemicals detected in passive sampler fabrication blanks (ng Sampler^{-1}) (*n*=2). Where no standard deviation is provided, levels were detected in only one blank.

	Chemcatcher's™						POCIS	
	SDB-RPS (0.2 µm pore PES membrane)		SDB-RPS (0.45 µm pore PES membrane)		SDB-XC (0.45 µm pore PES membrane)		0.45 µm pore PES membrane	
	Average	*S.D*	*Average*	*S.D*	*Average*	*S.D*	*Average*	*S.D*
Caffeine	4	0.7	16	17	7	2	20	3
DEET	1	0.1	4	0.9	1	0.1	2	0.2
Triclosan	3		2	0.7	2			
Ametryn					1			
Dicamba							2	0.2
Fluometuron	1							
Picloram					3			
Prometryn					1			
Terbutryn					1			

Table S5. Sampling rates normalised to surface area (R_s/A) published in other studies for polar contaminants by POCIS and Chemcatchers™.

Compound	POCIS (0.45 µm PES)		Chemcatcher (SDB-RPS) (0.1 or 0.2 µm PES)		Chemcatcher (SDB-XC) (0.1 or 0.2 µm PES)	
	Literature R_s /A (L dm^{-2} d^{-1})[a]	Reference	Literature R_s /A (L dm^{-2} d^{-1})[b]	Reference	Literature R_s /A (L dm^{-2} d^{-1})[d]	Reference
2,4-D	0.224	Alvarez et al. (2007)			0.289[e]	Tran et al. (2007)
Haloxyfop						
Triclopyr					1.201[e]	Tran et al. (2007)
Hydrochlorothiazide	0.116	MacLeod et al. (2007)				
Ametryn			0.881	Shaw et al. (2010)		
Bromacil						
Diuron	0.109 - 0.630	Aguilar-Martínez et al. (2009), Alvarez et al. (2004), Alvarez et al. (2007), Lissalde et al. (2011), Mazzella et al. (2007), Vermeirssen et al. (2012)	0.050 - 1.006	Shaw et al. (2009; 2010), Vermeirssen et al. (2009), Vermeirssen et al. (2012), Stephens et al. (2009)	0.157[e], 3.585	Tran et al. (2007), Vermeirssen et al. (2009)
Fluometuron			8.301[c]	Stephens et al. (2005)		
Prometryn	0.397	Thomatou et al. (2011)	0.057 - 0.792	O'Brien et al. (2011)		
Tebuthiuron			0.692	Shaw et al. (2010)		
Terbutryn	0.344 - 0.692	Aguilar-Martínez et al. (2009), Vermeirssen et al. (2012)	0.692, 0.509	Vermeirssen et al. (2009), Vermeirssen et al. (2012)	4.717	Vermeirssen et al. (2009)
Caffeine	0.107 - 0.659	Bartelt-Hunt et al. (2011), Bartelt-Hunt et al. (2009), Li et al. (2010), Vermeirssen et al. (2012)	0.245	Vermeirssen et al. (2012)		
Carbamazepine	0.487 - 1.22	Bartelt-Hunt et al. (2011), Li et al. (2010), MacLeod et al. (2007), Morin et al. (2012), Vermeirssen et al. (2012)	0.616, 1.572	Vermeirssen et al. (2012), Vermeirssen et al. (2008)		
Dapsone						
DEET	0.463 - 0.585	Bartelt-Hunt et al. (2011), Bartelt-Hunt et al. (2009)				
Codeine	0.718	MacLeod et al. (2007)				
Dicamba						
Picloram						
Triclosan	2.45 - 4.70	Li et al. (2010), MacLeod et al. (2007)				

[a] Literature values of R_s/A refer to standard POCIS configurations containing a surface area of either 41 or 45.8 cm^2 and a 0.1 µm pore size PES membrane. Values are for turbulent or flow conditions (> 0.03 m s^{-1}).

[b] Literature values of R_s/A refer to Chemcatcher configurations containing SDB-RPS Empore™ disks with a surface area (where stated) of 15.9 cm^2 and either a 0.1 or 0.2 µm pore PES membrane. Values are for turbulent or flow conditions (> 0.12 m s^{-1}).

[c] R_s/A determined with naked empore disks (no membrane).

[d] Literature values of R_s/A refer to Chemcatcher configurations containing SDB-XC Empore™ disks with a surface area (where stated) of 15.8 cm^2. Values are for naked (without a rate limiting membrane) samplers deployed under flow conditions (> 0.12 m s^{-1}).

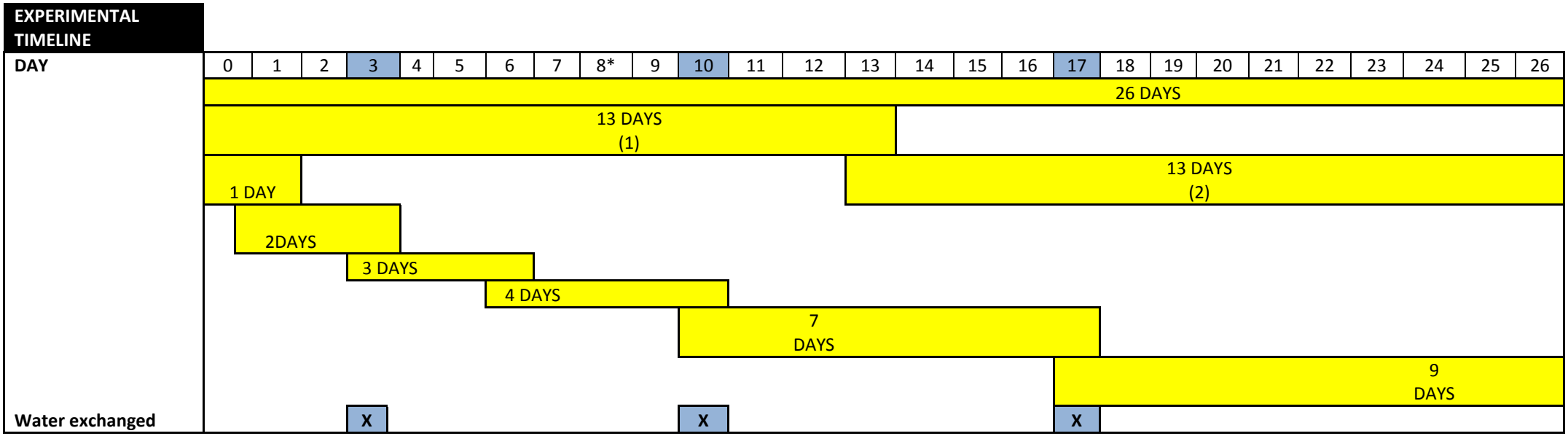
[e] Values are for samplers deployed under low / stagnant flow conditions (≤ 0.004 m s^{-1}) and containing a 0.2 µm pore size PES membrane.

