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Guidelines for passive sampling of hydrophobic contaminants in water using silicone rubber samplers

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This series presents detailed descriptions of methods and procedures relating to chemical and biological measurements in the marine environment. Most techniques described have been selected for documentation based on performance in ICES or other intercalibration or intercomparison exercises; they have been carefully evaluated and demonstrated to yield good results when correctly applied. They have also been subject to review by relevant ICES Working Groups, but this is not to be construed as constituting official recommendation by the Council.

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Contents

1 Abstract

This *ICES Techniques in Marine Environmental Sciences* provides advice on the use of silicone rubber passive samplers for the determination of freely dissolved non-polar contaminants in seawater. The level of detail offered may be helpful to first-time users of passive samplers, who wish to implement passive sampling methods in their monitoring programmes, and to more experienced users to review their current methods. The aspects covered by these guidelines include pre-extraction, spiking with performance reference compounds, deployment, retrieval, extraction, clean-up, chemical analysis, and calculation of aqueous concentrations.

Keywords. Passive sampler, water sampling, hydrophobic contaminants, free dissolved concentration, silicone rubber.

2 Introduction

Increasingly, passive sampling devices (PSDs) are being used for the monitoring of non-polar contaminants in water. There is a large variety of non-polar samplers, including semi-permeable membrane devices (SPMDs; Huckins *et al.*, 1990), low-density polyethylene (LDPE) strip samplers (Adams *et al.*, 2007; Booij *et al.*, 1998; Müller *et al.*, 2001), silicone strip samplers, Chemcatchers (Kingston *et al.*, 2000), and many others (ITRC, 2006; Kot *et al.*, 2000; Stuer-Lauridsen, 2005; Vrana *et al.*, 2005). The passive diffusion of hydrophobic contaminants from the water phase into the sampler forms the basis of the sampling process. At the initial stage of sampler deployment, contaminants are absorbed at a rate directly proportional to their aqueous concentration (linear uptake stage; Figure 1). As the sampling continues, the contaminant gradually approaches its equilibrium concentration in the sampler. Sampling kinetics is generally faster at greater flow rates and at higher temperatures, and can be quantified using the dissipation of performance reference compounds (PRCs) that are spiked into the sampler prior to deployment (Huckins *et al.*, 2002; details are given below). The British Standards Institution and the International Organization for Standardization have issued general guidelines for the use of PSDs in water monitoring (BSI, 2006; ISO, 2011).

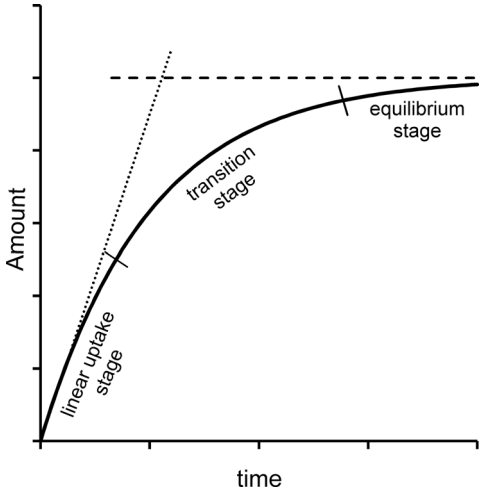

Figure 1. Contaminant amounts that are absorbed by passive samplers as a function of time (solid line). The approximate models for the linear uptake stage (short time limit) and the equilibrium stage (long time limit) are illustrated as dotted and dashed lines, respectively.

PSDs yield an integrated contaminant signal over a time window of days ($\log K_{ow} \approx 4$) to years ($\log K_{ow} \approx 7$). Therefore, the application of hydrophobic passive samplers in aquatic monitoring may reduce temporal variability when compared with batch water sampling, thus facilitating the identification of temporal trends. In addition, PSDs only sample the freely dissolved concentration of contaminants, which is highly relevant to the risk assessment of these compounds (Lohmann *et al.*, 2012). Results from studies with passive samplers are qualitatively similar to those from biomonitoring. It should be recognized, however, that contaminant uptake by passive samplers is simpler and better understood than contaminant accumulation by organisms, which is often complicated by food-mediated transport, biotransformation, and variation in the physiological state of the organisms. More information on the working principles of passive samplers can be found in Huckins *et al.* (2006) and in Greenwood *et al.* (2007). These publications also discuss and compare the advantages and limitations of passive sampling with biomonitoring.

The present guidelines summarize the use of passive sampling using silicone sheets. Silicone sheet samplers were chosen because accurate polymer–water partition coefficients (K_{pw}) are available for many contaminants (Smedes *et al.*, 2009). In addition, there is better agreement between hydrodynamic theory and experimental sampling rates for these samplers (Rusina *et al.*, 2010) than with SPMDs (Huckins *et al.*, 2006) and Chemcatchers (Vrana *et al.*, 2007). Further considerations for evaluating the pros and cons of specific PSDs can be found elsewhere (Lohmann *et al.*, 2012).

