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Solutions for present and future emerging pollutants in land and water resources management

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Internal Deliverable

ID T2.3 Guidelines describing passive sampling and analytical aspects of the procedure for relevant compounds

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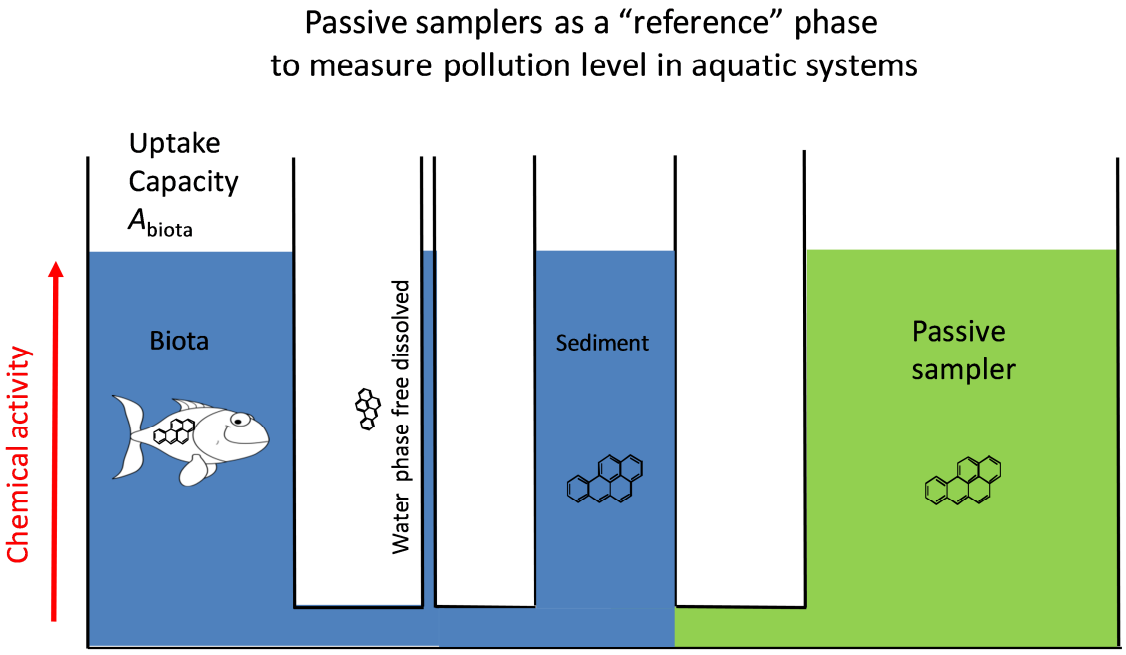
Branislav Vrana, Foppe Smedes, Klára Hilscherová, Tatsiana Rusina, Krzysztof Okonski, and Jiří Novák

Masaryk University, MU, Brno, Czech Republic

1 Summary

Passive sampling is a powerful tool that can conveniently be used for monitoring of organic compounds in water and other environmental compartments. It has been designed to provide estimates of freely dissolved concentrations which have been shown to be in many cases most appropriate to explain exposure and adverse effects in biota. Partition based passive sampling also allows direct comparison of measured water concentrations with concentrations in diverse compartments (e.g. water, sediment, biota), based on the assessment of chemical activity in those matrices. The time-integrating character of sampling in combination with the application of a sampling matrix (polymers) with well-defined and constant properties makes it possible to achieve a lower inherent variability of exposure information compared to traditional grab sampling of whole water. Thus, it is suitable for assessment of pollutant trends in water bodies. This internal deliverable of the SOLUTIONS project provides a practical guidance on the use of passive samplers for monitoring organic pollutants in water. Two categories of passive samplers are addressed. The first category comprises partition-based samplers for the measurement of non-polar contaminants, and the guidance sets focus on silicone rubber based samplers, which have been widely applied in the SOLUTIONS project. The second category encompasses adsorption passive samplers for monitoring more polar aquatic contaminants; the typically applied samplers are based on the use of sorbents designed for solid-phase extraction. This guidance should assist users of passive samplers, who wish to implement passive sampling methods in their research or monitoring work, as well as more experienced users in the use of the available methods according to the state-of-the art. The guideline addresses principles of passive sampling, sampler preparation, field deployment, laboratory processing, chemical analysis, calculation of aqueous concentrations and associated uncertainty considerations. Aspects of quality assurance are also addressed. Finally, practical examples of sampler operation and sample processing procedures are provided, which have been developed and applied within the SOLUTIONS project.

2 Graph


Passive samplers as a “reference” phase
to measure pollution level in aquatic systems
Uptake
Capacity
A_{biota}
Biota
Water phase free dissolved
Sediment
Passive
sampler
Chemical activity

1

3 Contents

4 List of Abbreviations

a-PSD	adsorption-based passive sampler
BDEs	brominated diphenyl ethers
CA	chemical activity
DCM	dichloromethane
DEE	diethylether
DEQ	degree of equilibrium
EPS	the “enhanced” passive sampling system
EQS	Environmental Quality Standards
GC/MS	gas chromatography/mass spectrometry
HCB	hexachlorobenzene
IIS	instrumental internal standard
K_{pw}	polymer-water partition coefficient or sorbent-water distribution coefficient
LDPE	low density polyethylene
LOD	limit of detection
LOQ	limit of quantification
NBFR	novel brominated flame retardants
OCP	organochlorine pesticide
OPFR	organophosphorus flame retardant
PAH	polycyclic aromatic hydrocarbon
PDMS	polydimethylsiloxane
p-PSD	partitioning-based passive sampler
PCB	polychlorinated biphenyl
PRC	performance reference compound
PS	passive sampler
RIS	recovery internal standard
SR	silicone rubber
QA/QC	Quality assurance/Quality control
SPMD	semipermeable membrane device
TWA	time-weighted average
WBL	water boundary layer
WFD	Water framework Directive 2000/60/EC

5 Introduction

Environmental quality is recognized as a high priority across the world, and measures towards its improvement have a positive effect on the quality of human life. Anthropogenic pollutants in the aquatic environment may have a negative effect not only on the ecosystems, but, ultimately, also on the human health. To control environmental pollution their concentrations are monitored in various compartments with the aim to detect trends, underpin risk assessment and support decisions on remedial actions. Data from chemical monitoring should be comparable between laboratories and provide accurate and representative information on pollutant levels and trends. Much emphasis has been placed on the chemical-analytical aspects of measuring pollutant levels in discrete samples but less attention has been paid to the underpinning sampling procedures, despite the very much larger uncertainties associated with this crucial phase of the monitoring process. Passive samplers present an innovative monitoring tool for the time-integrated measurement of bioavailable contaminant levels in the aquatic environment. Passive sampling is based on the deployment in situ, or use in the laboratory, of non-mechanical devices of simple construction capable of accumulating contaminants dissolved in water or other environmental media. The uptake of hydrophobic/lipophilic substances by passive samplers (PS) is based on a much better solubility of most organic substances in the material the samplers are made from, e.g. low density polyethylene (LDPE) filled with lipid (semipermeable membrane devices, SPMD) or without lipid, silicone rubber, i.e. polydimethylsiloxane (PDMS)-based materials, and polyoxymethylene. In addition to these partition samplers, adsorption-based samplers are also available that can accumulate the more hydrophilic substances. From the uptake by PS freely dissolved concentrations of substances in the water phase can be derived, often with extremely low limits of quantification (LOQ). These derived concentrations typically represent an average over a certain time period, often corresponding to the deployment period of the sampler (typically 2-6 weeks). These properties of PS present a potential value for use in regulatory monitoring.

This technology has a great potential because of the simplicity of the principles underlying its function, and structure. In contrast to active samplers, passive samplers have no moving parts, they normally do not require a power source for their operation, and are relatively inexpensive. In addition, these devices can be deployed in almost any environmental condition, thus making them ideal for pollutant monitoring even in remote areas with minimal infrastructure.

The implementation of passive sampling in monitoring programmes requires:

- Availability of samplers with well-defined and constant properties, which should preferably be commercially available
- Existence of guidelines for use and data interpretation
- Calibration data including sampler/water partition coefficients for partition samplers (definition in section 10) or an appropriate measure for accurate sampling rates for adsorption samplers (definition in section 11)
- Quality assurance/Quality control
    - Uncertainty/variability of the method should be known
    - Proficiency testing schemes for analysis and data interpretation should be available
    - Reference materials (or stations) for method testing should be available

The guidelines presented here cannot address all passive samplers that are currently being used by the scientific community, but they illustrate the use of two main types of passive samplers, namely partition-based samplers (p-PSD) for non-polar compounds, and adsorption-based samplers (a-PSD) showing the examples of two specific samplers that have been applied within the SOLUTIONS project. Although specific issues are expected when different types of samplers are applied, these guidelines address typical issues that apply for passive samplers in general.

The application of p-PSD for sampling hydrophobic compounds is illustrated using samplers based on **silicone rubber** (SR) sheets. SR sheet samplers were chosen for application within the SOLUTIONS project because accurate polymer – water partition coefficients (K_{PW}) are available for many contaminants [1]. In addition, there is a better agreement between hydrodynamic theory and experimental sampling rates for these samplers [2] than for SPMDs [3] and Chemcatchers [4]. Further considerations for evaluating the pros and cons of specific PSDs can be found elsewhere [5].

The application of a-PSD for sampling polar compounds is illustrated using samplers based on **Empore™ SPE disks**. The main criteria for their application in SOLUTIONS included a simple construction, a simple working principle, mechanical robustness and commercial availability.

6 Principles of passive sampling

Passive sampling is based on the deployment, in situ or use in the laboratory, of devices capable of accumulating contaminants from water or from other media present in the aquatic environment (sediment, aquatic biota etc.), but also other environmental media e.g. air. Transfer of contaminants from the

environment into the sampler is a spontaneous diffusion process that is driven by the difference in chemical activity (CA; for explanation see 7) of the monitored substance between the sampled medium and the sampler sorption phase. The accumulation of substance in the sampler takes place until thermodynamic equilibrium (in an open dynamic aquatic systems such as rivers a dynamic equilibrium or steady state is meant) established between the sampler and the water, or until the sampling process is interrupted. The sampler exposure period is usually several days to weeks. Passive sampling can be viewed as a special case of chemical extraction from the sampled medium that is performed in situ (Figure 1). During exposure in the field monitored substances are extracted, and their concentration in the sampler extract is then determined in the laboratory.

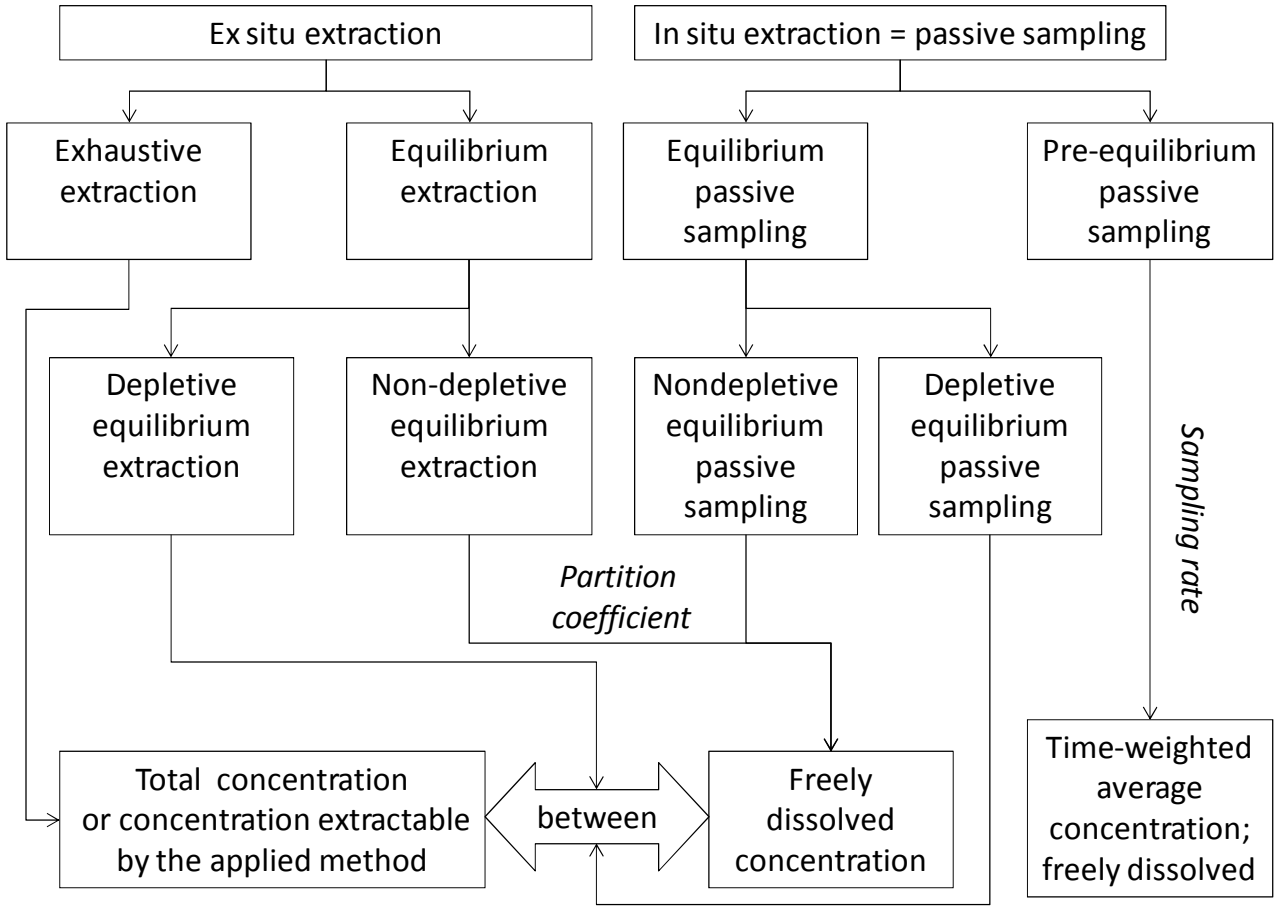


Figure 1 Various extraction modes applied in analysis of environmental pollutants. Passive sampling can be considered as a special case of extraction, performed in situ. Passive sampling combines sampling, sample isolation from the matrix, analyte pre-concentration and often sample conservation into a single step.

When the sampler's calibration parameters are known, it is possible to calculate the concentration of substances in the sampled medium from their amounts found in the sampler. At the initial stage of sampler deployment, contaminants are absorbed at a rate directly proportional to their aqueous concentration (linear uptake stage; Figure 3). In the linear uptake stage the obtained sample represents the concentration of the sampled substance in the sampled medium for a certain period of time. In this phase the sampler integrates contaminant peak events that occur during its exposure. The amount of a compound accumulated in the sampler is proportional to the time-weighted average of its concentration in the water phase during exposure. As the sampling continues, the concentration gradually approaches contaminant`s equilibrium concentration in the sampler.

A very important aspect of passive sampling is the option to express the equilibrium concentration in the form of CA [6] which then also applies to the sampled medium (see 7). Differences in CA are the driving force of spontaneous mass transfer between the various environmental compartments. In practice the results of passive sampling is expressed in free dissolved concentrations which are essentially proportional to CA. Due to the high sampler sorption capacity and integrative character of passive sampling free dissolved concentrations can be monitored in water at extremely low levels (down to the order of pg/L).

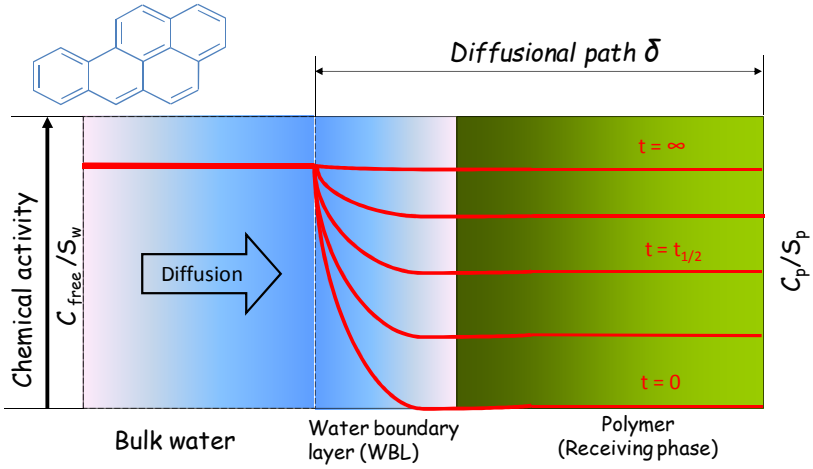


Figure 2 Functional principle of a passive sampler, showing a compounds`s chemical activity profiles during diffusion and accumulation from water (or other sampled medium; left hand side) to the sorbent (receiving phase) in time along the diffusional path δ. The chemical activity of a substance in a medium is given as ratio of concentration C and the subcooled liquid solubility/uptake capacity S. The high accumulation of the sampled substance in the sampler is achieved by the high solubility (or uptake capacity) in the receiving phase S_p.

In general, two types of passive samplers can be distinguished: partition passive samplers (p-PSD) and adsorption passive samplers (a-PSD). Although most requirements apply to both types of samplers, it is easier to discuss principles and application separately for both sampler types – see chapters 10 and 11.

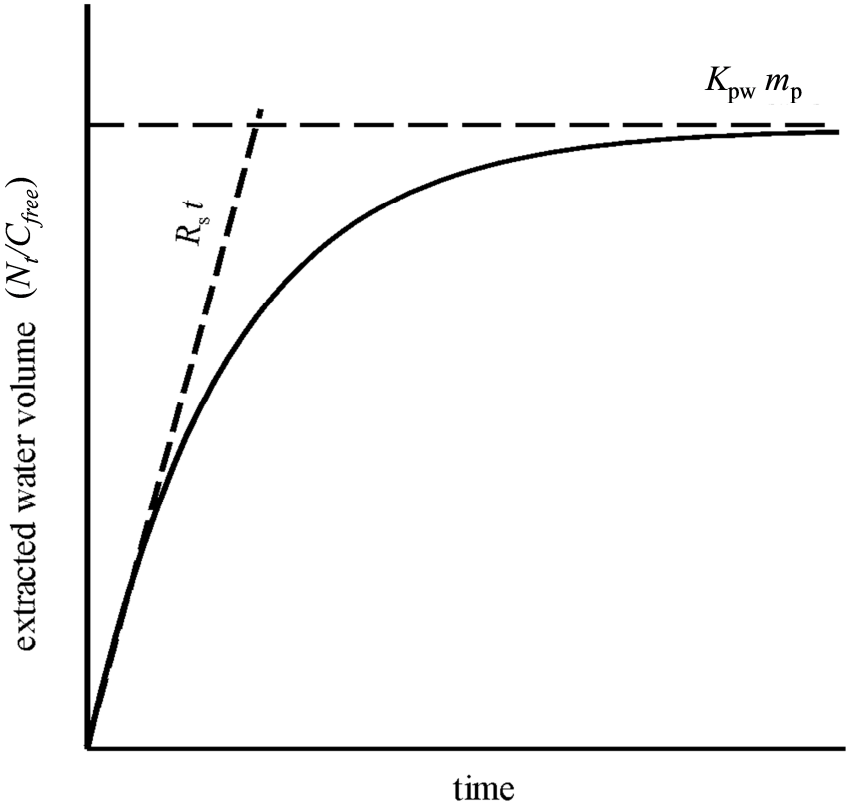


Figure 3 Effectively extracted water volume as a function of time. Here N_t is the uptake at time t and C_{free} the free dissolved concentration. For long exposure times the extracted volume is constrained by the sorption capacity of the passive sample ($K_{pw} \times m_p$), and at short exposure times by the product of sampling rate and time ($R_S \times t$). Adapted from [7].