Table S6. The logarithm of PES membrane-water sorption coefficients (log K_{mw}) for POCIS and Chemcatchers™ determined from the average from samplers deployed for 1,7,13 and 26 days, and literature log K_{mw} values for Chemcatcher™ (SDB-RPS).

	Chemcatcher™ (SDB-RPS)		Chemcatcher™ (SDB-XC)	Modified POCIS	Chemcatcher™ (SDB-RPS)
Membrane pore size (µm)	**0.2**	**0.45**	**0.45**	**0.45**	**0.1**
log K $_{mw}$					**(Vermeirssen et al., 2012)**
Pesticides					
2,4-D	3.60	3.61	3.51	3.83	
Ametryn					
Bromacil	2.43	2.16	2.45	2.99	
Dicamba					
Diuron	4.10	3.86	4.13	3.96	4.61
Fluometuron	3.57	3.34	3.65	3.66	
Haloxyfop	3.22	3.18	3.40	3.50	
Picloram	2.98	2.78	2.83	3.13	
Prometryn					
Tebuthiuron	2.39	2.14	2.38	2.99	
Terbutryn					3.48
Triclopyr	3.59	3.48	3.63	3.60	
PPCPs					
Caffeine	2.11[a]		2.29	2.83	2.09
Carbamazepine	2.43	2.24	2.42	3.18	2.47
Codeine					
Dapsone	3.17	2.97	3.23	3.20	
DEET	2.82	2.62	3.03	3.22	
Hydrochlorothiazide	1.87	1.63[a]	2.13	2.43	
Triclosan	4.61	4.48	4.50	4.30	

[a] K_{mw} derived from n =3

Where data are missing - there were insufficient data points to establish K_{mw}

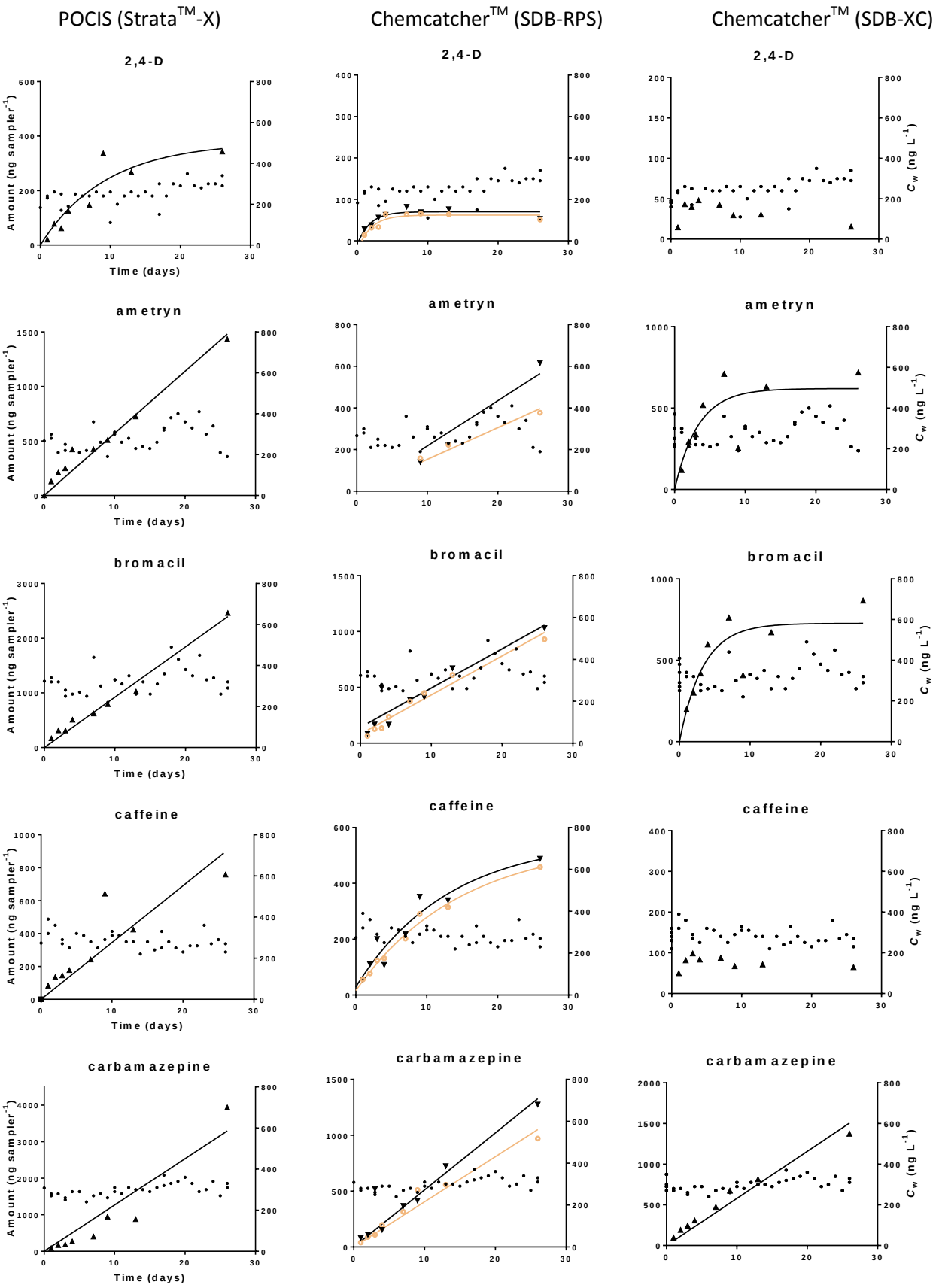


*** Codeine spiked from day 8**

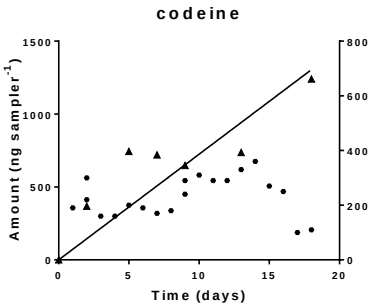
Fig. S1. Experimental timeline showing the deployment periods of passive samplers over 26 d in a 1400 L stainless steel water tank. Days in which the water was exchanged are marked with X.

