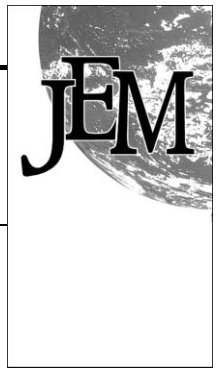

Development of an integrative passive sampler for the monitoring of organic water pollutants

Luise Wennrich,*[a] Branislav Vrana,[b] Peter Popp[c] and Wilhelm Lorenz[d]

[a]*Leibniz-Institute of Surface Modification, Permoserstrasse 15, D-04318 Leipzig, Germany. E-mail: luise.wennrich@iom-leipzig.de; Fax: +49 341 235 2584; Tel: +49 341 235 3184*
[b]*Department of Chemical Ecotoxicology, UFZ–Centre for Environmental Research Leipzig-Halle, Permoserstrasse 15, D-04318 Leipzig, Germany*
[c]*Department of Analytical Chemistry, UFZ–Centre for Environmental Research Leipzig-Halle, Permoserstrasse 15, D-04318 Leipzig, Germany*
[d]*Martin-Luther-University Halle-Wittenberg, Institute of Analytical and Environmental Chemistry, Kurt-Mothes-Strasse 2, D-06120 Halle (Saale), Germany*

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The development of convenient and competitive devices and methods for monitoring of organic pollutants in the aquatic environment is of increasing interest. An integrative passive sampling system has been developed which consists of a solid poly(dimethylsiloxane) (PDMS) material (tube or rod), acting as hydrophobic organic receiving phase, enclosed in a water-filled or an air-filled low-density polyethylene (LDPE) membrane tubing. These samplers enable the direct analysis of the pollutants accumulated during exposure in the receiving phase by thermodesorption–GC/MS, avoiding expensive sample preparation and cleanups. The capabilities of these sampling devices were studied for the sampling of 20 persistent organic pollutants (chlorobenzenes, hexachlorocyclohexanes, *p*,*p*′-DDE, PAHs, and PCBs) in laboratory exposure experiments. For the three sampler designs investigated the uptake of all target analytes was integrative over exposure periods up to 9 days (except PCB 101). The determined sampling rates range from 4 to 1340 μl h^{-1} for the water-filled samplers and from 20 to 6360 μl h^{-1} for the air-filled ones, respectively. The sampling rate of the analytes is dependent on their molecular weight, partition between water and sampler media (PDMS, polyethylene, water, air) and also of the sampler design. The passive samplers enable the estimation of time-weighted average (TWA) concentration of water pollutants in the lower ng l^{-1} to pg l^{-1} range.

Introduction

The monitoring of environmental pollutants in the ground and surface waters is of fundamental importance for both the protection of these ecosystems and the quality of human life. In particular the determination of persistent organic pollutants (POPs) is of ecotoxicological relevance due to their high toxic potential, their persistence and their tendency to bioaccumulate. As is known, these pollutants can be present in the aquatic environment both freely dissolved and particle-bound. For ecological risk assessment the bioavailable fraction is of substantial interest. This corresponds with the freely dissolved fraction. Using conventional sampling techniques (grab sampling) only the total content of the pollutants is obtained. Furthermore, the conventional sampling and analysis of grab water samples only provide information about pollutant burden at the moment of sampling.

Passive sampling techniques can overcome the problems mentioned above. These techniques allow the convenient determination of the time-weighted average concentration of the freely dissolved fraction of pollutants over several weeks or even months. Compared to conventional sampling the number of the samples and thus the expense of sampling and subsequent analysis can be reduced significantly. In addition, due to the accumulation of the pollutants over the whole sampling period, passive sampling allows the detection of even low analyte concentrations. Furthermore, the sampling devices are usually simple in design, small, inexpensive and require no power supply. This makes the technique inexpensive and suitable for use at remote sites. However, for the determination of TWA concentrations of organic pollutants in field studies samplers must be calibrated in laboratory experiments.

Today the passive sampling technique represents an attractive alternative to the conventional snap-shot sampling for water monitoring of semivolatile POPs. In the last few years various passive sampling devices were designed for monitoring of pollutants in the aquatic systems. These sampling devices are usually so-called membrane samplers. Such membrane samplers typically consist of a receiving medium with a high affinity for the organic contaminants enclosed by a diffusion-limiting semipermeable membrane.[1–4]

Semipermeable membrane devices (SPMDs), introduced by Huckins and co-workers,[5–9] attained the greatest importance and widespread application. Due to both their high membrane surface area and their relatively large volume of receiving medium SPMDs proved to be most effective in their capacity to accumulate lipophilic contaminants. The SPMD sampler consists of layflat low-density polyethylene tubing enclosing a thin film of triolein. The main disadvantage of the SPMD technique is the complex sample preparation procedure required to recover the accumulated pollutants from the collecting phase (triolein). This is achieved by dialysis using considerable amounts of organic solvents, followed by concentration of the extracts and an expensive cleanup before the chromatographic analysis.[9,10]

In the last few years several attempts have been made to develop passive sampling devices, which avoid the drawbacks mentioned above and also make passive sampling technology more attractive for routine monitoring programmes. Such passive samplers contain solid materials (granular adsorbents

and compact polymeric sorbents, like PDMS, respectively) instead of the liquid organic receiving phase. That allows the thermodesorption of the accumulated pollutants without additional sample preparation.

Hardy *et al.*[11–13] created a passive sampler consisting of a glass tube, sealed at one side with a silicone–polycarbonate membrane. Depending on the target analytes this sampler can be filled with various granular materials, such as activated charcoal, Tenax-TA, XAD-7, Chromosorb 103 and Porapak Q. After exposure, the granular receiving phase can be desorbed either with a suitable solvent or thermally. This sampler was successfully applied for the enrichment of more volatile organic compounds, like monocyclic aromatic compounds[13] and phenols,[12] whereas the less volatile compounds were not enriched effectively.

At the end of the nineties Gratwohl and Martin[14,15] patented a so-called ceramic dosimeter for the integrative sampling of organic compounds in ground water. This sampler consists of a porous ceramic tube which was filled with different grained adsorbents, *e.g.* the ion exchange resin Amberlite IRA-743 and Tenax. The porous ceramic tube enables only the dissolved analytes to pass the membrane. This sampler was applied for the monitoring of several PAHs in ground water. Concerning the subsequent thermodesorption of the analytes from Tenax difficulties appear due to the unexpected water permeability of the ceramic membranes.

In a recently published paper, Vrana *et al.*[16] described the application of a solid sorbent on the basis of PDMS as receiving phase in a membrane sampler. This so-called MESCO (*m*embrane-*e*nclosed *s*orptive *co*ating) sampler consists of a stir bar coated with a thin PDMS layer (Gerstel Twister, a commercially available device used for stir bar sorptive extraction, SBSE[17]) enclosed in a water-filled dialysis membrane bag from regenerated cellulose. After exposure of the sampler, the PDMS coated stir bar is taken from the enveloping membrane and can be directly analysed by thermodesorption–GC/MS. Thus, laborious and time-consuming sample preparation can be avoided.