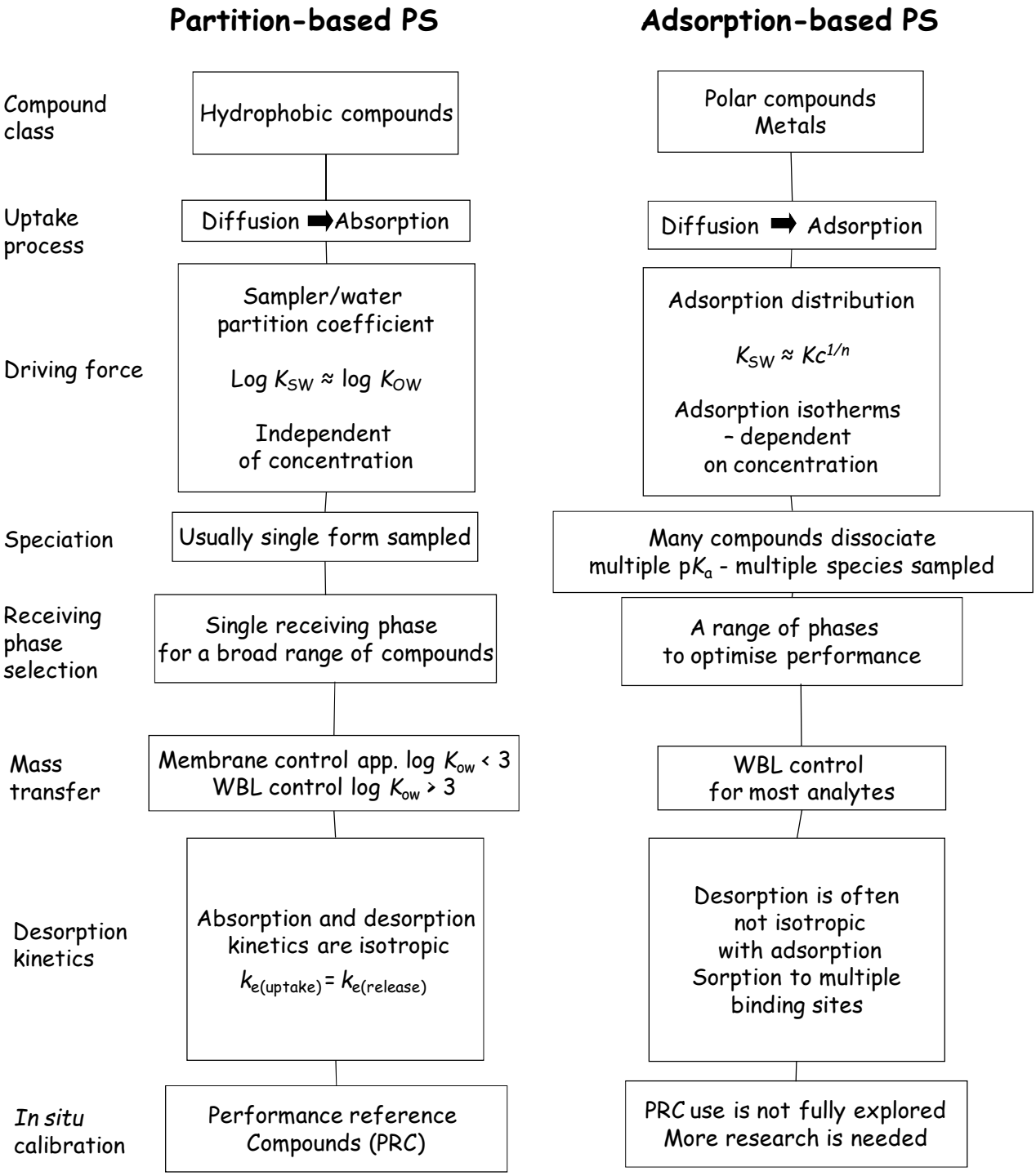


Figure 4 Comparing properties of partitioning and adsorption-based passive samplers.1

[1] WBL means the water boundary layer; k_e is the exchange rate constant of the compound between the sampler and the sampled medium.

7 Equilibrium partitioning theory and the chemical activity concept

In agreement with the equilibrium partitioning theory [8], it has been shown that exposure, bioconcentration and toxicity of hydrophobic organic compounds is related to the freely dissolved concentration (C_{free}) rather than to the total concentration that includes various quantities of compound bound to dissolved organic matter, colloids, or suspended particulate matter forms [9,10]. In contrast to C_{free}, whole water sample concentrations of organic chemicals allow for only limited conclusions on exposure of and risks to biota and thus hamper understanding of relationships between contamination and ecological status [11]. The key issue for exposure assessment is the knowledge of the driving force for spontaneous contaminant uptake to the organism from its environment. From the thermodynamic point of view the driving force for uptake is given by the difference of chemical`s CA (or fugacity) between the water and the organism. Because CA is directly proportional to C_{free}, i.e. $CA=C_{free}/S_W$ being the ratio between concentration and uptake capacity (here aqueous solubility of the subcooled liquid S_W), the importance of C_{free} for contaminant uptake and transport becomes evident. If the aqueous CA is known, this value also applies to all other matrices present in an aquatic ecosystem, provided they are at equilibrium with water:

$$CA = \frac{C_{free}}{S_W} = \frac{C_{sed}}{U_{sed}} = \frac{C_{biota}}{U_{biota}} = \frac{C_{lipid}}{U_{lipid}} \quad but \quad also = \frac{C_{passive\,sampler}}{U_{passive\,sampler}} \qquad (1)$$

Where C_x and U_x are the respective concentration and the uptake capacity of matrix ‘x’. A difference in CA is the driving force for a spontaneous chemical mass transfer between matrices, and also for uptake by organisms. This is valid even when the chemical is taken up via the food exposure route. However, when the food is digested and/or consumed in the catabolic processes within the organism, the internal CA will change (i.e. increase) and so will the uptake. With time, both processes (i.e. the uptake and the release) result in establishment of a steady state. The resulting CA ratio between predator and prey is biomagnification.

8 Site considerations

Prior to the start of a study with passive samplers, a number of issues should be considered, including the following. The suitability of site for the purpose of sampling should be assessed, i.e. if general status of water quality in the water body should be monitored, the site should be located outside mixing zones with point sources of pollution, e.g. discharges of effluents from industrial and municipal wastewater, polluted tributaries, contaminated sites etc. Secondly, it is useful to acquire information on turbulence-flow rates,

temperature, conductivity, pH, water depth, stratification, biofouling potential and turbidity at the exposure sites. Thirdly, the possibility that target compounds may undergo photolysis should be considered and, if so, whether deployment devices and site conditions (e.g. turbidity, natural shading and albedo or light reflectance from site surfaces) will adequately protect the samplers from sunlight. If not, further measures to avoid photolytic degradation may need to be implemented. Fourthly, the risks that samplers may be vandalized, stolen or otherwise interfered with, need to be assessed. Finally, a safe access to the sampling site and possibility to work on site with a minimised risk of sample contamination should be also considered.

9 Quality assurance and quality control

Quality assurance monitoring with passive sampling requires a series of quality control measures. These include the analysis of the reagents and solvents (**reagent blanks**), **preparation controls**, **field controls** and **recovery spikes**. Comparison of reagent blanks, preparation and field controls can help identify possible sources of contamination and take the necessary measures to ensure quality.

9.1 Reagent blank

According to the EN ISO 5667-23 [12], reagent blank is an aliquot of reagent used in treatment of passive sampling devices which is analysed following deployment in order to diagnose any contamination from the reagents used. The amounts detected in the reagent blanks can be subtracted from the amounts detected in analysis of exposed samplers, preparation controls, and field controls.

9.2 Preparation control

The term ’preparation control’ is not explicitly defined in the EN ISO 5667-23 norm, but it is essential for QC of the sampling process. The preparation control reveals amounts of target compounds that have been taken up during preparation, storage and subsequent analysis of the samplers. In order to allow mutual comparison of contaminant levels, it is crucial to use preparation controls and exposure samplers from the same production batch. Amounts of target compounds in the preparation controls should preferably be similar to those in the procedural blanks. Results of the preparation controls are used to estimate LOD/LOQ. For that purpose the amount of analyte found in the preparation control (**Error! Reference source not found.**) or the instrumental blank is substituted to Equation 5. If target compound amounts in preparation controls are much higher than in the reagent blank, the sampler preparation procedure should be critically assessed to identify and eliminate the causes of these elevated levels [13].

Look out!

Since the LOQ values for the water concentration are calculated using site-specific sampling rates, LOQs are also site-specific. The integrative character of passive sampling often allows reducing LOQs by extending the sampler exposure period.

The preparation controls are also analysed to give information on the spiked amounts of PRCs (N_0) in p-PSDs. The PRC fraction that remains in the sampler after exposure is determined as the ratio of PRC amount in exposed sampler to the amount find in preparation control (N_0).

9.3 Field control

According to the EN ISO 5667-23 [12], field control is a quality control passive sampling device to record any chemical accumulated in passive sampling devices during manufacture, assembly, storage, transportation, deployment, retrieval and subsequent analysis. In addition to preparation controls, the field controls reveal information on sampler contamination that occurred during deployment, transport and retrieval procedures.

Field controls may contain higher target analyte than the preparation controls, if sampler deployment/retrieval operations are conducted in highly contaminated areas near factories, highways, or on board ships, or when the working area is in an area with elevated air contamination. Since contaminant concentrations in field controls are always very site-specific, it is not recommended to use these controls for determining average blank levels and detection limits. Field controls should mainly be used to assess contamination from the atmosphere during transport and deployment/retrieval process in a qualitative manner. Elevated concentrations of analytes in field controls may indicate the need to revise/change the procedure of passive sampler deployment and retrieval.

9.4 Performance reference compound (PRC)

According to the EN ISO 5667-23 [12], PRC is a compound that is added to the sampler prior to exposure and has such an affinity to the sampler that it dissipates from the sampler during exposure, and that does not interfere with the sampling and analytical processes. Sampling kinetics can be quantified using the dissipation of PRCs that are spiked into the sampler prior to deployment.

9.5 Recovery spike

According to the EN ISO 5667-23 [12] recovery spike is a quality control passive sampling device, pre-spiked with known mass of analytical recovery standard, used to determine the recovery level of pollutant from passive sampling devices following deployment.

9.6 QA/QC for toxicological analysis

QA/QC applied for passive samplers for toxicological analysis is similar to those for chemical analysis. Preparation controls (9.2) and field controls (9.3) are processed together with exposed samplers and they are treated like samples. Reagent blanks (9.1) processed in the same way but without sheets. While toxicity recovery is a good way to test for the general applicability of an extraction and clean-up method, it does not provide any information on causes for insufficient recovery [14]. Thus, it is recommended that analytical recovery is assessed in addition to toxicity recovery, when recovery spikes (9.5) are analysed. The set of compounds used to monitor recovery should include those classes of chemicals that are known to cause the effect of concern. This approach will help to identify compound groups and properties that might be responsible for insufficient toxicity recovery [14].

Since PRCs (9.4) cannot be applied in samplers subjected to toxicological analysis, information on sampling rates cannot be derived directly for those samplers. Instead, an indirect method must be applied. Samplers of the same dimensions are spiked with PRCs and deployed in parallel with the samplers for toxicological analysis. Following exposure, those samplers are analysed for PRC loss during exposure and derived sampling rates are applied for samplers for toxicological analysis.

10 Partitioning-based PS devices

Partitioning-based PS devices (p-PSD) are made from hydrophobic polymeric materials with high permeability for the compounds to be sampled. p-PSDs absorb (or, more accurately, dissolve) substances from water because of much better solubility of the substances in the sampler material compared to water. Consequently, hydrophobic substances with low solubility in water are strongly accumulated in p-PSDs, while hydrophilic substances are concentrated to a much smaller extent. Following a sufficiently long exposure in the environment the absorbed concentration in the p-PSDs eventually attain equilibrium with the concentrations outside the sampler, e.g. water. From the equilibrated concentration in the p-PSD an aqueous phase concentration can be estimated using the sampler-water partition coefficients (K_{PW}).

However, in practice, with application of p-PSDs in water, equilibrium is only attained for substances with a log K_{PW} up to 5 or 6 when exposed long or under turbulent conditions. For more hydrophobic

substances the uptake is too slow (or actually the sampler uptake capacity too large) to attain equilibrium in typical exposure periods (2-8 weeks). In that case the estimated C_{free} relies on the measurement of the in situ water volume extracted by the p-PSD during the exposure period. This volume (or the sampling rate, when expressed per time unit) is derived from the release of selected substances dosed to the p-PSD prior to exposure. Basically, the rate of release, controlled by the diffusion through the water boundary layer at the sampler surface, is determined. The first order rate constant of the release under the given sampling conditions (temperature and turbulence) is equal to that of the uptake and can consequently be used for calculating C_{free} also in situations where equilibrium is not attained. Models and methods have been developed to estimate sampling rates [2,15], as well as K_{PW} [1], to derive C_{free} from sampler uptake.

10.1 Commercial availability

Materials that are typically applied in sampler construction include low density polyethylene filled with lipid (semipermeable membrane devices, SPMD) [3], pure low density polyethylene (LDPE), silicone rubber, i.e. polydimethylsiloxane (PDMS)-based materials, and polyoxymethylene (POM). The above mentioned polymer materials used for constructing p-PSD are widely available and mostly inexpensive. Preparing polymer-based passive samplers is a simple laboratory routine. Only SPMDs are commercially available including various deployment cages for a field deployment. However, the semipermeable membrane devices present a bi-phasic sampler (they consist of LDPE and triolein) and there is a general trend to apply mono-phasic and highly permeable p-PSDs [16], since for such samplers simplified contaminant uptake models are applicable [2], in which the internal sampler resistance to mass transfer can be neglected. LDPE and PDMS based polymers meet these criteria [17] but polyoxymethylene is an example of a polymer with very low internal diffusion [18] and published uptake models that neglect the internal resistance to mass transfer are not applicable for samplers based on that material. Presently, there is no commercial supplier of sampler materials that guarantees the constant and homogeneous material properties required for passive sampling. Ideally, commercial samplers should already be homogeneously dosed with performance reference compounds (PRC) and ready to deploy in the field [16].

10.2 Available guidance documents

The availability of guidance documents presents one of the steps required for a broader implementation of passive sampling in environmental monitoring.

Look in:

Several guidance documents, tips and tricks can be found in literature [3,19,20]. *For the application of SPMDs guidelines are available from USGS* [21]. *In 2011 an ISO norm on the application of passive sampling was published* [12]. *In 2012, a very useful guidelines for passive sampling of neutral hydrophobic substances specific for silicone polymers were published by ICES* [22].

10.3 Preparation, deployment, and retrieval

10.3.1 Preparation of samplers

A very detailed information on preparation of silicone rubber samplers has been provided in a freely available guidance document published by ICES [22] and we refer the reader to it. Silicone rubber can be obtained from different manufacturers but it has to be considered that sampler/water partition coefficients slightly vary between suppliers. AlteSil silicone [23] is one of the most widely used silicone material with reliable published sampler/water partition coefficients [1] and transferred to other materials by cross calibration [24]. Currently used silicone rubber sheets for passive sampling are applied in film thicknesses from 0.2 to 0.5 mm. Briefly, the sheets can be cut to a size appropriate for sampling, mounting holes can be made in it using a paper puncher. Those holes can be used for an easy mounting the sheets on sampler holder. The surface area for passive sampler is selected based on the information of expected analyte levels. Sampling rates are directly proportional to sampler`s surface area [25] and thus a larger surface area allows to lower the detection limits or allows to prepare sub-samples for analysis of more compound groups. Choosing a combination of sheet size and thickness allows modifying the sampler uptake capacity, which is for a particular compound given as a product of sampler/water partition coefficient (K_{pw}) and the sampler mass.

The silicone rubber sheets contain oligomers (short-chain polymers) that may interfere with the chemical analysis. These oligomers have to be removed prior to deploying the sheets. The sheets should therefore be loosely packed and extracted by Soxhlet with ethylacetate for at least 100 h. Details of the procedure are given in the mentioned guidance document [22].

10.3.2 Spiking samplers with PRCs

The dissipation of performance reference compounds (PRCs; 9.4) from exposed samplers is used to calculate the in situ sampling rates. Details of selection of PRCs and the spiking procedure is given in the guidance document [22]. PRCs should be compounds that do not naturally occur in the environment and

accurate experimental K_{pw} values should be available for them. It is recommended to use a minimum of six PRCs covering the range of logK_{pw} 3.5 – 5.5 at increments of approximately 0.3 log units. Additionally, one PRC can be included that will not be depleted at all (log K_{pw} > 6) and one that is expected to be depleted completely (log K_{pw} < 3.3) [22]. It was shown that PAHs are not always suitable PRCs due to photodegradation. Photodegradation is indicated by a higher loss of PRCs from the sampler during exposure than can be explained solely by the diffusive release from sampler to water. Monitoring such enhanced release of PRCs from samplers, such as d_{12}-chrysene and d_{12}-benzo[e]pyrene, may help to identify photodegradation [26].

10.3.3 Required number of samplers

A sampler batch should consist of samplers for all planned sampling sites. This number is increased by 10 % (but by at least four) preparation controls (9.2) and approximately 20% of field control samplers (9.3).

Look out!

For repeatability and mutual sample comparability, it is important that the batch consists of samplers that are homogeneous in quality and amounts of spiked PRCs. It is advised to perform a homogeneity check of the batch by analysing a number of randomly selected samplers for PRCs. Rapid analytical methods such as thermal desorption/GC-MS (10.5.3) enable a fast screening.

10.3.4 Sampler storage

SR samplers can be stored during their transport to and from the sampling site as well as in the laboratory in wide mouth amber glass jars of an appropriate size, firmly closed by a screw cap with a thin (ca 0.5 mm) taylor made stainless steel liner. Samples can be stored in a freezer at -20°C.

10.3.5 Deployment devices

10.3.5.1 Static deployment

Passive samplers can be deployed in water using various deployment devices. The purpose of deployment devices is to hold samplers at the desired position in the sampled water and protect them from being torn by currents, severe weather, or boat traffic, or eaten by aquatic organisms [20]. Some devices, e.g. cages from perforated steel plates also provide shading of the samplers reducing photo-degradation of analytes. Passive samplers can often easily be deployed in the field with limited costs using inexpensive

equipment, such as stainless steel or galvanised mesh frames (see Figure 5; left). More robust samplers may be required when the deployment is done under strong currents, where the sampler holders must protect the samplers from mechanical damage. When deploying samplers in marine environment, all components must be made of corrosion-resistant metals (e.g. stainless steel 316L or titanium alloys). Examples of various deployment devices can be found in the literature [20–22].

Figure 5. Examples of various deployment devices for silicone rubber sheets.

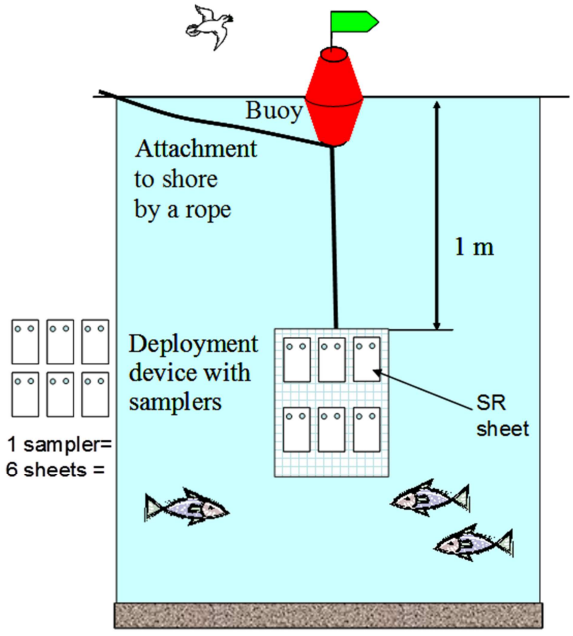


Figure 6. Example of deployment of silicone rubber sheets in water. If required (e.g. in strong currents), the deployment device may be also anchored to the ground using an anchor or a weight (not shown).

The sampler deployment devices should have a fixing eye that allows the device to hang on a buoy, bridge or quay. Knots in ropes can be secured with cable ties. An example of deployment is shown in Figure 6.