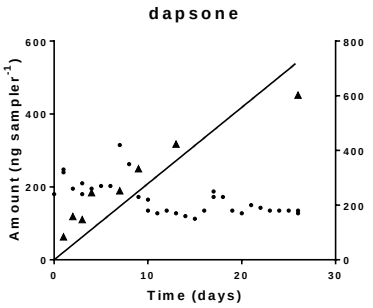
Fig S2. Photograph showing the position of Chemcatcher™ samplers (left) and a POCIS deployment cage (right) in the calibration water tank.

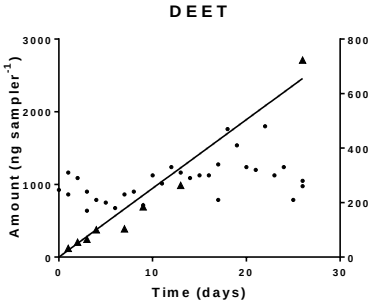
Fig. S3. Accumulation profiles for target chemicals in POCIS and Chemcatchers™ (triangles and circles) and concentrations in water (dots). For Chemcatcher™ (SDB-RPS) pink circles and black triangles represent samplers with 0.2 µm and 0.45 µm PES membranes, respectivley.

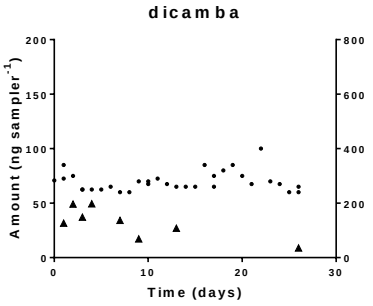


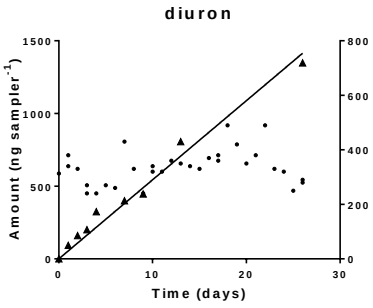
POCIS (Strata™-X)

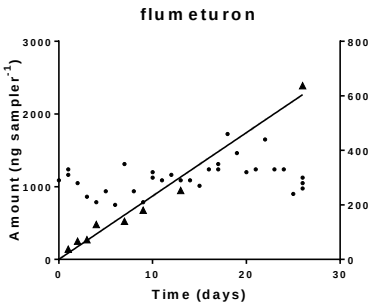




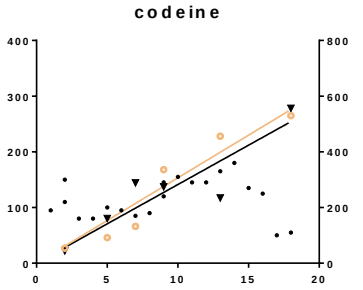


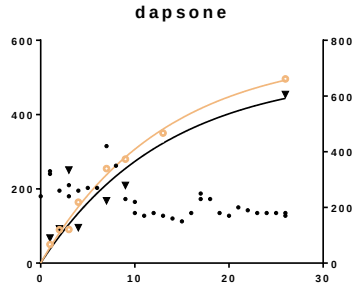


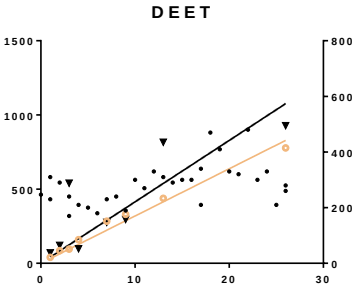


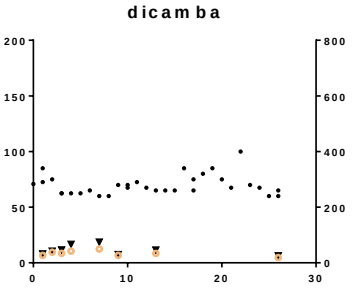


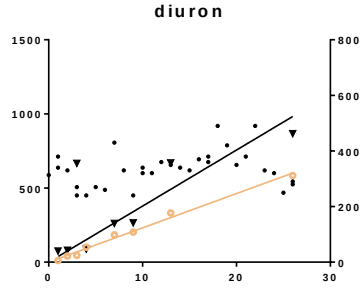
Chemcatcher™ (SDB-RPS)