Silicone rubber sheets (Altesil translucent) have been used for the monitoring of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and hexachlorobenzene (HCB) in coastal and estuarine waters in the Netherlands, parallel with biomonitoring using mussels (Smedes, 2007a). In addition, these samplers were used in a marine trial survey in which thirteen laboratories from nine European countries, and one from Australia, participated (Smedes *et al.*, 2007a, 2007b, 2007c).

2.1 Overview

Briefly, the method for determining aqueous concentrations of hydrophobic contaminants using silicone passive samplers is as follows. Silicone rubber sheets are deployed in seawater for a period during which they absorb non-polar organic chemicals from the water. The amount absorbed depends upon a number of factors, including the physical dimensions of the rubber sheets, the temperature and salinity of the water and its physical movement over the rubber sheets, and the polymer-water partition coefficients (K_{pw}). After retrieval, the non-polar organics are analysed in the rubber sheets. To determine the amount of water that the sheets have effectively sampled, the sheets are spiked with performance-reference compounds prior to deployment. Aqueous concentrations are calculated using the contaminant amounts that are absorbed and from the PRC amounts that are dissipated from the samplers. Details are given below of sampler pretreatment, deployment, retrieval, and extraction. In addition, clean-up and analysis of the extracts are described, followed by calculation methods and considerations for quality-control procedures and data reporting.

3 Preparation, deployment, and retrieval

3.1 Preparation of the sheets

Silicone rubber sheets, Altesil translucent, were obtained from Altecweb (www.altecweb.com) as 30×30 cm or 60×60 cm sheets. The most commonly used thickness was 0.5 mm. Other thicknesses are available, but may require different conditions for pre-extraction and analysis. The sheets were cut to a size of 5.5×9.0 cm. Mounting holes were made using a paper punch, by punching a hole at both sides of the sheet rim, at a distance of ca. 11 mm (Figure 2). This resulted in two holes with a centre-to-centre distance of 33 ± 1 mm. These holes were used for mounting the sheets on the sampler holder (Section 3.4, Figure 3). A different sheet size can be used if needed, and a different silicone manufacturer can be chosen, if the sampler–water partition coefficients are accurately known.

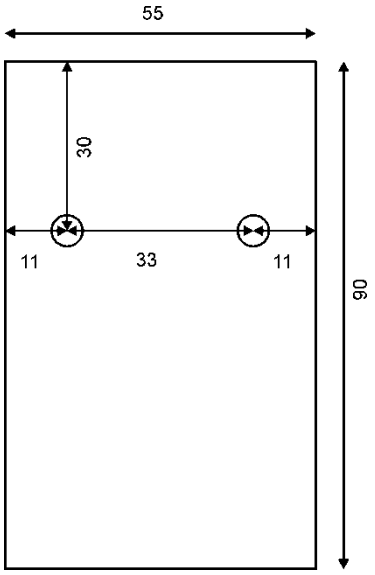

Figure 2. Sheet layout. Numbers represent the distance in mm.

The exposed surface area of 5.5×9.0 cm with two 5.5 mm diameter mounting holes was approximately 100 cm^2. Longer sheets are possible, but the suggested size excludes the risk that the exposed sheets stick to neighbouring sheets or (backwards) to themselves. Commonly applied surface areas for a passive sampler range from 300 to 600 cm^2 and, using the suggested sheet dimensions, 3–6 sheets simultaneously exposed make up a sampler. Large surface areas were used to lower the detection limits or allow analyses of more compound groups.

The silicone rubber sheets contain oligomers (short-chain polymers) that may interfere with the chemical analysis. These oligomers must be removed prior to deploying the sheets. The sheets were therefore soxhlet-extracted with ethylacetate for at least 100 h. Soxhlet operation can be interrupted during the night (for example, because of safety regulations), provided the sheets are fully covered with solvent during this period. Note that if sheets are packed closely in the soxhlet extractor, extraction efficiency may decrease and, in such a case, it is recommended to extend the extraction time to approximately one week. A realistic test to determine whether or not oligomers are sufficiently removed is to randomly select six sheets from the batch and extract these as described in Section 4.1. After evaporation of the extract to dryness, the residual weight should be insignificant. In case the residual weight is

measurable, e.g. more than 1 mg and the residue does not dissolve in 1 ml methanol, the pre-extraction was likely insufficient. Following the pre-extraction, the sheets were transferred to a wide-mouth bottle. Ethylacetate was removed from the sheets by soaking in methanol twice for 8 h, using approximately 4 ml of methanol per sheet.