PDMS is recommended as a receiving phase in extraction and thermodesorption as it has a number of benefits compared with other sorbents.[18] The predominant mechanism of analyte extraction into the polymer PDMS phase is absorptive partitioning, which means that displacement effects of the analytes which are characteristic for adsorbents play no role.

Although the MESCO sampler is a miniaturised version, this passive sampling approach enables lower quantification limits for hydrophobic POPs in the pg l^{-1} level. The application of regenerated cellulose as a porous hydrophilic membrane material enables the widening of the applicability to a broader polarity range of pollutants including low-hydrophobic substances (log $K_{OW} < 4$). Unfortunately, this material has relatively low chemical and thermal stability and is subject to microbial degradation,[3] which potentially leads to the damage of the sampler in the field.

The aim of the work presented here was to develop and to test a membrane sampler combining the advantages of the MESCO sampler with those of more stable membranes, such as low-density polyethylene. LDPE membranes were successfully applied in SPMDs. These membranes are hydrophobic, resistant to solvents and biodegradation and they can be heat-sealed. Furthermore, the commercially available stir bars as receiving phase should be substituted by less expensive PDMS materials with a significantly enhanced volume to increase the maximum exposure time of the passive sampler in the field.

Theory

Previously, models have been developed describing the uptake kinetics of organic contaminants in water by passive samplers constructed as solvent filled dialysis membranes,[19] triolein filled polyethylene membranes[20] or membrane enclosed sorptive coatings[16] and can analogously be adapted for the description of the function of samplers designed in this study. These consist of a hydrophobic solid receiving phase (PDMS) enclosed in water-filled or air-filled semipermeable membrane made of nonporous LDPE.

The mass transfer of an analyte in a sampler includes several diffusion and interfacial transport steps across all barriers, *i.e.* the stagnant aqueous boundary layer, possible biofilm layer, the membrane, the inner fluid (aqueous or gas) phase, and the receiving organic phase as rate control step is not assumed *a priori*.

It can be shown that in the initial uptake phase, chemical uptake is linear or time-integrative. Under these conditions the concentration of a chemical in the organic phase is directly proportional to the product of the concentration in the surrounding aqueous medium C_W [kg m^{-3}] and the exposure time t [s]. For practical application, uptake can be described by eqn. (1)

$$M_S(t) = M_0 + C_W R_S t \quad (1)$$

where M_S [kg] is the amount of analyte accumulated in the receiving phase and M_0 [kg] the initial amount of analyte in the sampler. R_S [m^3 s^{-1}] is the sampling rate of the system:

$$R_S = k_{ov} A \quad (2)$$

where k_{ov} [m s^{-1}] is the overall mass transfer coefficient and A [m^2] is the membrane surface area. Sampling rate can be determined experimentally under fixed conditions at constant analyte concentration. Under environmental conditions, when the water concentration changes during the exposure, the term C_W represents a TWA concentration during the deployment period.

As described by Huckins *et al.*,[21] the uptake of an analyte into the passive sampler is linear and integrative approximately until the concentration factor of the sampler (ratio $C_S(t)/C_W$) reaches half-saturation. If sampling rates R_S and organic receiving phase/water partitioning coefficients K_{SW} are available, the maximum exposure time in which the sampling device works integrative under field conditions can be estimated using eqn. (3):

$$t_{50} \sim \ln 2 K_{SW} V_S / R_S \quad (3)$$

where t_{50} is the first-order half-time of the uptake curve and V_S the volume of the receiving phase.

Experimental

Chemicals and materials

The test substances (Table 1) include several groups of semivolatile persistent organic pollutants: hexachlorocyclohexanes (HCHs), chlorinated benzenes (CBs), 2,2′-bis(4-chlorophenyl)-1,1′-dichloroethylene (*p,p′*-DDE), PAHs, and PCBs.

HCH, chlorobenzene, PCB and PAH reference standards were obtained from Promochem (Wesel, Germany). The solvents *n*-hexane, methanol and dichloromethane (for organic trace analysis) were purchased from Merck (Darmstadt, Germany). HPLC-grade water was supplied by Baker (Deventer, The Netherlands). Layflat LDPE membrane tubing (layflat, 30 mm; wall thickness, 80 μm) was achieved from Polymer-Synthese-Werk GmbH (Rheinberg, Germany). Silicone tubing (3.0 mm × 3.6 mm) was obtained from Reichelt (Heidelberg, Germany). Silicone rod material (2.0 mm id) was purchased from Goodfellow (Bad Nauheim, Germany). Stir

Table 1 Selected physicochemical properties of the test analytes

Compound	Abbreviation	No.	MW[a]	log K_{OW}[b] at 25 °C	log K_{MW}[c] at 25 °C	K_{AW}[d] at 25 °C	D_A[e]/cm^2 s^{-1} at 20 °C	D_W[f]/cm^2 s^{-1} at 20 °C
1,2,4,5-Tetrachlorobenzene	TeCB	1	215.9	4.5	4.0	4.9×10^{-2}	0.06	6.2×10^{-6}
Pentachlorobenzene	PeCB	2	250.3	5.2	4.6	3.4×10^{-2}	0.057	5.8×10^{-6}
Hexachlorobenzene	HCB	3	284.8	5.5	4.8	5.3×10^{-2}	0.0543	5.5×10^{-6}
α-HCH	α-HCH	4	290.8	3.7	3.2	5.0×10^{-4}	0.05	6.2×10^{-6}
β-HCH	β-HCH	5	290.8	3.8	3.3	1.8×10^{-5}	0.05	6.2×10^{-6}
γ-HCH	γ-HCH	6	290.8	3.7	3.2	2.1×10^{-4}	0.05	6.2×10^{-6}
δ-HCH	δ-HCH	7	290.8	4.1	3.6	1.8×10^{-5}	0.05	6.2×10^{-6}
PCB 28	PCB 28	8	257.5	5.6	4.9	8.2×10^{-3}	0.0542	5.1×10^{-6}
PCB 52	PCB 52	9	292.0	6.1	5.2	8.2×10^{-3}	0.054	4.9×10^{-6}
PCB 101	PCB 101	10	326.4	6.8	5.6	1.4×10^{-2}	0.054	4.7×10^{-6}
p,*p*′-DDE	*p*,*p*′-DDE	11	318.0	5.7	5.0	1.7×10^{-3}	0.05	5.0×10^{-6}
Acenaphthylene	Ace	12	152.2	4.0	3.5	3.4×10^{-3}	0.063	6.5×10^{-6}
Acenaphthene	Acenaph	13	154.2	4.0	3.5	4.9×10^{-3}	0.063	6.3×10^{-6}
Fluorene	Flu	14	166.2	4.2	3.7	3.2×10^{-3}	0.06	6.0×10^{-6}
Phenanthrene	Phe	15	178.2	4.5	4.0	1.3×10^{-3}	0.058	5.8×10^{-6}
Anthracene	Ant	16	178.2	4.6	4.4	1.6×10^{-3}	0.058	5.9×10^{-6}
Fluoranthene	FLU	17	202.3	5.1	4.5	4.2×10^{-4}	0.055	5.5×10^{-6}
Pyrene	Pyr	18	202.3	5.1	4.5	3.7×10^{-4}	0.055	5.6×10^{-6}
Benzo[*a*]anthracene	BaA	19	228.3	5.9	5.1	2.3×10^{-4}	0.052	5.1×10^{-6}
Chrysene	CHR	20	228.3	5.7	5.0	2.6×10^{-5}	0.052	5.1×10^{-6}

