

Supporting Information

"Membrane enclosed sorptive coating - a novel integrative passive sampler for monitoring organic contaminants in water"

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The flow-through system

The experimental setup of consisted of an one meter high glass column (7.5-cm inner diameter) with a sieve-like perforated bottom (openings 0.5 cm diameter). The column was covered with dark foil to prevent photodegradation of analytes during exposure. The volume of the column was 5 L. The exposure water was pumped from the bottom to the top of the column. Test chemicals were dissolved in methanol (400 $\mu\text{g L}^{-1}$) and the appropriate amounts of stock solution (80 to 200 $\mu\text{L min}^{-1}$) were delivered into exposure water in a 1-L chamber positioned at the bottom of the column using a peristaltic pump (Minipuls 3, Gilson, USA). The water in the chamber was mixed using a magnetic stirrer with the turning speed of 600 min^{-1} . The resulting methanol concentration in the exposure water did not exceed 0.01% (v/v). Water was fed to the chamber using a membrane pump (Prominent, Germany) at 90 L h^{-1} . The passive sampler string was fixed in the column in a vertical position using teflon rings fastened at the top and the bottom of the column.

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Processing and analysis of water samples

The residues in the water samples were extracted using solid-phase extraction (SPE). 0.3 g of sorbent Lichrolut (R) was placed into a glass column with a teflon frit at the bottom (height 110 mm, diameter 10 mm). The sorbent was activated before use by passage of 10 mL methanol followed by 100 mL double-distilled water. 2 l of the aqueous sample was passed through the column at 30 mL min⁻¹ (underpressure). After entire sample has passed through the column, the sorbent was dried by aspirating ambient air through the column. Residues were eluted with hexane. 50 µL of nonane was added, extracts were evaporated to dryness under gentle stream of nitrogen, and redissolved to 200 µL in hexane before GC/MS analysis.

Spiking studies of water at multiple concentrations for the SPE procedure were conducted to determine recoveries for the test compounds. A procedural blank and four recovery solutions (5 - 20 ng L⁻¹) were extracted concurrently with aqueous samples. The recovery standards were analysed alongside spiking standards and a mean percentage recovery for the four spiking concentrations was calculated. Mean percentage SPE recoveries of the test compounds were between 39 and 83% for SPE. For acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene and hexachlorobenzene the recovery rates of SPE were not reproducible, therefore concentration of these substances was determined using SPME technique (see below). In experiment 3 (Table 2), aqueous concentrations of these substances were not determined. Chemical concentrations found in water samples were corrected for losses during the sample handling using recovery rates derived from spiking studies.

The quantification of acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene and HCB in water was carried out with an SPME device (Supelco 65 µm-polydimethylsiloxane-divinylbenzene (PDMS-DVB) solid phase microextraction fibre assembly) in combination with a gas chromatographic system. For the microextraction of analytes from the aqueous samples 480 mL of aqueous solution was placed to a 500 mL closed Erlenmeyer flask and the SPME fibre was lowered to the solution. The flask content was agitated by a glass magnetic stirrer at 1000 min⁻¹ for 60 min at room

temperature. For the external calibration, double-distilled water was spiked with the substance mixture dissolved in methanol. The calibration was carried out at four concentration levels (5 to 30 ng L⁻¹, double determination).

The quantitation and qualitative control of the compounds of interest in SPE extracts and on SPME fibers was made by GC (HP 5890), interfaced to a mass spectrometric detector (280°C), and a capillary column (60 m × 0.25 mm i.d.) with a non-polar stationary phase DB5MS (thickness 0.25 μm). A splitless mode of injection was used. Injection volume of SPE extracts was 1 μL. Temperature conditions: injector 250°C, column 60°C (1 min) - 30°C/min - 150°C - 4°C/min - 280°C - (39 min). Helium was used as carrier gas (0.65 mL min⁻¹). Data were obtained in the selected ion monitoring (SIM) mode for achieving maximum possible sensitivity. Quantification of the residues was accomplished using a ten-point external standard curve.

