

This is the final draft of the contribution published as:

Chepchirchir, B.S., Zhou, X., Paschke, A., Schüürmann, G. (2020):
Polyethersulfone as suitable passive sampler for waterborne hydrophobic organic compounds
– Laboratory calibration and field test in the Sosiani river, Kenya
Sci. Total Environ. **699**, art. 134056

The publisher's version is available at:

<http://dx.doi.org/10.1016/j.scitotenv.2019.134056>

Polyethersulfone as suitable passive sampler for waterborne hydrophobic organic compounds – Laboratory calibration and field test in the Sosiani river, Kenya

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Highlights

- Polyethersulfone (PES) is a cost-efficient single-phase sampling material
- Uptake of waterborne hydrophobic organic compounds in PES is practically irreversible
- Performance reference compounds are not applicable due to their nearly irreversible sorption in PES

Keywords: Passive sampling, Polyethersulfone, Organochlorine pesticides, Polychlorinated biphenyls, Polycyclic aromatic hydrocarbons, Linear Solvation Energy Relationships

Abstract

We report the application of polyethersulfone (PES) membrane as a cost-saving and less labour-intensive single-phase passive sampler for waterborne hydrophobic organic compounds (HOCs) like organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs). The uptake kinetics of 31 HOCs from water to porous polyethersulfone (PES) membranes and their partitioning behaviour were investigated in laboratory studies. Sampling rates (R_s) of HOCs with PES were determined in a range from 1.15 to 12.9 L/d. The uptake of test chemicals and the elimination of analogous (pre-loaded) performance reference compounds (PRCs) showed anisotropy, both under laboratory and field conditions, implying that PRCs are not suitable for determining *in situ* sampling rates with PES. The PES-water partition coefficients (K_{pw}) are, on average, ten times higher than the related K_{ow} . A Linear Solvation Energy Relationship for modelling the measured $\log K_{pw}$ with PES under inclusion of all available published data yields a poor fit in comparison to what is usually obtained with homogeneous polymers like polydimethylsiloxane or low-density polyethylene. At least a strong linear relationship was found between $\log R_s$ and $\log K_{pw}$ for the narrow $\log K_{ow}$ range of HOCs investigated in this work which can be used for interpolation to other HOCs in this range. The PES membranes were also tested in a field trial in a tropical river against the well-established silicone rubber (SR) sheets. With laboratory-based R_s for PES generated under field-relevant temperature and water flow velocity it was possible to obtain time-weighted average concentrations in the lower ng/L range which are comparable (within a factor of two) with those derived from accumulated amounts in SR sheets (using *in situ* sampling rates).

1 Introduction

In a foregoing paper (Chepchirchir et al., 2017) we described the application of silicone rubber (SR) sheets as a robust passive sampler to characterize the spatial and temporal variability of waterborne HOCs in a tropical river. One major disadvantage of this material is the time- and solvent-consuming cleaning procedure that is required before use. Other polymer materials like polyethersulfone (PES) or low-density polyethylene (LDPE) are more efficient in pre-cleaning and processing. A porous PES membrane, for example, is usually used with the polar organic chemical integrative sampler (POCIS) (Alvarez et al., 2004) and the Chemcatcher version for polar target compounds (Kingston et al., 2000, Charriau et al. 2016) to cover sorbent material and to act as a protective and partly diffusion-limiting layer. Kingston et al. (2000) demonstrated that such a PES protective membrane retarded the accumulation of dieldrin, PCB 52, PCB 153 and phenanthrene in the inner receiving phase of the sampler. Later it was shown that PES membranes also sorb some pesticides, estrogens, and bisphenol A to a higher extent than the sorbent material (Tran et al., 2007; Vermeirssen et al., 2012; Morin et al., 2018;). By taking advantage of this fact, PES tubes (hollow fibres) were successfully applied for micro-extraction of several polar and non-polar chemicals ranging from caffeine to octocrylene (Prieto et al., 2012) and of polar chlorinated pesticides (Prieto et al., 2014) from water samples. Posada-Ureta et al. (2017) successfully calibrated PES tubes as passive sampler for more hydrophobic compounds including triclosan, dichlorodiphenyltrichloroethane (DDT), two phthalates and two organophosphorous pesticides in waters of different salinity, and applied them in an intertidal estuarine environment. Mijangos et al. (2018) investigated such PES tubes further as field samplers for emerging micro-pollutants (herbicides, hormones, life style products,

corrosion inhibitors, perfluoroalkyl substances, personal care products and pharmaceuticals) in seawater.

Given the wide log K_{ow} range of sorbed analytes, the aforementioned studies suggest strong sorption in PES and the potential for its application as a single-phase sorbent to a wider range of analytes than those sampled by the POCIS and the polar Chemcatcher version. Indeed, Endo and Matsuura (2018) showed PES to be a strong sorbent for some neutral organic compounds, with the PES-water partition coefficients ~ 2.5 log units larger than those of K_{ow} . Additionally, Harman et al. (2008) observed the uptake of PAHs and carbazoles in POCIS sorbent at very low ng/POCIS levels, which were characterized by high variability and poor linear fit. We hypothesize that these compounds would sorb strongly to the PES membrane and only appear in the sorbent after a longer lag time.

We assessed the potential of PES as a sorbent for PAHs, PCBs, and OCPs by deploying it in parallel to SR in Sosiani river, Kenya, to measure time-weighted average (TWA) concentrations of these compound classes on a comparative basis. Prior to field deployment of PES, we carried out a laboratory calibration experiment to determine PES-water partition coefficients (K_{pw}) and sampling rates (R_s) at field conditions, and to test the suitability of performance reference compounds (PRCs) for determining *in situ* R_s of PES.

2 Experimental

2.1 PES calibration experiment

Reagents used in the uptake calibration experiment are given in section S1 of the Supplementary data. Altogether we investigated 16 PAHs, 6 PCBs, and 8 OCPs. The

calibration experiment was carried out using a continuous flow design. Setup and details are shown in Fig. 1. The “pre-contaminated” apparatus was flushed with spiked tap water (25 ng/L nominal concentration for each target compound). PES strips measuring 1.0 cm by 9.0 cm were cut out from 20.3 cm × 25.4 cm sheets of the Supor-200 membrane with 0.2 μm pore size (Pall Corp.) and pre-cleaned in ethyl acetate and methanol. Subsequently, they were spiked with PRCs (seven deuterated PAHs and four PCBs) during three days in 400 mL methanol-water (1:1, v/v) mixture and thereafter stored dry at 4 °C until use (see section S2 for details). Eight strips were fixed onto a rotatable clamp which was rotated at a speed of 130 r.p.m., equivalent to river flow velocity of 0.34 m/s under field conditions. Spiked water was pumped through the 1.4 L experimental vessel with a flow volume rate of 5 mL/min to ensure a nearly constant exposure concentration of analytes during the test period. The experiment proceeded at an average room temperature of 23.5 °C continuously for 14 days with short interruptions during membrane removal and replacement which were done at day 2, 4, 7 (in duplicate), 10, 12 and 14. The effectively exposed surface area of a PES strip was only $\approx 14 \text{ cm}^2$, because 1 cm on each end of the strip was covered by a clip (Fig 1). The removed PES strips were patted dry with lint-free tissue and stored at 4 °C until extraction. Later, they were extracted twice in 15 mL ethyl acetate, then the extracts were concentrated to 1 mL and analysed by GC-MS as outlined in section S3.