[a]Molecular weight. [b]Octanol–water partition coefficient.[22,23] [c]Membrane–water partition coefficient estimated from eqn. (4).[28] [d]Henry's Law constant.[22,23] [e]Diffusion coefficient in air.[25] [f]Diffusion coefficient in water.[24] [g]δ_T = length of the diffusion path in the transfer medium = 0.3 cm.

bars for SBSE (PDMS coating: 0.5 mm thickness, 10 mm length) were obtained from Gerstel (Mülheim/Ruhr, Germany).

Physicochemical properties of substances

Henry's Law constants K_{AW} at 25 °C of substances under investigation were taken from the literature.[22,23] Almost equal values of aqueous diffusion coefficients D_W were estimated for the tested group of compounds ranging from 5×10^{-6} to 7×10^{-6} cm^2 s^{-1}.[24] Diffusion coefficients of the test analytes in air D_A at 20 °C range from 0.05 to 0.06 cm^2 s^{-1}.[25] An approximated value of 10^{-10} cm^2 s^{-1} was used as diffusion coefficient of the analytes in the LDPE membrane D_M.[26,27] The membrane/water partition coefficients K_{MW} were estimated from a predictive equation derived by Hofmans:[28]

$$\log K_{MW} = -0.0956(\log K_{OW})^2 + 1.7643 \log K_{OW} - 1.98 \quad (4)$$

Preparation and test of the sampler components

The materials provided for receiving phases in the passive sampling devices (silicone tubes and rods) were obtained from the manufacturers as endless materials. In order to obtain reproducible results the tubes and rods were carefully cut with a scalpel in pieces of each 40 mm length and then weighed. Outliers in the weight (CV > 1%) were discarded.

In order to clean and condition the silicone tubing and rods, in each case ten of these were placed into a vial (50 ml) containing 50 ml of *n*-hexane and horizontally shaken for 2 h (tubing) or 4 h (rods). The materials were dried in a desiccator under vacuum and then thermally conditioned for 3 h at 250 °C in a nitrogen flow of about 50 ml min^{-1}. For cleaning and conditioning of the stir bars these were placed separately into small vials filled with 2 ml of a mixture of dichloromethane and methanol (1 : 1) for 1 h. Then they were dried in a desiccator and subsequently heated at 250 °C for 90 min in a nitrogen flow. For cleaning of the layflat LDPE tubing, 3 pieces of this material with a length of each 1 m were put into a glass vessel (500 ml) containing 500 ml of *n*-hexane and shaken for 24 h. Then the solvent was rejected and the procedure was repeated once. The wet tubing was dried in a desiccator.

To investigate the applicability of some PDMS materials as organic receiving phases in the sampling devices these were tested within the complete extraction and thermodesorption procedures. For this purpose, the conditioned receiving phases were separately shaken in each 50 ml water spiked with the test analytes (100 ng l^{-1} of each compound). This solution was prepared by spiking a water sample with a mixture of test analytes dissolved in methanol. The vials containing the tubes and the rods were horizontally shaken for 2 h at 200 motions per min. The stir bars were stirred at 1000 rpm in Erlenmeyer flasks for 2 h. After extraction, the receiving phases were taken from the water sample, rinsed with a small volume of water, and dabbed dry with a lint-free tissue. It should be noted that the small water droplets inside the tubes should be carefully removed. The accumulated analytes were determined using thermodesorption–GC/MS as described later. The completeness of the desorption of the enriched analytes (carry over) was revised by a second desorption under equal conditions.

Membrane samplers

The membrane samplers used in this study (Fig. 1) consist of a layflat LDPE membrane tubing (length, 50 mm) enclosing a

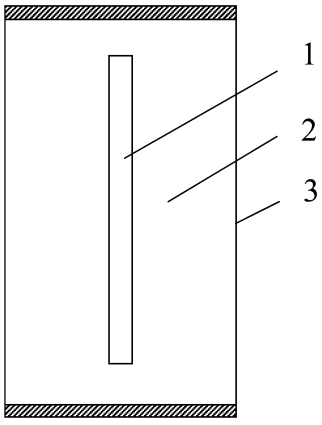

Fig. 1 Schematic diagram of the passive sampling device described here. The receiving phase (component 1, silicone tubes or rods) is enclosed in low-density polyethylene membrane tubing (component 3) filled with the transfer medium (component 2, water or air) and heat-sealed at each end.

silicone tube (length, 40 mm; referred to as tube sampler) or a silicone rod (length, 40 mm; referred to as rod sampler). The layflat LDPE tubing with the receiving phase inside was water-filled (about 8 ml) or air-filled and heat-sealed at both ends. For both samplers the volume of the receiving phase (about 125 µl) and the effective membrane surface area (30 cm^2) were equal. In order to enable a simultaneous exposure of a set of samplers, they were connected to a string.

Laboratory exposure experiments

A set of passive samplers were exposed to contaminated water with a nominal analyte concentration of each 50 ng l^{-1} in a flow-through exposure system. This system consisted of an exposure chamber, an 1 m high glass column (inner diameter 7.5 cm) with a perforated bottom. To prevent photodegradation of the analytes during exposure the column was covered with dark foil. In a mixing chamber (1 l) positioned at the bottom of the exposure column tap water (60 l h^{-1}) and the appropriate amount of the test analytes dissolved in methanol (400 µg l^{-1}) delivered by a peristaltic pump (Gilson, USA) were carefully mixed using a magnetic stirrer. The resulting methanol concentration in the exposure water did not exceed 0.01% (v/v). Tap water was fed to the mixing chamber by a membrane pump (Prominent, Germany). The spiked water flowed from bottom to top through the exposure chamber. Using a heating–cooling system the water temperature in the exposure chamber was held constant at the predetermined temperature. The passive sampler string was fixed in the exposure column in a vertical position.