3.2 Spiking with PRCs

The dissipation of performance reference compounds (PRCs) from exposed samplers was used to calculate the *in situ* sampling rates (Section 6.1). Candidate PRCs are all deuterated PAHs, including biphenyl and several PCBs (1, 2, 3, *4, 10, 14, 21, 29, 30, 50, 55, 78, 104*, 112, 143, *145, 155*, 198, and *204*; italic numbers represent PCB congeners for which experimental K_{pw} values are available; K_{pw} values of the other PCBs can be calculated from Smedes *et al.* (2009)). It is suggested to have 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 (logK_{pw} >6) and one that is expected to be depleted completely (logK_{pw} <3.3).

The amount of PRC should be chosen such that the concentration in the extract does not exceed the calibration range, but it should be high enough that after depletion from the sampler, a residual 10% can still be measured accurately. The amount of spike substance to be added to the samplers is calculated as the number of samplers (number of sheets divided by the number of sheets per sampler) times the amount per sampler. The amounts of PRCs that are finally detected in the spiked samplers can be up to ~30% less than the dosed amounts, because of losses during the spiking procedure. This spiking procedure, described below, is for a convenient amount of samplers, but it can be adjusted proportionally for other amounts of samplers.

To spike the sheets, 0.6 l of methanol is added to not more than 0.6 kg of sheets (~200 sheets measuring 5.5 × 9.0 × 0.05 cm) in a 2.5 l wide-mouth glass bottle and the spike solution is added. This bottle is shaken under stepwise addition of water, ending in 50% methanol following the scheme in Table 1. Although a high percentage of the added PRCs is absorbed by the silicone sheets, minor amounts remain present in the solution (50% MeOH) that is discarded, particularly for PRCs with small partition coefficients. The variation of PRC amounts between sheets is ca. 5%.

Table 1. Dilution scheme after spiking of 0.6 kg sheets.

Time (h)	Volume MeOH (ml)	Added water volume (ml)	Total water volume (ml)	water content (% v/v)	Step time (h)
0	600	0	0	0	
24	600	74	74	11	24
48	600	76	150	20	24
72+	600	107	257	30	>24
120+	600	143	400	40	>48
168+	600	200	600	50	>48

After discarding excess solvent, the wet sheets are packed in airtight (amber glass) jars (100 ml) with lids lined with aluminium or stainless steel foil. The lids are tightened and the jars stored at −20°C. The samplers do not have to be frozen during transport, but should be kept in the dark to prevent photolysis of the deuterated PAHs.

3.3 Required number of samplers

Each sampler batch consists of samplers for all planned stations. This number is increased by 10% (but by at least four) preparation controls, which are not deployed but are used to assess any uptake by the samplers during preparation, to determine the initial concentration of the PRCs before exposure, and to calculate limits of determination (LOD) and quantitation (LOQ). In addition, the inclusion of ca. 20% field control samplers is suggested. Field controls are samplers that are not deployed, but are exposed to air during deployment and recovery of exposed samplers. The required number of sheets (n_{sheets}) is then calculated using the number of stations (n_{station}) by:

$$n_{\text{sheets}} = [1.2\ n_{\text{station}} + \text{MAX}(n_{\text{station}}/10, 4)] \times n_{\text{sheets per sampler}}. \quad (1)$$

3.4 Deployment device

Details of a sampler holder and deployment frame are illustrated in Figure 3. Sampler sheets are fitted on two neighbouring mounting stems of the sampler holder and are kept in place by a fixing rod (Figure 3, middle and bottom). The configuration presented in Figure 3 allows for mounting six sheets per holder. One or more sampler holders are fitted on a deployment frame (Figure 3, top), which is designed to protect the sampler holder against damage caused by bumping. No protective mesh is needed.

A swivel connector gives rotational freedom to the sampler frame. A shackle or rope is used to fit the sampler frame to whatever object is selected in the field (e.g. jetty, buoy, tree branch, or bottom lander). The shackle is secured with a pin, cable strap, or stainless steel wire. Knots in ropes are secured with cable straps and tape. Figure 3 shows the system used in the ICES trial survey (Smedes *et al.*, 2007a). Alternative frames and sampler holders may be used as required, on the condition that the sampler holder is protected against damage caused by bumping. All components are made of corrosion-resistant metal (e.g. stainless steel 316L). Consultation of physical oceanographers or a marine mechanics workshop is helpful.

3.5 Deployment

Sampling locations are selected, depending on the aim of the programme, but also considering practical issues, such as the availability of suitable mooring sites, for example, quays, jetties, or buoys. If using navigation buoys, be aware that antifouling may have been applied and make sure that the deployments do not interfere with the buoy maintenance schedule. Long ropes will wind up around nearby objects. Floating objects may collide with the sampler frame.

Typically, a sampling depth of 2 m below the surface is appropriate to coastal waters. If the local water depth is less than 3 m, then the half depth can be chosen. In tidal areas, the shallowest depth, i.e. low water spring tide, should be considered, to prevent exposure to air during lowest low tide. The risk of vandalism or theft should be considered, and appropriate measures should be taken to minimize this risk (e.g. by hiding, camouflaging, using secure areas, or using locks).