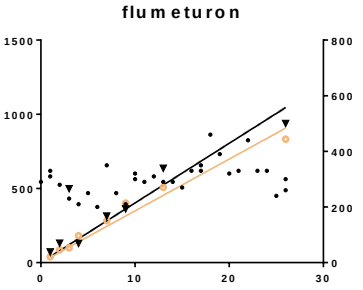




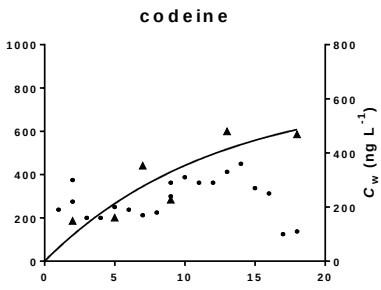


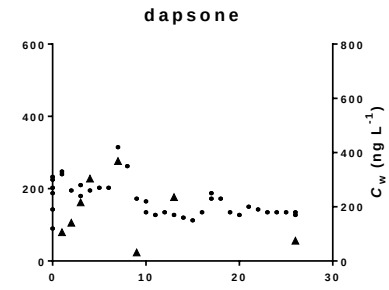


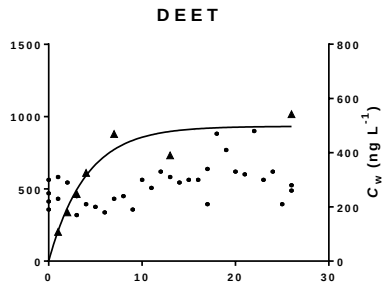


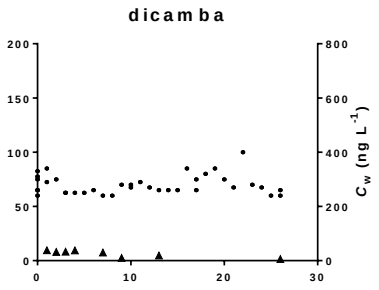


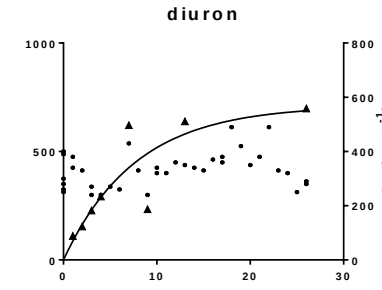
Chemcatcher™ (SDB-XC)

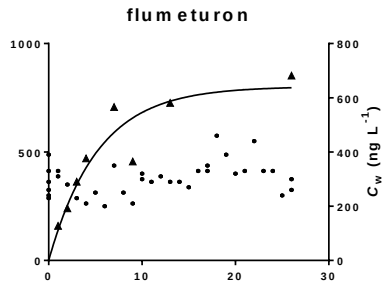




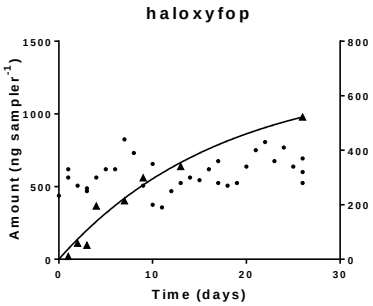


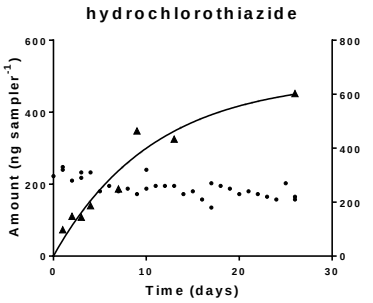


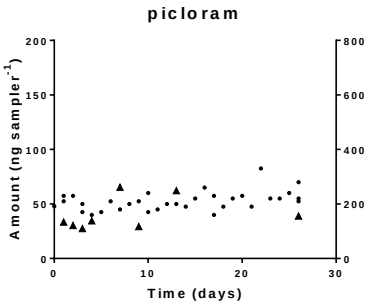


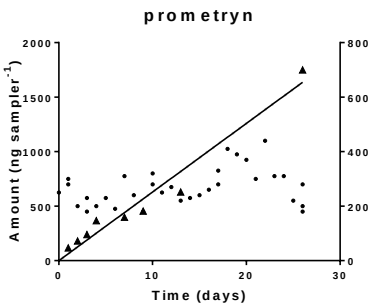


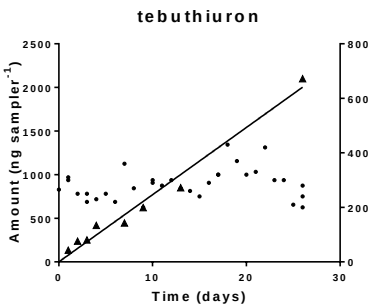
POCIS (Strata™-X)



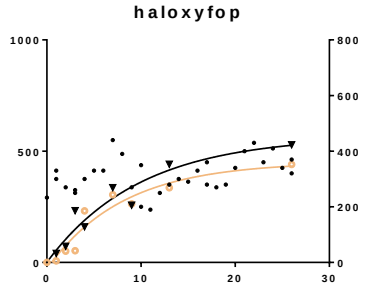


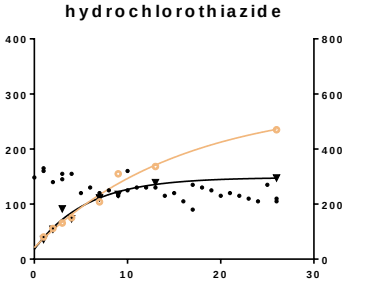


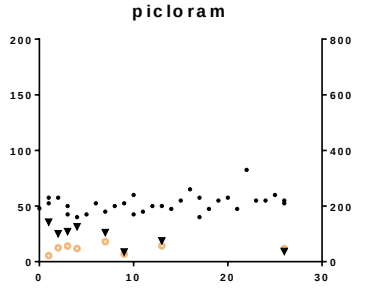


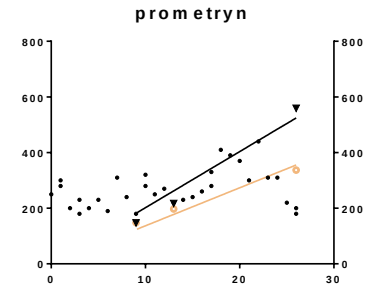


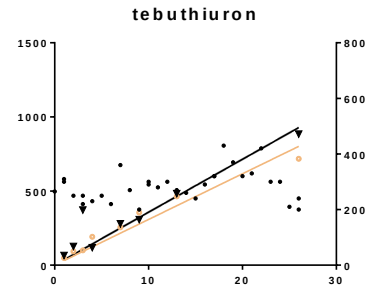
Chemcatcher™ (SDB-RPS)