The exposure experiments were performed at 14 and 8 °C, respectively, and at a linear flow velocity of the water of 0.38 cm s^{-1} (see Table 2). The samplers were removed one by one after predetermined exposure times. (The maximum exposure times varied between 176 and 236 h.) Then the receiving phases were immediately taken out of the enveloping LDPE tubing and carefully dried. The loaded receiving phases were stored in closed small glass vials at −18 °C in a freezer until thermodesorption–GC/MS analysis. Investigations concerning the loss of analytes during storage of the loaded receiving phases under these conditions resulted in the conclusion that these could be neglected.

In order to determine the concentration of the analytes under investigation in the water during exposure, samples were taken from the exposure column at each time when samplers were removed and analysed as described below.

Processing of the water samples

The extraction of the water samples taken from the exposure column was performed using SBSE. The procedure was as follows: 50 ml of the water sample was filled into an Erlenmeyer flask (50 ml), the stir bar was lowered in the flask and then the sample was stirred at 1000 rpm for 2 h. After this the stir bar was taken out, washed with water and dried. For external calibration, spiked water samples containing 10, 30, 50, 70, and 100 ng l^{-1} of each analyte were prepared using a mixture of test analytes dissolved in methanol and extracted as described above. It should be noted that the content of methanol in the calibration solutions should be held constant (<1%).

Thermodesorption–GC/MS analysis

The pollutants accumulated during the exposure experiments in the receiving phases of the passive samplers and in the stir bars were analysed using thermodesorption–GC/MS. The solid receiving material was placed into an empty glass desorption tube. Thermodesorption–GC/MS was performed on an Agilent Technologies system 6890/5973 (Palo Alto, CA, USA) equipped with a Gerstel thermodesorption device with auto-sampler. For cryofocusing of the analytes prior to the transfer into the capillary column a Gerstel cold injection system (CIS 4) with an empty liner was used. During thermal desorption the CIS 4 was cooled with liquid nitrogen to a temperature of −150 °C. For the desorption of the analytes from the receiving phases and the stir bars the following conditions were chosen: desorption temperature, 250 °C; helium flow rate, 100 ml min^{-1} and desorption time, 10 min. The transfer lines both from the thermodesorption device to the CIS 4 and from the GC to the MS ion source were set to 250 °C. After desorption of the receiving phase and cryofocusing of the analytes, the CIS 4 was heated to 250 °C at a rate of 12 °C s^{-1}, whereas the system was used in the splitless mode with a splitless time of 1.5 min. An HP-5 MS capillary column (30 m, 0.25 mm id, 0.25 µm film thickness) was employed with the following temperature program: 50 °C, 3 min isothermal, 15 °C min^{-1} to 160 °C, then at 3 °C min^{-1} to the final temperature of 280 °C, and held for 8 min. Helium was used as carrier gas at a linear velocity of 39 cm s^{-1}. The single ion monitoring (SIM) mode applying one or two characteristic ions per analyte was chosen for the detection.

For external calibration of the accumulated pollutants in the receiving phases, a plug of silanised glass wool (length, about 4 cm) which was positioned in the heated zone of a desorption tube was spiked with the calibration solution (2 µl). The desorption tube was flushed for 1 min with a nitrogen flow of 30 ml min^{-1} to allow the main part of the solvent (methanol) to evaporate and then thermally desorbed. In order to control analyte losses during the evaporation of methanol at external calibration, the flush time was varied in the range of 30 to 120 s. This investigations resulted in no significant decrease of the peak areas with increased flush time. Quantification of the analytes sorbed in the receiving phase was performed using a six-point calibration.

Results and discussion

Assessment of PDMS materials

In a preliminary study the applicability of some commercially available PDMS materials—silicone tubes and silicone rods—as organic receiving phase in the passive sampling devices were investigated to achieve information about the extraction efficiency, the repeatability, completeness of the thermodesorption process (carry over), and the handling of the materials. For this purpose, each eight pieces of the receiving phases were object of the complete extraction and thermodesorption procedures (see the Experimental section—Preparation and test of the sampler components). Additionally, stir bars were included in the experiments, because they should serve on the one hand for comparison and they were employed for the analysis of the water samples on the other hand. The results of

Table 2 Conditions of the flow-through exposure experiments

Experiment no.	Sampler design used	Nominal concentration/ng l^{-1}	Temperature/°C	Flow velocity/cm s^{-1}	Exposure period/h
1a	Water-filled tube sampler	50	14	0.38	176
1b	Air-filled tube sampler	50	14	0.38	224
1c	Water-filled rod sampler	50	14	0.38	224
2	Water-filled tube sampler	50	8	0.38	236

Table 3 Mean peak areas (n = 8), coefficients of variation (CV in %) and carry over (%) of different receiving phase materials obtained from extraction and thermodesorption–GC/MS analysis

	Stir bars			Tubes			Rods		
Compound	Peak area × 10^{-3}	CV (%)	Carry over (%)	Rel. peak area[a] (%)	CV (%)	Carry over (%)	Rel. peak area[a] (%)	CV (%)	Carry over (%)
1,2,4,5-Tetrachlorobenzene	947	5.2	0.32	1.03	9.1	4.09	0.65	8.8	5.27
Pentachlorobenzene	965	6.0	0.15	0.65	6.8	1.36	0.68	6.5	4.37
Hexachlorobenzene	1004	6.9	0.12	0.65	15.5	nd	0.73	3.8	3.62
α-HCH	391	7.6	0.05	0.72	6.1	nd	0.85	5.2	3.03
β-HCH	57	9.6	3.00	1.33	4.5	2.25	1.71	19.7	4.28
γ-HCH	305	8.7	0.11	0.64	6.3	0.40	0.84	6.8	3.52
δ-HCH	117	8.5	0.86	0.85	7.8	2.64	1.10	20.6	0.70
PCB 28	1565	9.3	0.18	0.46	5.9	0.81	0.75	5.0	4.21
PCB 52	898	10.3	nd	0.43	5.2	0.28	0.74	6.9	4.73
PCB 101	510	11.1	0.09	0.36	11.1	0.33	0.67	16.5	6.07
p,p'-DDE	376	10.9	nd	0.36	13.2	0.09	0.65	20.5	5.78
Acenaphthylene	1272	5.5	0.26	1.00	6.9	1.31	0.82	7.4	3.41
Acenaphthene	1496	6.5	0.54	0.84	6.6	1.46	0.61	14.9	4.02
Fluorene	1287	7.6	0.50	0.72	7.3	1.36	0.84	4.6	3.72
Phenanthrene	2058	9.3	1.19	0.63	7.3	0.98	0.80	5.8	3.94
Anthracene	1386	9.8	0.14	0.54	5.9	0.42	p.i.		
Fluoranthene	1673	11.5	0.12	0.41	3.6	0.46	0.65	19.9	4.82
Pyrene	1643	11.2	0.12	0.41	6.7	0.44	0.55	20.9	5.17
Benzo[*a*]anthracene	281	12.8	nd	0.62	18.9	0.18	0.85	28.6	3.53
Chrysene	364	8.8	nd	0.52	14.0	0.25	0.89	25.5	3.97