200 mL of water were taken daily from the experimental vessel using a 250 mL Erlenmeyer flask to check the aqueous concentrations to which the PES strips were exposed. 40 mL methanol and a 24 μL pre-cleaned PDMS-coated stir-bar (Twister from Gerstel) were added to such a water sample. The flask was then covered with aluminium foil to prevent photolysis of analytes and stir-bar sorptive extraction proceeded for 24 h using an inductive-drive stirrer (Thermo Scientific Variomag) at 600 r.p.m. The Twister was removed using

forceps, gently patted dry and stored at -20 °C until analysis. Twister analyses were done using a thermal desorption unit coupled to a GC-MS system (see also section S3).

2.2 Pre-deployment preparation of the field samplers

PES sheets were cut into 6.5 cm × 10.0 cm pieces giving an exposure surface area of ≈ 130 cm² per sampler. The samplers were pre-cleaned as described in section S2, and then wrapped in pre-cleaned aluminium foil and stored at 4 °C until field deployment. The stainless steel wire meshes (approx. 25×8 cm with 5×5 mm squares of 0.5 mm thick wire) used in deployment of membranes were also cleaned in acetone and stored. The pre-deployment preparation procedure for SR (AlteSil™ silicone sheets, translucent 30 × 30 cm, 0.5 mm thick; obtained from Altec Products Ltd., Victoria/UK) has already been described in an earlier paper (Chepchirchir et al., 2017). Briefly, SR sheets (i.e. 5.5 × 9.0 cm strips) were first cleaned by Soxhlet extraction in ethyl acetate over a period of five days, and thereafter soaked twice in methanol for 8 h. PRCs were then spiked onto the clean sheets by equilibrating in a 400 mL methanol-water mixture (1:1, v/v) for seven days. Finally, the SR sheets were dried and stored at 4 °C until deployment.

2.3 Field deployment and retrieval

Field performance of PES in comparison to SR was tested by deploying both sorbents in parallel at two stations along Sosiani river, Kenya (Station 1: 0.51601, 35.27061; Station 2: 0.51175, 35.25866). As its name suggests, the river is rocky and turbulent, and can be considered to be well mixed especially during low flow rates from December to February. This period marks the dry season with an average monthly rainfall of 25.4 mm and a mean temperature maximum of 24.7 °C and a minimum of 10.7 °C (<https://en.climate-data.org/africa/kenya/uasin-gishu/eldoret-926351/#climate-graph>). The river flow

velocity was on average 0.34 m/s. The two sampling stations were located along the river adjacent to Eldoret town. The sampling campaign was carried out from December 2014 to January 2015.

Given that the average water depth along the river during the sampling period was 0.8 m, the samplers could not be deployed in standard cages, thus a home-made approach was designed. Accordingly, three PES membranes were secured onto a wire mesh for protection against abrasion. The mesh was then tied on both ends onto a polypropylene rope, onto which nine SR sheets were also fixed. The rope was then first anchored onto boulders that were readily available at the river bed to ensure that the samplers remained immersed in water at approximately two-thirds of the depth below the water surface, and then further fastened onto wooden pegs at the river banks. Field exposure duration was 30 days. During retrieval, PES membranes were carefully removed from the wire mesh, then both PES and SR samplers were rinsed in river water to remove excess biofouling and debris, patted dry, wrapped in aluminium foil and transported in a cooler box at 4 °C. The samplers were stored at -20 °C until extraction.

2.4 Extraction and analysis of field-exposed samplers

A PES field sampler consisted of one sheet ($\approx 130 \text{ cm}^2$ surface area) and three samplers were exposed per sampling station. The samplers were patted dry and placed in a 100 mL Erlenmeyer flask into which 15 mL ethyl acetate was added, then the membranes were extracted on an orbital shaker (Edmund Bühler, Germany) during 20 min at 90 rpm. The extract was transferred to a 40 mL evaporation tube, then the extraction process was repeated once using fresh solvent. All the extracts and rinsing amounting to approximately 40 mL were then concentrated to 2 mL on a Turbo Vap® II (Zymark). The extract was

cleaned and dried by passing through a glass column packed with anhydrous sodium sulphate into a 40 mL evaporation tube. The column was rinsed twice each with 5 mL ethyl acetate, then the cleaned extract was further concentrated to 1 mL under a cold gentle stream of nitrogen, transferred into a PTFE-capped glass vial and analysed by liquid injection on a GC–MS (see section S3 for details).

A SR sampler unit consisted of three sheets ($\approx 300 \text{ cm}^2$ surface area), yielding triplicate samplers each per sampling station. The sheets were extracted twice with 100 mL methanol at room temperature over 12 h and 8 h, respectively. The extracts were concentrated to 2 mL on a Turbo Vap® II (Zymark), then 20 mL of ethyl acetate were added and the extracts were cleaned and further concentrated to 1 mL and analysed by GC-MS (see section S3).

2.5 Determination of aqueous concentrations

TWA concentrations (c_w) based on PES and SR application were estimated using the general (curvilinear) uptake model given by Booij et al., 2007:

$$c_w = \frac{m_t}{K_{pw} \cdot m_p \left[1 - \exp\left(-\frac{R_s \cdot t}{K_{pw} \cdot m_p}\right) \right]} \quad (1)$$

where m_t in [ng] is the sorbed amount, m_p in [kg] is the sampler mass, and t in [d] is the field-exposure duration. The inherent assumption for applying this uptake model is constancy of R_s that holds for water boundary layer controlled uptake kinetics. This is only an approximation for polymer controlled (or mixed mode) uptake kinetics (cf. e.g. Tcaciuc et al. 2015). For SR, *in situ* R_s (Table S5 in section S9) were determined from fractions of

remaining PRCs as already described in our earlier paper (Chepchirchir et al., 2017). K_{pw} values were obtained from literature (Smedes et al., 2009).

c_w from PES-accumulated amounts were also calculated with Eq. 1 using laboratory-determined sampling rates and partition coefficients. R_s values for PES were determined using time-dependent sorbed amounts (m_t) and average water concentrations (c_w) during the laboratory calibration experiment as follows:

$$R_s = \frac{m_t}{c_w \cdot t} \quad (2)$$

For evaluating field results, these lab-derived sampling rates were multiplied by a factor of 9.3, which is the ratio of surface areas of field-exposed PES sheet (130 cm²) vs. lab-calibrated PES strip (14 cm²).