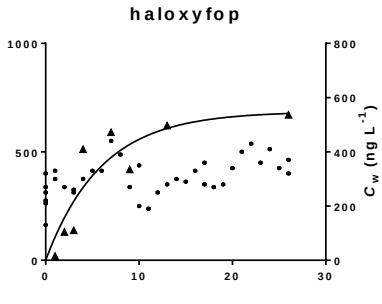


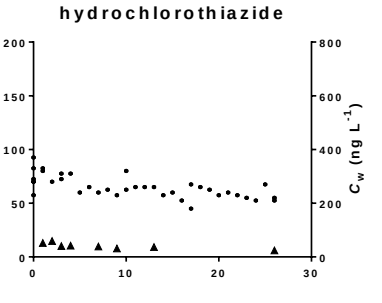


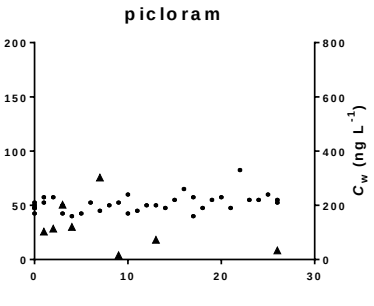


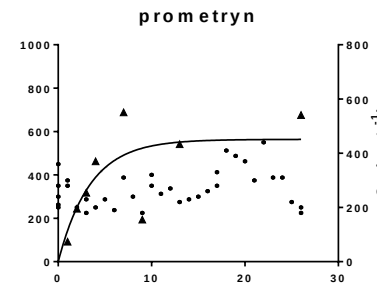


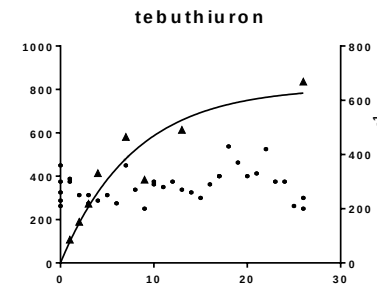
Chemcatcher™ (SDB-XC)



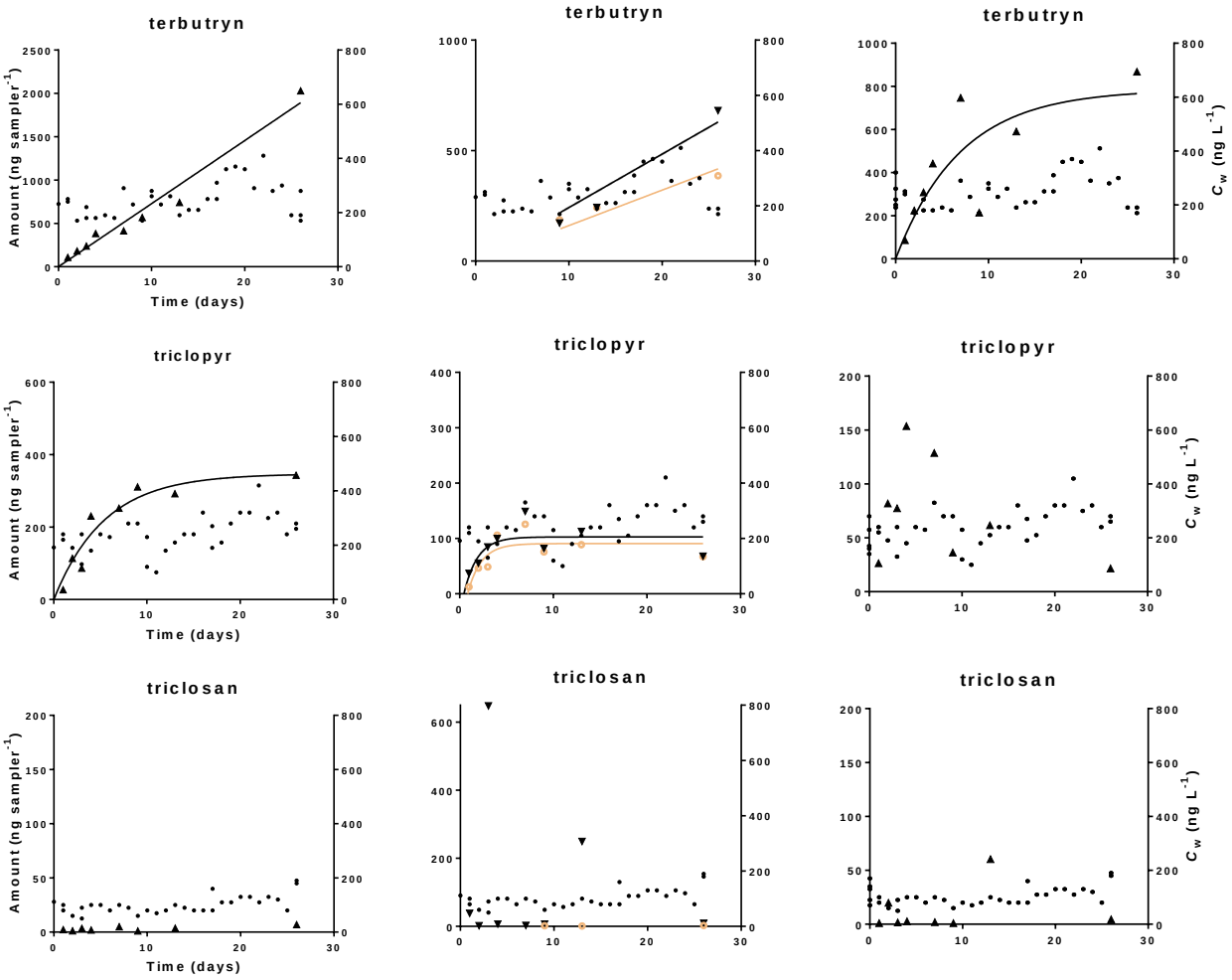








POCIS (Strata^{TM}-X) Chemcatcher^{TM} (SDB-RPS) Chemcatcher^{TM} (SDB-XC)



*Codeine was spiked in the calibration tank system from day 8. Therefore uptake profile was established from deployments over 2, 5, 7, 9, 13 and 18 days (*n*=6).

* Uptake profiles for ametryn, prometryn and terbutryn with Chemcatchers^{TM} (SDB-RPS and SDB-XC) were determined from *n*=3 (i.e. days 10, 13 and 26).