[a]Related to the mean peak areas of the stir bars (n = 8). [b]nd = not detectable. [c]pi = peak interference.

these investigations are summarised in Table 3. The carry over provides information about the completeness of the thermodesorption process. For this purpose, the already thermally desorbed materials were desorbed again and the peak areas of the first and second desorption were compared, setting the areas of the first desorption to 100%. It should be noted that the volume of the PDMS phase of the stir bars (24 µl) and the other materials (125 µl) differ considerably. The extraction yields (relative peak areas) of the analytes investigated using tubes and rods were in the range of 0.37 to 1.33 compared to stir bars. From the three receiving phases, the best repeatability was found for the stir bars. The variation coefficients of the peak areas of the individual analytes extracted from the spiked solution by the 8 stir bars ranged from 5 to 13%. Comparing the tubes and the rods, the first ones showed a better repeatability with variation coefficients from 4 to 19% (tubes) and from 4 to 29% (rods), respectively. The values for the carry over of the stir bars indicate that the thermodesorption of the most compounds under the given conditions was nearly quantitative (<1% except β-HCH and phenanthrene). The values for the tubes were slightly higher (in most cases lower than 1.5%). In contrast, the carry over of the rods was significantly increased (between 3.0 and 6.1%). The reasons for this finding we assume in the significantly larger thickness of the PDMS layer of the rods (2 mm id) compared to the other materials (tubes, 0.3 mm; stir bars, 0.5 mm). Thus, an increased time is needed for the quantitative diffusion of the analyte molecules dissolved in the PDMS phase to the surface area of the rods. For this reason the silicone tubes were favoured as receiving phase material in the passive sampler devices. However, it was found that the handling of the rods is more convenient, especially by the preparation of the air bubble-free water-filled samplers and in consideration of drying (removing of the small water droplets on the inner surface area of the tubes). Therefore, in one exposure experiment rod samplers were included, too.

Calibration experiments

The capabilities of the passive sampling devices described here for the long-term water monitoring of the target analytes were investigated by performing exposure experiments in a flow-through exposure apparatus. In Table 2 the experimental conditions are summarised. Over the exposure periods the analyte concentrations in the water as well as the temperature and the flow rate of the water were held constant. As described above, during the exposure experiments water samples and passive samplers were taken from the exposure column at time intervals to determine the analyte concentrations in the water (C_W) and the amounts accumulated in the samplers (M_S).

The mean concentration of the individual analytes in the water samples within the exposures (C_W) were in the range of 78 to 131% of the nominal concentration (except *p,p'*-DDE in experiment 1). The calculated coefficients of variation of the average analyte concentrations were at maximum 11%.

The experimentally determined time courses of the accumulated amounts of individual analytes on the receiving phases (M_s) were fitted by the linear regression analysis. According to eqn. (1) the adjustable parameters are the slope ($C_W R_S$) and the intercept (M_0) of the linear uptake curve. The quality of the fit was characterised by the standard deviations of the optimised parameters, as well as the correlation coefficient (R) and the fit standard deviation (SD). Typical uptake curves are shown in Fig. 2.

Using tube samplers the uptake of all compounds was linear over the whole exposure time in all experiments. The correlation coefficients of the regression were in the range of

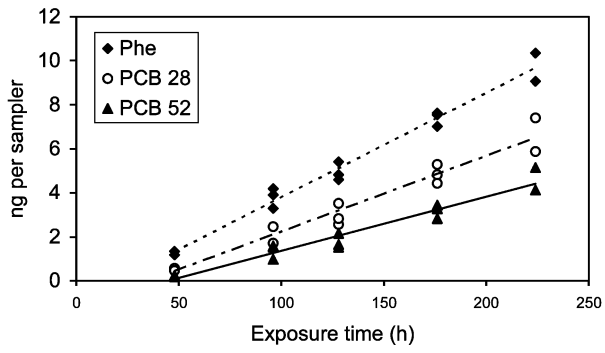

Fig. 2 Uptake of selected analytes by the air-filled tube sampler obtained from a flow-through exposure at 14 °C (nominal analyte concentration, 50 ng l^{-1}). For abbreviations see Table 1.

0.867 to 0.988. The variation coefficients of the calculated slope did not exceed 20%.

Using rod samplers (experiment 1c) the uptake of all analytes was linear except PCB 101. The correlation coefficients of the regression ranged from 0.698 to 0.990. The variation coefficients of the slope were in maximum 34%.

The uptake curves of the analytes show partly negative intercepts. From the theory[16] negative intercepts can be explained by the presence of a lag phase. This can be interpreted as the time needed for the analyte to pass the LDPE membrane. The duration of the lag phase or the so-called delay time is affected by the diffusivity of analyte and thickness of individual barriers (membrane and diffusion layers of fluid media). Moreover, steady-state flow of analyte from water to the receiving phase is not established immediately. However, the time to reach steady-state flux in the sampler can be estimated by the magnitude of the variable l^2/Dt, where l is the film thickness, D is the diffusion coefficient and t is time.[29] If the variable is less than unity, a steady-state flux is assumed. Using the thickness of the polyethylene membrane of 100 μm and a typical diffusion coefficient of small non-polar molecules in LDPE membranes of 10^{-10} cm^2 s^{-1}, steady-state should be achieved after one or two days in the polyethylene membrane. This corresponds well with the lag phase observed in our experiments. In most cases the calculated lag phases were in the range between 5 and 30 h, however, for the PCBs lag phases up to 48 h were found. In aqueous and air boundary layers, steady-state should be established after few minutes only. To use the sampler for the monitoring purposes, analytes should approach steady-state in the individual compartments quickly with regard to the duration of experiments, *i.e.* duration of the transition phase should not be much longer than 10% of the exposure period.

Sampling rates. The sampling rates R_S of the three types of passive samplers obtained in the exposure experiments 1 and 2 are given in Table 4. According to eqn. (1) the R_S values were calculated by dividing the slope of the linear uptake curve by the mean analyte concentration C_W in the water during exposure. The variances of the R_S values were calculated from both the coefficients of variation of the slope and of the analyte concentration in the aqueous phase, according to the law of error propagation.

Over the range of the controlled exposure conditions, the R_S values of the analytes under investigation covered a range of 2 to 3 orders of magnitude. For example, for the water-filled tube sampler at 14 °C the R_S values were in the range of 5 to 1340 μl h^{-1}. Comparing the sampling rates of the PAHs it can be seen that the values decrease with increasing molecular weight (size), increasing hydrophobicity (log K_{OW} ranged from 4.0 to 5.9) and decreasing water solubility of the compounds. A similar behaviour, significantly decreased sampling rates with increasing chlorination grade, was found for the chlorinated benzenes and the PCBs.