10.3.5.2 Enhanced passive sampling

The "enhanced" passive sampling system (EPS; Figure 7) has been designed to obtain enhanced passive sampler uptake rates in order to achieve sufficient sensitivity despite the short time available for sampling [27]. The system can be applied for increasing sampling rates of compounds that are accumulated in samplers under water boundary layer control (WBL) [7]. The increase in water flow velocity in the vicinity of sampler reduces the resistance to mass transfer in the WBL, resulting in faster chemical uptake. The uptake principle in the EPS remains the same as in classical static passive sampling and the monitoring results can be evaluated using usual passive sampler calibration parameters. Various passive samplers of hydrophobic and polar compounds can be mounted to the EPS device, but they should consist of thin sheets containing sorbent material with a sufficient analyte uptake capacity, such as silicone rubber and LDPE sheets for sampling hydrophobic compounds, or Empore™ disks for sampling polar compounds. In addition to situations where only short deployment periods are possible the EPS is useful in lakes or water bodies where natural flow velocities and consequently sampling rates are low. The EPS shows limited bio-fouling and photo-degradation is no issue.

The EPS device consists of a rectangular stainless steel plate box. During operation the box remains open from two sides and it is fully immersed in water. One end of the box is connected to a submersible pump (cca 9 $m^3 h^{-1}$) that forces water at high flow velocity (1-2 m s^{-1}) through the exposure chamber. A submersible temperature and light intensity logger is attached to the box during the entire exposure. Samplers are mounted to the EPS device just before exposure and removed immediately after recovery. The top of the EPS device is deployed approx. 0.5 m below the water level. The operation procedure of the EPS device is provided in Annex 2. The submersible pump that is needed for EPS operation must be connected to an electric power supply, which must be available on site.

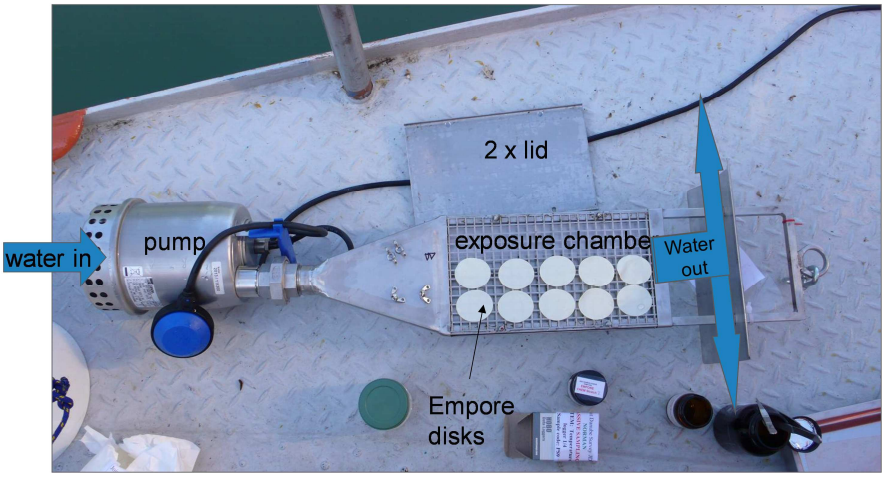


Figure 7. Design of the "enhanced" passive sampling system (EPS). The EPS device consists of a rectangular stainless steel plate chamber. Samplers are placed on a wire mesh support inside the chamber and the box is closed by two lids. During sampling, each sampler is exposed to water only from one side. The box always remains open at the left-hand and the right-hand side. The left-hand side of the box is connected to a submersible pump (ca 9 $m^3 h^{-1}$) that forces water at high flow velocity (1-2 m s^{-1}) through the sampler exposure chamber. During operation the EPS device is fully immersed in water.

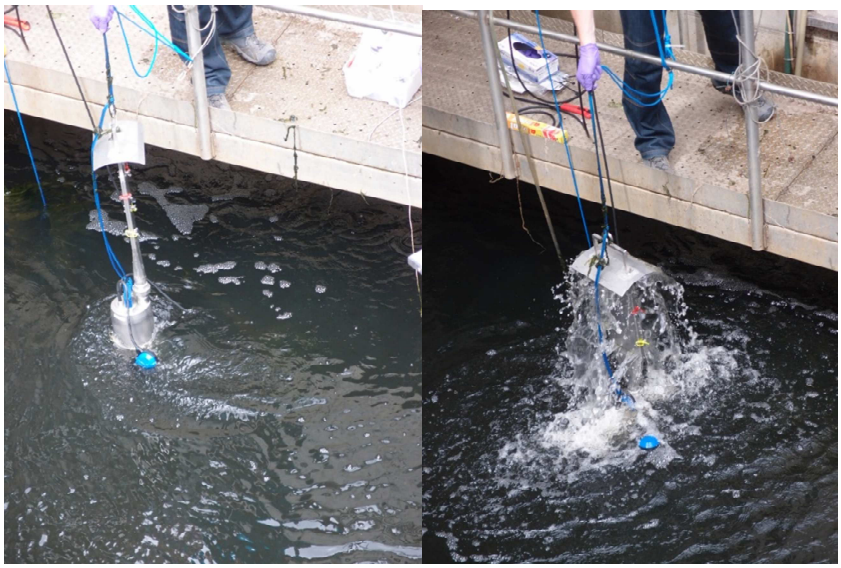


Figure 8. The "enhanced" passive sampler (EPS) during deployment to water for sampling. The submersible pump (visible at the bottom of the device at the left picture) forces water at high flow velocity

through the sampler exposure chamber above it. The water stream jetting from the exposure chamber is visible at the right picture. During operation the EPS device is fully immersed in water. In the photographs it is lifted from water for a better visibility.

10.3.5.3 Mobile passive sampling device

The above mentioned “enhanced” passive sampling system (EPS) can be applied as a mobile device for temporally and spatially integrative sampling of trace organic pollutants. In such case the EPS is used in a concept similar to that of a Ferry-Box [28] to obtain a representative picture of pollution situation along defined stretches or transects of large water bodies including rivers, lakes or seas. The EPS enhances the uptake rate of contaminants into passive samplers, thereby allowing reduction of the exposure time needed for accumulation of sufficient chemicals for analysis.

During the Joint Danube Survey 3 the “enhanced” passive sampling system was installed on board of the expedition ship Argus and the application of temporal- and spatial- integrative passive sampling approach resulted in samples that provide a representative picture of pollution situation in eight defined stretches of the Danube river [27]. The EPS device was deployed on the frontal deck of the Argus (Figure 9). For sampling, the device was immersed in a flow-through system that consisted of a 600 L stainless steel tank. The river water in the tank was exchanged at a rate of about 3 m^3 h^{-1} by a high performance pump. The water intake to the chamber was by a vertical steel pipe positioned in front of the ship. The water sampling depth was about 0.5 m below the water level.

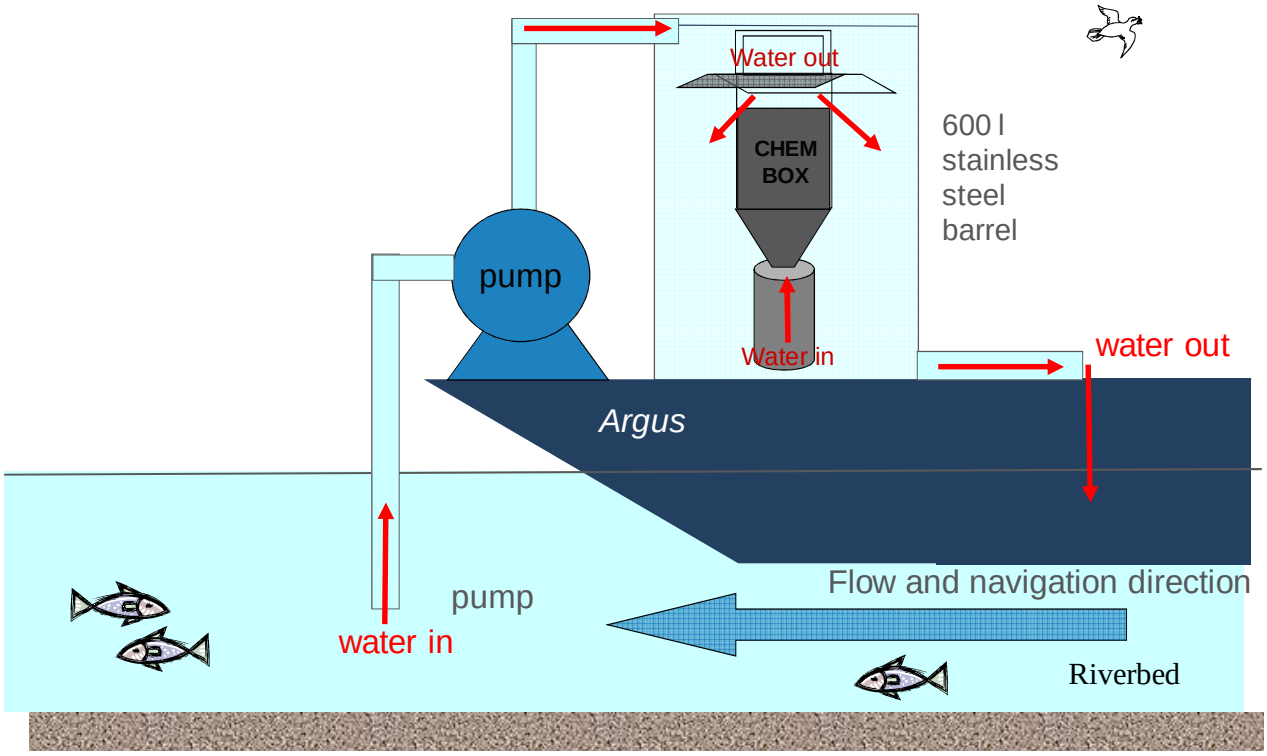


Figure 9. A mobile „enhanced" passive sampling device in operation.

The device was operated only during the cruising of the ship or when the ship anchored outside harbors (e.g. for sampling) in areas not visibly impacted by point sources of pollution such as discharge pipes, industrial areas next to the river, or oil films visible on the water surface. The device was switched off before the ship entered harbors and switched on again when the cruise resumed. Samplers were mounted to the EPS device just before exposure and removed immediately afterwards.

Each individual water sampling period took approximately 5 days. During that period the ship moved downstream along a defined stretch. The obtained sample contained water pollutants integrated in time and space along that stretch. Eight stretches of the Danube were sampled with three sampler types (SR, LDPE and ED).

Mobile exposures can also be performed by other means, e.g. by towing samplers fastened to the end of a benthic trawl net [29].

10.3.6 Deployment and retrieval

The following items are required for sampling: Sampler holders, labeled samplers (including field controls; 9.3**Error! Reference source not found.**) stored in their transport containers, tweezers with rounded tips, a stainless steel plate or serving tray that can be used for handling the samplers during

deployment and retrieval (low risk of contamination), cable ties, milli-Q water, ropes, anchors, buoys, pH- temperature- and conductivity- meter, a bucket on a rope, vinyl gloves, clean scourers, paper tissues and a camera to document the sampling operation and the state of samplers before and after deployment.

For deployment:

1. The field controls are unpacked and placed on the metal plate on a secure place (wind should not take them). It is suggested to remove the field control sheets from their container and expose them to air on clean steel, glass, or ceramic surface during the time required for deployment, and later during recovery of the exposed samplers and their cleaning process. Time is registered.
2. Samplers are taken from their transport container and fixed to the deployment device.
3. When all samplers are mounted, the deployment device with samplers is immersed in water as quickly as possible.
4. The sampler deployment device is secured in water using a rope, buoy and anchor (for various options see 10.3.4.
5. The field controls are packed in their original transport containers and time is registered. Field control samplers should be placed in freezer as soon as possible.

For retrieval:

1. The field controls are unpacked and placed on the metal plate on a secure place. Time is registered.
2. The deployment device with the samplers is retrieved from water and placed at a secure and clean place.
3. Samplers are collected from the deployment device and placed on a clean plate, tray or whatever was collected for their cleaning purpose.
4. Local water and a clean scourer can be used to clean the samplers as good as possible in the shortest possible time.
5. Samplers are dried with a paper tissue and put back in the corresponding container.
6. Samplers and field controls are packed in their original transport containers and time is registered.
7. Samplers are stored according to storage instructions (mostly frozen at -20°C) and sent to the processing laboratory.

For deployment it should be made sure that the used material is clean. Before mounting the samplers all the fixing gear to fix the samplers is prepared. Samplers should be mounted just before exposure (and removed from the sampler directly after recovery). Usually non-sharp tweezers are required for mounting

the sheets and a clean working place to sort the samplers on: either a stainless steel serving tray, a large glass Petri or a ceramic dish.

Data on sampling are recorded on a sampling form. An example of such form is provided in **Annex 1**. During recovery the same parameters are recorded as at the time of deployment.

Depending on the season and place of deployment the recovered sampler can be clean or totally covered by biofilm and other adherent organisms. It is suggested to document the situation by taking pictures of the recovered samplers. Cleaning of the samplers is best done immediately after recovery using local water. Samplers that are almost clean are first wiped with a soaking wet tissue and subsequently patted dry with tissue and transferred to the transport container in which they were delivered. If fouling organisms grow on the sampler they should be scraped off as completely as possible. Further residues can be removed using a very wet scourer. A nylon type (as used in kitchen) without foam sponge and washed with methanol is appropriate. Local water is best used for sampler cleaning. Samplers are preferably kept under local water as much as possible. Gloves should certainly be used if local water is so contaminated that contact needs to be avoided, otherwise properly washed and extensively rinsed hands contaminate less than gloves may do. The cleaning should be done in the shortest time possible. It is not necessary to brush a sampler as clean as new, but the cleaner it is, the better. The situation can be documented using a camera. After cleaning the samplers are patted dry with a tissue. Then the samplers are placed to their transport container. Finally, when the recovered samplers are placed back in the storage container they should be stored in dark, and as soon as possible transferred to a freezer, until analysis or dispatch to the analysing laboratory.

	***Look out!*** *Cleaning of the samplers is best done immediately after recovery using local water. Immersing samplers during the cleaning process to water collected from the sampling site minimizes their exposure to air and associated analyte losses or sample contamination. Analyte losses are linearly related to the time of the cleaning process on air but not likely if samplers are immersed in local water. Water from the sampling site contains analytes with similar concentrations to the water samplers were exposed to during deployment. Local water is consequently more suitable than distilled water brought from the laboratory.*

10.4 Shipment of samplers to laboratory

Ideally, samplers should be sent to the processing laboratory using a transport mean with the shortest transport period. The use of heat insulated shipping containers and ice packs are advised to maintain low

temperatures during transport. Temperature loggers can be added to the package if monitoring of a temperature-controlled supply chain is required. When sending samples the receiving laboratory should be informed at forehand. The physical address, not only the P.O. Box, should always be included on the label. Secondly, it is wise to have the phone number with international suffix of sending and receiving contact on the address label. Sampling material can go separate from samplers by regular mail service, which is less expensive. Samples can also be sent by regular mail in a small package that may be transported faster than a large one. Alternatively a courier service can be used.

10.5 Laboratory processing for chemical analysis

Several schemes for extracting the samplers may be applied, including Soxhlet extraction, cold-extraction or thermal desorption. Other extraction methods (such as accelerated solvent extraction, microwave extraction etc.) may be used as well, provided they were tested for compatibility with the sampler construction materials under applied extraction conditions. Performance of the applied method should always be tested using recovery spikes (9.5).

Before extraction, samplers are taken from the freezer and warmed up to laboratory temperature. Individual SR sheets are then taken out from their storage containers (10.3.4) with clean tweezers and patted with a dry paper tissue to remove residual water.

Before extraction, the sheets are placed in an appropriate extraction vessel (a flask, Soxhlet extraction chamber or thermal desorption tube – for details see chapters (10.5.1-10.5.3). Recovery internal standards (RIS) can be dripped on the sheets or added to the sheets in the Soxhlet thimble or extraction flask at the beginning of the extraction/desorption[2]. Preparation controls (9.2) and field controls (9.3) are treated like samples. Reagent blanks (9.1) processed in the same way but without sheets. Recovery spikes (9.5) are preparation controls that are spiked prior to extraction with known amounts of analytes. They are treated like samples.

10.5.1 Soxhlet extraction

Using a pair of tweezers, samplers are concertina folded so that they fit into a Soxhlet extraction chamber with maximum surface exposed to solvent. The volume of Soxhlet extractor is selected approximately 5-

[2] Annex 1 provides an example of application of various recovery internal standards before extraction of silicone rubbers exposed during the Joint Danube Survey (JDS3), and which were then subjected to analysis of a broad range of analyte classes.

10 times larger than the volume of the extracted sheets[3]. The contact of sheets inside the chamber should not be too dense, otherwise the extraction efficiency may be reduced. One reagent blank (9.1) and one procedural recovery spike sample (9.5) should be included in each batch of samplers. SR samples are then spiked with recovery internal standards (RIS) by dripping RIS solutions on the surface of the SR sheet inside the Soxhlet extractor. An equal amount of RIS solution as dosed to all samples is also collected in a vial that is later analysed in parallel with the samples as reference. This approach allows the RIS solution to be non-quantitative.

Soxhlet extraction with methanol, acetonitrile or their mixture is recommended for silicone rubbers [22]. Typically, Soxhlet extraction can be accomplished within 8 hours. If the sheets do not fit into one Soxhlet apparatus, extractions can be done sequentially by replacing the extracted sheets after 8 h and continuing the extraction with the same portion of solvent [22]. Using combination of solvents forming a positive azeotrope [30] may be beneficial for reducing the boiling point [22]. Azeotrope tables are accessible via different web pages [30]. Boiling point of the extraction solvent can also be reduced when Soxhlet extraction is performed at a reduced pressure. It is not necessary to discard the silicone rubber sheets after extraction. If they have not been physically damaged they may be thoroughly extracted and reused again. The benefit of reusing the silicone rubber sheets is that they normally contain less silicone oligomers than those applied for the first time.

	***Look out!*** *Extraction with non-polar solvents is not recommended, because these solvents cause considerable swelling of the sheets (ethylacetate up to 200% and hexane up to 400%) and may extract any oligomers that have not been removed during pre-extraction. It is strongly recommended to test the analyte recovery of Soxhlet extraction from silicone rubbers to methanol before applying the procedure to real samples. Decomposition of some analytes (e.g., some hexachlorocyclohexane isomers) may occur while boiling in methanol.*

An example of Soxhlet extraction procedure applied to silicone rubber samplers exposed in the Danube river during the Joint Danube Survey 3 [27] is given in ***Annex 2***.

[3] For example, for the extraction of an AlteSil silicone rubber sheet with dimensions 14×28 cm and 0.5 mm thickness with an approximate mass of 24 g, a 200 ml soxhlet extraction chamber is the appropriate size.

10.5.2 Cold extraction

The second method to extract the sheets is a cold-extraction procedure. Sheets are transferred to a 300 or 500 ml Erlenmeyer flask with glass stopper. Methanol (approximately 10 times the volume of extracted sheets) is added and the flask is shaken gently overnight. Subsequently, the extraction is repeated with fresh solvent for 8 h, after which the two extracts are combined.

	***Look out!*** *Note that a cold extraction procedure is a batch process. Thus, several extraction steps are usually required to achieve complete analyte extraction. Note that several subsequent extractions with a smaller volume of solvent are more efficient than a single extraction step with a larger solvent volume. Use of cold extraction is advised only if Soxhlet extraction is not applicable e.g. because of thermal lability of analytes.*

10.5.3 Thermal desorption

PDMS, the main component of silicone rubber, is thermally stable, inert and can be used in a broad temperature range (it behaves as a sub-cooled liquid between 20 and 320 °C). After sampling, the analytes can be introduced quantitatively into the analytical system by thermal desorption [31]. The possibility to recover and transfer volatile and semi-volatile analytes from PDMS by thermal desorption coupled to gas chromatography enabled the development of miniaturised sample preparation approaches without the need of toxic solvents, including solid phase micro-extraction (SPME) [32] and stir bar sorptive extraction (SBSE) [33].

The diffusion coefficients of most non-polar analytes with a molecular mass up to 1000 in silicone rubber are high enough to assure their homogeneous distribution by diffusion in a rubber sheet during an exposure lasting several weeks at temperatures above 10°C [34,35]. Therefore, it is possible to cut (using a sharp and clean knife or a hole puncher) a small piece (approximately 10 mg) of the sampler, insert it into a thermal desorption liner and process it by thermal desorption coupled online to a gas chromatograph with a mass spectrometer. The mass of analysed material is determined by weighing the piece of polymer after the thermal desorption. An example of such application is given by Vrana et al. (2016) [36].

