CHAPTER 24
NOVEL PASSIVE SAMPLERS FOR MONITORING ORGANIC POLLUTANTS IN SURFACE AND GROUND WATER BASED ON MEMBRANE-ENCLOSED SILICONE MATERIAL

Albrecht Paschke1, Branislav Vrana1, Peter Popp2, Luise Wennrich3, Wilhelm Lorenz3, and Gerrit Schüürmann1

1 UFZ-Department of Chemical Ecotoxicology
2 UFZ-Department of Analytical Chemistry, UFZ Centre for Environmental Research Leipzig, Germany
3 Institute of Analytical and Environmental Chemistry, Martin-Luther-University Halle-Wittenberg, Germany

ABSTRACT
In the last five years we have used semi-permeable membrane devices (SPMDs) in several field campaigns for time-integrative and biomimetic sampling of persistent organic micropollutants (chlorinated hydrocarbons, polycyclic aromatics, etc.) in brooks, rivers, lakes and groundwater wells around Leipzig. These devices are expensive and their processing is time- and solvent-consuming. Therefore we have developed novel types of passive samplers consisting of a membrane which encloses coarse silicone material or polydimethylsiloxane (PDMS) coatings (embedded in a fluid) as the collecting phase. We tested different commercially available materials like 100 µm PDMS fibres from Supelco, Twister bars from Gerstel, silicone tubes and rods from Goodfellow. Also different fluid compositions in the membrane bag were tested. In laboratory flow-through experiments we determined the sampling rates with different sampler types under standard conditions. Preliminary field trials have shown the applicability of the new samplers but have also indicated necessary improvements concerning especially the membrane enclosure used.

The general advantages of the new developed passive samplers are i) the simple removing of the collector phase; ii) its processing without further clean-up steps by direct thermodesorption or solvent microextraction; iii) the possibility to spike the collecting phase before deployment with so-called performance reference compounds and iv) that, in addition to chemical target or non-target analysis, the collecting phase can also be subject to biological effect screening (after digestion using an appropriate solvent). Provided further field tests succeed, some of the new samplers will be inexpensive and multifunctional alternatives to established passive samplers (SPMDs, dosimeters) for monitoring persistent (more hydrophobic) organic compounds in aqueous environmental compartments.
1 INTRODUCTION
Monitoring of environmental pollutants in ground and surface waters is of fundamental importance for the protection of ecosystems and human health. Especially the determination of persistent organic pollutants (POPs) is of relevance due to their tendency to bioaccumulate and their high toxic potential. These pollutants are present in the aquatic environment both truly dissolved and particle-bound. Of primary interest for risk assessment is the bioavailable fraction which corresponds to the truly dissolved fraction. With conventional sampling techniques (grab sampling) only the total content of the pollutants is obtained. Furthermore, analysis of grab samples provides only information about pollutant burden at the moment of sampling.

Passive sampling techniques can overcome these problems. They allow the determination of time-weighted average (TWA) concentration of the truly dissolved fraction of pollutants over several weeks or even months. Compared to conventional sampling the number of the samples and thus the expense for sampling and subsequent analysis can be reduced significantly. In addition, due to the long accumulation period, passive sampling allows the detection of very low concentrations of target analytes. Furthermore, the sampling devices are usually simple in design and do not require power supply, etc. This makes such techniques suitable for field use, even at remote sites. However, for the calculation of TWA concentrations in the monitored water phase from the collected amounts of analytes it is essential to know the specific sampling rates of the sampler or to determined them in additional laboratory experiments.

In the last few years various passive sampling devices were designed for monitoring of pollutants in the aquatic systems. These sampling devices can be classified as diffusion samplers and permeation samplers, depending on the rate-limiting step of analyte transport into the collecting phase [1-3].

Among the permeation samplers, the so-called semipermeable membrane devices (SPMDs), introduced by Huckins and co-worker [4,5], attained the greatest importance and wide-spread application. A SPMD consists of layflat low-density polyethylene tubing enclosing a thin film of triolein. SPMDs proved to be most effective in their capacity to accumulate lipophilic contaminants. We have used the commercially available standard SPMDs in several field campaigns for sampling of chlorinated hydrocarbons, polycyclic aromatics, etc., in brooks, rivers, lakes and groundwater wells around Leipzig, Germany [6-8]. The main disadvantage of this sampler type is, beside the relatively high price, the complex sample preparation procedure required to recover the accumulated pollutants from the collecting phase (tri olein). This is achieved by dialysis using considerable amounts of organic solvents, followed by preconcentration and expensive cleanup of the extracts before the chromatographic analysis [6, 9, 10].