Originally, higher chlorinated PCBs (PCB 138, PCB 153 and PCB 180) and EPA PAHs with high molecular weights (benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenz[*ah*]anthracene and benzo[*ghi*]-perylene) were to have been included in the exposure studies, too. However, in previous investigations it was found that these compounds were accumulated in the receiving phase only in very small amounts (near the detection limits). Therefore an accurate determination of the sampling rates was precluded.

The sampling rates of the samplers described here are low (0.12 to 32 ml per day for the individual analytes using the water-filled tube sampler) compared with those of other sampling devices, such as standard SPMDs[21] (1 to 8 l per day). That means, the sampling efficiency of the SPMDs is about 3 orders of magnitude higher. Nevertheless, the sensitivity of the two methods should be approximately the same, because in the case of the samplers described here, the total amount of the analyte accumulated in the receiving phase is transferred to the GC/MS. In contrast, only a small portion of the obtained SPMD extract (usually 1–2 μl) is injected.

Comparing the sampling rates given in Table 4 with those of the MESCO sampler[16] it can be seen that the R_S values are in the same order of magnitude (in the μl h^{-1} range), as expected, but the MESCO sampling rates are more uniform. Additionally, for the PCBs and PAHs with high molecular weights R_S values could be determined, too. That means that measurable amounts of these analytes were accumulated in the PDMS material during the exposure. The main difference between these both sampling devices is in the membrane material employed. The membrane of the MESCO sampler consists of porous hydrophilic polymeric material (molecular weight

Table 4 Sampling rates R_S of the 3 passive sampler designs derived from flow-through exposures at different temperatures (nominal analyte concentration 50 ng^{-1})

	Water-filled tube samplers				Air-filled tube samplers		Water-filled rod samplers	
	T = 8 °C		T = 14 °C		T = 14 °C		T = 14 °C	
Compound	R_S /μl h^{-1}	CV (%)	R_S/μl h^{-1}	CV (%)	R_S/μl h^{-1}	CV (%)	R_S/μl h^{-1}	CV (%)
1,2,4,5-Tetrachlorobenzene	737	9	647	9	6355	9	480	11
Pentachlorobenzene	201	11	192	11	4314	11	214	14
Hexachlorobenzene	21	13	56	22	904	14	87	18
α-HCH	229	11	185	13	136	8	283	9
β-HCH	31	16	69	11	34	17	69	14
γ-HCH	120	10	141	11	72	8	195	10
δ-HCH	44	11	96	10	24	9	138	11
PCB 28	96	10	57	15	921	13	64	20
PCB 52	52	12	41	18	621	13	33	35
PCB 101	5	13	[a]		104	15	4	80
p,p′-DDE	4	14	5	20	53	14	5	21
Acenaphthylene	988	9	730	9	1398	8	507	7
Acenaphthene	897	9	671	9	2226	7	481	7
Fluorene	907	9	1342	11	1876	6	753	8
Phenanthrene	541	10	269	11	929	8	259	11
Anthracene	515	11	265	14	988	12	125	12
Fluoranthene	69	10	56	9	122	10	37	14
Pyrene	42	11	34	10	99	13	30	15
Benzo[*a*]anthracene	13	15	10	19	31	16	8	14
Chrysene	9	14	9	19	20	13	6	27

[a]PCB 101 could not be determined in this experiment.

cutoff 1000). Thus, the analytes pass the membrane by diffusion through the water-filled pores. In contrast, the membrane of the samplers used in this study consists of nonporous polyethylene. The organic analytes can pass such a nonporous polymeric membrane only by dissolving in the polymeric phase and subsequent diffusion through the membrane layer. (LDPE membranes can be passed only by truly dissolved organic molecules with cross-sectional diameters up to about 1 nm.[20]) Thus, the diffusion coefficients of the individual organic substances in the polymer D_M and the membrane/water partition coefficients K_{MW} are of crucial importance for the sampling efficiency.

Influence of the transfer medium on the sampling rates. In order to investigate the influence of the medium, which is contained in the sampling device together with the receiving phase, water-filled and air-filled tube samplers were exposed together under the same conditions. The determined sampling rates and variances are listed in Table 4. Comparing the R_S values in the columns 4 and 6 it can be seen that the values of most of the analytes for the air-filled sampler are significantly higher as for the water-filled ones with exception of the four HCH isomers. Thus, for the chlorobenzenes and the PCBs the R_S values are increased 10- to 20-fold and for the PAHs up to 4-fold, respectively.

The comparability of experimentally derived sampler uptake rates to actual values during environmental sampling generally depends on the similarity of laboratory and site exposure conditions. When sampler calibration and field conditions are dissimilar, the magnitude of the differences in lab and field uptake rates for an analyte depends on the source of analyte rate control. Thus, examination of potential rate-limiting barriers is important.

The overall mass transfer coefficient is expected to be affected by the diffusion of solutes in individual phases (water, membrane, the inner transfer medium [air or water], and the PDMS, respectively) and by their partitioning into the PDMS and the LDPE membrane, since accumulation of hydrophobic analytes is expected also in the hydrophobic membrane. From the theory,[30,31] it is assumed that the overall resistance ($1/k_{ov}$), to the uptake of a chemical is given by the sum of particular barrier resistances to mass transfer [eqn. (5)]:

$$\frac{1}{k_{ov}} = \sum_i \frac{\delta_i}{K_{iw} D_i} \qquad (5)$$

where δ_i is the particular barrier thickness, D_i is the diffusion coefficient in the barrier and K_{iw} is the partition coefficient between the i-th phase and water.

For water-filled tube sampler, the overall resistance ($1/k_{ovWS}$) is then given by eqn. (6):

$$\frac{1}{k_{ovWS}} = \frac{\delta_B}{D_W} + \frac{\delta_M}{D_M K_{MW}} + \frac{\delta_W}{D_W} + \frac{\delta_S}{D_S K_{SW}} \qquad (6)$$

The subscripts B, M, W and S represent the boundary aqueous layer at the surface of the sampler [B], the membrane [M], the transfer aqueous layer inside the sampler [W], and the receiving organic phase [S].

The resistance to mass transfer in the air-filled tube sampler can be described analogously by eqn. (7):

$$\frac{1}{k_{ovAS}} = \frac{\delta_B}{D_W} + \frac{\delta_M}{D_M K_{MW}} + \frac{\delta_A}{D_A K_{AW}} + \frac{\delta_S}{D_S K_{SW}} \qquad (7)$$

where the subscript A denotes the air layer between the receiving phase and the membrane, and K_{AW} is the dimensionless Henry's Law constant.