Thermal desorption/GC/MS allows a rapid analysis of analytes and performance reference compounds in exposed sampler without the use of organic solvents. However, the procedure can be applied only for thermally stable compounds that do not decompose during the thermal desorption step. Moreover, since

only a small fraction of the total sample is subjected to thermal desorption and subsequent instrumental analysis, the method is typically not suitable for analysis of compounds present in silicone rubber below 10 ng g^{-1} [36]. It is highly recommended as a fast screening approach for determining levels of PRCs (9.4) in exposed samplers. Because sampling rates can be calculated from the retention of PRCs in the exposed samplers (10.6), the volume of water extracted by the sampler can be estimated. Based on the known enrichment factor of analytes in the passive sampler, the extraction procedure of the whole sampler can be adjusted, if needed.

	***Look out!*** *When thermally desorbing silicone rubber based materials or other polymers, carefully check the maximum thermal desorption temperature in order to avoid material decomposition. Materials may be desorbed only in a stream of an inert gas to avoid oxidation and damage. Silicone rubbers may during the thermal desorption process release siloxane oligomers which then condense in the gas chromatograph and cause a persistent contamination of the instrument. It is advised to carefully extract the silicone rubbers before use as described in 10.3 and test the material for "bleeding" of siloxanes e.g. by scanning the presence of large "ghost" peaks of various cyclic siloxanes in chromatograms (presence of ions with m/z 73, 147, 207, 221, 281, 295, 355, 429)*[37]*. Incomplete thermal desorption of strongly adsorbing compounds with high boiling point may lead to carryover effects.*

10.5.4 A clean up step for the removal of silicone oligomer traces

In case some of the undesired siloxane oligomers remain in the extracts, an additional clean-up of the extract with C18-bonded silica cartridges (made of glass) described by Smedes and Booij [22] can be considered. The procedure has been tested for clean-up of hexachlorobenzene, PCBs and PAHs, but needs to be adapted when applied for other compounds.

10.5.5 Volume reduction and solvent exchange of extracts

Volume reduction of extracts is best done using a Kuderna-Danish apparatus but rotary vacuum evaporation is also possible, providing the loss of compounds by volatilisation is negligible. Sometimes a solvent exchange is required, e.g. when an extract in methanol or acetonitrile must be transferred to a non-polar solvent in order to perform a normal phase silica clean-up. For such a solvent exchange and extract evaporation to dryness should be avoided and the use of azeotropes should be considered. Note that the azeotropic solvent exchange does not work when nitrogen blow-down is used for concentrating

the extract [22]. Azeotrope tables are accessible via different web pages [30]. A practical eexample of an efficient solvent transfer from methanol or acetonitrile to hexane are given by Smedes and Booij [22].

A solvent keeper, which is a less volatile solvent remaining in the vessel and keeping the analytes dissolved while a more volatile solvent is evaporated with a high boiling point (e.g. nonane or isooctane) can help to avoid losses preventing evaporation to dryness. It is also useful when it also can be used as injection solvent.

10.5.6 Sample cleanup and instrumental analysis

Clean-up of the extracts and instrumental analysis can be carried out according to standard laboratory methods. An example of a sample clean-up procedure applied to silicone rubber samplers exposed in the Danube River during the Joint Danube Survey 3 [24] is given in Annex 2. Extracts in non-polar solvents are suitable for direct use in common clean-up and analytical methods as applied to water, biota, or sediment extracts.

Look in:

Useful references to analytical methods that are applicable for analysis of WFD priority substances are available in the CIRCA public document library – guidance documents [38,39].

http://ec.europa.eu/environment/water/water-framework/facts_figures/guidance_docs_en.htm

10.6 Calculations

For estimating aqueous contaminant concentrations from their uptake by the p-PSD estimates of the substance specific sampled/extracted volume of water (sampling rate if expressed per time unit; R_s) and sampler-water partition coefficients K_{pw} are required [40].

The calculation of aqueous concentrations involves several steps that are detailed below and, briefly, are as follows. First, the water sampling rates are calculated using the PRC fractions that are retained (i.e. the ratio of PRC amounts at the end and at the beginning of the exposure). Small retained PRC fractions indicate fast sampling rates and vice versa. These sampling rates are then used to calculate the aqueous concentrations of the other analytes.

10.6.1.1 *Estimation of the sampling rate*

The magnitude of R_S may be controlled by transport through the water boundary layer (WBL-controlled uptake), or by transport in the polymer (membrane-controlled uptake). In case of WBL controlled uptake the release rates of PRCs mirrors the compound uptake rates under local hydrodynamic conditions, and sampling rates can be estimated including a measure of their precision [15]. This also would cover the effect of fouling that has been shown to have little effect on the final water concentration estimate [41].

In situ sampling rates can be obtained from the retained PRC fractions (*f*) according to [22]:

$$f = \frac{N_t}{N_0} = exp\left(-\frac{R_s t}{K_{pw} m_p}\right) \quad (1)$$

where N_0 is the dosed amount measured in a reference sampler, N_t is the amount in the sampler after exposure, R_s is the (equivalent) water sampling rate (L d^{-1}), t is the exposure time (d), m_p is the mass of the sampler (kg), and K_{PW} (L kg^{-1}) is the sampler:water partition coefficient.

	***Look out!*** *Since the retained fraction of PRCs f (equation 1) in the sampler is calculated as an amount ratio, it is not necessary to calibrate the instrument for measurement of true PRC amounts. It is sufficient to demonstrate linearity of instrumental response to PRC concentration. For the purpose of calculating the f value, ratio of PRC internal standard corrected peak area is sufficient in most cases.*

For evaluation whether the uptake may be controlled by membrane the knowledge of analyte diffusion coefficient in the sampler polymer material (D_p) is required. It is necessary to consider the membrane controlled mass transfer especially for compounds with low K_{pw} values (log K_{ow} <3.5), since the resistance to mass transfer is inversely proportional to the K_{pw} value, and, as a result, for hydrophilic compounds the resistance to mass transfer in polymer may become dominant [25]. Membrane control may also dominate in situations with extremely low WBL resistance, e.g. at extremely high water flow velocities (>10 m s^{-1}).

For neglecting the membrane resistance to mass transfer, the following criterion should be fulfilled:

$$R_s << \frac{AD_p K_{pw}}{\delta_m} \quad (2)$$

where R_S is the sampling rate for WBL-controlled uptake, calculated from PRC dissipation as described below, A is the sampler surface area, and δ_m is the thickness of the applied polymer sheet (if exposed from one side only, otherwise half-thickness is taken into the calculation).

Rusina et al. (2007, 2010) [2,17] have demonstrated that the sampling rates of compounds fully controlled by the WBL decrease weakly with increasing molar mass (M).

$$R_S = \frac{B}{M^{0.47}} \tag{3}$$

where B is a proportionality constant that depends on the water flow conditions and includes unit conversions. The model considers the decrease of diffusion coefficients in water with the increasing molecular weight. Because the meaning of constant B is rather abstract, it is practical to calculate the sampling rate for a compound with a certain molar mass (M), e.g. 300 g mol^{-1}, using Equation (3).

The combination of equations (1) and (3) results in a model equation that enables calculation of WBL-controlled sampling rate of a compound from its molar mass and the retained PRC fractions using unweighted non-linear least-squares estimation according to [15]:

$$f = \frac{N_t}{N_0} = exp\left(-\frac{Bt}{K_{pw}M^{0.47}m_p}\right) \tag{4}$$

where the retained PRC fractions (f) is the dependent variable, ($K_{pw}\times M^{0.47}$) is the independent variable and B is the adjustable parameter, respectively.

Figure 10 shows curves where the retained PRC fraction is fitted to the denominator in the exponent of equation 4. For longer exposures the curve shifts to higher K_{pw} values. At the longest exposure, i.e. 18 d, PRCs with logK_{pw} up to 5.5 are dissipated meaning that all samples substances up to that K_{pw} have attained equilibrium. At the other end little or no dissipation was observed from logK_{pw}=7, which means that uptake still is in the linear phase and C_{free} estimations rely on the sampling rate.

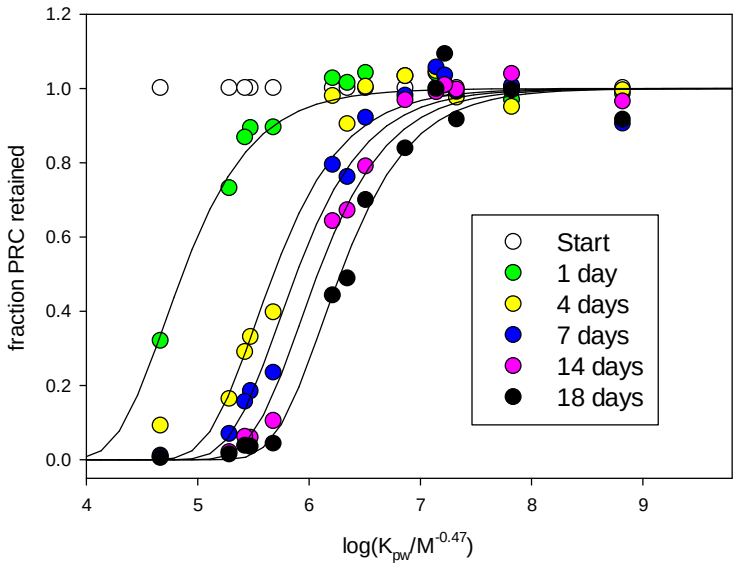


Figure 10 Retained PRC fractions as a function of $logK_{pw} \times M^{0.47}$ *after 0-18 days of exposure of a Twister™ stir bar made of PDMS at 20°C in water in an open system. The model fits for water boundary layer controlled uptake* $R_s = B \times M^{-0.47}$ *(Equations 3 and 4) are shown as drawn lines. Adapted from* [42].

10.6.1.2 Sampler-water partition coefficients

The second important parameter for calculation of water phase concentrations is the sampler-water partition coefficient K_{pw}. Since the solubility of hydrophobic substances in water is affected by temperature and salinity, the K_{pw} values are also affected by these parameters. Most of the published K_{pw}s are determined under controlled laboratory conditions in a system containing pure water at 20°C. Application of temperature and salinity specific K_{pw}s showed that within the naturally occurring water salinity and temperature range the variation of K_{pw} values is limited to a factor 2 [43]. However, the necessity of such correction is questionable because from the physicochemical point of view, the chemical bioconcentration factor should not be regarded as a rigid constant either, but as a parameter that is related to the thermodynamic state of the investigated system, including its temperature, pressure, salinity etc. Sampler-water partition coefficients increase with the decreasing temperature [43] and analogically, chemical bioconcentration factor should be higher at lower temperature [44]. Similarly, in both cases the driving force for spontaneous contaminant partitioning from water to the sampler polymer or to a living organism tissue (by partitioning to lipids or proteins) increases with increasing salinity. Since both the abiotic partition coefficients (K_{pw}) as well as the bioconcentration factor values (BCFs) are expected to be likewise affected by temperature and water salinity, their ratio should not be much

dependent on those environmental variables. Calculation of free dissolved concentrations in water (C_{free}) using K_{pw} that has not been corrected for temperature and/or salinity results in a concentration estimate in a system at 20°C and zero salinity. We believe that such estimate of C_{free} can then be directly compared with an environmental quality standard (EQS) value which had been derived without taking into account potential effects of temperature and salinity on aquatic organism exposure [45,46].

Theory of partition passive sampling and available calibration data

Look in:

The theory and modelling of partition passive sampling is in detail described in the works of Huckins et al. [3]*, Booij et al. (2007)* [25] *and an overview is provided also by Lohmann et al. (2012)* [5]*. Rusina et al. (2007, 2010)* [2,17] *have demonstrated that the sampling rates of compounds fully controlled by the WBL decrease weakly with increasing molar mass (M). Booij and Smedes (2010)* [47] *derived an improved method for estimating in situ sampling rates of nonpolar passive samplers using PRCs. Apell et al. (2015)* [48] *developed a mathematical model that relates environmental, polymer and chemical properties that control the sampling rate and provided a guidance on how to use the model to select an appropriate polymer, deployment time and a suite of PRCs.*

Polymer-water partition coefficients K_{pw} *of many compounds are available for various* ***silicone rubber based*** *polymers from Smedes et al. (2009)* [1]*, Yates et al.* [49]*, Jonker et al. (2015)* [43]*, and a data compilation is available in Difilippo and Eganhouse (2010)* [50].

K_{pw} *values for* ***LDPE*** *have been published by Müller et al. (2001)* [51]*, Adams et al. (2007)* [52]*, Smedes et al. (2009)* [1]*, Fernandez et al. (2009)* [53]*, Hale et al. (2010)* [54]*, and a critical review has been provided by Lohmann et al. (2012)* [55].

For evaluation whether the uptake may be controlled by the membrane diffusion coefficients of analytes in sampler polymer are required. Diffusion coefficients for LDPE and silicone rubber based polymers are available from Rusina et al. (2010) [34] *and Narváez Valderrama (2016)* [35].

For characterizing new polymers, for which K_{pw} values are not yet available, ***polymer–polymer partitioning*** *can be used as the basis for a deeper insight into partitioning differences of compounds between polymers, calibrating analytical methods, and consistency checking of existing and calculation of new partition coefficients* [24].

	***Look out!*** *Note that accurate K_{pw} values are especially important for PRCs and compounds that approach equilibrium during exposure (approximately with log K_{pw}<5). For those compounds calculation of concentration in water is depending on knowing the sampling rate, but is derived from the ratio of concentration found in sampler and the K_{pw}.* *The use of accurate K_{pw} values is less critical for compounds that are in the linear uptake stage (see above), and K_{pw} values that are approximated using logK_{pw} - logK_{ow} regression have sufficient accuracy in such case.*

10.6.1.3 Calculation of concentrations in the aqueous phase

The concentration in the water phase C_w is calculated according to [3,7]:

$$C_w = \frac{N_t}{K_{pw} m_p \left[1 - exp\left(-\frac{Bt}{K_{pw} M^{0.47} m_p}\right)\right]} \qquad (5)$$

An example of a C_{free} calculation is shown below.

	***Look out!*** *In cases when sampler contamination occurs during transport and manipulation in the field, the amount in preparation control (*9.2*) N_0 and field control (*9.3*) N_f may be under certain conditions subtracted from the amount in the exposed sampler N_t. Such approach is shown in chapter 10.7.1.*

An example of calculation of concentration in the water phase from the amount accumulated in silicone rubber passive sampler

*The example illustrates the calculation of free dissolved concentration of pyrene from its amount in an exposed silicone rubber passive sampler. A passive sampler made of AlteSil silicone rubber with the mass m = 10 g was exposed for 42 days in surface water at water temperature of 20°C. The sampler was spiked before exposure with 70-700 ng PRCs (d_{10}-biphenyl and PCB1, 2, 3, 10, 14, 21, 30, 50, 55, 78, 104, 145 a 204). PRCs and polycyclic aromatic hydrocarbons were analysed in the exposed sampler and in the preparation control (***Error! Reference source not found.***). The amount of pyrene in the sampler after exposure was 2800 ng. Calculate pyrene concentration in water phase.*

Solution:

Fraction *f* is calculated as the ratio of a PRC between the amount found in the exposed sampler and the preparation control (see Table below).

PRC compound	log K_{pw} [1]	M	*f*
Biphenyl-D10	3.63	164	0
PCB 1	4.22	189	0.00
PCB 2	4.41	189	0.01
PCB 3	4.36	189	0.01
PCB 10	4.58	223	0.01
PCB 14	5.11	223	0.03
PCB 21	5.22	258	0.10
PCB 30	5.71	292	0.08
PCB 50	5.38	258	0.40
PCB 55	6.15	327	0.49
PCB 78	5.99	292	0.60
PCB 104	6.07	292	0.70
PCB 145	6.62	361	0.84
PCB 204	7.59	430	0.98

The nonlinear regression of f using equation 4 yields B=138 ± 7 d^{-1}, corresponding to R_s (at M=300 g mol^{-1}) of 9.5 ± 0.5 L d^{-1}.

N_t = 2800 ng is the amount of pyrene found in the exposed sampler
K_{pw} = $10^{4.68}$ L/kg is the sampler/water partition coefficient
B = 138.4 d^{-1} is the optimized parameter
m = 10 g = 0.01 kg is the mass of sampler
M = 202.2 g/mol is the molar mass
t = 42 d is the sampler exposure time

The calculated concentration of pyrene in the water phase is:

$$C_w = \frac{2800}{10^{4.675} \times 0.01 \times \left(1 - \exp\left(-\frac{138.4 \times 42}{10^{4.675} \times 202.506^{0.47} \times 0.01}\right)\right)} = 9.293 \frac{ng}{L} = 9293 \frac{pg}{L}$$

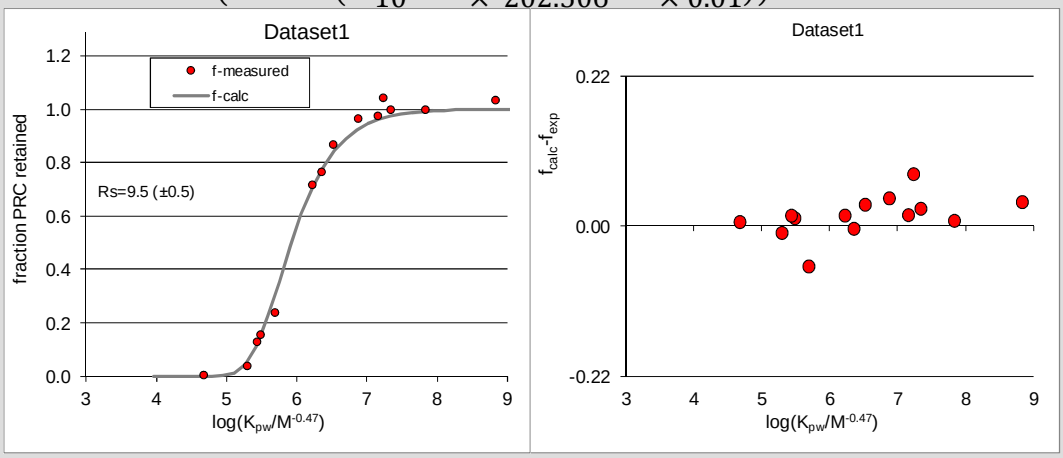


Figure 11. Retained PRC fractions as a function of log(K_{pw} $M^{0.47}$). The model fit (Equation 4) is displayed as a drawn line.

10.7 QA/QC for partitioning-based PS devices

10.7.1 Use of control samples and blanks

The amount of analytes, determined in reagent blank (9.1) can be subtracted from the amount measured in exposed samplers, preparation controls (9.2) and field controls (9.3).

Correction of the analyte amount in exposed passive sampler (N_t) using preparation controls (N_0) or field controls (N_f) is not a simple subtraction. For compounds that reach partition equilibrium between sampler and water during exposure, their amount in the sampler at the end of exposure is not affected by the amount that was in the sampler during its preparation, i.e. the amount in the preparation control (9.2). In contrast, for compounds with a high uptake capacity ($K_{pw} \times m_p$) their amount in the exposed sampler is given by the sum of amount in the control and the amount accumulated in the sampler during exposure [56]. Subtraction of the analyte amount in the controls from the amount found in the exposed sampler can be done for compounds in the linear uptake phase during the entire exposure, which can be assessed from the PRC elimination data. A conservative sample rejection criterion is to set the minimum amount in exposed samplers to ten times the amounts detected in the field controls, and to review sampler construction and transport operations if this condition is not met [13].

If the user decides to perform correction, a scheme for control subtraction from exposed samplers is described below and it may be used with caution. It should be emphasized, however, that this method has not been assessed critically and accepted by the whole passive sampling community.