K_{pw} values were determined by dividing the maximum sorbed concentrations (c_{PES}) by the average aqueous concentrations during the calibration experiment as follows:

$$K_{pw} = \frac{c_{PES}}{c_w} \quad (3)$$

2.6 Quality assurance

During preparation, field deployment and retrieval, duplicate samplers were exposed to air in the vicinity of the working area. These blanks were extracted and analysed analogous to the field-exposed samplers. In addition, procedural blanks were also processed similarly but without the samplers. Only a few compounds were detected in blanks but at concentrations below the limits of quantitation, except for naphthalene and 2-methylnaphthalene. Given that uptake remained largely in the linear phase and that sorption and desorption may not

occur simultaneously as seen in the case of PRCs (section 3.1), the blank values for these compounds were subtracted from measured concentrations.

3 Results and discussion

3.1 Unsuitability of PRCs in determining *in situ* sampling rates for PES

The PRC spiking procedure for three days (section 2.1) yielded sufficient amounts sorbed on the PES strips (in the order of 3 µg per PES strip). Analysis of desorption data for PRCs showed that in general, 0–20% of all the PRCs were dissipated during the 14 days experimental duration (Fig. 2 shows an example). Desorption of PRCs was also tested under field conditions in the Saale river, Germany for a duration of 30 days. Results showed that < 20 % of the original amounts dissipated in 64 % of the spiked PRCs (Table S2). The range of desorbed amounts for all the PRCs was 6–35 % of the initial amounts. Fractions of dissipated PRCs were generally outside the acceptable range of 20-80 % as proposed by Huckins et al. (2002). Additionally, chemical uptake versus PRC desorption was not isotropic as can be seen in Fig. 2. An isotropy between PRC desorption and chemical uptake for the same class of compounds as investigated in this study has been demonstrated with other passive samplers such as silicone rubber (Rusina et al., 2010), which has led to successful application of PRCs in determining *in situ* sampling rates (Chepchirchir et al., 2017). In the current study, PRCs could not be used to account for the field variability in uptake rates in PES and were unsuitable for determining *in situ* sampling rates. A number of intrinsic PES properties may favour the uptake of compounds, for example, the presence of micro-/nano-voids and/or unrelaxed free volume regions (Fig. S1 in section S4 shows voids $\geq 0.3 \mu\text{m}$) may enhance the sorption of organic chemicals. This is because the narrow pores

offer multiple contact points within the PES matrix for the sorbate, leading to increased sorption energies that favour sorption (Saquing et al., 2010). Pre-existence of cavities (pores) that can accommodate incoming sorbates may identify the pores as preferred sorption sites (Lu and Pignatello, 2004). However, the narrow pores may also hinder the desorption of chemicals from the PES matrix. By drawing analogy from sorption/desorption hysteresis reported in natural organic matter and other glassy polymers, the anisotropy observed in this study can be caused by strong sorptive bonds and mass transfer limitations (Lu and Pignatello, 2004; Pignatello and Xing, 1996); see Chepchrichir (2017) for further discussion.

3.2 PES-water partition coefficients

K_{pw} for the analytes were calculated using Eq. (3), but could not be calculated using uptake (k_u) and elimination (k_e) rates (i.e. $K_{pw} = k_u/k_e$) since release of spiked compounds was slow and exhibited anisotropy similar to PRCs (Fig. S2a + b in section S5). Hence K_{pw} values reported here should be considered as “apparent” partition coefficients because we could not verify establishment of distribution equilibrium between water and PES. The obtained log K_{pw} values are shown in Table 1. These log K_{pw} values were not significantly different from each other, implying PES is a non-selective sampler for these compounds. On average, the K_{pw} are ten times higher than the respective K_{ow} , indicating strong sorption of the HOCs to PES. Such strong sorption has also been observed e.g. with triphenyl phosphate (Li et al., 2018), phenols, estrogens, bisphenol-A and carbendazim (Morin et al., 2018), and other compounds (Endo and Matsuura, 2018; Vermeirssen et al., 2012). The apparent K_{pw} values for PES were ≈ 1.5 log units higher than those of the rubbery SR for the same set of compounds (Smedes et al., 2009). Saquing et al. (2010) also made a similar finding, where

the glassy PVC had a higher partition coefficient for toluene ($K_{pw}= 809.2$ L/kg) than the rubbery PE ($K_{pw}= 70.7 - 123.1$ L/kg). For PES, the high apparent K_{pw} for the HOCs can be attributed to a number of factors: specific intermolecular interactions between aromatic rings of adsorbate molecules with the phenyl groups of PES, a high surface area of the porous filter (Fig. S1), multiple pathways for the sorption process, and the possibility of PES undergoing plasticization when immersed in an aqueous media due to interactions of the polar sulfonate groups with water. The latter scenario may cause a depression of the glass transition temperature (T_g) making the polymer more flexible (Schult and Paul, 1997; Endo and Matsuura, 2018).

Uptake curves (for examples see Fig. S2) show that some compounds attained apparent equilibrium, while uptake for others remained largely in the linear range during the experiment. Slowed equilibration of other compounds in PES has also been observed in other studies (Vermeirssen et al., 2012; Endo and Matsuura, 2018). Non-achievement of equilibrium for most compounds can be explained by the diffusion process in the porous membrane. Considering the structure of PES (Fig. S1), it is possible that for some compounds, the uptake during the first few days is a combination of sorption in the amorphous regions and a hole-filling process. Sorption to dissolution sites is faster due to the higher diffusion coefficients, but as these regions fill up, sorption is slowed down in the condensed phases (pores) due to lower diffusivities in these regions, and this slowed process may give an impression of equilibrium attainment. Glassy polymers generally have lower diffusion coefficients than rubbery polymers with the ratio of diffusion coefficients ($D_{rubbery}/D_{glassy}$) ranging from 10^2 to 10^8 , increasing with penetrant diameter (Saquing et al., 2010). The occurrence of both dissolution and pore sorption sites implies PES has a high

sorption capacity, in which case equilibrium may not be attained within the practical time scale of an experimental set up (Booij et al., 2016).

Given the hydrophobic nature of PES backbone (contact angle of a water droplet = 56°), it is expected that hydrophobicity would primarily determine the partitioning of HOCs from the aqueous phase (Jermann et al., 2009; Zhao et al., 2013). However, our study could not establish an explicit relationship between K_{pw} and K_{ow} when all data were considered.