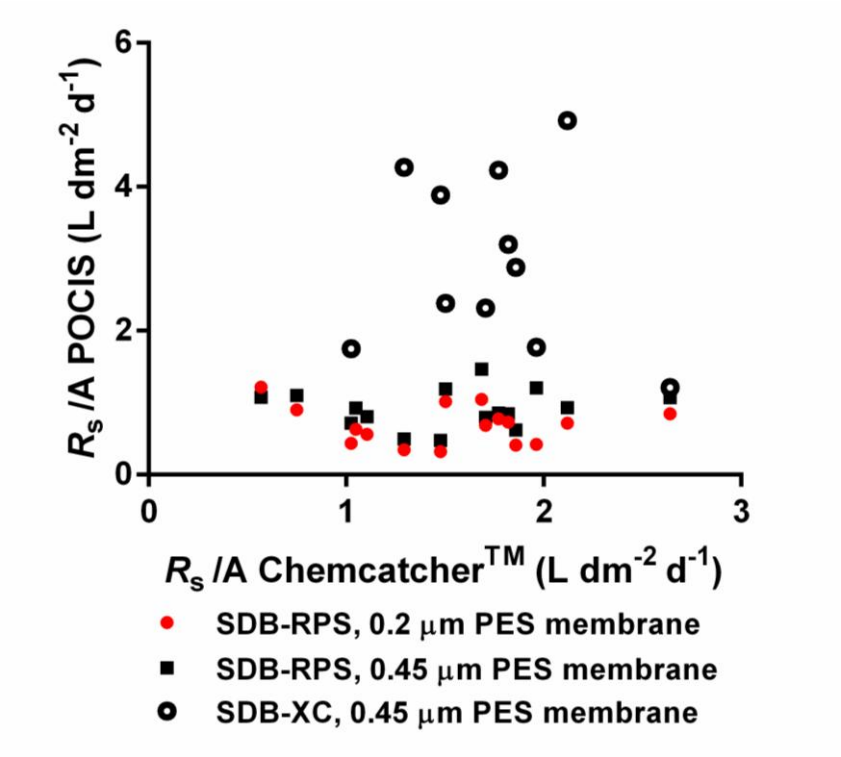


Fig. S4. Sampling rates normalized on surface area (R_s/A; L dm^{-2} d^{-1}) for target chemicals with POCIS vs. Chemcatchers^{TM}, showing no correlation.

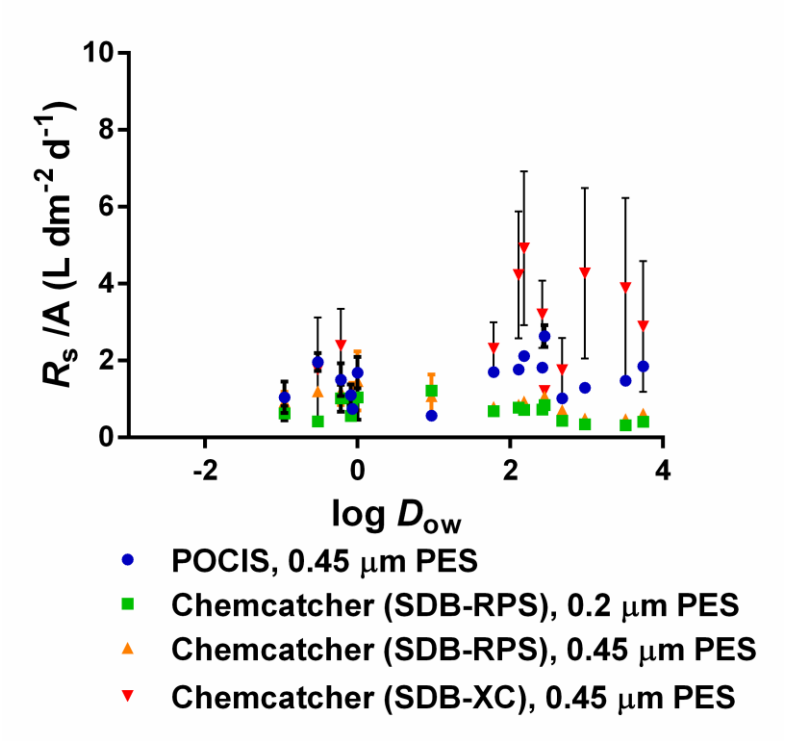


Fig. S5. Sampling rates normalised on surface area (R_s/A; L dm^{-2} d^{-1}) vs. log D_{ow} for target chemicals with POCIS and Chemcatchers™.

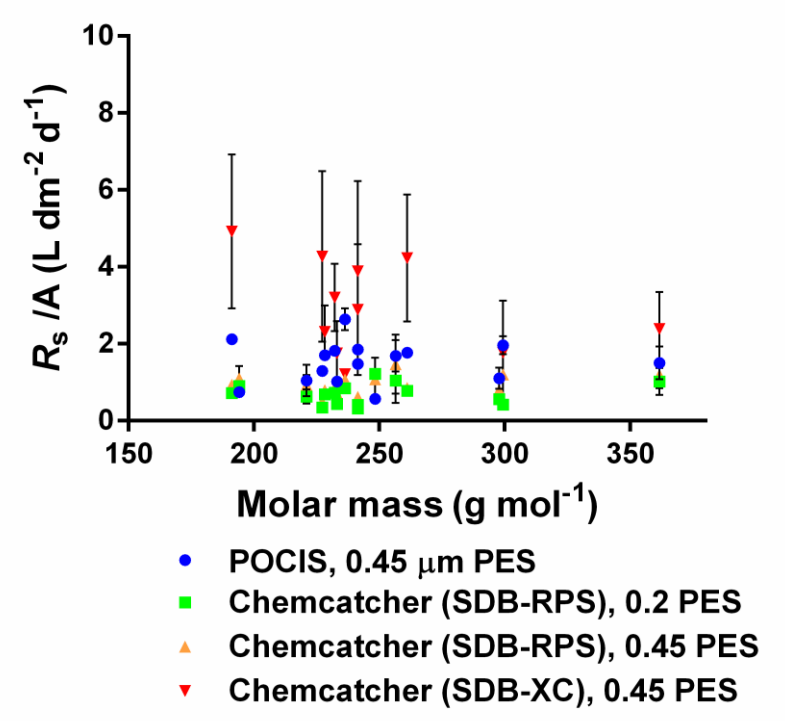


Fig. S6. Sampling rates normalized on surface area (R_s/A; L dm^{-2} d^{-1}) vs. molar mass for target chemicals with POCIS and Chemcatcher™.