It is likely that the differences in the sampling rates determined under the same exposure conditions for two sampler designs differing from each other only in the composition of the filling medium (water or air) are caused by differences in the partial resistance to mass transfer in this medium. These particular resistances are described by the corresponding terms δ_W/D_W and $\delta_A/D_A K_{AW}$ in eqn. (6) and (7), respectively. The diffusion paths of analyte molecules through the inner transfer medium are approximately the same for both sampler designs (*i.e.* $\delta_W \approx \delta_A$). Practically, the exact distance between the membrane and the PDMS rod or tube cannot be measured because the PDMS rod or tube was not in a fixed position inside the membrane. This distance may vary between 1 and 5 mm and an approximate average value of $\delta_T = 3$ mm was taken for calculations of particular resistances of the inner medium to mass transfer of an analyte. Note that for both sampler designs, the mass transfer by convection in the inner transfer medium is assumed to be negligible. Thus, the differences in sampling rates for an analyte may originate in unequal transfer medium permeability for the two sampler designs.

To examine the effect of the inner transport medium on the mass transfer in the sampler, the sampling rate ratio for two sampler designs (R_{SAS}/R_{SWS}) determined for the same analyte under equal exposure conditions can be expressed using a combination of eqn. (2), (6) and (7):

$$\frac{R_{SAS}}{R_{SWS}} \approx \left(A + \frac{\delta_T}{D_W}\right) \Big/ \left(A + \frac{\delta_T}{D_A K_{AW}}\right) \qquad (8)$$

where $A = \delta_B/D_W + \delta_M/D_M K_{MW} + \delta_S/D_S K_{SW}$ and δ_T is the length of the diffusion path in the inner transfer medium. The sampling rate ratio is then modulated by the value of analyte's diffusion coefficient in water, the diffusion coefficient in air and the Henry's Law constant, respectively. We assume that the diffusion in membrane and/or the inner transfer medium are dominant diffusion limiting steps. The aqueous boundary layer at the surface of the sampler and in the PDMS layer present only a small part of the total diffusion path. Therefore, the term A in eqn. (8) can be rewritten $A \approx \delta_M/D_M K_{MW}$

In order to prove the applicability of eqn. (8) for prediction of the R_{SAS}/R_{SWS} ratio from the physicochemical properties of analytes, a correlation of estimated and measured ratio was performed using linear regression analysis [eqn. (9)]:

$$(R_{SAS}/R_{SWS})_{calc} = -1.153 + 2.023(R_{SAS}/R_{SWS})_{exp} \qquad (9)$$

$n = 19$; SD = 8.68; $r = 0.85$; $P < 0.0001$

The fit yields a good correlation (see also Fig. 3). However, the calculated ratio overestimates the experimental value on average by a factor of 2. The systematic error is likely introduced into the calculation by using an imprecise value of the distance between membrane and PDMS phase δ_T. A simulation of the effect of varying δ_T on the estimated R_{SAS}/R_{SWS} ratio showed that a 5-fold increase in δ_T from 1 to 5 mm results in a variation in the average slope of the linear dependence of calculated to measured R_{SAS}/R_{SWS} from 0.9 to 2.8. Despite this imprecision, experimental and estimated data correlate well for the whole range of simulated δ_T. Thus, it appears that the observed differences in experimental R_S values for two sampler designs can be explained based on physicochemical properties of analytes and theoretical considerations to mass transfer in samplers.

The calculation of particular resistances shown in eqn. (6) and (7) allows also recognizing the dominant barriers to mass transfer. Any step or layer with more than 50% of the total resistance is considered rate limiting. The comparison relative contribution of individual barriers to the total resistance for each compound shows that the uptake rate control depends not only on the sampler construction, but also on the analyte properties (Table 5). The estimation of the rate limiting barrier will be verified by experiments in the future.

Comparison of the tube and rod sampler. A comparison of the water-filled tube and rod samplers (Table 4, column 4 and

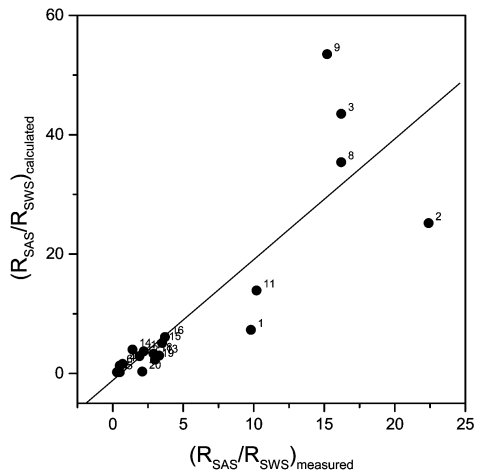

Fig. 3 Calculated *versus* experimental sampling rate ratio (R_{SAS}/R_{SWS}) for two sampler designs differing from each other only in the composition of the filling medium (air or water). The experimental ratio was determined for the two designs under the same exposure conditions in a flow-through experiment at 14 °C. The theoretical ratio R_S was calculated using eqn. (8). The line represents the linear regression given in eqn. (9).

8) shows that the sampling rates are similar. For the tube sampler the R_S values of PAHs are generally higher than those for the rod sampler. The variances of the sampling rates show increased values especially for the three PCBs for the rod sampler (PCB 28, 20%; PCB 52, 35% and PCB 101, 80%). A similar behaviour could be observed for chrysene (variation coefficient, 27%). The reason for this finding we assume in the relatively large thickness of the PDMS layer of the rods (2 mm id) and the associated deferred and incomplete desorption of these analytes. Because of the lower variances using the tube sampler this one has been favoured.

Effect of the temperature. In order to study the influence of the temperature on the sampling rates, the water-filled tube samplers were exposed at two different temperatures (14 and 8 °C; see Table 4). A significant decrease (*t*-test) of the sampling rates with decreasing temperature was observed for hexachlorobenzene, β-HCH and δ-HCH. In contrast, the more volatile PAHs, acenaphthylene, acenaphthene, phenanthrene, and anthracene, show a significant increase of the R_S values with decreasing temperature. The R_S values of the other PAHs (except fluorene) determined at the two exposure temperatures have no significant differences. The prediction of the temperature effect on the sampling rates is difficult because of the complexity of the system. Both thermodynamic and kinetic parameters affecting the sampling rate are temperature dependent.