The evolution of analyte amount in the sampler (N_p), in which no further contamination occurs during transportation and manipulation during field deployment/retrieval can be described by a general equation [7,56]:

$$N_t = N_0 \, exp\left(-\frac{R_s t}{K_{pw} m_p} \right) + C_w K_{pw} m_p \left(1 - exp\left(-\frac{R_s t}{K_{pw} m_p} \right) \right) \qquad (6)$$

The term

$$DEQ = \left(1 - exp\left(-\frac{R_s t}{K_{pw} m_p} \right) \right) \qquad (7)$$

can be described as degree of equilibrium attained during sampler exposure (*DEQ*).

The first term in the sum presents the amount of analyte in the sampler at the time of its preparation (N_0), which corresponds to the amount in the preparation control (9.2). This term can be interpreted as a (time-dependent) blank level that can be subtracted from the amount detected in the exposed samplers. After sampler exposure, depending on the compound properties, the term can approach two limit values. For compounds, which quickly attain equilibrium between sampler and water, this term becomes a value close to zero with increasing time. In contrast, for compounds, which only very slowly achieve equilibrium, this term remains constant and equal to N_0 during entire exposure.

In cases when sampler contamination occurs during transport and manipulation in the field, the amount in preparation control (9.2) N_0 and field control (9.3) N_f can be subtracted from the amount in the exposed sampler N_t according to equation:

$$N_{t\_corr} = N_t - \left[\left(N_o + 0.5 \times \left|N_f - N_0\right|\right)(1 - DEQ) - 0.5\left(N_f - N_0\right)\right] \qquad (8)$$

The corrected amount of analyte in exposed sampler N_{t_corr} can then be used for calculation of water concentration. The calculation is based on an assumption that the contamination of field control does not occur in a single event, but continuously at a constant rate during all operation steps including manipulation, transport and storage of samplers. At the time of preparation the sampler was contaminated by the amount N_0. During transport to the sampling site and sampler deployment, additional contamination can be derived from one half of the difference between the field and preparation control, i.e. $0.5\times(N_f - N_0)$. The second half of contamination, i.e. $0.5\times(N_f - N_0)$ is expected to be added to the sampler during the operations of sampler retrieval and transport from the field to laboratory. A portion of the amount of contamination, contained in the sampler at the start of the field exposure (i.e. $N_0+0.5\times(N_f-N_0)$) is eliminated from the sampler during its exposure in the sampled water i.e. $[N_0+0.5\times(N_f-N_0)] \times(1-DEQ)$.

10.7.2 Interlaboratory studies, learning exercises and proficiency testing schemes

The Marine Chemistry Working Group (MCWG) and Working Group on Marine Sediments WGMS, operating within ICES, organised in 2006 the ICES “Passive sampling Trial survey and Intercalibration”. The exercise was joined by 13 laboratories that performed passive sampling of water and sediment at 30 stations [57]. The laboratory inter-calibration aspect was covered by performing all sampling using duplicate samplers deployed in parallel; the participating laboratories analysed one of the samplers from

their nearest station and the replicate samplers from all stations were analysed by a central laboratory. Comparing concentrations reported by the participants and by the central laboratory a CV around 20% was derived for the analytical interlaboratory variation (excluding substances occurring in samples at concentrations close to their LODs). This is considered as a good result because the CV also included the variation originating from sampling with replicate samplers that was shown to range between 5 and 13 % [58]. Sampling rates calculated from PRC dissipation showed an overall CV of 30%. The resulting mean variability of estimated water concentrations variability was around 35 %. Of course, with respect to the result accuracy, the uncertainty of the applied sampler-water partition coefficients needs to be taken into account. It should be noted that for over 2/3 of the labs it was the first time they applied passive sampling and none of them had ever analysed the PRCs before. Instructions and sampling material (silicone polymer) that was received from the central laboratory may have contributed to achieve the respectable obtained quality.

AQUAREF, the French national reference laboratory for the surveillance of aquatic environment, organised an interlaboratory study on passive sampling in 2010. Among other investigated parameters, the study included passive sampling of polycyclic aromatic hydrocarbons. Participants used their own passive samplers, and sampling was tested at one freshwater and one marine site [59]. Various samplers were applied but 11 out 20 participants used SPMDs. The average between laboratory reproducibility was estimated around 90% and was similar when only one sampler type (SPMDs) was considered.

Within NORMAN (a network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances) an interlaboratory study on passive sampling was conducted in 2011 [60,61]. PBDEs were included in the exercise from the group of hydrophobic substances. In this exercise participants deployed their own sampler in triplicate and also received from the organiser triplicate silicone rubber polymer passive samplers that were exposed in parallel. The triplicate provided samplers showed good within laboratory variations (6-20%) indicating that passive sampling was repeatable. The between laboratory results of PBDE amounts accumulated in sampler showed a variability of around 100%, which demonstrated difficulties the participating laboratories experienced with sampler analysis. Also for the conversion from sampled chemical amounts to aqueous concentrations laboratories did not show agreement and this almost doubled variability in the between laboratory results. This is likely due to insufficient experience of the participating laboratories with the analysis of PRC compounds and application of models for translation of passive sampler data into aqueous concentrations. The latter source of uncertainty was confirmed when the organiser applied a uniform method for the conversion of the participant’s data to the aqueous phase. Such approach resulted

in much better comparable C_{free} estimates (CV~ 25%). This test was performed on data from nine laboratories that reported PBDE as well as PRC data for the provided sampler. Among the five laboratories that matched very well, three had joined the ICES Passive sampling Trial survey earlier. In conclusion, between laboratory variability can be reduced when participating laboratories are experienced in the method application. Moreover, the variability can also be significantly reduced by providing study participants with appropriate guidance and training.

Quasimeme (Quality Assurance of Information for Marine Environmental Monitoring) is a community of practice for marine environmental measurements that incudes proficiency testing schemes dedicated for monitoring. In 2014 Quasimeme ran a first inter-comparison exercise with silicone passive samplers exposed in parallel in a European estuary. The target analytes included PCBs, PAHs, PBDEs and participants determined the release of PRCs by estimating the fraction retained in the exposed sampler compared to a non-exposed sampler. In average the between laboratory reproducibility was around 30%. Evaluation showed that the between-laboratory CV was lower than the one predicted by the Horwitz[62] function. Quasimeme has organised next rounds of the proficiency testing in 2015 and 2016.

Accuracy of passive sampling results is related to the quality of partition coefficients. As literature values shows some variation [50,63], both the OSPAR/ICES and the AQUAREF/NORMAN [16] recommended organisation of an inter-laboratory comparison for the determination of partition coefficients in order to obtain a measure of its uncertainty. The ICES Marine Chemistry Working Group is currently working on the production of guidelines for the determination of partition coefficients.

11 Adsorption PS devices

Adsorption PS devices (a-PSD) generally contain adsorptive materials that are also applied in solid phase extraction of hydrophilic substances from water. In an a-PSD a thin layer of such material is applied separated from the water phase by a filter or a membrane. Some a-PSD do not contain filters or membranes, but they consist of disks containing adsorbent powder dispersed in a thin layer of porous supporting material (e.g. Empore™ SPE disks). Like for a p-PSD the substances diffuse through the water boundary layer and the membrane or filter, but accumulation in the binding material is by an adsorption process and not by dissolution. Adsorption of strongly hydrophilic substances is possible since binding can take place by a number of interactions between the surface of the material and the chemical, e.g. van der Waals, π−π interactions, hydrogen bonding, and Coulomb forces [64]. After extended exposure the uptake rate is reduced not only by equilibration but it can be limited also by saturation of the sorption sites of the adsorbent applied. Also uptake of nontarget compounds and other interfering natural compounds contributes to saturation and competes for sorption sites with target substances. Differences between p-PSD and a-PSD are illustrated in Figure 4. To avoid or reduce this effect exposure periods are kept shorter than with partition PS. Although extensive laboratory derived calibration datasets have been reported for a-PSDs, literature shows limited agreement [65,66]. Because of knowledge gaps on the detailed understanding of mass transfer and sorption processes, conversion of chemical uptake by such samplers to aqueous concentrations is associated with larger uncertainty [16]. In spite of these shortcomings, a-PSDs samplers can give valuable results with regards to substance screening to determine whether water bodies are potentially at risk and as an alternative method in situations where classical monitoring approaches based on low frequency spot sampling fail. In water bodies with highly variable concentrations estimates of time weighted average substance concentrations from integrative adsorption passive sampling will improve temporal representativeness of monitoring.

11.1 Commercial availability

Various a-PSDs are available of which the “Polar Organic Chemical Integrative Sampler“ (POCIS) is the most known [67]. The POCIS comes in two versions: one for pharmaceuticals and one for pesticides. The latter contains a mixture of several adsorption phases including a carbonaceous material. Little advantages were observed using specific adsorbents [68]. Another a-PSD is the Chemcatcher®, available in several configurations that contain various commercially available sorbent particle loaded Empore™ SPE disks as receiving phase, which can be used with or without an additional diffusion membrane [69]. Furthermore, Baker provides so-called Speedisk which is a high diameter (5 cm) SPE cartridge intended

for concentrating water samples in the laboratory. The Speedisk™ performance as a passive sampler proved to be as good as that other designed passive samplers. A Speedisk™ has a configuration similar to that of a Chemcather® but is equipped with a glass fibre filter where other passive sampler types use polethersulfone membranes. A range of Speedisks™ containing sorbent materials suitable for sorption of different compound groups is available. Within SOLUTIONS project, passive samplers based on Empore™ SPE disks (Sigma-Aldrich; hereinafter referred to simply as Empore disks) have been applied in the Danube case study and their performance characteristics as passive samplers have been characterized. Empore disks can be used without any membrane protection, which simplifies the chemical uptake process, its description and modelling.

11.2 Available guidance documents

The uncertainty/validity of the a-PSD methods is presently a major barrier for its implementation in monitoring schemes where strict method performance criteria are set [70].

Look in:

Although there is a large number of publications on development, calibration and application of a-PSD [19,71–74]*, not many official guidelines are available. A very general ISO guideline was developed in 2011* [12] *and a guidance how to use a POCIS sampler can be found at the USGS website* [21] *and at Wikipedia* [75]*. The information contains practical advices on sampler use but the data interpretation part is not sufficient, since clear deterministic methods for estimation of sampled water volumes in field situations are often missing.*

11.3 Deployment, and retrieval

Passive samplers can be deployed in water using various deployment devices and for deployment of a-PSD the same general rules apply like for p-PSD, as has been discussed earlier (10.3.4). In contrast to the p-PSD samplers made of flexible elastomers, a-PSD devices are typically constructed from materials that are more fragile and may easier be mechanically damaged. This needs to be considered in construction of deployment devices, which should allow free water motion around sampler but minimise the risk of sampler damage by strong water currents, floating debris etc. Examples of various sampler deployment devices are shown in Figure 12.

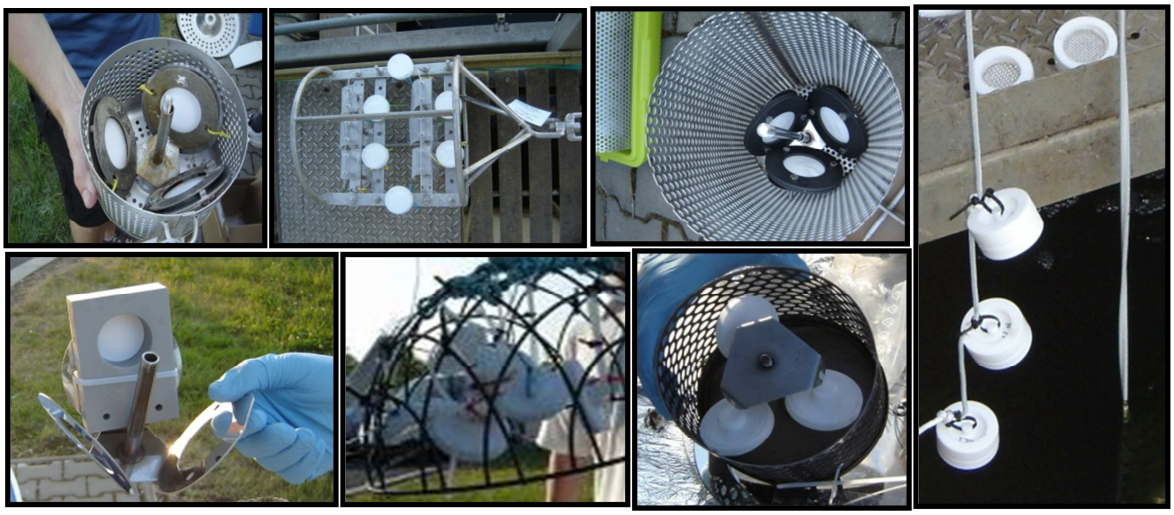


Figure 12. Examples of various deployment devices for adsorption-based samplers.

11.4 Laboratory analysis

Laboratory analysis can be carried out according to standard laboratory methods that are applied in processing water samples after their solid phase extraction. An example of a sample processing procedure applied to SDB-RPS Empore disk based samplers that were exposed in the Danube River during the Joint Danube Survey 3 [24] is given in Annex 4. Extracts in polar solvents are suitable for direct use in common instrumental methods (e.g. LC/MS) as applied to water.

11.5 Calculations

Sampling rates have been widely studied for POCIS samplers in the laboratory as well as in the field but the resulting extensive laboratory derived calibration datasets that have been reported for POCIS in literature show a high variability and do not seem to be robust, when exposure conditions such as temperature, flow velocity or sampler orientation towards water flow are slightly changed [65,72,73]. The uptake process is not yet well understood, sampling rates are typically substance specific, and models are scarce that allow to estimate sampling rates for compounds from their physicochemical properties [76]. Also it appeared that target substances often adsorb to the commonly applied polyethersulphone membranes [77], which further complicates modelling of the extraction kinetics and analyte distribution in the sampler. So even with extensive calibration an uncertainty of around factor two should be considered for POCIS samplers [78]. The translation of laboratory calibrations to the field would be limited to a factor of two [79].

Recent research also focuses on the use of a hydrogel layer for controlling the uptake, as is applied in DGT samplers for metals, and may result in a more controllable chemical uptake [80]. Basically, the sampler is coated by a hydrogel layer that acts as a defined artificial water boundary layer much thicker than the natural water boundary layer of which the thickness is variable depending on the hydrodynamics. The consequence is, however, that the uptake rate of such sampler is also effectively reduced, which decreases the sensitivity of the method. In current situation, the user has the option to select sampling rates available in literature for estimating water concentration from passive sampling data, but he has to consider that the result is affected by the relatively high uncertainty of sampling rates [66].

11.5.1 *In situ* calibration

In the current situation when deterministic methods for estimation of sampled water volumes in field situations are missing for a-PSDs, the *in situ* calibration of passive samplers can be applied to improve the accuracy of results produced by passive samplers. The *in situ* calibration approach is based on monitoring of compounds of interest in water by two comparable methods, namely by time proportional composite water sampling, and by passive sampling. The *in-situ* calibrated sampling rates (field R_s) can then be derived from the regression of water concentration vs. sampled mass on the passive sampler [81]. Moschet et al. [81] evaluated this approach for 322 micro-pollutants in several rivers using Chemcatcher sampler. They concluded that only substances with relatively constant river concentrations can be quantified accurately in the field by passive sampling if substance-specific field R_S are determined. For that purpose, the proposed *in-situ* calibration is a very robust method and the substance specific empirical R_S can be used in future monitoring studies in rivers with similar environmental conditions (i.e., flow velocity, temperature, pH). A similar approach has been applied also for other a-PSDs configurations [82–84].

11.5.2 Estimate of in situ sampling rates using co-deployed partition based samplers with PRCs

Since calibration of a-PSD using PRCs has only a limited applicability (usually for a narrow range of conditions and for limited number of substances [65,85]) other options need to be explored to assess chemical mass transfer to a-PSD in the field.

For a-PSD configurations, without the use of a protective polymer membrane which complicates the uptake mechanism, it is reasonable to co-deploy them in the field together with partition based passive samplers (p-PSD) in a similar sampler deployment arrangement (e.g., flat sheets oriented in a similar way

in the water stream and deployed in a sampler holder with the same geometry). Unlike for a-PSD, for p-PSD devices the in situ sampler calibration using PRCs is a widely applied approach.

Data obtained by two co-deployed samplers can be directly compared, when assuming that certain criteria are fulfilled:

1. **Substances suitable for cross-calibration.** A group of compounds must be identified that accumulates well in both applied sampler types, namely in the a-PSD sampler, and in the p-PSD. Those substances should be measured in both exposed samplers. Such substances should be present at most sampled sites at measurable concentrations. Polycyclic aromatic hydrocarbons or alkylphenols are example compound classes.
2. **Integrative uptake.** For the substances identified in point 1 the sampler uptake capacity should be high and their integrative uptake in both samplers over the whole exposure should be guaranteed. The two sampler types may differ in the surface area, the quality and the mass of sorbent material applied. This implies that the mass of those compounds found in both sampler depends solely on their sampling rates R_S and not on their sampler uptake capacities ($K_{pw} \times m_p$). In other words, for the substances intended for cross-calibration sampling should be integrative and the samplers far from the thermodynamic equilibrium with the sampled water.
3. **WBL controlled uptake** should apply for substances identified in point 1 in both passive samplers. The sampling rate R_S is a product of mass transfer coefficient and the active sampler surface area. In most applied samplers the main barrier to mass transfer is the WBL, and from theory, similar mass transfer coefficients are expected. Although for many a-PSD the WBL controlled may not apply for all substances, it is likely for hydrophobic compounds [7]. To minimise the chance of a membrane controlled uptake, use of protective or diffusion membranes should be avoided. It should be taken into account that higher sampling rates are achieved in absence of diffusion membranes; as a consequence the integrative uptake is shorter than when using samplers protected by membranes.

In order to estimate the in situ R_S of the a-PSD, the following steps are followed:

1. For the p-PSD device WBL-controlled sampling rates are determined from PRC release using the approach outlined in 10.6.1.1.
2. The substances that fulfil the above criteria (e.g. PAHs) are determined in both compared passive samplers (e.g., in the a-PSD, and the p-PSD).

3. The surface specific uptake of those compounds (ng cm^{-2}) is compared for the two different samplers.
4. When a significant correlation in uptake is found, it is assumed that surface specific sampling rates (actually, the mass transfer coefficients) are proportional by the same factor and the regression can be used to estimate sampling rates of the a-PSD:

$$\frac{N_{a-PSD}/A_{a-PSD}}{N_{p-PSD}/A_{p-PSD}} = F \tag{9}$$

$$R_{S,a-PSD} = F \times \frac{A_{a-PSD}}{A_{p-PSD}} \times R_{S,p-PSD} \tag{10}$$

The obtained WBL controlled sampling rate estimate $R_{S,a\text{-}PSD}$ should be from theory [7] a function of the compound`s diffusion coefficient in water and can be estimated for any compound from its molar mass M using the equation 3.

The concentration in the water phase C_w from its amount in a sampler operating in the linear uptake mode is calculated according to [7]:

$$C_w = \frac{N_t}{R_s t} \tag{11}$$

However, for long exposure times the extracted volume is constrained by the sorption capacity of the passive sample ($K_{pw} \times m_p$) and in such case, the more general equation 5 should be applied.