Moreover, literature K_{pw} values for other compounds (Vermeirssen et al., 2012; Prieto et al., 2014) yielded a similarly poor correlation to $\log K_{ow}$. This fact indicates that hydrophobicity is indeed not the key parameter determining this partitioning process. It is possible that specific mechanisms such as π - π interactions between the aromatic rings of the HOCs and PES and hydrogen bonding through the polar sulfonyl groups dominate the uptake process. Hitherto, comparative values from literature for the compounds under investigation in this work are nonexistent. However, a recently published study by Endo and Matsuura (2018) demonstrated a weak correlation between $\log K_{pw}$ and $\log K_{ow}$ (ranging from 0 to 3.5) for ten neutral compounds investigated. The determined K_{pw} values are ~ 2.5 log units larger than of the K_{ow} values. These authors attempted also to fit a linear solvation energy relationship (LSER) with Abraham's descriptors (Abraham et al., 2004; Endo & Goss, 2014) to the $\log K_{pw}$ for the neutral compounds (including the experimentally determined $\log K_{pw}$ reported by Vermeirssen et al., 2012). Altogether, their dataset contained only 21 substances and resulted in a relatively poor fit ($R^2 = 0.66$, $SD = 0.57$). With our K_{pw} values and other recently published data (Prieto et al., 2014; Li et al., 2018, Morin et al., 2018), we could extend the model base considerably (90 compounds). However, this extended model (see section S6 for details) shows poor fit when compared with homogeneous polymers like PDMS (Sprunger et al., 2007) or LDPE (Liu et al., 2017). Without performing rigorous

statistical testing, the compiled PES data appears to resemble a cluster correlation. As already pointed out by Endo & Matsuura (2018), non-attainment of equilibrium, nonlinear sorption isotherms and a mixed mode of absorption and adsorption with PES could be possible contributing reasons for this performance deficit of the LSER model. It is also possible that the types of chemical interactions covered by the Abraham model are not the most relevant ones for the solute sorption from water into PES.

3.3 Sampling rates

Sampling rates were estimated by linear regression (Eq. 2) using all or part of sorbed amounts that showed linearity in the uptake curve. The water analyses, i.e. stir-bar sorptive extraction followed by thermodesorption and GC-MS (as described under 2.1,) confirmed a mean aqueous concentration of 25 ng/L per analyte in the exposure vessel over the duration of the uptake experiment. Sampling rates (Table 1) ranged from 1.15 L/d (methoxychlor) to 12.9 L/d (chrysene). Similarly to apparent PES-water partition coefficients, $\log R_s$ values are not correlated with $\log K_{ow}$. Modelling using the Abraham model was not successful (see section S6 for details).

In an attempt to to interpolate sampling rates with PES for other HOCs, we first tried to correlate the R_s values with the related K_{pw} values. A very strong log-linear relationship resulted: $\log (R_s/[L/d]) = 1.04 (0.04) \log K_{pw} - 6.25 (0.27)$ ($n = 30$, $R^2 = 0.96$, $SD = 0.05$); see Fig. 3. However, this relationship is useful only in the narrow $\log K_{pw}$ range between 6.0 and 7.0. The data pairs reported by Vermeirssen et al. (2012) in the $\log K_{pw}$ range between 2.0 and 5.0 (see S6.b for selection and transformation of original data) give with $\log (R_s/[L/d]) = 0.16 (0.04) \log K_{pw} - 1.83 (0.14)$ ($n = 17$, $R^2 = 0.47$, $SD = 0.12$) only a poor linear relationship. The unusual strong inter-correlation obtained with our target substances

can be explained by the fact that their elimination rate constants are very low (cf. foregoing sections) and hence $\log K_{pw}$ is, similarly to $\log R_s$, proportional to $\log k_u$.

A further inspection of the data regarding the diffusional mass transfer in the PES membrane can be found in Chepchrichir (2017). Two variants of an intraparticle diffusion model are used, originally developed by Weber and Morris (1963) and applied already to explain adsorption in cyclodextrin–polysulfone (Baruah et al., 2015) and POCIS–nylon (Belles et al., 2014) samplers. Additionally, structural differences between PES and SR and their implication on sorption capacity and permeability are discussed more detailed in Chepchrichir (2017).

3.4 Comparison of sorbed amounts of PAHs in PES and SR in the field

In the field exposed samplers we could quantify only PAHs but no other target HOCs included in our GC-MS analysis. This confirms our foregoing field results (Chepchrichir et al. 2017) and is also consistent with an UNEP report (UNEP 2016) which stated altogether a minor level of pollution with aqueous organic micropollutants in most of the African rivers. Published data on the pollution of the Sosiani river with HOCs could not be found. Fig. 4 shows the total sorbed amounts of PAHs from the two sampling stations, grouped by the number of rings and normalized to 100 cm² of sorbent material. The accumulated 4- and 5-ringed PAHs in the two sorbents were at an approximately 1:1 ratio. For the lower molecular weight PAHs, PES showed greater sorption than SR.

3.5 Freely dissolved concentrations determined using PES and SR in the Sosiani river

As already discussed, PRCs could not be applied to PES. Therefore, to minimize the errors introduced when using laboratory results to estimate field values, the calibration experiment

as described in section 2.1 was conducted at field conditions, at a temperature of ≈ 24.0 °C and a flow velocity of 0.34 m/s. Sampling rates obtained in the calibration experiment were converted to the larger surface area of field-exposed PES sheets and then used to estimate TWA c_w at the two sampling stations, assuming comparable and constant flow velocities.

For the SR samplers, PRCs were used to determine *in situ* sampling rates. The estimation of R_s from dissipated PRCs was done by non-linear least squares regression, and is already described in our earlier paper (Chepchirchir et al., 2017). The values obtained at the two sampling sites are listed in Table S3 of section S7.

c_w determined using PES could be calculated for lower molecular weight members up to benzo[b+k]fluoranthene. Higher molecular weight members were either undetectable or their concentrations were below the TWA sampling limits. These sampling limits (SL) are given in Table S5 for both sampler types. Freely dissolved concentrations determined using PES and SR were generally comparable within a factor of two (see Fig. 5 and Table S4 in section S8). A more detailed analysis of the agreement between the two sampler materials using the Bland-Altman method (Bland & Altman, 1986 and 1999) is visualised with a plot of the difference between the results of the two methods against their average in Fig. S5. This approach indicates the limits within 95% of the differences will lie. At station 1, the PES-based results may be approximately 7 ng/L above or 4 ng/L below the SR-based results. For station 2, we have similar limits, PES can be 5 ng/L above or 4 ng/L below SR. Generally, it is not a statistical decision if this is acceptable for water monitoring, but depends on the environmental quality standards (EQS) to which the sampling results should be compared. If we, for example, relate our sampling results for anthracene, fluoranthene and benzo[a]pyrene to the maximum allowable concentrations for these compounds in

inland waters (in force as EQS in the European Union; European Commission, 2008) then it becomes obvious that our field results are two to three orders of magnitude below these EQS values. In additional consideration of the low TWA sampling limits for the applied PES sampler formats and the acceptable coefficients of variations of our results (< 5% for station 1 and < 15% for station 2) we feel confident that PES sheets can be used (besides SR) as a cost-efficient alternative for long-term monitoring of hydrophobic organic compounds in surface waters.