Sample contamination from the air and instruments is to be avoided. Exposure of the samplers to the air should be minimized. Therefore, sampler holders (with the fixing rod (Figure 3) temporally fitted in place by a cable strap) and mooring ropes are installed prior to mounting the samplers. All instruments must be cleaned prior to use. The jars with the samplers are opened above a clean working surface. This working surface can be a stainless steel board, a glass sheet, a glass chopping board,

or a large glass Petri dish. Sampler sheets may stick to these surfaces. Sticking is minimized by wetting the surfaces with water collected from the site or with ultra pure water. A convenient alternative is a stainless steel wire mesh (1 cm). Samplers are transferred to the holders using two pairs of blunt tweezers.

Mount the sheets on the holder as follows. At deployment, cut the cable strap that keeps the fixing rod in place and pull out the rod. Take all of the sheets from the jar and separate them using tweezers. Then transfer the sheets onto the holder with the short side facing upwards. Guide the fixing rod through the holes on the stem and fasten it with a cable strap.

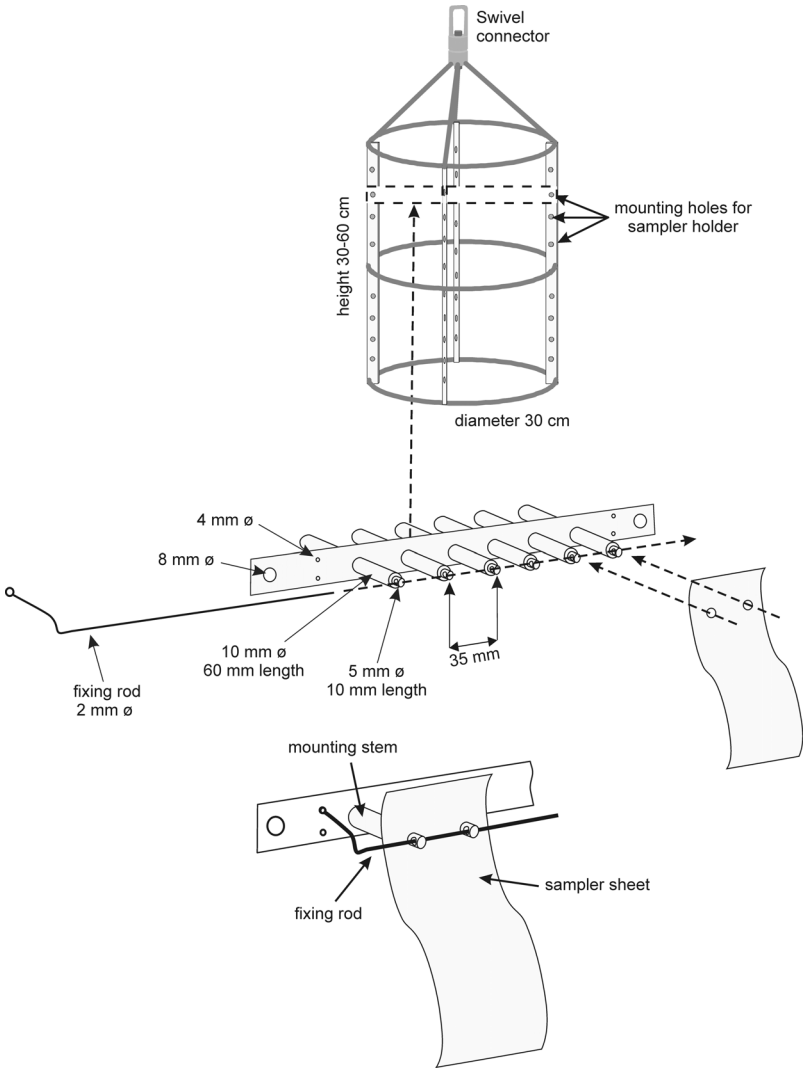

Figure 3. Schematic drawing of deployment frame and sampler holder used in ICES passive sampling trial survey.

Appropriate exposure times depend on the properties of target compounds, their concentration in the body of water, the purpose of monitoring, and the local hydrodynamic conditions and temperatures. Absorbed amounts that can be expected after the exposure can be estimated (Equation 6, Section. 6.3), by selecting an approximate sampling rate for the exposure site. For 600 cm^2 of sampler surface in turbulent marine coastal waters, sampling rates of 30–60 l day^{-1} are observed, whereas in quiescent open sea areas, sampling rates decrease to 4–10 l day^{-1}. From

this information and the required limits of detection, the optimal exposure period can be estimated.

Some important background data on the exposures should be recorded. This information is needed in the final data processing and interpretation.

- Geographical position, local water depth, exposure depth
- Date and time of deployment
- Salinity
- Water temperature
- Photograph of the deployment site

Data loggers can be deployed together with the samplers for recording the water temperature and salinity.