Based on widely applied relationships such as the Wilke–Chang equation and the Heyduk and Laude equation[32] analyte diffusion coefficients in water are expected to be directly proportionally to temperature. On the other hand, the phenomenon of reduced or nearly constant solute permeability with increasing temperature has been observed in nonporous polymers such as LDPE.[33] Typically, increased temperature should enhance mass transfer in all media and the uptake of target analytes should exhibit Arrhenius dependences. However, in membrane systems, non-ideal solute-polymer interactions may affect activation energy required for molecular diffusion, increasing complexity of the temperature–R_S relationship. Also, partition coefficients K_{iw} may decline enough with increasing temperature to offset increases in diffusion coefficients.[34]

Maximum exposure time t_{50}. Maximum exposure time in which the passive sampling device accumulates a pollutant integrative under field conditions can be estimated according to eqn. (3) and the sampling rates R_S from the exposure experiments. As described in an earlier paper,[16] the determination of distribution constants K_{SW} for the analyte partitioning between PDMS coating and aqueous sample in batch experiments causes difficulties. Therefore, the apparent distribution constants $K_{f(PDMS)}$, obtained from SPME experiments with PDMS coated fibers (100 μm) was used as a substitute for the K_{SW} values in the estimation.[16] The results of the t_{50} estimation for the water-filled tube sampler are given in Table 6. From the calculation results that for acenaphthylene, acenaphthene and fluorene the passive sampler may accumulate integrative about 2 to 3 weeks. Maximum exposure times from 3 to 10 weeks were estimated for HCHs. For the other PAHs investigated, HCB, DDE and PCBs, the t_{50} values may

Table 5 Estimation of the main barrier to mass transfer in water-filled and air-filled passive sampler designs according to eqn. (6) or (7)

	Water-filled sampler			Air-filled sampler		
Compound	Membrane (%)	Water (%)	Rate limiting barrier	Membrane (%)	Air (%)	Rate limiting barrier
1,2,4,5-Tetrachlorobenzene	14	86	W	99	1	M
Pentachlorobenzene	4	96	W	93	7	M
Hexachlorobenzene	2	98	W	92	8	M
α-HCH	49	51	W+M	79	21	M
β-HCH	43	57	W+M	10	90	A
γ-HCH	49	51	W+M	62	38	M
δ-HCH	27	73	W	5	95	A
PCB 28	2	98	W	60	40	M
PCB 52	1	99	W	41	59	M + A
PCB 101	0	100	W	34	66	A
p,p′-DDE	1	99	W	20	80	A
Acenaphthylene	33	67	W	94	6	M
Acenaphthene	32	68	W	96	4	M
Fluorene	23	77	W	90	10	M
Phenanthrene	13	87	W	66	34	M
Anthracene	11	89	W	66	34	M
Fluoranthene	4	96	W	15	85	A
Pyrene	4	96	W	14	86	A
Benzo[a]anthracene	1	99	W	3	97	A
Chrysene	1	99	W	0	100	A

[a]W = Water. [b]M = Membrane. [c]A = Air.

Table 6 Estimated maximum exposure times t_{50} of the analytes using water-filled tube samplers in the field at 14 °C

Compound	log $K_{f(PDMS)}$	t_{50}/day
Hexachlorobenzene	4.3[a]	1283
α-HCH	3.2[b]	29
β-HCH	2.7[b]	24
γ-HCH	3.2[b]	40
δ-HCH	3.3[b]	74
PCB 28	4.7[a]	3158
PCB 52	5.0[a]	8761
p,*p*′-DDE	5.2[a]	108749
Acenaphthylene	3.40[c]	12
Acenaphthene	3.63[c]	23
Fluorene	3.71[c]	14
Phenanthrene	3.96[c]	121
Anthracene	3.98[c]	129
Fluoranthene	4.71[c]	3287
Pyrene	4.86[c]	7625
Benzo[*a*]anthracene	5.26[c]	63769
Chrysene	5.69[c]	188469

[a]Data from reference 16. [b]Data from reference 36. [c]Data from reference 35.

be several months and more. The results of the t_{50} calculation indicate that the passive sampler under investigation enables the estimation of TWA concentrations of pollutants from the amounts accumulated during field exposures of several weeks.

As described above, the change of the inner transfer medium (from water to air) used in the samplers results in significantly increased sampling rates for most of the analytes investigated (except the HCH isomers) and thus, according to eqn. (3), in decreasing t_{50} values. It could be estimated, that the air-filled tube sampler may integrative sample the low molecular weight PAHs (acenaphthylene and acenaphthene) only up to one week. However, in the calibration experiment linear uptake were found to be up to nine days for these compounds.

Sensitivity. The calculated sampling rates were used to estimate the potential of the sampling devices under study to detect low TWA concentrations of the target analytes. Based on eqn. (1), the minimum quantifiable TWA concentration of the analytes in ambient water were estimated, whereas the M_S values were replaced by the limits of quantification $M_{S(LOQ)}$. According to the correlation mentioned above, the sensitivity of the entire analytical method depends on the sampling rate R_S and the exposure time of the sampler. That means, presuming the integrative uptake of the analyte from the sampler over the entire exposure period, the sensitivity improves with increasing exposure time. Assuming an exposure of 10 days, limits of quantification in the range of 3 pg l^{-1} (fluorene) to 2.4 ng l^{-1} (*p*,*p*′-DDE) could be estimated for the water-filled tube sampler (at 14 °C). The use of the air-filled tube sampler enables a significant improvement in sensitivity for most of the target analytes except the HCH isomers. Therefore this sampler design is recommended if very low concentrations of pollutants are expected in the field. These results demonstrate that the sampling devices described here enable the detection of the target analytes in the lower ng l^{-1} to pg l^{-1} range.

Conclusions

Based on a previously described sampler (MESCO)[16] a new passive sampler was designed which has on one hand the advantages of the earlier one, and overcomes its weakness (the low chemical and thermal stability as well as biodegradability of the dialysis membrane from regenerated cellulose) on the other hand. The membrane was substituted by a stable, in the SPMD technique successfully applied, LDPE membrane. Moreover, the stir bars used as receiving phase were substituted by less expensive PDMS materials (tubes and rods), which enabled additionally a significant increase of the PDMS volume and thus the accumulation capacity. The study of the PDMS materials regarding reproducibility and completeness of enrichment and thermodesorption yielded in comparable good results of tubes and stir bars.

The investigation of the capability of three versions of the sampler (water-filled tube and rod sampler as well as air-filled tube sampler) resulted in the new samplers enabling the effective accumulation of the POPs under study and thus the estimation of low TWA concentrations of these water pollutants. The first comparison of samplers which differ only in the filling medium (water and air, respectively) was done, to our knowledge. This resulted in a significant increase of the sampling rates of most of the analytes and thus in enhanced sensitivities for the air-filled sampler. This finding could be confirmed by calculation of the sampling rates based on physico-chemical parameters.

The new samplers are stable in field exposure (as tested in on-site experiments) and enable longer exposure times compared with the MESCO sampler because of their enlarged accumulation capacity.

However, there is a lack in efficient sampling of analytes with larger molecular size, such as PCBs and PAHs with high molecular weights because of the application of the non-porous LDPE membranes.

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