Table 1. Results of the linear regression analysis of the accumulated amount of test compounds in the Twister-receiving phase of the passive sampler versus time, mean aqueous concentrations of analytes (C_w) during exposure, and the observed lag phase in the initial uptake period (t_{lag}). Passive samplers were exposed for 7 days to a constant aqueous analyte concentration (20 ng L^{-1} ; nominal) at 19°C (experiment 1).

Compound	n	r^2 adjusted	S.D.	intercept [ng]	C.V. %	slope $\times 10^3$ [ng h $^{-1}$]	C.V. %	C_w [ng L $^{-1}$]	C.V. %	t_{lag} [h]
HCB	14	0.94	0.01	0.00	6405	1.4	7	12.2 ^a	7	-
γ -HCH	14	0.94	0.05	-0.09	38	4.5	7	13.5	41	20
p,p-DDE	14	0.96	0.04	-0.17	18	5.0	6	16.6	7	33
PCB28	14	0.96	0.04	-0.15	17	4.6	5	13.7	49	33
PCB52	14	0.96	0.03	-0.13	17	4.0	5	14.7	32	32
PCB101	14	0.96	0.03	-0.12	17	3.5	6	15.4	13	35
PCB138	14	0.97	0.02	-0.12	14	3.4	5	15.3	7	36
PCB153	14	0.96	0.02	-0.11	15	2.9	5	15.0	6	37
PCB180	14	0.95	0.02	-0.12	14	2.7	6	24.4 ^b	8	46
Acenaphthylene	14	0.97	0.06	-0.19	21	8.3	5	17.3 ^a	7	22
Acenaphthene	14	0.96	0.03	-0.11	23	4.5	5	16.0 ^a	8	24
Fluorene	14	0.97	0.05	-0.19	18	7.1	5	18.1 ^a	7	27
Anthracene	14	0.96	0.05	-0.15	23	6.3	5	13.6 ^a	15	24
Phenanthrene	14	0.95	0.04	-0.15	19	4.3	7	13.3 ^a	10	35
Fluoranthene	14	0.93	0.07	-0.23	22	6.5	7	16.6	11	35
Pyrene	14	0.96	0.06	-0.23	19	7.8	5	15.4	15	29
Benzo[a]anthracene	14	0.93	0.11	-0.41	19	10.5	7	17.7	4	39
Chrysene	14	0.93	0.10	-0.36	21	9.8	7	15.2	8	37
Benzo[b]fluoranthene	14	0.96	0.06	-0.30	14	7.3	6	16.2	5	41
Benzo[k]fluoranthene	14	0.93	0.09	-0.37	17	7.9	8	15.9	8	46
Benzo[a]pyrene	14	0.95	0.06	-0.27	15	6.5	6	16.7	7	42
Indeno[1,2,3-cd]pyrene	14	0.95	0.04	-0.22	15	4.8	6	16.3	5	45
Benzo[g,h,i]perylene	14	0.93	0.04	-0.18	17	3.9	7	16.5	9	45

^aThe aqueous concentration was determined using SPME - technique.

^bThe nominal concentration of PCB 180 was 40 ng L^{-1}

Table 2. Results of the linear regression analysis of the accumulated amount of test compounds in the Twister-receiving phase of the passive sampler versus time. Passive samplers were exposed for 7 days to a constant aqueous analyte concentration (20 ng L⁻¹; nominal) at 14°C (experiment 2).