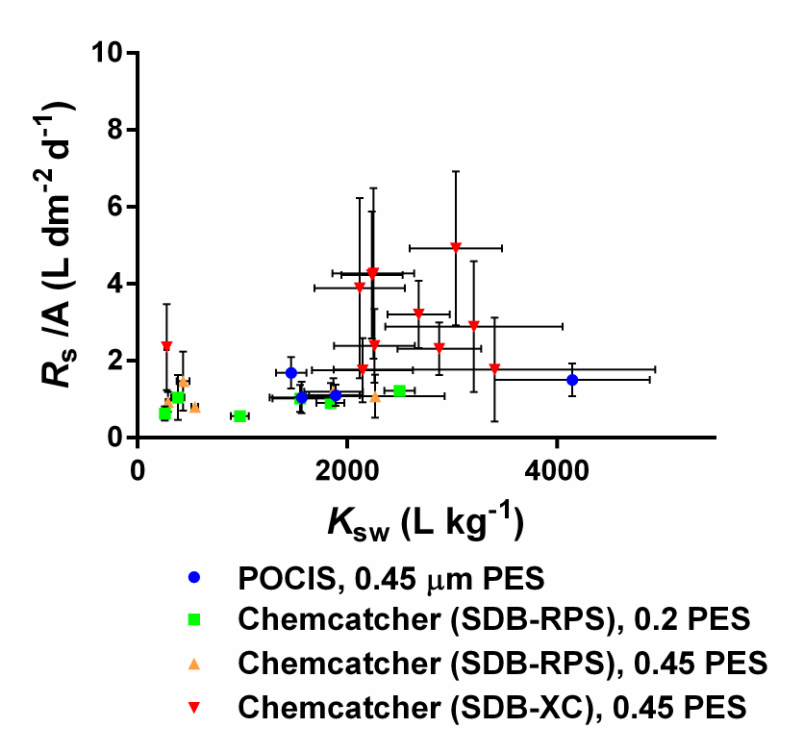
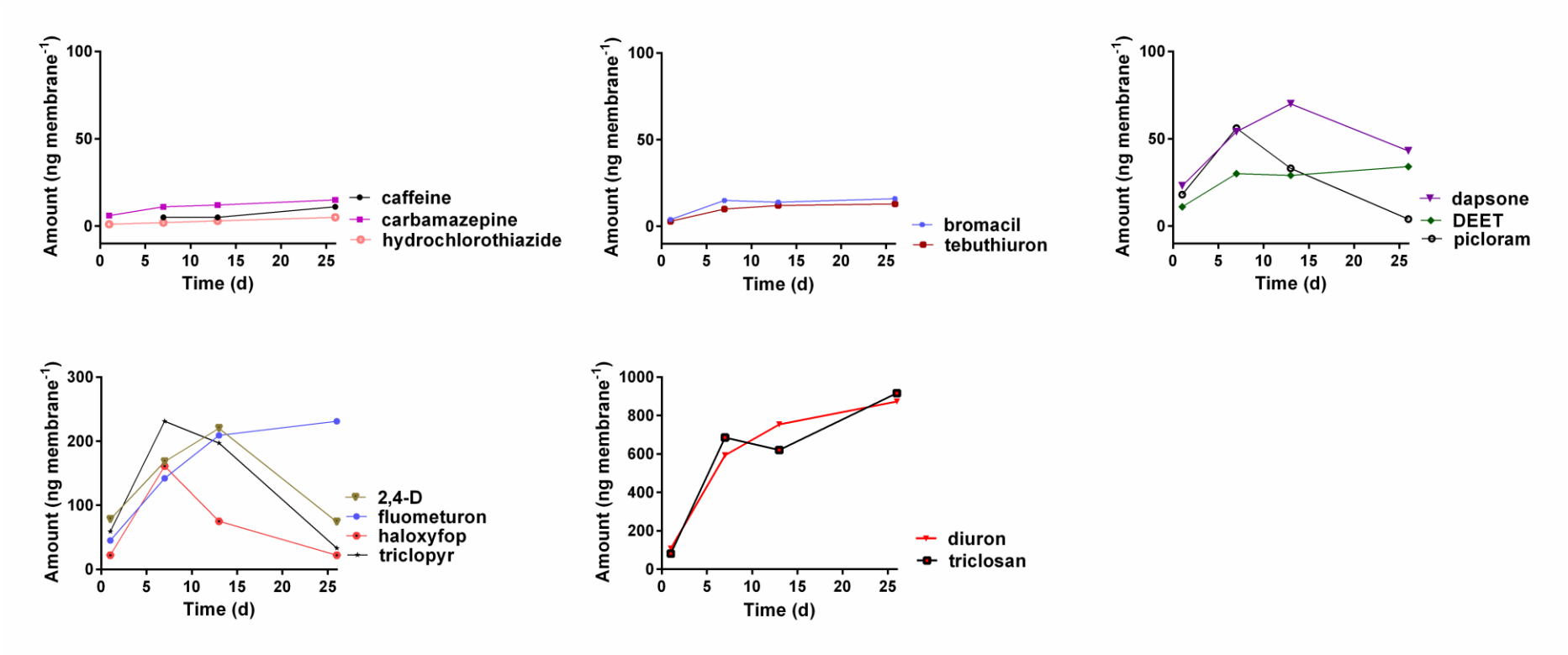
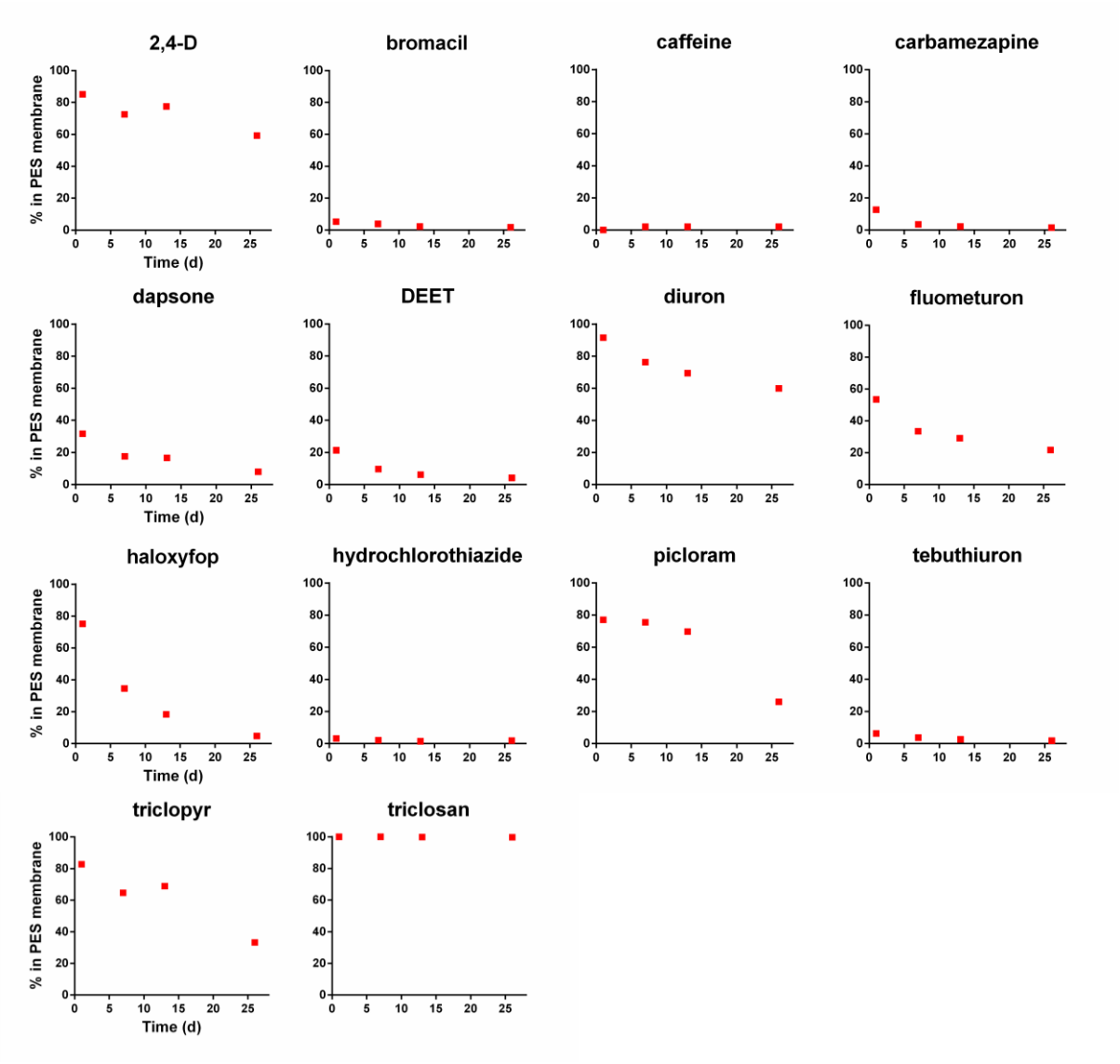