In the last decade several attempts have been made, to develop devices, which avoid the drawbacks mentioned above and make the passive sampling technology more attractive also for routine monitoring programmes. Such passive samplers contain solid materials (granular adsorbents and compact polymeric sorbents) instead of the liquid organic receiving phase. That allows thermodesorption of the accumulated pollutants without additional sample preparation.

Hardy et al.[11-13], e.g. 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 com-
pounds, like monocyclic aromatic compounds [13] and phenols [12], whereas the less volatile compounds were not enriched effectively.

Grathwohl and co-worker[14-15] designed a new 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. with ion exchange resin Amberlite IRA-743 or Tenax, and was tested 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 tube.

Our work in the last years was concentrated on the development and test of permeation samplers for POPs in aqueous systems by taking advantage of commercially available polydimethylsiloxane (PDMS) coatings or silicone material (tubes, rods) as the collecting phase. PDMS is recommended as a receiving phase in extraction and thermodesorption as it has a number of benefits compared with other sorbents [16]. The predominant mechanism of analyte extraction into the polymer PDMS phase is absorptive partitioning, that means, displacement effects of the analytes which are characteristically for adsorbents play no role.

This contribution summarizes the actual state of our research and gives some perspectives.

2 SAMPLER WITH PDMS-COATED SPME FIBRE [17]

Fig. 1 shows in principle the design of this permeation sampler. We tested e.g. membrane bags (13 cm × 2.5 cm) of 100 µm thick low-density polyethylen (LDPE) tubing (Polymer-Synthesewerk Rheinberg, Germany), heat-sealed at both ends, in combination with 100-µm PDMS fibres (Supelco, Deisenhofen, Germany) as collector phase (= 0.68 µL) and 25 mL of a 40/60-isopropanol/water mixture (v/v) as inner fluid. The coil spring prevents the fibre coating from direct contact with the membrane.

The performance of the new sampler was tested by time-dependent exposure in a flow-through system (described elsewhere [18]) at 19 °C (upstream flow: 36 L/h; nominal water concentration for each test substance: 50 ng/L; exposure times: up to 360 h) The obtained sampling rates are summarized in the second column of Table 1 (for details on SPME fibre desorption and gas chromatographic analysis, see [19]). A serious problem of this sampler is that the polymer-coated glass fibre tip is very fragile and difficult to
handle during removal from and re-insertion into the steel needle of the commercial SPME syringe device.

3 SAMPLER WITH PDMS-COATED STIR BAR [18, 20]
The PDMS-coated stir bar contained here as collector phase is known under the trademark Twister (Gerstel, Mühlheim/Ruhr, Germany) and commonly used for solvent-free microextraction like a SPME fibre but with a larger extraction capacity. Fig. 2 gives a diagram of the sampler. Specifically, we tested dialysis membrane bags of regenerated cellulose Spectra/Por 6 with a molecular weight cutoff of 1 kDa (3 cm × 1.8 cm), sealed at each end with a 35-mm Spectra/Por enclosure, in combination with Twister bars of 15 mm length coated with a 500 µm thick layer of PDMS (= 24 µL) and 3 mL bidistilled water as filling.

Figure 2: The permeation sampler with PDMS-coated Stir bar

Regenerated cellulose as a porous hydrophilic membrane material enables to widen 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, which potentially leads to the damage of the sampler in natural surface waters. This sampler type was also tested in a flow-through apparatus (under the same conditions like above, see [18] for experimental details). The determined sampling rates are given in the third column of Table 1.
TABLE 1
Sampling rates (SR) of the permeation samplers with PDMS-coated SPME fibre and Twister bar for selected POPs (not directly comparable, see text)