4 Conclusions

PES sorbed the HOCs (log K_{ow} range 3.4 - 7.4) with the uptake curves for most compounds remaining in the linear range until the end of sampler exposure period (14 days). Thus, true equilibrium could not be verified during this study and further experiments need to be conducted for K_{pw} determination/examination. Nevertheless, the calculated 'apparent' K_{pw} values were ≈ 1.2 and ≈ 1.5 log units larger than the respective K_{ow} and the K_{pw} for SR, which indicates the strong sorption properties of PES. The uptake of our test chemicals and the elimination of analogous (pre-loaded) PRCs displayed anisotropy, implying that PRCs are not suitable for determining *in situ* sampling rates with PES. Further experiments should be done to find out the causes of anisotropy. On the other hand, the practically irreversible sorption found for the investigated HOCs may imply that PES acts as an 'infinite' sink and is thus a suitable material not only for water purification but also useful as cost-efficient single-phase passive sampler. The uptake mechanism in PES needs further investigation and more sampling rates should be generated in well-designed laboratory calibration experiments to cover a broader range of environmental conditions and exposure scenarios. Further field tests of PES sheets against other well-established passive samplers (SR, LDPE)

and long-term composite water sampling, for example using a continuous flow integrative sampler (Llorca et al., 2009), are also necessary to get a more representative picture on the performance of the PES sampler.

Competing interests

The authors declare that they have no competing interest.

Acknowledgements

We thank Uwe Schröter (UFZ) for technical support in the laboratory and Dr. Matthias Schmidt (UFZ/ProVIS) for preparing micrographs of PES membranes with the scanning electron microscope and furthermore the National Environmental Management Authority Eldoret office, Kenya, for fieldwork support. B.S.C. is grateful to the Ministry of Higher Education Science and Technology (MOHEST), Kenya and the German Academic Exchange Service (DAAD) for the doctoral scholarship.

Finally we want to thank the anonymous reviewers of the manuscript, esp. reviewer 4, who helped considerably to improve the paper Furthermore, we are gratefully acknowledge Julia Kostin (UFZ) for improving the English of the text.

Appendix: Supplementary data

Supplementary data to this article can be found online at <http://...???...>

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Table 1: Some chemical properties of the investigated HOCs, experimentally determined sampling rates and apparent PES-water partition coefficients. Error sign (\pm) represent the standard deviation from the mean. R_s values are for 14 cm² PES strip.

Name of chemical	CAS No.	M [g/mol]	$\log K_{ow}^a$	V_{LeBas} [cm ³ /mol]	R_s [L/d]	$\log K_{pw}^b$ [L/kg]
Naphthalene	91-20-3	128.8	3.37	147.6	2.23 \pm 0.88	6.37 \pm 0.02
Acenaphthylene	208-96-8	151.4	4.00	165.7	2.72 \pm 0.49	6.43 \pm 0.06
Acenaphthene	83-32-9	154.9	3.92	173.0	2.48 \pm 0.54	6.41 \pm 0.07
Phenanthrene	85-01-8	177.8	4.57	199.0	5.36 \pm 1.12	6.71 \pm 0.05
Anthracene	120-12-7	177.8	4.54	197.0	6.12 \pm 1.14	6.82 \pm 0.04
Fluoranthene	206-44-0	204.2	5.22	217.0	8.14 \pm 1.66	6.81 \pm 0.01
Pyrene	129-00-0	204.2	5.18	214.0	6.23 \pm 1.34	6.72 \pm 0.01
Benz[a]anthracene	56-55-3	229.1	5.91	248.0	8.45 \pm 2.90	6.98 \pm 0.02
Chrysene	218-01-9	229.1	5.86	251.0	12.79 \pm 2.73	7.03 \pm 0.01
Benzo[b]fluoranthene	205-99-2	251.2	5.90	268.9	11.58 \pm 2.80	6.99 \pm 0.02
Benzo[k]fluoranthene	207-08-9	251.2	6.11	268.9	4.10 \pm 1.04	6.56 \pm 0.08
Benzo[a]pyrene	50-32-8	251.2	6.04	263.0	4.94 \pm 1.26	6.69 \pm 0.06
Indeno[1,2,3-cd]pyrene	193-39-5	275.4	6.50	283.5	4.26 \pm 1.11	6.60 \pm 0.09
Benzo[ghi]perylene	191-24-2	275.4	6.50	277.0	1.61 \pm 0.48	6.09 \pm 0.09
2-Methylnaphthalene	91-57-6	141.3	3.86	169.8	4.66 \pm 0.88	6.64 \pm 0.08
2,7-Dimethylnaphthalene	582-16-1	154.9	4.26	192.0	6.17 \pm 1.03	6.75 \pm 0.08
PCB 28	7012-37-5	257.0	5.67	247.3	5.56 \pm 0.81	6.75 \pm 0.05
PCB 52	35696-99-3	295.1	5.84	268.2	3.54 \pm 0.51	6.45 \pm 0.04
PCB 101	37680-73-2	323.6	6.38	289.1	4.42 \pm 0.67	6.65 \pm 0.03
PCB 138	35065-28-2	363.1	6.83	310.0	5.23 \pm 1.05	6.73 \pm 0.02
PCB 153	35065-27-1	363.1	6.92	310.0	5.00 \pm 0.84	6.69 \pm 0.03
PCB 180	35065-29-3	398.1	7.36	330.9	4.30 \pm 0.89	6.65 \pm 0.03
o,p'-DDE	3424-82-6	316.2	6.00	305.2	4.93 \pm 0.89	6.70 \pm 0.02
p,p'-DDE	72-55-9	316.2	6.51	305.2	6.52 \pm 1.07	6.81 \pm 0.02
o,p'-DDD	53-19-0	323.6	5.87	312.6	3.90 \pm 0.79	6.61 \pm 0.06
p,p'-DDD	72-54-8	323.6	6.02	312.6	2.42 \pm 0.66	6.40 \pm 0.09
o,p'-DDT	789-02-6	354.8	6.79	333.5	1.66 \pm 0.38	6.25 \pm 0.06
p,p'-DDT	50-29-3	354.8	6.91	333.5	3.07 \pm 0.72	6.50 \pm 0.07
Hexachlorobenzene	118-74-1	281.8	5.50	221.4	3.47 \pm 0.78	6.54 \pm 0.08
Methoxychlor	72-43-5	346.7	5.08	354.3	1.15 \pm 0.46	6.17 \pm 0.05

^a values obtained from Smedes (2009)

^b apparent partition coefficients.