Fig. S7. Sampling rates normalized on surface area (R_s/A; L dm^{-2} d^{-1}) vs. sorbent-water sorption coefficients (K_{sw}; L kg^{-1}) for chemicals with POCIS and Chemcatchers^{TM}.



*Profiles for ametryn, prometryn, terbutryn, codeine were not determined due to insufficient data points. No accumulation in dicamba was observed in PES.

Fig. S8. Accumulation of target chemicals in PES membranes (0.2 µm pore size) from Chemcatcher™ (SDB-RPS).



*Profiles for ametryn, prometryn, terbutryn, codeine were not determined due to insufficient data points. No accumulation in dicamba was observed in PES.

Fig. S9. Percent accumulation in PES membranes (0.2 µm pore size).

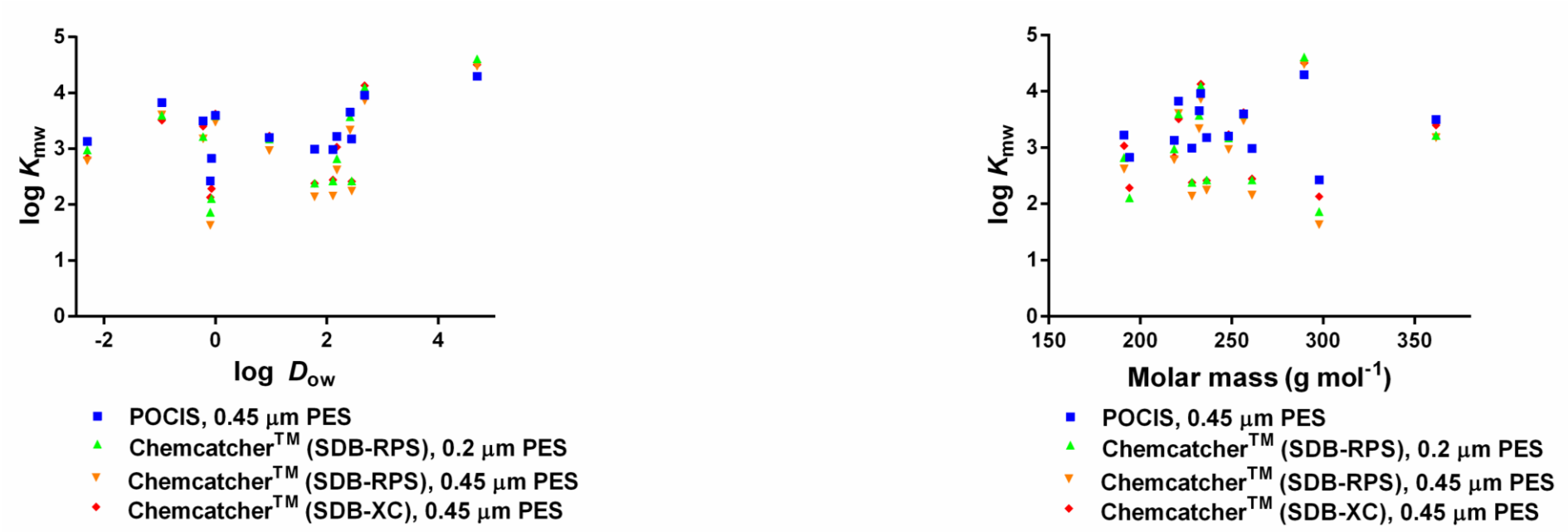


Fig. S10. The logarithm of PES membrane – water sorption coefficients (log K_{mw}) vs. log D_{ow} (left) and molar mass (right) for target chemicals with modified POCIS and Chemcatchers^{TM} (SDB-RPS and SDB-XC).