On sites where sample contamination from the air is possible (e.g. urbanized and industrial areas, deployment from ships), field controls can be used to check for contamination during sampler deployment and retrieval operations. To this end, the field control samplers are removed from their jars and spread out on a stainless steel wire mesh >5 cm above the working surface during the process of deployment. They are replaced in their jars after the sampler deployment is complete.

3.6 Recovery after deployment

During recovery, the same parameters are recorded as at the time of deployment, amended by a qualitative description of the biofouling, which may be useful for interpreting deviant results, such as unexpectedly high or low sampling rates or low concentrations of biodegradable analytes. Depending on the season and place of deployment, the recovered sampler can be clean, covered by a thin biofilm, or totally overgrown with organisms. The degree of biofouling can be documented by taking a picture of the recovered sheets. A clean working surface is required for handling the samplers, and local exposure water is used for rinsing and cleaning. Sheets that are almost clean are first wiped with a wet tissue paper and subsequently patted dry with tissue paper. If significant fouling has occurred, the biofouling is scraped off the sampler as completely as possible. Remaining residues can be removed using a scourer that has been immersed in local water. A nylon kitchen scourer without sponge, rinsed with methanol and water, is appropriate. Only use gloves if the local exposure water is so contaminated that skin contact must be avoided. Properly washed and rinsed hands pose a lower contamination risk than gloves do. The cleaning should be done in the shortest time possible (e.g. less than 5 min) to minimize the risk of sample contamination from the air. It is not feasible to clean them to look like an unexposed sampler, but all surface fouling should be removed. After deployment, sheets are generally slightly coloured yellow to green. If a particular location was selected for exposing a field control, then this control should also be exposed to air during the entire cleaning procedure. However, these controls should not be cleaned with local exposure water.

The recovered samplers are placed back in a storage jar with lids lined with aluminium foil and stored in the dark, in a cooling box, and are transferred as soon as possible to a freezer (−20 °C). For samplers that were not cleaned in the field, heavy biofouling sometimes can be broken off after freezing, as the frozen fouling layer will be stiff, whereas the sheets remain flexible. If necessary, additional cleaning in the laboratory can be done in the same way as described above, but using ultra-pure water.

4 Analysis

4.1 Extraction

During all concentration steps, extreme care should be taken to prevent evaporation of the sample extract close to dryness, because the matrix content (the amount of co-extracted non-target organic matter) of the sample extracts is too low to act as a keeper. When azeotropes are used for solvent transfer, extracts do not have to be reduced to very small volumes.

Two schemes for extracting the samplers may be applied. Excess water should be removed by patting the samplers dry with a paper tissue (if this was not done earlier, see above). Recovery standards can be dripped on the sheets or added to the sheets in the soxhlet thimble or extraction flask at the beginning of the extraction. Preparation controls and field controls are treated like samples. The procedural blank and recovery are processed in the same way but without sheets.

The simplest and safest way to extract the 3–6 sheets that make up one sampler is to put them together, loosely or concertina-folded, in a soxhlet apparatus and extract with methanol/acetonitrile (1:2 v/v) for 8 h. This solvent mixture has a number of convenient properties.

- It has little ability to extract oligomers.
- Acetonitrile boils at 85°C. Addition of 19 volume% methanol decreases the boiling point to 64°C; lower than methanol.
- Acetonitrile forms an azeotrope with water; therefore the extract is dried during Kuderna Danish concentration.
- When the initial methanol content is >19% by volume, Kuderna Danish concentration ends in methanol, which is suitable for clean-up with C18-bonded silica (Section 4.2).

Rather than a mixture, pure methanol or pure acetonitrile can be used. 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. A procedural blank and procedure recovery are done in the same way, but without sheets.

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 (150 ml) 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.

The exact sampler mass must be determined after extraction. This is the total air-dried weight of all sheets that comprise one sampler.

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.

4.2 Optional clean-up for the removal of silicone oligomer traces

Although oligomers should have been quantitatively removed from the sheets during pre-extraction, traces of these oligomers possibly appear as interferences in some applications. Oligomers in the extracts may cause considerable problems, for example, by blocking high-performance liquid chromatographic (HPLC) columns

and by coating gas chromatographic (GC) liners. If the presence of silicone oligomers is discovered only after the exposures, an additional cleansing of the extract with C18-bonded silica cartridges (glass version) can be considered. This ensures the removal of oligomer traces and also removes other highly hydrophobic matrix compounds, e.g. lipids. Concentrate the methanol extract to <2 ml. Pre-rinse a glass column containing 300–500 mg C18-bonded silica with 6–10 ml methanol/acetonitrile (1:2). Transfer the extract to the column and elute with 6–10 ml methanol/acetonitrile. This will elute HCB, all PCBs, and all PAHs up to coronene. The elution volume for other compounds must be tested separately.