Captions to Figures

Fig.1: Setup of the continuous flow calibration apparatus (left) with a 22 L glass flask for storage of spiked tap water, a pump for generating continuous water flow (all connecting tubes made of stainless steel), a glass vessel for sampler exposure, a stirrer for rotating the samplers and the stainless steel clamp (right) for fixing and rotating the PES strips. (The clamp disks have a diameter of 5 cm).

Fig. 2: Plot of uptake of acenaphthene (blue diamonds) and elimination of [D₁₀]acenaphthene (red squares) against time. m_0 is the amount at $t=0$ (pre-loaded). m_{\max} is the maximum accumulated amount and m_t the amount in PES at time t .

Fig. 3: Linear regression of the experimentally determined $\log R_s$ vs. $\log K_{pw}$ for the 30 tested HOCs with PES (see text for details)

Fig. 4: Comparison of the sum of sorbed amounts of PAHs with PES and SR at the two field sampling stations (normalized to 100 cm² sorbent material).

Fig. 5: Comparison of the TWA concentrations of 17 PAHs in the Sosiani river obtained from PES samplers (with lab-based R_s values) and from SR samplers (with PRC-based *in situ* R_s). The red dots (for station 1) and the blue squares (for station 2) are pairs of mean values ($n = 3$ for each sampler). The respective standard deviations are shown as “error bars”. The line above the diagonal is the 2:1 line and below the 1:2 line.