An example of calculation of *in situ* sampling rates of an adsorption passive sampler using co-deployed partition based samplers with PRCs

The example illustrates the estimation of WBL controlled sampling rate of a sampler made of SDB-RPS Empore disks from the sampling rate obtained using co-deployed (in the same sampling device) AlteSil silicone rubber (SR) sheet spiked with PRCs. Sampling was performed using the EPS device (17.1) deployed during the Joint Danube Survey 3 as a mobile passive sampler on the river stretch between Bratislava and Budapest [27]. *Figure 14 shows an excellent correlation of uptake of polycyclic aromatic hydrocarbons in both samplers. Using the approach outlined in 11.5.2 sampling rates in the Empore disk sampler can be for this situation estimated as:*

$$R_{S,Empore} = 0.76 \times \frac{A_{Empore}}{A_{SR}} \times R_{s,SR} = 0.76 \times \frac{173}{392} \times R_{s,SR} = 0.34 \times R_{s,SR}$$

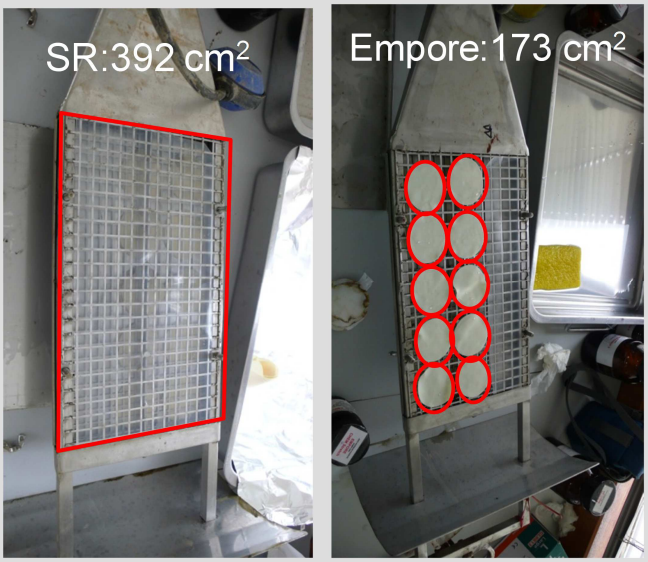


Figure 13. Co-deployed AlteSil silicone rubber and SDB-RPS Empore disks in an EPS device.

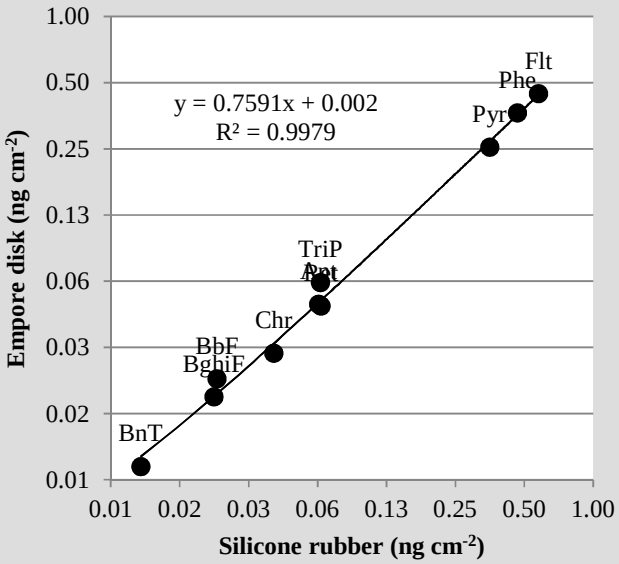


Figure 14. Comparison of surface specific uptake (ng cm^{-2}) of polycyclic aromatic hydrocarbons into AlteSil SR and SDB-RPS Empore disks. The line shows linear regression of data. Analysis was performed only with substances that were in the linear uptake stage in silicone rubber. A $\log_2$ scale is used on both axes for a better data visibility.

	***Look out!*** *In case of a-PSD the uptake rate is reduced not only by equilibration but it can be limited also by saturation of the sorption sites of the adsorbent applied. Also uptake of non-target compounds and other interfering natural compounds contributes to saturation and competes for sorption sites with target substances. Effects of pH and ionic strength on sorption distribution of polar compounds in adsorbents are more pronounced than in case of non-polar compound partitioning to elastomer polymers. Finally, the sorption capacity of adsorbents is limited by the available surface area and typically, K_{pw} values are not constant with increasing concentration in water phase but non-linear sorption isotherms apply* [64]. *To avoid or reduce those effects, sampling with a-PSD is preferably performed in the linear uptake mode and exposure periods are kept shorter than with p-PSD, typically only 2-4 weeks.Note that when samplers without a diffusive membrane or filter are applied, the integrative period may be even shorter for compounds with low K_{pw} values.* *Exemplary provisional adsorbent – dissolved phase distribution coefficients (K_{pw}) (L kg^{-1}) for selected pharmaceuticals and adsorbent materials, determined during SOLUTIONS project, are provided in Annex 5. K_{pw} values for a range of pesticides have been recently published by Ahrens et al.* [86].

11.6 QA/QC of adsorption passive sampling including interlaboratory studies

The guidances on passive sampling referred to earlier, all include advice on the use of various blank samplers, with and without exposure and directions to check recovery of the chemical extractions like would be done for water spot sampling [87]. A comprehensive kind of proficiency testing exercise was the NORMAN Inter-Laboratory Study (NORMAN-ILS) organised in 2011. The study was intended as a learning exercise and to determine the variability in all the separate steps in the passive sampling process. About 30 laboratories joined the exercise and passive sampling of several groups of substances including pharmaceutical, currently used pesticides, perfluorinated compounds, steroid hormones and some others was tested. The report of the NORMAN-ILS is available [60] and a summary has been published [61]. The overall conclusion was that the between laboratory variation was about 5 times larger than the within laboratory variability. The within laboratory variability was generally low and, because it was derived from uptake of replicate samplings using provided parallel exposed POCIS samplers, consequently also the sampling process could be considered equally repeatable or better. In addition to samplers provided by the organiser, participants in parallel exposed their own samplers. In case when the uptake in different samplers was based on the same mechanism/principle, the surface specific uptake was quite similar for

the participants' and the provided samplers, which means that the passive sampling process is, within limits, repeatable in different sampler types. The different approaches laboratories used to derive concentrations in the aqueous phase from the sampler uptake also caused a considerable variation. Summarising, the analytical inter-laboratory variability was the largest source of variation, followed by approaches applied for conversion of passive sampler uptake to aqueous concentrations. The sampling process itself had surprisingly good repeatability and preparation of homogenous reference materials from field exposed samplers seems to be very feasible.

The poor reproducibility of laboratory analysis may have been caused by the fact that many participants were not yet experienced in analysing substances in passive samplers. Blueprints for improving analytical performance are widely available and it can be assumed that this can be resolved. In the past, the approach helped to improve accuracy of trace organic pollutant analysis in water samples.

That leaves the calibration to achieve an accurate estimation of the sampled water volume yet unresolved. Considering the effort already made to solve this issue the uncertainty that comes along with present available a-PSDs must probably be accepted for now.

Nevertheless, even when accepting the uncertainty of a factor two, adsorption passive sampling can still be the method of choice preferred to spot sampling. In present discussions it has been a common practice to compare the inter-laboratory uncertainty of a-PSD with the intra-laboratory method performance parameters, i.e. accuracy (trueness and precision) of the analyte amount found in the sample collected by spot-sampling. With passive sampling the same level of accuracy as with spot sampling is achievable only in the limit case. However, when the assessment of uncertainty is extended by including the variability of sampling in the field, there is a considerable chance that, in spite the uncertainty associated with a-PSDs, the annual average (AA) concentration calculated from continuous passive sampling with a monthly sampler exchange frequency will be more robust than the AA calculated from monthly spot sampling. This is because results from a-PSDs are in most cases time- integrative and accidental concentration variations are recorded by samplers, whereas those are certainly missed with low frequency spot sampling.

The implementation of a-PSD would be facilitated if the legislation set clear criteria for representativeness of samples used in compliance monitoring.

12 Sample processing for toxicological analysis

Several schemes for extracting the samplers may be applied, including Soxhlet extraction and cold-extraction in a similar way as described in chapter 10.5. The main difference between the methods applied for chemical and toxicological analysis is that during sample processing recovery or other internal standards should not be added, since those may interfere with the bioassays and cause false positive response in tests.

The same rules for solvent transfer apply as described in chapter 10.5.5. The procedure for silicone rubber sheets may be rather simple, since their extraction to methanol is advised. Methanol is a solvent miscible with water and compatible with many bioassays. Adsorption based samplers are also often extracted to methanol. Therefore transfer of extracts to other solvents may be skipped in such case. Useful information on solvent transfer of extracts intended for toxicological analysis can be found in Brack et al. (2016) [14].

Look out!

*Samplers intended for toxicological analysis should not be spiked with PRCs (9.4**Error! Reference source not found.**) since bioassays may give undesired positive response to those compounds. When passive samplers for chemical and toxicological analysis are exposed simultaneously, they should be clearly distinguishable and their mix-up during sample processing must be avoided. This can be done best by placing them separately in labelled deployment cages, labelling them by a tag, or samplers made of polymer sheets may be cut to a shape that allows an easy identification. When PRC-spiked and non-spiked samplers are exposed next to each other, it is important that a direct physical contact between them is avoided. Since polymer materials used in sampler construction have mostly a very good permeability (diffusivity×solubility) for the sampled chemicals and PRCs, samplers for toxicological analysis may become cross-contaminated with PRCs from PRC-spiked samplers during a direct contact. A layer of water between samplers has typically a high resistance to mass transfer (low permeability), and thus, the risk of sampler contamination by PRC from an adjacent sampler is minimized. Moreover, samplers are deployed in open deployment devices with a fast water exchange and PRCs that diffuse out of the spiked samplers are quickly and effectively diluted in water to concentrations that are not detectable.*

13 Reporting

The report of obtained estimates of concentrations in the water phase should include the information about the exposure site, the deployment and recovery. In addition, it is relevant to provide data on the analytical chemistry (recoveries, procedural blanks, amounts in the controls), as well as on the calculation

methods that were used. The latter is important to allow users of the data to recalculate the aqueous concentrations in case better calculation methods or improved sampler calibration parameters become available [22]. The ISO 56667-23 [12] specifies the minimum information that should be provided for each analyte in the passive sampling device set.

14 Conclusions

Passive sampling is a powerful tool to complement and in many cases replace monitoring of organic compounds in water and other environmental compartments. Passive sampling devices are able to deal with variable concentrations and, because of the large accumulation of substances from the sampled medium into the sampler, they can also achieve very low limits of quantification. This internal deliverable of the SOLUTIONS project provides a practical guidance on the use of passive samplers for monitoring organic pollutants in water. The guidance should facilitate practical implementation of passive sampling devices in monitoring activities performed within the framework of the SOLUTIONS project and beyond. It is intended to facilitate the selection of an appropriate sampling device based on the study objectives (e.g. trend monitoring or checking compliance with environmental quality standards), information on physico-chemical properties of monitored compounds and characteristics of the monitored water body. The availability of such guidance documents presents one of important prerequisites for the intended future implementation of passive sampling in regulatory monitoring programs. Further conditions include the availability of calibrated passive samplers for relevant substance groups, a task that is also being performed within the SOLUTIONS project. The SOLUTIONS project provides also a platform for field testing activities using novel passive samplers, their comparison with other novel monitoring tools developed within the project, such as the large volume solid-phase extraction method, and their application in case studies in selected European river basins.

15 References

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16 Annex 1. An example of a sampling record form

SAMPLING RECORD

SAMPLER: _____

Sampling site		
GPS coordinates	**Latitude**	**Longitude**
	DEPLOYMENT	**RECOVERY**
Who		
Date and time		
Duration of the deployment and recovery process (exposure to air for field control)		
Conductivity		
pH		
Water and air temperature		
Flow		
Water velocity		
Water depth		
Picture –time of snapshot		

17 Annex 2. Operation manual for the “enhanced” passive sampling device

The “enhanced” passive sampling system (EPS; Figure 7) has been designed to obtain enhanced passive sampler uptake rates in order to achieve sufficient sensitivity despite the short time available for sampling [27]. The system can be applied for increasing sampling rates of compounds that are accumulated in samplers under water boundary layer control (WBL) [7]. The increase in water flow velocity in the vicinity of sampler to 1-2 m s^{-1} reduces the resistance to mass transfer in WBL, resulting in faster chemical uptake. The uptake principle in the EPS remains the same as in classical static passive sampling and the monitoring results can be evaluated using usual passive sampler calibration parameters.

17.1 The EPS device

The sampling device (Figure 15) consists of a rectangular stainless steel plate box. During operation the box remains open from two sides. One end of the box is connected to a high volume immersible pump that forces water at a high speed through the box during the sampling operation. During operation, water ejected from the pump enters the box through a slit on the front end and exits through another slit on the opposite side. A protective “roof” plate is placed in front of the exit opening. This prevents the exiting water to jet stream up. Instead, the roof plate leads the upward flow of water back along the sides.

Two walls of the device box consist of a stainless steel square mesh (14×28 cm) with cca 10 mm eye size. During sampling operation passive sampler sheets are laid on these “mesh walls” from the outside the box. After placing of the samplers, the two “mesh walls” will be closed by two stainless steel plate lids from both sides. The lids stay in place during the sampling operation.

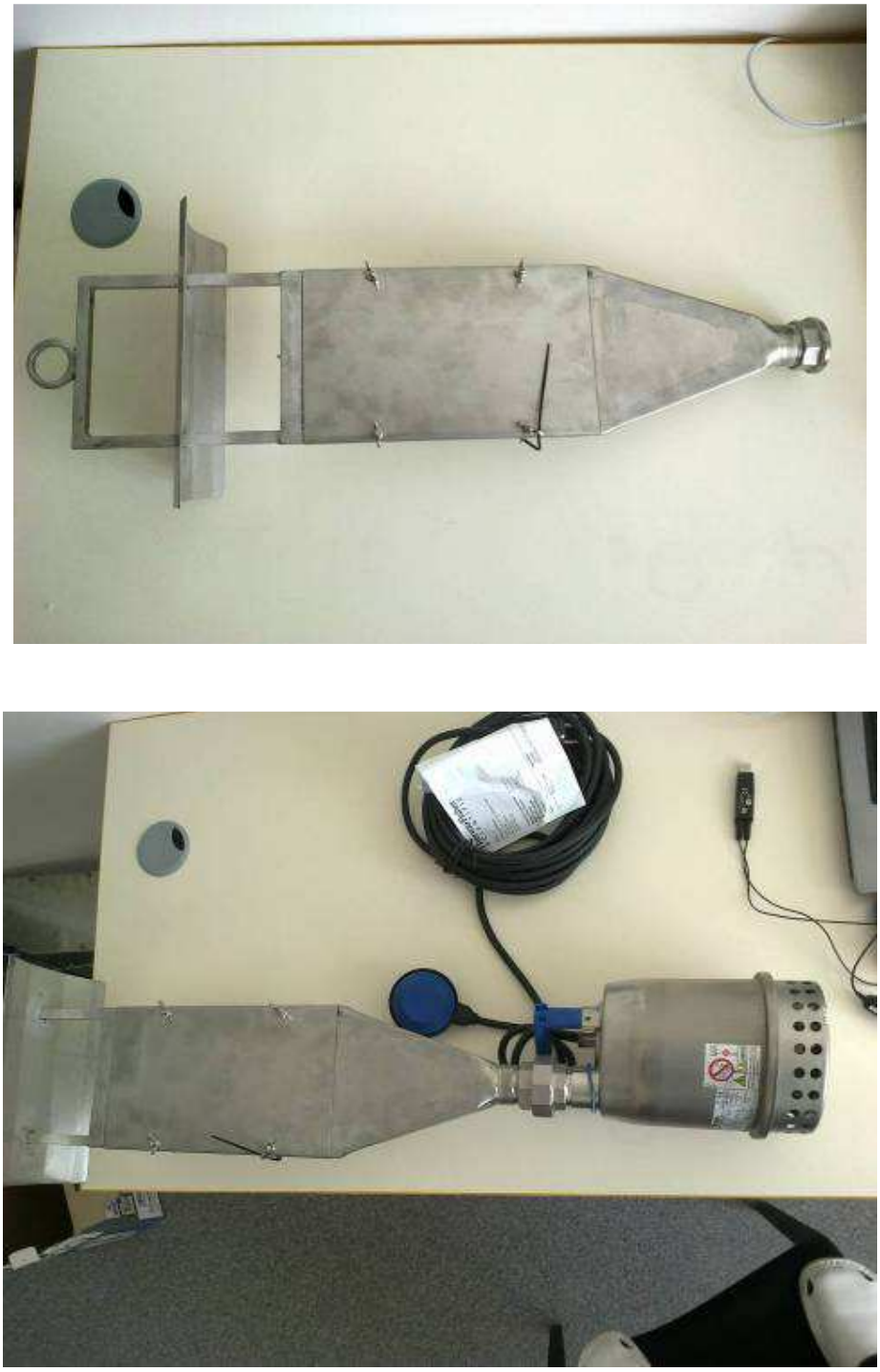

Figure 15. The "enhanced" passive sampling device. Top: the device, bottom: the device mounted on a submersible pump.

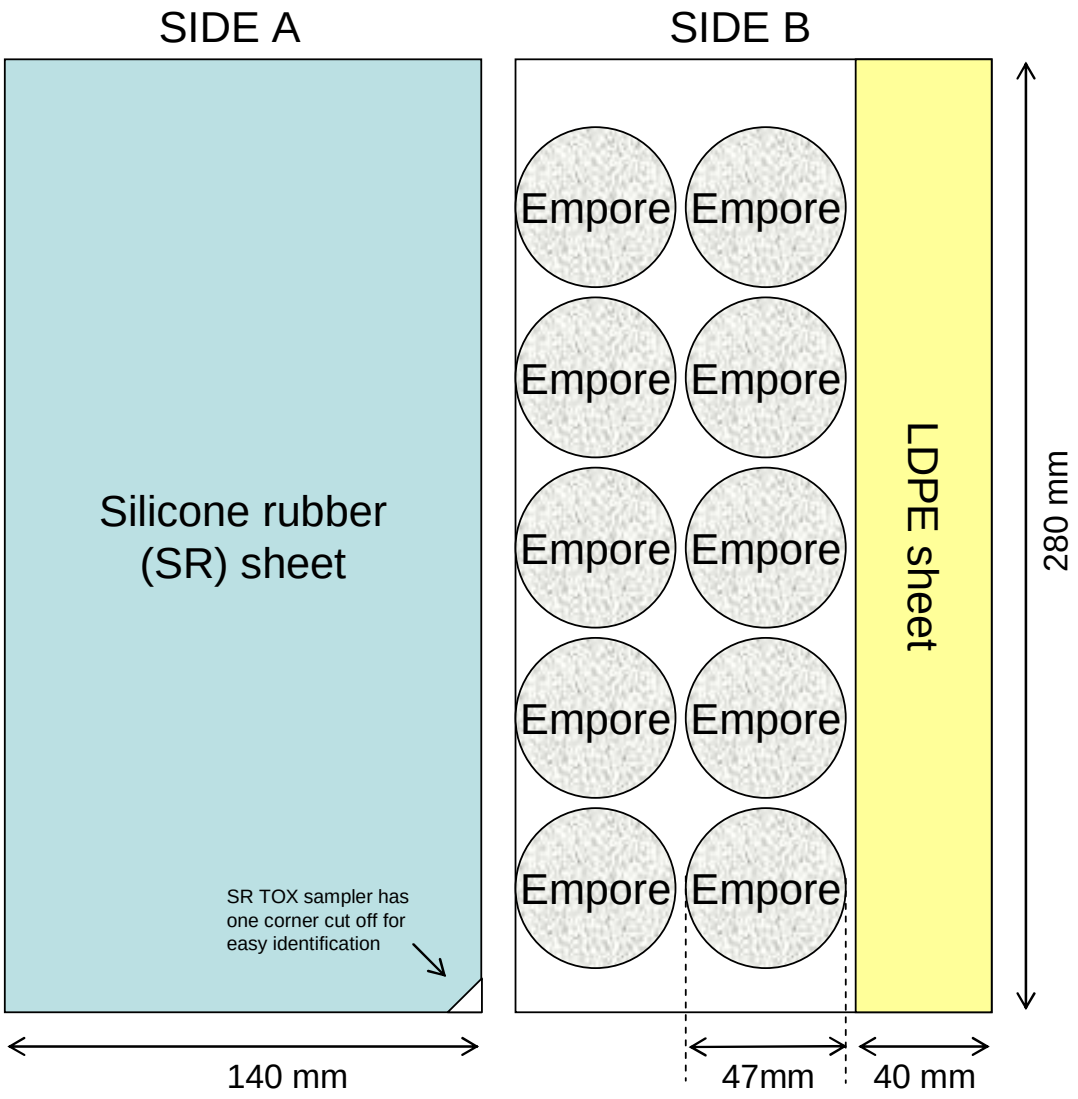

Figure 16. An example of positioning of various passive samplers in the sampling box during operation. For an easy identification of samplers mounted in the EPS device, the polymer sheets comprising a sampler may be cut into a specific shape. In the picture a silicone rubber sampler intended for later toxicological analysis is denoted in the drawing as "SR TOX" and it has one sheet corner cut off for an easy and unambiguous identification.