4.3 Solvent transfer to non-polar solvents

After concentrating the extract to 2 ml, the solvent in the concentrate will be methanol, even when the sheets were extracted with methanol/acetonitrile (1:2; see Section 4.1). Solvent transfer of methanol to hexane can be done by concentrating the extract to 2 ml, then adding 10 ml hexane for each millilitre of methanol. Add boiling stones and boil the (two-phase) mixture down to 2 ml on a water bath. Repeat the procedure if two phases are still present. If the two phases remain, the lower phase is probably not methanol, but water. If this is the case, add 20 ml hexane, vortex 1 min, remove the water phase with a capillary pipette, and concentrate the hexane phase to 2 ml. (Note that the azeotropic solvent exchange from methanol to hexane does not work when nitrogen blow-down is used for concentrating the extract.)

A less convenient method to exchange the solvent is solvent extraction in a separation funnel. Concentrate the methanol to <50 ml, transfer the extract to a separation funnel, and add ultra-pure water until the methanol-water phase contains less than 20% methanol by volume. Extract the aqueous phase twice with 100 ml of hexane. Emulsions can be broken, after removal of the separated water phase, by dropping some methanol on them. The combined hexane extracts are concentrated prior to clean-up.

4.4 Clean-up and analysis

Clean-up of the extracts and instrumental analysis can be carried out according to standard laboratory methods. 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.

5 Usage of blanks and control samples

For the first stage of the data processing, it is important to distinguish between preparation and field controls (Section 3.3) and procedural blanks. The preparation controls are primarily analysed to give information on the spiked amounts of performance reference compounds (N_0). Second, the preparation control reveals which target compounds have been taken up during preparation and storage of the samplers. Additionally, the field controls provide information on sampler contamination during deployment and retrieval procedures.

The amounts detected in the procedural blanks can be subtracted from the amounts detected in analysis of exposed samplers, preparation controls, and field controls.

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. If those amounts in the preparation controls are much higher than the procedural blank, the preparation procedure should be critically assessed to identify and eliminate the causes of these elevated levels (and subsequent higher LOD/LOQ). Correction of the amount in exposed samplers using preparation controls is a not simple subtraction. For compounds that reach equilibrium, the amount of target compounds after exposure will not be influenced by the preparation blank, whereas for very hydrophobic compounds, the amount after exposure is the sum of preparation blank and uptake during exposure. As a rule of thumb, amounts of target compounds in preparation controls less than one-tenth of those in the exposed samplers are acceptable and no correction of the amounts in the exposed samples is needed.

Field controls may demonstrate elevated contaminant levels (compared with the preparation controls) for PAHs, if sampler deployment/retrieval operations are conducted near factories, highways, or on board ships, or when the working area is in the plume of engine exhausts. Because elevated levels in field controls can be highly site-specific, it is not recommended to use these controls for determining average blank levels, detection limits, and quantification limits. Instead, these controls may be used to assess contamination from the atmosphere during transport and deployment/retrieval in a qualitative manner. Elevated levels in the field controls, for example, may indicate that revision of transport and deployment/retrieval operations is necessary. A possible correction scheme for exposed samplers is described in Annex 1, but it should be emphasized that there is no agreement so far within the passive sampling community whether or not this correction scheme should be applied at all. For the time being, the safest approach is to accept only absorbed amounts in the exposed samplers that are ten times higher than the amounts in the preparation controls and the field controls, and to take measures to reduce the amounts in the controls if these are too high.

6 Calculations

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. In addition to a comprehensive model, approximate (but simpler) uptake models are given for the limiting cases when the sampling is far from equilibrium or close to equilibrium. Such models could contribute to insight and may be used to verify the correctness of the calculation. Finally, the time window over which the sampling has been time-integrative is evaluated.

6.1 Assessment of PRC amounts

The PRC data are screened prior to calculating sampling rates. Detection limits for the PRCs may depend on the amounts of other compounds present in the extract. Therefore, all PRC responses should be inspected carefully for possible interferences from other analytes, particularly if the PRC concentration in the extract is low. Each PRC peak that reveals no interference from other compounds is acceptable for further processing. For the model fitting procedure described below, results at or below the limit of detection can even be included.