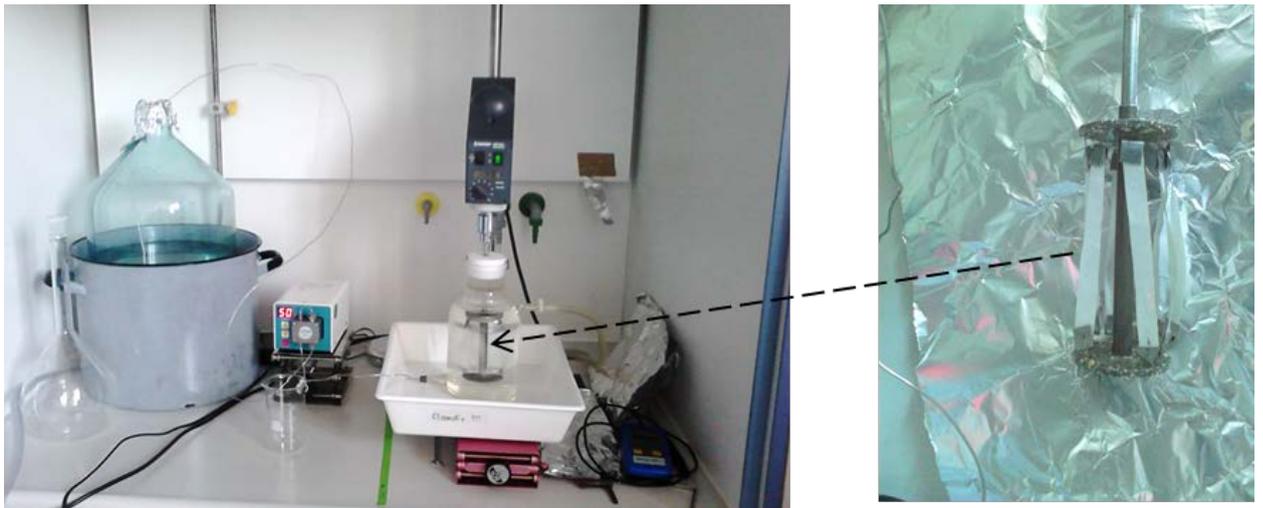


Figure 1

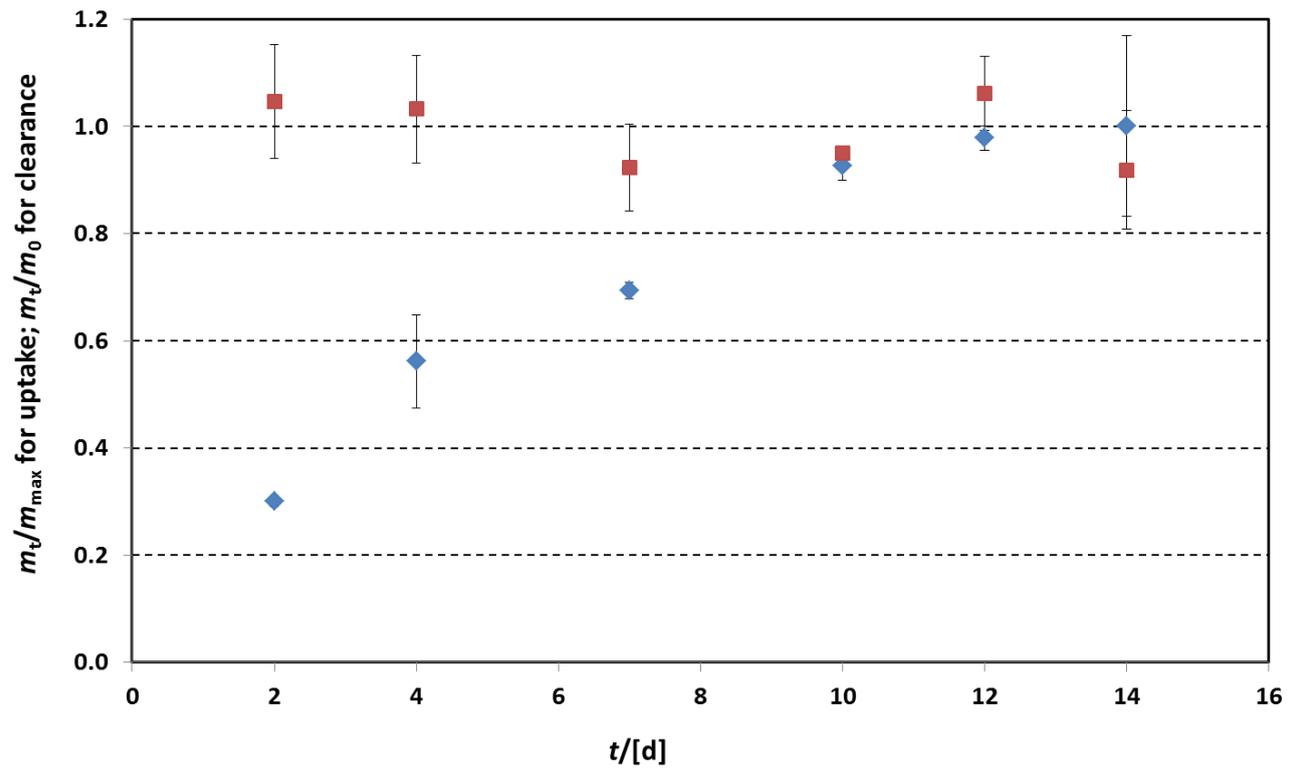


Figure 2

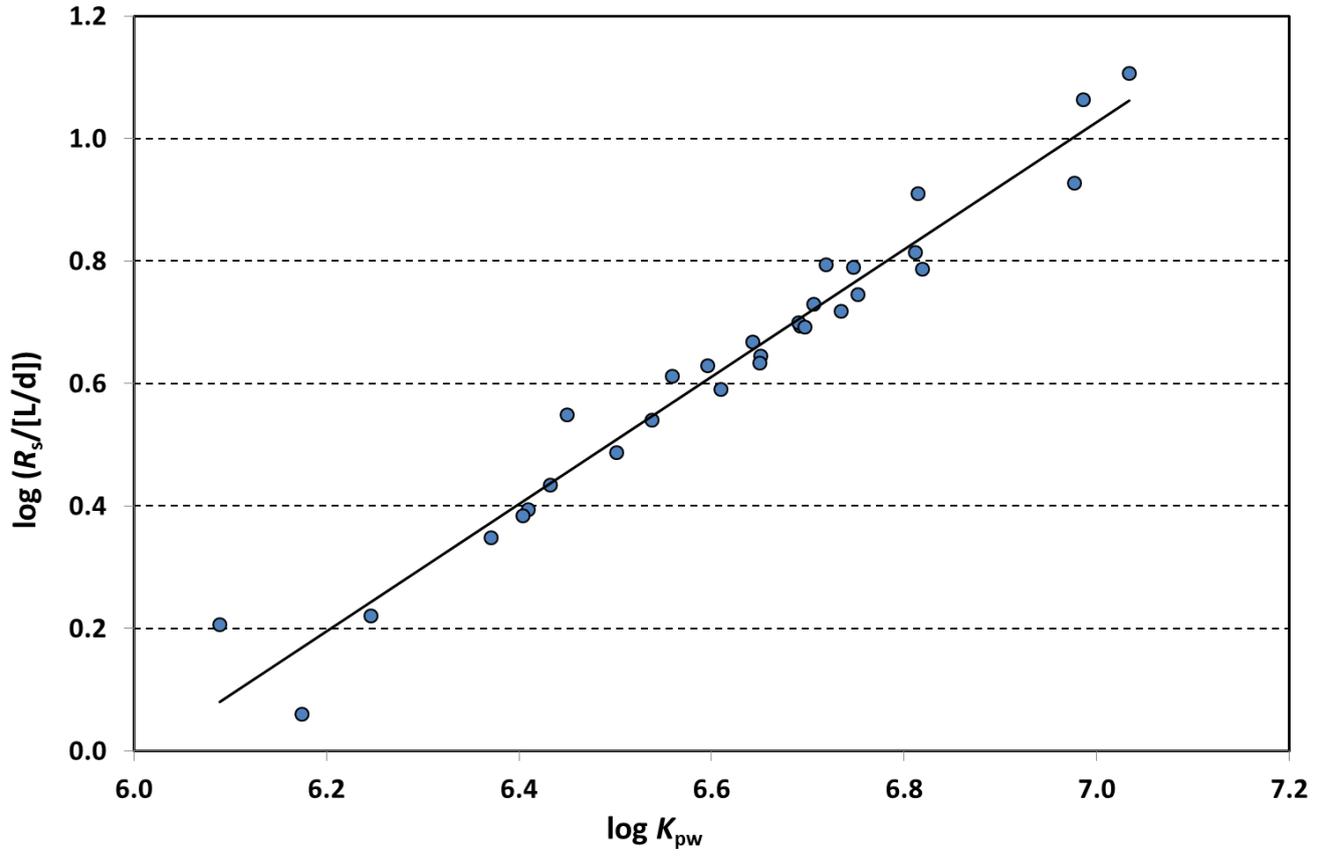


Figure 3

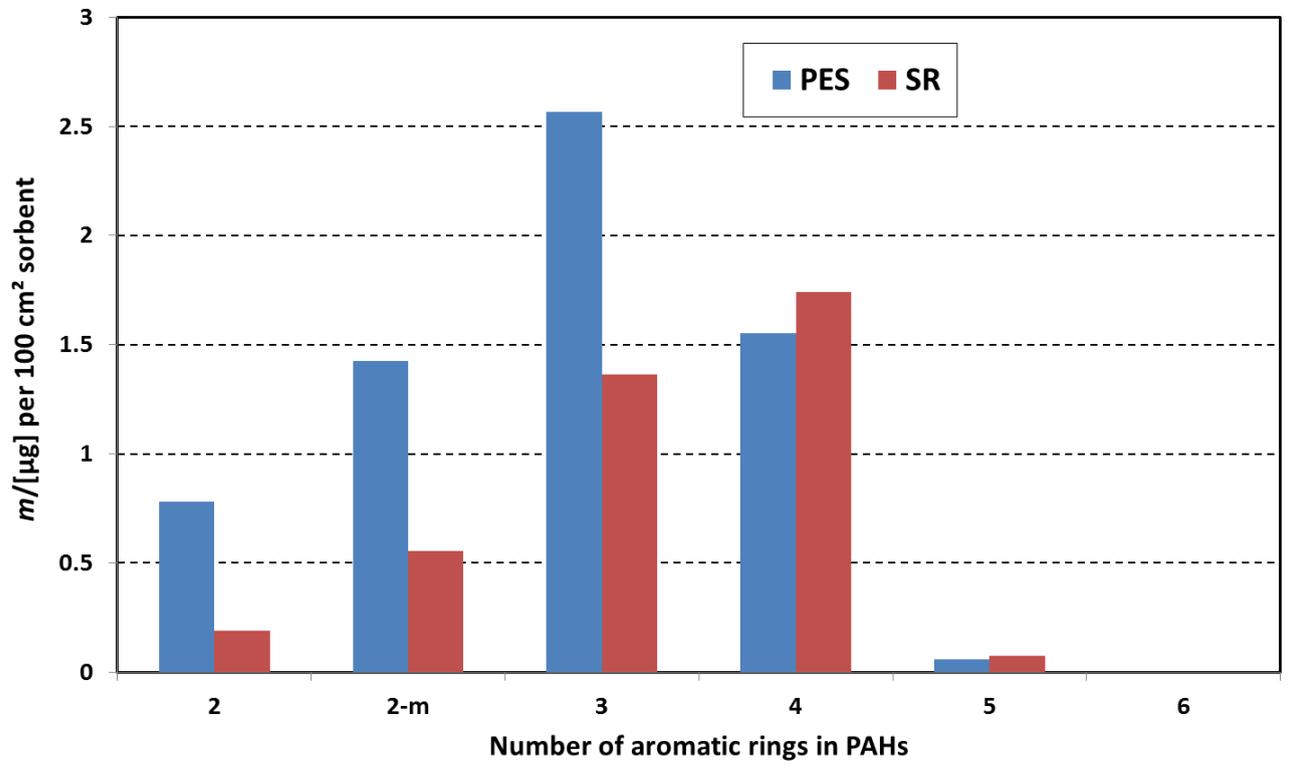


Figure 4

Polyethersulfone as suitable passive sampler for waterborne hydrophobic organic compounds – Laboratory calibration and field test in the Sosiani river, Kenya