17.2 Passive samplers applicable in the EPS device

Various passive samplers of hydrophobic and polar compounds can be mounted to the EPS device, but they should consist of thin sheets containing sorbent material with a sufficient analyte uptake capacity,

such as silicone rubber and LDPE sheets for sampling hydrophobic compounds, or Empore™ disks for sampling polar compounds. An example is given here of a concurrent deployment of three passive samplers in the EPS device that enables to sample compounds with a broad range of physicochemical properties. The three types of passive samplers that are mounted into the EPS device during operation are: silicone rubber sheets, Empore disks, and LDPE sheets.

Containers with passive samplers will be labelled with a unique description containing information on purpose of the sampler (exposure sampler or field blank) and the sampling station and sampling period for which it is intended.

17.2.1 Silicone rubber sampler

The sampler consists typically of a single AlteSil silicone rubber sheet with dimensions 14×28 cm and 0.5 mm thickness, but samplers from other silicone rubber based materials, with smaller sheet dimensions, and with smaller sheet thickness can be applied as well. Samplers are suitable for accumulation of hydrophobic compounds from the water phase during exposure. Samplers intended for later chemical analysis may be spiked with a number of Performance Reference Compounds (PRCs; **Error! Reference source not found.**) that will be partially released during exposure. Samplers for a later toxicological analysis should not be spiked with any chemicals during their preparation since adding chemicals to the sampler may interfere with the later toxicological analysis.

17.2.2 Empore disks

The sampler consists of 10 solid phase extraction disks SDB-RPS Empore™ SPE disks (Sigma-Aldrich; hereinafter referred to simply as Empore disks) with 47 mm diameter. Samplers are suitable for accumulation of hydrophilic compounds from the dissolved phase, especially compounds that are present neutral or in a cationic form in the dissolved phase. Pre-conditioned Empore disks samplers are prepared according to the procedure described in Annex 3.

17.2.3 Low density polyethylene (LDPE) sheets

The sampler consists typically of LDPE sheets 4×28 cm. Samplers accumulate hydrophobic compounds from the dissolved phase.

17.3 Material, equipment and facilities

An electricity sockets with 220 V voltage is required on site. A list of material required for operation of the EPS device:

1. An EPS sampling device.
2. A submersible pump that is compatible with the device. For example, the submersible pump BEST ONE-10 [88] has been tested and showed a good performance with the EPS device. In case of pump fault or sampler damage, an additional backup EPS device with pumps should be available.
3. A waterproof extension cable (20 m) to connect the pump to a 220V power source that must be available on site.
4. Equipment to hang the passive sampler (rope, shackles, cable ties, stainless steel screws).
5. Submersible temperature loggers. In case the logger is triggered by a magnet, it is necessary to take it to the sampling site. Submersible temperature logger should be attached to the EPS device during the whole exposure. The battery and memory capacity should be sufficient for an operation during the whole sampling campaign. A light sensor on the logger is a useful feature that enables to monitor eventual exposure of samplers to sunlight (e.g. during deployment and recovery operations).
6. Containers with passive samplers (17.2). Samplers should be labelled and a list of samples provided. Until exposure the sampler containers are stored in a freezer.
7. Two non-sharp tweezers
8. A clean stainless steel baking tray or a clean plate from an inert material that can be used sort the samplers on (wrapped in aluminium foil and stored in a clean place when not in use)
9. Methanol washed sponge for cleaning of silicone rubber and LDPE sampler sheets after exposure.
10. Beaker to take some local water
11. Vinyl gloves
12. Lint-free tissue paper to dry the SR and LDPE sheets
13. A bottle with Milli-Q water
14. For sampler recovery the original containers in which the samplers came before exposure
15. A camera to document the procedure

17.4 Mounting of samplers in the EPS device

For deployment the material used should be clean. A workspace is required of about 1 m to lay the sampler BOX device horizontally during mounting and dismounting samplers. Non-sharp tweezers are required for mounting the sheets and a clean working place to sort the samplers on: a stainless steel baking tray. Samplers should be mounted just before exposure (and removed from the sampler directly after recovery). The data on sampling on should be recorded on a sampling form.

1. All listed material for sampling is prepared.
2. Only the first time during a sequential deployment of several samplers, the EPS device should be connected with the submersible pump and fixed strongly. Care should be taken especially to avoid losing the sealing O-rings.
3. The pump should be disconnected from electricity.
4. Start of the mounting time is recorded.
5. The container with SR field control (8.8.3) is open and placed on the clean steel baking tray during the sampler mounting operation.

6. The screws on the EPS device are released and one lid on the device is open. The butterfly nuts that hold the lid should be stored safely in the stainless steel dish and their contamination or loss during deployment should be avoided.
7. The container with SR passive samplers is opened and a sampler is taken out using a pair of tweezers.
8. The passive sampler is mounted into the EPS device according to Figure 19.
9. The lid on the EPS is closed using the 4 butterfly nuts. The EPS device is turned so the side with the other lid is up.
10. Points 4.-9. are repeated with LDPE and Empore disks samplers- they are mounted on the other side of the EPS device. Positioning in the box should be done according to Figure 16. During exposure, all samplers are exposed from one side to the same water.
11. Empore disks are mounted in the EPS device as follows: The lid of the device on the floor so that it's bended sides show up as shown in Figure 22. Using tweezers, glass fibre filter (47 mm glass fiber filter disks) supports are placed on the lid in positions where Empore disks will be placed. Empore disks are placed on the top of the glass filters. Since both filters and the Empore disks are wet, they will stick to the lid. The lid is taken from both sides and slowly turned upside down. Care has to be taken that the disks are not released. Finally, the lid is placed back in its position. The Empore disks should always be in direct contact with the mesh. The glass fibre filter is only a support to help filling up the gap between the lid and mesh so that the samplers are not washed away by the water current during exposure.
12. All butterfly nuts should be secured against loosening by pulling cable ties (tie wraps) through the holes in butterfly nut wings on both sides of the box as shown in Figure 20.
13. The submersible temperature logger is fixed to the frame bar of the box above the roof using a cable tie. In the protocol the code of the logger is written down. The code is usually visible on the back side of the logger under a transparent plastic. The logger is activated. The memory and battery capacity should allow logger operation without interruption during the whole duration of the campaign. After a successful logger start at the beginning of the sampling operation the logger remains attached to the EPS device and no other operation is needed, except wiping the light sensor window with a paper tissue each time the device is pulled out from water. Also functionality of the logger should be checked regularly (usually, the logger that is in operation give signals – a flashing light diode). The logger is only removed from the device at the end of the whole campaign. A label is placed on the logger to identify to which device it was attached.
14. The box is hung on a rope that will be used for deployment. The depth of sampler deployment below the water level should be kept constant during all exposures. The device should remain submerged during the sampling operation and also the device should be fixed safely (where possible, double fixing with a steel and a nylon rope). Precautions should be made that the EPS devices (if several are operated side by side) does not get entangled into each other and avoid them turning around axis during exposure. This can be done by fixing each device by two ropes fastened at different positions on the shore.
15. The electric cable of the submersible pump is connected to the 220V socket and the pump is switched on. Caution should be taken to avoid touching the device while the EPS device is in operation and the pump is on.
16. Start of exposure is recorded.
17. Field controls are returned back to their containers. Containers of exposure samplers should be stored closed.
18. The sampling protocol should be filled in. An example is given in Annex 1.

Look out!

There is a risk of an electric shock when the device is in operation. Caution should be taken and touching any wet parts of the EPS device should be avoided while the pump is connected to electricity.

17.5 Recovery of samplers from the EPS device

19. All listed material for sampling is prepared.
20. The pump is disconnected from electricity.
21. Gloves should be used if local water is contaminated and physical contact with it needs to be avoided, otherwise properly washed and extensively rinsed hands contaminate less than gloves may do.
22. Start of sampler recovery is recorded.
23. The EPS device is pulled from water. The device is placed horizontally on a desk or a clean surface with the one lid up.
24. The clean stainless steel tray is prepared for placing the samplers after taking out from the EPS device. The tray should be filled with local water.
25. The submersible logger device should be checked if it is still active (led diode indicator). It is only replaced if it is not active.
26. The containers with field controls are opened and placed on a clean surface.
27. The screws on the EPS device are released and one lid on the box is opened.
28. The dedicated passive sampler containers are opened – those are the same in which the samplers were delivered for deployment.
29. The exposed sampler is taken out from the EPS device using tweezers
30. The recovered situation is documented by taking picture with a camera of the recovered samplers.
31. Silicone rubber samplers are put to the steel tray filled with local water for cleaning purpose. Empore disks are normally not cleaned after exposure.
32. Local water and the provided pre-cleaned scourer/sponge is used to clean the samplers as good as possible in the shortest possible time. The samplers should be kept under local water as much as possible.
33. Samplers are dried by patting with a lint free paper tissue and put in the corresponding transport and storage jar; the lid is closed. The cleaning should be done in the shortest time possible, e.g. less than 5 minutes.
34. The field controls are packed in their corresponding containers and time is recorded
35. The device is then turned so that the other lid shows up.
36. Points 27.-35 are repeated with LDPE and Empore disks samplers.
37. LDPE sheets should be only gently cleaned using a paper tissue – the scourer/sponge would scratch it!
38. Empore disks should not be cleaned. Any water in the storage vials should be poured out before exposed Empore disks are inserted in it.
39. If the sampling campaign is designed to deploy several samplers in a time sequence, another set of samplers is mounted.
40. The sampling protocol is filled in.
41. The recovered samplers are placed back in the storage containers ad they should be stored in the dark, and as soon as possible are transferred to a freezer, until analysis or dispatch to the analysing laboratory.

Figure 17. Opening and closing lids on the EPS device.

Figure 18. The EPS device with an open lid on one side.

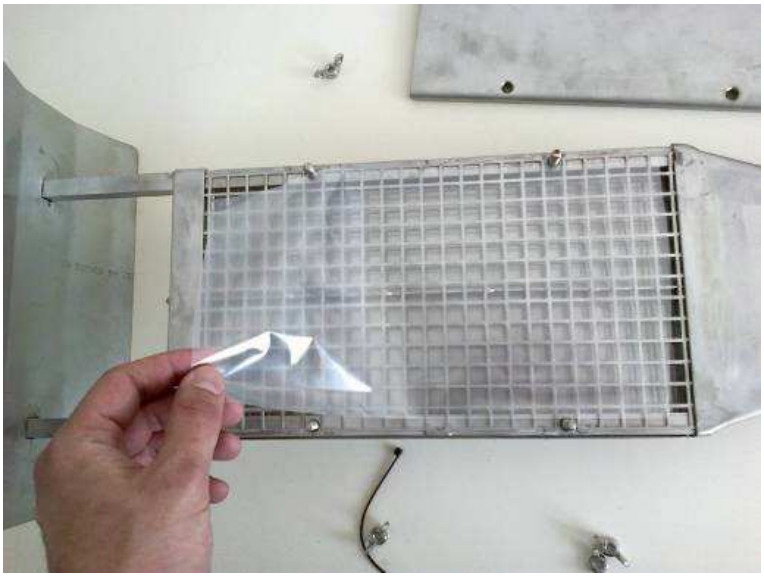

Figure 19. Mounting a SR sheet in the EPS device. Note this should preferably be done by tweezers or using gloves.

Figure 20. Cable ties to protect butterfly screws against loosening during exposure. Cable ties must be closed.

Figure 21. A fixing eye to hang the box device on a rope during exposure.

Figure 22 Mounting Empore disks into the EPS device.

18 Annex 3 An example of a sample processing procedure of silicone rubber samplers

The sampler consists of a single AlteSil silicone rubber sheet with dimensions 14×28 cm and 0.5 mm thickness. Samplers were applied during the Joint Danube Survey 3 to accumulate compounds from the dissolved phase during exposure to Danube water [27].

1. Before extraction, samplers are taken from the freezer and warmed up to laboratory temperature. Individual SR sheet were taken with clean tweezers and patted with a dry paper tissue to remove residual water.
2. Using a pair of tweezers, the SR sheets are folded as concertina so that they fit into a 200 mL Soxhlet extraction chamber (Figure 23). 6 SR sheets are placed in 6 parallel Soxhlet extractors as one extraction batch. 1 reagent blanks and 1 recovery spike is extracted in each batch.
3. SR samples are spiked with recovery internal standards (RIS) by dripping RIS solutions on the surface of the SR sheet inside the Soxhlet extractor according to Table 1. An equal amount of RIS as dosed to all samples is also collect in a vial that are analysed in parallel with the samples as reference. This approach allows the RIS solution to be non-quantitative.
4. Pre-cleaned boiling stones are added + 250 mL methanol into a 250 mL round bottom flask of a Soxhlet extraction apparatus.
5. Compounds sorbed in the SR sheet are extracted for 8 hour in methanol using Soxhlet extraction.
6. The SR sheets are taken out from the Soxhlet extraction chamber. They are placed on a clean stainless steel baking tray in the fume cupboard overnight to evaporate the remaining solvent. Weight m_1 of the dry SR sheet after extraction is recorded.
7. The volume of the extract in methanol is reduced to cca 4-5 mL using Kuderna-Danish evaporation apparatus (Figure 24).
8. To remove any particles, sand or any residual natural organic material that might be co-extracted from the surface of SR during extraction a small bunch of glass wool + 0.3g anhydrous Na_2SO_4 is put into an empty glass Pasteur pipette. The filled pipette is washed with three times 1 mL methanol. The extract is quantitatively transferred to the Pasteur pipette by rinsing the round bottom flask 3 times with 2 mL methanol. Finally, the filled pipette is washed with three times 1 mL methanol. The filtered extract is collected in methanol to a pre-weighted (m_2) labeled 100 mL point flask that contains boiling stones. The volume is reduced in point flask to approximately 1.5-2 mL using Kuderna-Danish evaporation apparatus.
9. The total weight of the 100 mL point flask with the 2 mL extract in methanol (m_4) is recorded. The weight is compared with the desired value (m_3). If necessary, the volume of the extract is further reduced under soft nitrogen flow or methanol is added to have exactly 2 mL of extract.

18.1 Sample division for analysis by liquid chromatography

10. 10% (200µL) of the extract in methanol is collected using a 200 µL syringe into pre-weighed 2mL minivial (m_5) for analysis of pharmaceuticals (Ph), polar pesticides (Pe); non-target screening (NTR) and the total weight is recorded (m_6).
11. 10% (200µL) of the extract in methanol is collected using a 200 µL syringe into pre-weighed LC vial (m_7) for analysis of steroids, alkylphenols and bisphenol A (St) and record the total weight of the extract (m_8)**.**

12. The used syringes are washed with hexane and add to the remaining extract of 1.6 mL (80%) in 100 mL point flask to transfer to hexane according to procedure below and process by further cleanup steps for GC/MS analysis. For details see the splitting scheme in Figure 25.

Table 1 Recovery internal standard (RIS) mixture composition added to exposed silicone rubber samplers before their extraction.

Compound group analysed	**Compound added as RIS**	**RIS Concentration [ng mL^{-1}]**	**Spike volume[µL]; solvent**	**Amount spiked/sample [ng]**
Polycyclic aromatic hydrocarbons Polychlorinated biphenyls Alkyl- and Aryl-phosphates	Naphtalene-D_8	5000	50; hexane	250
	Phenanthrene-D_{10}	5000		250
	Perylene-D_{12}	5000		250
	PCB 4	1000		50
	PCB 29	1000		50
	PCB 185	1000		50
	^{13}C-triphenylphosphate	5000		250
Brominated diphenyl ethers (BDEs) Novel brominated flame retardants (NBFRs)	A mix of BDEs-^{13}C and a mix of NBFRs-^{13}C-	40	50; hexane	2
Pharmaceuticals, Currently used pesticides	Alachlor-D_{13}	500	100; acetonitrile	50
	Diuron-D_6	500		50
	Simazine-D_{10}	500		50
	Caffeine-C_{13}	500		50
	Triclosan-C_{13}	500		50
Steroids Alkylphenols	17α-ethinylestradiol -D	25	100; acetonitrile	2.5
	n-nonylphenol	25		2.5

Figure 23. Soxhlet extraction of folded silicone rubber sheets.

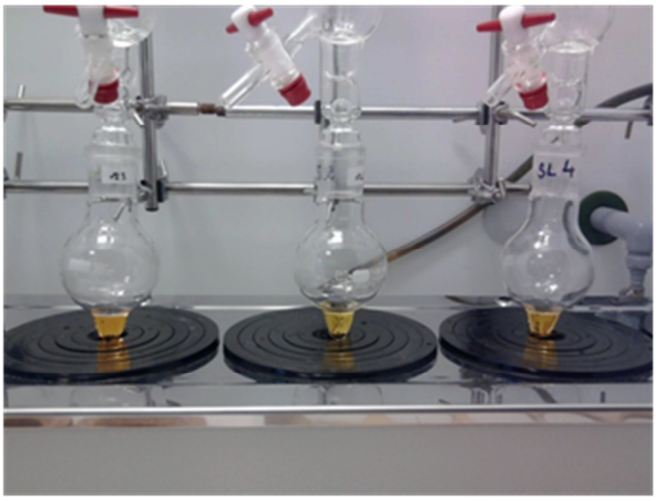

Figure 24. Kuderna-Danish apparatus for volume reduction of sampler extracts

18.2 Sample processing for analysis by gas chromatograph

13. The remaining extract 1.6 mL (80% of the total volume) is transferred from methanol to hexane. For that purpose 20 mL of hexane are added to the remaining extract in a 100 mL point flask and Kuderna-Danish apparatus is used to reduce the volume to 1.5-2 mL (control with the desired weight in hexane m_9). If necessary the volume of the extract is further reduced under soft nitrogen flow or hexane is added to have exactly 1.6 mL of final extract. The weight of point flask with 1.6 mL in hexane is recorded (m_{10}).

18.3 Sample division for analysis by gas chromatography

14. 5% (100µL) of the extract in hexane are collected using 100 µL syringe into pre-weighed labeled GC minivial (m_{11}) for non-target screening (NTR) and the total weight (m_{12}) is recorded.

15. 5% (100µL) of the extract in hexane are collected using 100 µL syringe into pre-weighed labeled GC vial (m_{13}) for non-target screening (NTR) (by a different method) and record the total weight (m_{14}) is recorded.
16. From the remaining 1.4 mL extract in hexane in point flask 400 µL are taken to a pre-weighted 20 mL labeled vial (m_{15}) for a non-destructive clean up (see the non-destructive procedure 18.4) and the total weight m_{16} is recorded.
17. The remaining 1 mL stays in the 100 mL point flask and is subjected to destructive clean up (see the procedure 18.5).

18.4 Non-destructive extract cleanup

The cleanup is used for analysis of PAHs, PRCs, NBFR, organophosphate flame retardants and musks.

18. For each sample a small piece of glass wool and an aliquot of 5g activated silica gel (pre-extracted in DCM and baked at 150°C for 12h) is prepared.
19. Glass columns *d*=1 cm, 30 cm long are used for cleanup.
20. The column is conditioned with 15 mL of diethylether (DEE) followed by 15 mL of hexane.
21. The 1 mL extract (from step 17) in hexane is quantitatively transferred to the column by washing 3 times the point flask with 0.5 ml hexane.
22. Compounds are eluted and collected in 100mL labeled evaporation point flask with:
    a) 40 mL 100% DEE b) 10 mL 100% acetone (for alkylphosphate elution)
23. Instrumental internal standard (IIS) is added to point flask according to Table 2.
24. The DEE and acetone are evaporated using Kuderna-Danish apparatus down to about 1 mL.
25. Transfer the extract in DEE and Acetone to hexane by adding 20mL of hexane and boiling using Kuderna-Danish evaporation unit and concentrate till ~1.5-2 mL. The extract is in hexane.
26. The volume of hexane is reduced using soft nitrogen flow down to 0.3-0.4 mL.
27. The extract is quantitatively transferred to GC pointed mini vials (1mL volume) and reduce the volume to have 400 µL (the same as volume splitted).
28. The extract is analysed using GC-MS for PAHs, musks, PCBs, PRCs and organophosphorus flame retardants.