6.2 Estimation of the sampling rate

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

$$f = \frac{N_t}{N_0} = \exp\left(-\frac{R_s\, t}{K_{pw} m}\right), \tag{2}$$

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 is the mass of the sampler (kg), and K_{pw} ($l\,kg^{-1}$) is the sampler-water partition coefficient. K_{pw} values for a number of silicone rubbers for freshwater may be obtained from Smedes *et al.* (2009). For exposures in marine and estuarine exposures, the salting out effect on K_{pw} has to be quantified according to:

$$\log K_{pw} = \log K_{pw}^0 + k_s\, I, \tag{3}$$

where I is the molar ionic strength, $\log K_{pw}^0$ is the partition coefficient at $I = 0$, and k_s is the Setschenow constant. Jonker *et al.* (2010) demonstrated that the k_s of PAHs is ca. $0.35\,l\,mol^{-1}$ for PAHs with three to six aromatic rings, in agreement with the literature review by Xie *et al.* (1997), who demonstrated that k_s is reasonably constant for compounds with Le Bas molar volumes $>150\,cm^3\,mol^{-1}$. The ionic strength of seawater with an absolute salinity of $35.17\,g\,l^{-1}$ and a temperature of 10 °C equals $0.715\,mol\,l^{-1}$. The ionic strength is approximately linear with the salinity (i.e. within 1%) and the temperature effect on I may be neglected. For average seawater, the salting out effect causes an increase in K_{pw} by 0.25 log units. No experimental data exist yet for the effect of temperature on the partition coefficient of silicone rubbers.

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). Rusina *et al.* (2007, 2010) have demonstrated that the R_s of PAHs and PCBs is fully controlled by the WBL and decreases weakly with increasing molar mass (M).

$$R_s = \frac{B}{M^{0.47}}, \tag{4}$$

where B is a proportionality constant that depends on the hydrodynamic conditions and is linearly proportional to the surface area of the sampler. By combining Equation 2 and 4, the retained PRC fractions are given by:

$$f = \exp\left(-\frac{B\ t}{K_{pw} M^{0.47} m}\right). \tag{5}$$

Although a range of units may be used for the variables and constants in Equation 5, it is advisable to stick to the units mentioned above and commonly used in the passive sampling literature: t in days, K_{pw} in $1\,kg^{-1}$, m in kg, and M in $g\,mol^{-1}$. The constant B can be obtained by fitting f as a function of $K_{pw}M^{0.47}$ using unweighted non-linear least-squares estimation (Booij and Smedes, 2010). This method makes use of all PRC data and is quite insensitive to outliers. Two examples of the result of this fitting procedure are displayed in Figure 4. Because the constant B is difficult to interpret, it makes sense to calculate the sampling rate for a compound with a molar mass (M) of $300\,g\,mol^{-1}$, using Equation 4. The R_s^{300} for station 1 is five times larger than for station 2 and reflects the higher flow velocities at this location. The precision of these PRC-based R_s estimates was 15% and 21%, respectively.

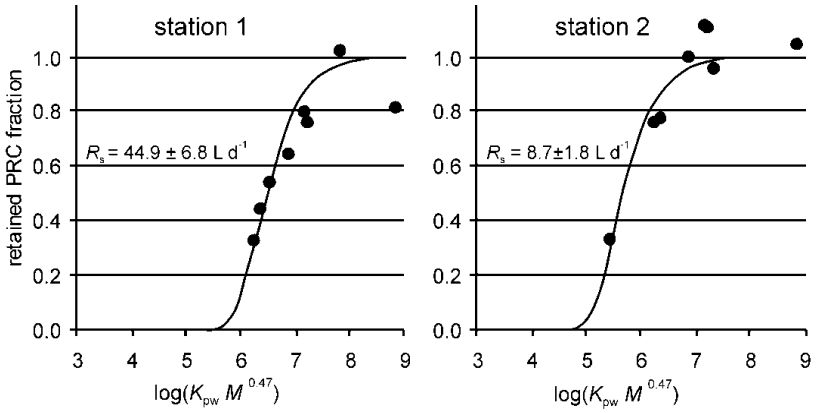

Figure 4. Retained PRC fractions as a function of log($K_{pw}M^{0.47}$). The model fit (Equation 5) is displayed as a drawn line.

6.3 Concentrations in the aqueous phase

The uptake of target compounds is given by (Booij *et al.*, 2007; Huckins *et al.*, 2006):

$$N_t = K_{pw} m\ C_w \left(1 - \exp\left(-\frac{R_s\ t}{K_{pw} m}\right)\right). \tag{6}$$

Aqueous concentrations can therefore be calculated using the absorbed amounts by:

$$C_w = \frac{N_t}{K_{pw} m \left(1 - \exp\left(-\frac{R_s\ t}{K_{pw} m}\right)\right)}. \tag{7}$$

To use the proportionality constant B obtained from the PRC data (see above) for calculating C_w from the absorbed amounts, Equations 4 and 7 are combined to give

the general equation that covers the linear uptake stage, the transition stage, and the equilibrium stage and takes into account the dependence of R_s on M:

$$C_w = \frac{N_t}{K_{pw}\, m\left(1-\exp\left(-\frac{B\, t}{K_{pw} M^{0.47} m}\right)\right)}. \quad (8)$$

Many K_{pw} values can be obtained from Smedes *et al.* (2009) and Smedes and Beeltje (2010). It should be noted that accurate K_{pw} values are especially relevant to PRCs and compounds that approach equilibrium. 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 calculated using logK_{ow} have sufficient accuracy in this case.