<table>
<thead>
<tr>
<th>Substance</th>
<th>SR of sampler with SPME fibre [mL/h]</th>
<th>SR of sampler with Twister bar [mL/h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-HCH</td>
<td>0.50</td>
<td>0.40</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>2.21</td>
<td>0.25</td>
</tr>
<tr>
<td>Anthracene</td>
<td>1.45</td>
<td>0.22</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>1.46</td>
<td>0.25</td>
</tr>
<tr>
<td>Pyrene</td>
<td>1.18</td>
<td>0.27</td>
</tr>
<tr>
<td>Benzo[a]anthracene</td>
<td>0.88</td>
<td>0.37</td>
</tr>
<tr>
<td>PCB 28</td>
<td>7.03</td>
<td>0.15</td>
</tr>
<tr>
<td>PCB 52</td>
<td>8.85</td>
<td>0.15</td>
</tr>
<tr>
<td>PCB 101</td>
<td>6.30</td>
<td>0.13</td>
</tr>
<tr>
<td>PCB 138</td>
<td>4.55</td>
<td>0.09</td>
</tr>
<tr>
<td>PCB 153</td>
<td>3.12</td>
<td>0.10</td>
</tr>
</tbody>
</table>

**SAMPLER WITH SILICONE ROD/TUBE [20, 21]**

This sampler type combines the advantage of a high-capacity collector phase with those of more stable membranes, such as LDPE. These membranes are hydrophobic, resistant to solvents and biodegradation and they can be heat-sealed. Furthermore, the expensive (and fragile) Twister bar is substituted here by relatively cheap silicone material (pieces of a tube or rod) as collector phase. (Additional investigations have shown the usefulness of these materials for an effective preconcentration of POPs from water samples and the applicability of thermodesorption-GC/MS analogously to the processing of Twister bars [21, 22].) The significant enhanced volume of collector phase (> 100 µL) increases the maximum exposure time of the passive sampler in the field.

Different configurations of the new sampler were exposed to spiked water in a flow-through system at 14 °C (upstream flow: 60 L/h; nominal concentration: 50 ng/L for each test chemical; exposure times: up to 176/236 h). The membrane bags (5 cm × 3 cm) consists of 80 µm thick LDPE tubing (Polymer-Synthesewerk Rheinberg, Germany). As collector phase either 4 cm long pieces of silicone tube (with 3.6 mm O.D., 3.0 mm I.D.; Reichelt, Heidelberg, Germany) or 4 cm long pieces of silicone rod (2.0 mm O.D., Goodfellow, Bad Nauheim, Germany) were used. The silicone material was embedded in 8 mL water in one series of experiments or in air for another series (see [21] for further experimental details). The sampling rates calculated from the determined mass uptake are given in Table 2.
TABLE 2
Sampling rates (SR) of the permeation samplers with different silicone materials and fluid fillings for selected POPs (see text for details)

<table>
<thead>
<tr>
<th>Substance</th>
<th>SR of sampler with rod+water [mL/h]</th>
<th>SR of sampler with tube+water [mL/h]</th>
<th>SR of sampler with tube+air [mL/h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-HCH</td>
<td>0.28</td>
<td>0.18</td>
<td>0.14</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>0.09</td>
<td>0.06</td>
<td>0.90</td>
</tr>
<tr>
<td>Anthracene</td>
<td>0.12</td>
<td>0.26</td>
<td>0.99</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>0.04</td>
<td>0.06</td>
<td>0.12</td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.03</td>
<td>0.03</td>
<td>0.10</td>
</tr>
<tr>
<td>Benzo[a]anthracene</td>
<td>0.01</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>PCB 28</td>
<td>0.06</td>
<td>0.06</td>
<td>0.92</td>
</tr>
<tr>
<td>PCB 52</td>
<td>0.03</td>
<td>0.04</td>
<td>0.62</td>
</tr>
<tr>
<td>PCB 101</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Remarkable higher sampling rates were obtained with air as fluid filling of the membrane bags. This can be explained by a detailed consideration of the mass-transfer resistances [21]. Tube and rod material yielded similar results but the variances in SR were lower for the tube-containing sampler. A practical drawback of the latter material in combination with water as fluid filling is that remaining water droplets (inside the tube) can disrupt the GC/MS analysis.

4 PROSPECTS
The thermodesorption of POPs (and of many other accumulated analytes) from the collector phases (PDMS fibre, Twister bar, silicone tube/rod) can be substituted by solvent microextraction [23-25]. This can have some advantages: i) it makes a thermodesorption/cold injection system unnecessary before gas chromatographic analysis; ii) this enables repetition of analyses and iii) the obtained extracts can be subject to biological effect screening.

Extensive field campaigns with the new samplers are indispensable to demonstrate their applicability under real-world conditions. Furthermore, additional exposure experiments under controlled conditions in the laboratory are necessary to verify/obtain the sampling rates for a wide range of water contaminants.

REFERENCES