Table 2 Instrumental internal standards added to extract portion for analysis of PAHs, organophosphate flame retardants, PCBs, PRCs and musks.

Compound	IIS Concentration [ng/ml]	Spike volume [µl]	Amount spiked/sample [ng]
Terphenyl	4000	50	200
PCB 121	200		10

18.5 Destructive extract cleanup and analysis of PCBs, OCPs, PBDEs

The remaining 1 mL extract is cleaned up for analysis of OCPs, PCBs, PRCs and BDEs using activated silica gel modified with sulfuric acid, activated and non-activated silica.

29. Silica gel is pre-extracted 8-10h in DCM and baked at 150°C for 12h. To prepare 44% modified silica gel 100g activated silica gel are used and 44 mL (79g) sulphuric acid are added in a round bottom flask. The mixture is manually shaken until there are no agglutinated clumps and silica gel looks homogeneous. The flask is placed in thermostat overnight. Storage period is up to 14 days.
30. Glass columns d=1 cm, 30 cm long are used for cleanup.
31. The column is filled from the bottom to top with: glass wool+1g activated silica gel+ 8g sulphuric acid modified silica gel + 1g non-activated silica gel.
32. The column is conditioned with 20 mL hexane:DCM (1:1 v/v).
33. 1 mL extract in hexane is quantitatively transferred to the column by washing 3 times the point flask with 0.5 mL hexane:DCM (1:1 v/v).
34. Compounds are eluted in 100mL labeled evaporation point flask with 30 mL hexane:DCM (1:1 v/v).
35. Instrumental internal standard (IIS) solution is added to the extract according to Table 3.
36. The hexane-DCM mixture is evaporated using Kuderna-Danish glassware to approximately 1.5-2 mL.
37. The extract is transferred to hexane by adding 20 mL of hexane and boiling using Kuderna-Danish evaporation unit and concentrates to approximately 1.5-2 ml .The extract is in hexane.
38. The extract in hexane is further evaporated to about 0.3-0.4 mL under a gentle N_2 stream.
39. The extract is quantitatively transferred to pointed 1mL GC minivials and evaporated further under soft N_2 flow to ~100µl.
40. Samples are analysed by GC-MS for PCBs, BDEs, OCPs.

Table 3 Instrumental syringe internal standards added to SR extract portion for analysis of PCBs, OCPs, PBDEs.

Compound	IIS Concentration [ng/ml]	Spike volume [µl]	Amount spiked/sample [ng]	Final V, ml	Final conc, ng/ml
MBDE-MXFR (^{13}C-PBDE 77, 138)	100	0.01	1	0.1	10
PCB 121	200	0.05	10	0.1	100

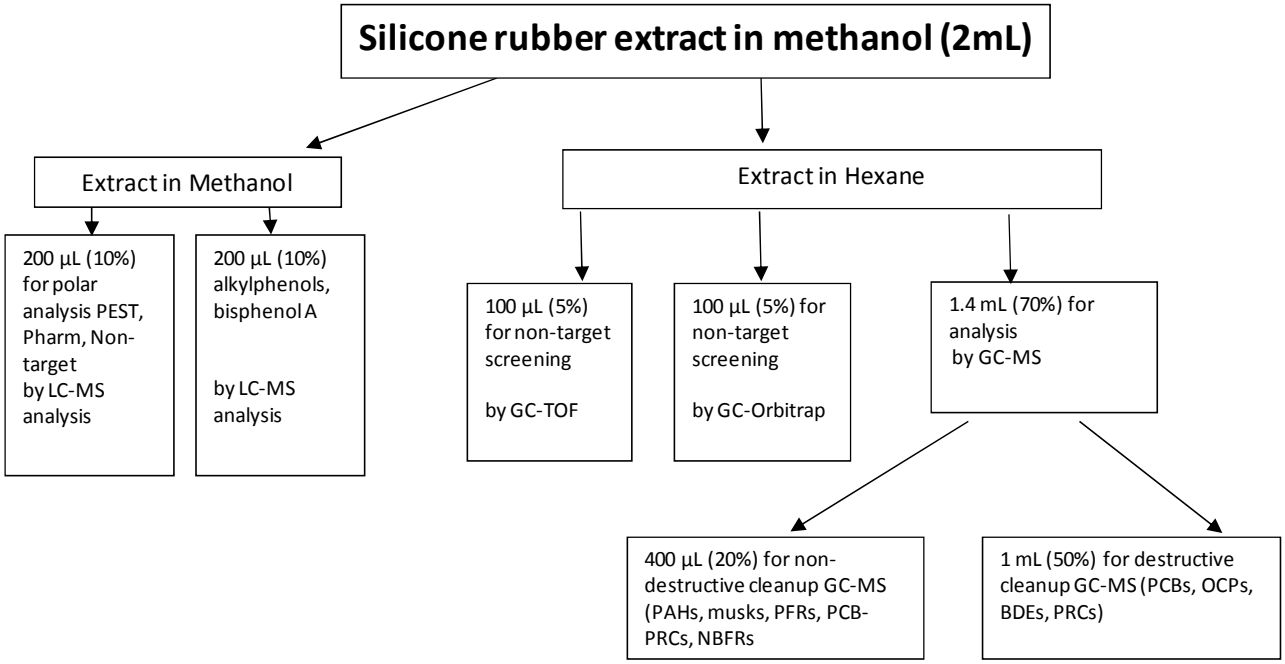

Figure 25. Division of the silicone rubber sampler extract for various methods of sample cleanup and subsequent instrumental analysis.

19 Annex 4 An example of a sample processing procedure of adsorption based passive samplers based on Empore disks

The sampler consists of 10 Empore™ SPE Disks SDB-RPS ø 47 mm (Sigma-Aldrich) (hereinafter referred to simply as Empore disks) without spiking by any compound (PRC or other). Samplers were applied during the Joint Danube Survey 3 to accumulate polar compounds from the dissolved phase during exposure to Danube water [27]. Empore disks were stored in a labeled 100 ml wide mouth glass jar closed by a plastic screw cap (with an aluminum liner inside).

19.1 Sampler preparation

Before sampling, Empore disks are washed and conditioned by subsequently immersing them in a) 100 mL acetone; b) 100 mL isopropanol; c) 100 mL methanol and d) 2x 100 mL milliQ water. The conditioned discs are stored immersed in milliQ water that is filled to the 100 ml glass jar. Samplers are dispatched to the sampling site in a portable cooling box and are kept in a refrigerator at 4°C until deployment. After field exposure Empore disks are placed in the same transport/storage flask in which they were delivered. The milliQ water in the transport/storage vial is discarded during sampler deployment. At the end of exposure no water is added to the samplers. Samplers are placed in the freezer at -20°C immediately upon delivery to the laboratory. With each sampler batch, a number of preparation controls (9.2), field controls (9.3) and reagent blanks (9.1) and laboratory spikes (9.5) is processed.

Sample processing consists of several steps: Spiking with recovery internal standards, freeze drying of Empore disks, solvent extraction and sample division for various instrumental analytical methods.

19.2 Spiking Empore discs with recovery standards

1. All Empore disk samples intended for chemical analysis are first spiked with recovery internal standards (RIS) (C_{13} caffeine, C_{13} triclosan, M8PFOA, M8PFOS, Alachlor-d_{13}, Diuron-d_6, Simazine-d_{10}, D-EE_2, n-nonylphenol) by adding RIS solution in methanol to each jar with Empore disks according to Table 4. An equal amount of recovery standards as dosed to all samples is also collect in a vial that will be analysed in parallel with the samples as reference
2. In addition, recovery spike samples (9.5) are spiked with a standard mix of target compounds according to Table 5.

Table 4 Recovery internal standards (RIS) applied

Compound	RIS Concentration [ng mL^{-1}]	Spike volume [µL]	Amount spiked/sample [ng]
C_{13} caffeine	400	100	40
C_{13} triclosan	400		40
M8PFOA	80		8
M8PFOS	80		8
Alachlor-d_{13}	1000		100
Diuron-d_6	1000		100
Simazine-d_{10}	1000		100
D-EE_2	40	100	4
nonylphenol	80		8

Table 5 Procedural recovery standards added to recovery spike samples

Standard	Concentration [ng mL^{-1}]	Spike volume [µL]	Amount spiked/sample [ng]
Mix of currently used pesticides	400	100	40
Mix of pharmaceuticals	400	100	40
Steroid(estrogen) mix	40	100	4

19.3 Freeze drying

Freeze drying is applied to remove excess water from the exposed Empore disks. Note that one sampler consists of 10 Empore disks, thus the volume of water retained by the disks after exposure is not negligible.

3. For freeze drying a set of approx. 20 screw cap lids are prepared that fit on the original 100 mL bottles that were used for sample storage. The lids should be provided with a small whole (2-3 mm) in the middle, inside with an aluminum foil liner. Alternatively, the screw caps on the jars with samples can be only slightly released (but not removed).

4. The samples are collected closed in their original transport/storage vials, caps are also labeled[4] and the weight is recorded (m_1). The screw caps are then exchanged for those in point 3, covered temporally with aluminum foil and placed to a freezer at -80°C for at least 1 hour to pre-cool as deep as possible. The original caps are meanwhile safely stored – e.g. placed in a clean zip-lock bag to avoid contamination.
5. Before usage of freeze drier is cleaned inside by wiping with ethanol 2-3 times to remove possible contamination.
6. Vacuum pump of the freeze dryer is turned on and left on for 0.5 h. When it reaches the desired temperature the first batch of jars with Empore disks is quickly transferred (remove the covering foil) from the deep freezer to the freeze dryer and immediately the vacuum is turned on.
7. Preparation controls (9.2) samples stay in the freeze dryer during the entire processing of Empore disks (to record the worst case scenario of contamination).
8. The Empore disks are freeze dried for 24 hours.
9. The prescribed operation procedure is followed to bring the samples back to normal pressure and laboratory temperature.
10. Samples are closed with the original screw caps (labeled on the top). The flasks with the dried disks inside are weighed. The weight $\boldsymbol{m_2}$ is recorded**.** If storage is necessary, the closed flasks are place to a zip-lock bag and stored in a freezer until processing.

19.4 Extraction

11. **1st extraction**: Analytes retained on the disks (note that one sampler consists of 10 Empore disks) are extracted by adding 70 ml acetone. Extraction is performed 3 times by overnight (12 h) slow shaking at room temperature.
12. The acetone extract is transferred to a collection flask – a 250 ml round bottom flask (with compatible ground joint) for the volume reduction using vacuum rotary evaporation.
13. The three extracts from step 11 are combined.
14. After extraction leave the 100ml glass bottles with extracted disks are left open in the fume cupboard overnight to evaporate the residue of the acetone from the samples. Then the 100ml glass bottles are placed for 1h to a drying oven at 50°C. The lids are put back and after cooling down to laboratory temperature weigh is immediately recorded (m_3). Difference between m_1 and m_2 (water content of disk) m_3 is compared with m_2 (water remained or extracted mass from the disks or losses due incomplete drying or sorbent loss during manipulation).
15. The Empore disks are removed from the 100ml glass bottles. The empty 100ml sample glass bottles with lid are weighed (m_4). The mass of sorbent material (10 Empore disks) is calculated as $m_s=m_2-m_4$.
16. The volume of extract is reduced to about 3-4 mL using vacuum rotary evaporation.
17. To remove particles that released from Empore disk during extraction a small bunch of glass wool + 0.3g anhydrous Na_2SO_4 are placed into an empty glass Pasteur pipette. The filled pipette is washed with three times 1 ml acetone. The extract is quantitatively transferred to the Pasteur pipette by rinsing the round bottom flask 3 times with 2ml acetone. Finally, the filled pipette is washed with three times 1 mL acetone. The filtered extract in acetone is collected to a 100 mL pointed round bottom flask. The volume of acetone is reduced to cca 1 mL using vacuum rotary evaporation.
18. To transfer the extract to methanol 20 mL methanol are added and the volume of the extract is reduced to approximately 0.5 mL using vacuum rotary evaporation.

[4] Most of the sample lids already have labels.

19. The extract is transferred (with a Pasteur pipette) to a pre-weighed (record weight = m_5; with labeled cap) clean 4 mL amber glass vial with a screw cap. The evaporation flask is rinsed twice with about 0.5 mL methanol. The volume (mass) is adjusted to 2 mL (desired weight = m_5 + 1.58g) (by adding methanol from further rinses of the evaporation flask in drops by a Pasteur pipette or syringe on a balance up to a desired weight).[5] The vial is immediately closed until next steps and the weight with cap is recorded (m_6).

19.5 Sample aliquotation

Final samples are in methanol.

20. The sample is divided into GC/LC vials in aliquots for different types of analysis using a syringe. Vial/septum type should be checked and recommended by those who will perform the instrumental analysis (to avoid contamination). The preparation of aliquots is described in the next steps.
21. Sample for analysis of (Ph) Pharmaceuticals, (Pe) Polar pesticides + perfluorinated compounds; (NTR) non-target screening by LC/MS: 250 µL of sample taken from step 19 = 12.5%.
22. Sample for analysis of alkylphenols + steroids + bisphenol A (St): 250 µL of sample are taken from step 19 = 12.5%.
23. Storage/backup = 62.5%. The weight of vial + extract that remains in the vial is recorded (m_7) and remaining mass of extract $m_R = m_7 - m_5$ is calculated. The remaining sample is closed and stored in a freezer.
24. The samples are stored according instructions by those who will perform analysis. Spiking with internal (syringe) standards should be performed by persons who will perform instrumental analysis, unless agreed in a different way.
25. The procedure is repeated for each sample.

Table 6. Typical recoveries of selected currently used pesticides from Empore™ SPE Disks SDB-RPS using procedure described in Annex 4

Compound	Mean recovery (%)
Acetochlor	81%
Alachlor	92%
Atrazine	91%
Azinphos metyl	94%
Carbaryl	91%
Chlorpyrifos	90%
Chlortoluron	91%
Clopyralid	83%
Dimethachlor	92%
Dimethoate	93%
Diuron	97%
Fenoxaprop ethyl	91%
Fluroxypyr	112%

[5] Density of methanol is 0.792 g cm^{-3}

Compound	Mean recovery (%)
Malathion	85%
Metazachlor	93%
Metolachlor	98%
Metribuzin	52%
Pendimethalin	86%
Pirimicarb	94%
Prochloraz	91%
Propiconazole	94%
Pyrazon	93%
Tebuconazole	98%
Terbufos	35%
Terbuthylazin	92%
Tribenuron-methyl	100%

Table 7. Typical recoveries of selected steroid hormones and alkylphenols from Empore™ SPE Disks SDB-RPS using procedure described in Annex 4

Compound	Mean recovery (%)
estrone (E3)	108%
17-α-estradiol (E2α)	93%
17-β-estradiol (E2β)	91%
17-α-ethinylestradiol (EE2)	89%
estriol (E1)	94%
4-nonylphenol	111%
4-t-octylphenol	90%

Table 8 Typical recoveries of selected pharmaceuticals from Empore™ SPE Disks SDB-RPS using procedure described in Annex 4.

Compound	Mean recovery (%)
acetaminophen	88%
DEET	73%
caffeine	88%
carbamazepine	85%
sulfomethoxazole	79%

20 Annex 5. Provisional adsorbent – dissolved phase distribution coefficients (*K*pw) (L kg^{-1}) for selected contaminants.

Table 9 Sorbent/water distribution coefficient (log Kpw) of selected pharmaceuticals on the SDB-RPS Empore disk sorbent. The values were derived by equilibrating 100 ml of solution containing a nominal analyte concentration of 10 µg L-1 with 100 mg adsorbent at pH=7 and 20°C.

Compound	**CAS**	**p*Ka***	**log K_{ow}**	**log K_{pw}**
ibuprofen	15687-27-1	4.91	3.97	2.74±0.27
ketoprofen	22071-15-4	4.45	3.12	2.83±0.27
naproxen	22204-53-1	4.15	3.18	2.84±0.27
triclocarban	101-20-2	-	4.90	2.75±0.28
clofibric acid	882-09-7	3.37	2.90	3.37±0.27
acetaminophen	103-90-2	9.38	0.46	2.93±0.01
DEET	134-62-3	-	2.02	3.47±0.23
caffeine	58-08-2	10.4	-0.07	3.15±0.02
carbamazepine	298-46-4	13.9	2.45	3.12±0.02
sulfamethoxazole	723-46-6	1.6; 5.7	0.89	3.09±0.01
atenolol	29122-68-7	9.60	0.16	2.01±0.17
diclofenac	15307-86-5	4.15	4.51	3.04±0.04
ciprofloxacine	85721-33-1	6.09	0.28	0.85±0.16

Table 10 Sorbent/water distribution coefficient (log K_{pw}) of selected pharmaceuticals for the Oasis HLB sorbent. Experimental conditions were the same as described in Table 9.

Compound	**CAS**	**log K_{pw}**
ibuprofen	15687-27-1	5.75±0.21
ketoprofen	22071-15-4	5.83±0.20
naproxen	22204-53-1	5.70±0.17
triclocarban	101-20-2	4.30±0.14
clofibric acid	882-09-7	4.06±0.14
acetaminophen	103-90-2	2.99±0.41
DEET	134-62-3	6.02±0.41
caffeine	58-08-2	3.83±0.43
carbamazepine	298-46-4	5.45±0.24
sulfamethoxazole	723-46-6	4.40±0.44
atenolol	29122-68-7	4.09±0.37
diclofenac	15307-86-5	5.41±0.40
ciprofloxacin	85721-33-1	4.61±0.32

Table 11 Sorbent/water distribution coefficient (log Kpw) of selected pharmaceuticals for the Oasis MAX sorbent. Experimental conditions were the same as described in Table 9.

Compound	**CAS**	**log K_{pw}**
ibuprofen	15687-27-1	5.76±0.05
ketoprofen	22071-15-4	6.01±0.04
naproxen	22204-53-1	5.80±0.06
triclocarban	101-20-2	5.51±0.26
clofibric acid	882-09-7	6.05±0.03
acetaminophen	103-90-2	2.74±0.02
DEET	134-62-3	5.18±0.13
caffeine	58-08-2	3.41±0.02
carbamazepine	298-46-4	4.13±0.06
sulfamethoxazole	723-46-6	5.20±0.04
atenolol	29122-68-7	1.64±0.01
diclofenac	15307-86-5	5.27±0.22
ciprofloxacin	85721-33-1	4.02±0.29

Table 12 Sorbent/water distribution coefficient (log Kpw) of selected pharmaceuticals for the XAD7 sorbent. Experimental conditions were the same as described in Table 9.

Compound	CAS	log K_{pw}
ibuprofen	15687-27-1	2.25±0.36
ketoprofen	22071-15-4	2.12±0.35
naproxen	22204-53-1	2.38±0.36
triclocarban	101-20-2	3.09±0.35
clofibric acid	882-09-7	1.01±0.35
acetaminophen	103-90-2	2.11±0.15
DEET	134-62-3	2.25±0.19
caffeine	58-08-2	1.45±0.21
carbamazepine	298-46-4	3.09±0.03
sulfamethoxazole	723-46-6	3.04±0.05
atenolol	29122-68-7	3.39±0.08
diclofenac	15307-86-5	2.34±0.34
ciprofloxacin	85721-33-1	3.09±0.11

Table 13 Sorbent/water distribution coefficient (log Kpw) of selected pharmaceuticals for the AlteSil silicone rubber. Experimental conditions were the same as described in Table 9.

Compound	CAS	log K_{pw}
ibuprofen	15687-27-1	1.96±0.10
ketoprofen	22071-15-4	0.67±0.13
naproxen	22204-53-1	1.08±0.11
triclocarban	101-20-2	2.52±0.08
clofibric acid	882-09-7	-0.33±0.12
acetaminophen	103-90-2	-0.26±0.10
DEET	134-62-3	2.19±0.18
caffeine	58-08-2	0.65±0.11
carbamazepine	298-46-4	1.86±0.03
sulfamethoxazole	723-46-6	0.30±0.27
atenolol	29122-68-7	0.46±0.33
diclofenac	15307-86-5	1.94±0.04
ciprofloxacin	85721-33-1	0.39±0.18