It is instructive to consider the limiting cases when the sampling is far from equilibrium (linear uptake stage) or close to equilibrium (equilibrium stage, see also Figure 1). Far from equilibrium (i.e. $[R_s\, t]/[K_{pw}\, m] \ll 1$), Equation 8 reduces to:

$$C_w \approx \frac{N_t}{R_s\ t}, \quad (9)$$

because $1-\exp(-x) \rightarrow x$, when $x \rightarrow 0$. This happens when the exposure time is short, when the sampling rate is small, or when the analyte is very hydrophobic (K_{pw} is large). In these cases, the calculated C_w is insensitive to uncertainties in the K_{pw} values that are used. Close to equilibrium (i.e. $[R_s\, t]/[K_{pw}\, m] \gg 1$), Equation 8 reduces to:

$$C_w = \frac{N_t}{K_{pw} m}, \quad (10)$$

because $1-\exp(-x) \rightarrow 1$, when $x \rightarrow \infty$. This happens when the exposure time is long, when the sampling rate is high, or when the analyte's K_{pw} value is small (e.g. naphthalene). In these cases, the calculated C_w is insensitive to uncertainties in the R_s values that are used. It should be emphasized that Equation 8 is always accurate and covers both limiting cases. The correctness of calculations using Equation 8 can be checked using Equations 9 and 10 for, respectively, high and low hydrophobic compounds.

The time window (τ) over which the sampler is capable of integrating potentially variable analyte concentrations may be estimated from:

$$\tau = \frac{K_{pw} m}{R_s}. \quad (11)$$

6.4 Reporting

The report of obtained C_w estimates should include the following information about the exposure site and the deployment and recovery.

- geographical position, local water depth, exposure depth
- object used for sampler frame attachment
- date and time of deployment and retrieval
- salinity at deployment and retrieval
- water temperature at deployment and retrieval
- description of the biofouling after the exposure
- photograph of the exposure site and of the sampler after exposure.

Additionally, 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 K_{pw} data become available. This includes:

- K_{pw} values that were used;
- analytical recovery;
- sampler mass;
- PRC/analyte amounts in solvent blanks;
- PRC/analyte amounts in preparation controls;
- PRC/analyte amounts in field control samplers (if applicable);
- PRC/analyte amounts in exposed samplers;
- fractions of retained PRCs;
- value of B, including its uncertainty;
- R_s estimate at $M = 300$ g mol^{-1}, including its uncertainty.

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Annex 1: Further comments on amounts detected in the controls

The amounts in the preparation controls may be used to determine blank levels and detection/quantification limits, but caution is needed to interpret these blank levels correctly. It has been reported that the amounts of compounds that quickly equilibrate with the samplers can be higher in the preparation controls than in the exposed samplers (Røe Utvik *et al.*, 1999). The reason for this observation is that compounds are released from the sampler if their initial concentration in the sampler is higher than their equilibrium concentration and if their equilibration time is similar to, or shorter than, the deployment time of the sampler. The evolution of analyte amounts (N_t) in the sampler is governed by (Booij *et al.*, 2007; Vrana *et al.*, 2001)

$$N_t = N_0 \exp\left(-\frac{R_s\, t}{K_{pw} m}\right) + C_w K_{pw}\, m\left(1-\exp\left(-\frac{R_s\, t}{K_{pw} m}\right)\right). \qquad \text{(A1)}$$

The first term represents the dissipation of the initial amount (N_0) during exposure. This term can be interpreted as a (time-dependent) blank level that can be subtracted from the amount detected in the exposed samplers. For quickly equilibrating compounds, this term goes to zero and for slowly equilibrating compounds this term is more or less constant, i.e. equal to N_0. The blank correction can subsequently be used to estimate C_w, using Equation 8 from the main text that modifies to:

$$C_w = \frac{N_t - N_0 \exp\left(-\frac{B\, t}{K_{pw} M^{0.47} m}\right)}{K_{pw}\, m\left(1-\exp\left(-\frac{B\, t}{K_{pw} M^{0.47} m}\right)\right)}. \qquad \text{(A2)}$$

It should be emphasized, however, that this method has not been assessed critically and accepted by the passive sampling community. Equation A2 should only be used as a last resort. The necessity to apply Equation A2 indicates that sampler preparation procedures should be improved to reduce the analyte levels in the preparation controls.

8 Abbreviations and technical terminology

GC	gas chromatography
HCB	hexachlorobenzene
HPLC	high-performance liquid chromatography
K_{ow}	octanol-water partition coefficient
K_{pw}	polymer-water partition coefficient
LDPE	low-density polyethylene
LOD	limit of determination
LOQ	limit of quantitation
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PRC	performance reference compound
PSD	passive sampling device
SMPD	semi-permeable membrane device
v/v	ratio by volume
WBL	water boundary layer

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