Compound	n	r ² adjusted	S.D.	intercept [ng]	C.V. %	slope×10 ³ [ng h ⁻¹]	C.V. %	C _w [ng L ⁻¹]	C.V. %	t _{lag} [h]
HCB	12	0.66	0.02	0.02	89	0.8	21	17.5 ^a	10	-
γ-HCH	12	0.79	0.05	0.10	52	2.9	15	15.7	45	-
p,p-DDE	12	0.80	0.06	-0.06	96	3.7	15	25.6	23	-
PCB28	12	0.78	0.09	-0.13	64	4.7	16	9.5	55	-
PCB52	12	0.79	0.07	-0.10	63	3.7	16	9.3	36	-
PCB101	12	0.76	0.06	-0.07	91	3.2	17	12.2	23	-
PCB138	12	0.84	0.04	-0.07	49	2.8	13	10.6	26	-
PCB153	12	0.81	0.04	-0.09	57	2.4	14	10.3	26	-
PCB180	12	0.83	0.03	-0.08	35	1.9	14	16.5	30	44
Acenaphthylene	12	0.88	0.12	-0.11	106	9.6	11	17.3 ^a	7	-
Acenaphthene	12	0.90	0.04	0.06	73	3.5	10	16.0 ^a	8	-
Fluorene	12	0.82	0.10	-0.03	336	6.4	14	18.1 ^a	7	-
Anthracene	12	0.84	0.09	-0.05	190	6.2	13	13.6 ^a	15	-
Phenanthrene	12	0.85	0.05	-0.10	50	3.3	13	13.3 ^a	10	-
Fluoranthene	12	0.88	0.06	0.03	215	4.4	11	20.2	29	-
Pyrene	12	0.88	0.07	0.03	244	5.6	11	20.7	28	-
Benzo[a]anthracene	12	0.84	0.07	0.02	326	4.5	13	21.1	30	-
Chrysene	12	0.85	0.07	0.01	496	4.6	13	21.2	29	-
Benzo[b]fluoranthene	12	0.82	0.08	-0.07	116	5.1	14	21.6	21	-
Benzo[k]fluoranthene	12	0.83	0.07	-0.11	66	4.6	14	21.7	24	-
Benzo[a]pyrene	12	0.81	0.08	-0.07	109	4.7	15	15.7	11	-
Indeno[1,2,3-cd]pyrene	nd ^b									-
Benzo[g,h,i]perylene	nd									-

^aThe aqueous concentration was determined using SPME - technique.

nd - no data

Table 3. Results of the linear regression analysis of the accumulated amount of test compounds in the Twister-receiving phase of the passive sampler versus time. Passive samplers were exposed for 4 days to a constant aqueous analyte concentration (50 ng L^{-1} ; nominal) at 19°C (experiment 3).

Compound	n	r^2 adjusted	S.D.	intercept [ng]	C.V. %	slope $\times 10^3$ [ng h $^{-1}$]	C.V. %	C_w [ng L $^{-1}$]	C.V. %	t_{lag} [h]
HCB	6	0.95	0.12	-0.08	127	13.6	10	no data	-	-
gamma-HCH	6	0.89	0.26	-0.13	163	19.5	15			-
p,p-DDE	6	0.80	0.13	-0.08	132	6.9	22	31.1	11	-
PCB28	6	0.74	0.23	-0.12	157	10.3	25	31.1	11	-
PCB52	6	0.81	0.16	-0.09	155	8.8	21	46.6	10	-
PCB101	6	0.81	0.14	-0.09	130	7.6	21	39.6	17	-
PCB138	6	0.78	0.13	-0.10	107	6.4	23	48.6	22	-
PCB153	6	0.78	0.11	-0.09	106	5.5	23	36.7	50	-
PCB180	6	0.68	0.06	-0.04	123	2.3	29	36.5	36	-
						0.0				-
Acenaphthylene	6	0.81	0.38	-0.21	153	20.2	21	no data		-
Acenaphthene	6	0.81	0.31	-0.15	176	16.6	21	no data		-
Fluorene	6	0.75	0.34	-0.15	188	15.4	25	no data		-
Anthracene	6	0.75	0.33	-0.16	171	15.0	25	no data		-
Phenanthrene	6	0.74	0.34	-0.13	222	15.1	26	no data		-
Fluoranthene	6	0.74	0.39	-0.19	171	17.4	25	39.2	10	-
Pyrene	6	0.72	0.45	-0.21	177	19.1	27	30.1	15	-
Benzo(a)anthracene	6	0.75	0.55	-0.28	167	25.5	25	36.8	25	-
Chrysene	6	0.76	0.46	-0.22	174	21.5	24	38.9	14	-
Benzo(b)fluoranthene	6	0.97	0.17	-0.12	120	23.3	8	42.5	17	-
Benzo(k)fluoranthene	6	0.97	0.11	-0.06	147	14.3	8	39.5	17	-
Benzo(a)pyrene	6	0.95	0.18	-0.06	248	19.7	10	29.0	29	-
Indenopyrene	6	0.81	0.33	0.08	333	18.0	21	37.0	10	-
Benzo(g,h,i)perylene	6	0.88	0.13	0.02	474	9.3	16	35.9	31	-