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Supplementary Data

S1 PES calibration experiment – reagents used and setup

S2 Pre-cleaning of PES membranes

S3 Instrumental analysis

S4 Scanning electron micrographs of PES

S5 Uptake and elimination of selected target compounds and PRCs in PES

S6 PES-water partition coefficients and sampling rates estimated using LSER models

S7 *In situ* sampling rates and partition coefficients for PAHs to SR

S8 Comparison of field concentration based on PES and SR

References (if not already listed in the article)

S1. PES calibration experiment – reagents used and setup

Reagents used were the following: chromatographic analysis grade cyclohexane, isopropanol, ethyl acetate, methanol and acetone (Merck, Darmstadt), anhydrous sodium sulphate (Merck, Darmstadt), PAHs mix 9 (100 ng/μL in cyclohexane) and pesticide mix 13 (10 μg/mL in toluene) from Dr. Ehrenstorfer, Augsburg; PRCs ([D₁₀]acenaphthene, [D₁₀]fluorene, [D₁₀]phenanthrene, [D₁₀]anthracene, [D₁₀]pyrene, [D₁₂]chrysene, [D₁₂]perylene, PCB 29, PCB 54, PCB 77 and PCB 81 from Dr. Ehrenstorfer, Augsburg), [D₁₀]fluoranthene internal standard (Dr. Ehrenstorfer, Augsburg) and pure forms of the analytes listed in Table 1 of the main text. Standard solutions of individual analytes were prepared in methanol at concentrations ranging from 2–3 mg/mL. From these standard solutions, working mixtures (100 ng/mL and 25 ng/mL) of all the analytes were prepared in methanol and stored at 4 °C. A mixture of the PRCs (1.5 mg/mL) were prepared in methanol.

S2. Pre-cleaning of PES membranes

PES membranes were pre-cleaned in appropriate solvents to remove impurities. Initially, several solvents were tested based on solubility and swelling of PES in the solvent to determine their appropriateness for use in cleaning and extraction. The results (Table S1) indicate the inappropriateness of chlorinated and some aprotic solvents which resulted in membrane solubility probably due to stress-induced cracking or solvent-induced crystallization (Benhalima et al., 2012; Hansen, 2002). Toluene effected no change in mass while a slight increase was observed in cyclohexane likely due to retention of trapped solvent. The membrane became brittle in toluene and acetonitrile. Thus ethyl acetate and methanol were selected as pre-cleaning solvents in that order.

Prior to use, pre-cleaning was done by immersing all PES strips in ethyl acetate in a wide-mouthed 200 mL glass bottle. The bottle was placed on an orbital shaker and the membranes were extracted during 48 h at 90 rpm, then all the solvent was replaced with methanol and the membranes were further extracted during 24 h at 90 rpm followed by air drying in a fume hood to constant weight. The clean PES strips were wrapped in pre-cleaned aluminium foil and stored at 4 °C until use.

Table S1: Performance of PES membrane in various solvents

Solvent	Solubility ^a	Swelling ^b (%)		Change in mass ^c (%)
		24 h	48 h	
Acetonitrile	-	61	61	-0.2
Dimethyl sulfoxide	+	n.d.	n.d.	n.d.
Dichloromethane	+	n.d.	n.d.	n.d.
Ethyl acetate	-	53	58	-0.4
Tetrahydrofuran	+	n.d.	n.d.	n.d.
Toluene	-	71	77	0.0
Cyclohexane	-	37	40	0.4

^aSolubility of PES membrane in the solvent at room temperature (+, soluble; -, insoluble);

^{b,c}calculated as a percentage relative to the initial value; n.d., not determined.

S3. Instrumental analysis

PES and SR extracts were analyzed on a 6890 Agilent gas chromatograph (GC) coupled to a 5973N Agilent mass selective detector (MSD) and a Gerstel multipurpose sampler. Analytes were separated on a DB-5MS capillary column (60 m by 0.25 mm by 0.25 μm) (Chrompack). The GC was operated in splitless mode with an injection volume of 2.0 μL . Helium flowing at 1.1 mL/s was used as the carrier gas. The oven temperature programme was: initially at 60 °C held for 1 min, then increased to 180 °C at a rate of 10 °/min, then to 220 °C at 2 °/min and finally to 280 °C at 10 °/min held for 30 min. Total runtime was 44 min. Electron ionization was used for spectra acquisition at 70 eV ionization energy. The MSD transfer line, ion source and quadrupole temperatures were set at 300 °C, 230 °C and 150 °C respectively. Mass spectra were acquired in both scan (m/z 35 to 700) and selected ion monitoring (SIM) modes. External calibration was used for analyte quantitation. The analytical figures of merit were calculated from the respective compound peak in the chromatogram of the lowest external calibration level (representing typically 0.1 – 1 pg of each target analyte) using the “signal-to-noise” tool of the Agilent Chemstation software. It calculates the signal-to-noise ratio of the selected peak. If this ratio is then related to the mass injected for this peak, one can calculate the three-fold of noise (~ limit of detection = LOD) and the ten-fold of noise (~ limit of quantification = LOQ) in mass units. For our target analytes in the order of 20 (e.g. naphthalene, fluoranthene, phenanthrene) over 40-60 pg (for the PCBs and DDX) to 100 pg for methoxychlor (see also Table S6).

Analytes sorbed onto Twisters were desorbed by thermal desorption on a GC (6890N, Agilent) coupled to a MSD (5973, Agilent), a thermal desorption unit (Gerstel) and a HP-5MS (5% phenylmethylsiloxane column; 60 m by 0.25 mm by 0.25 μm) (Chrompack). Oven temperature programme was: 60 °C held for 5 min then increased at a rate of 15 °/min to 180 °C then at 10 °/min to 220 °C then finally at 15 °/min to 300 °C held for 30 min. Helium was used as the carrier gas. Chromatograms were obtained in SIM mode. LOD and LOQ were calculated as described above and in the same orders of magnitude.

S4. Scanning electron micrographs of PES

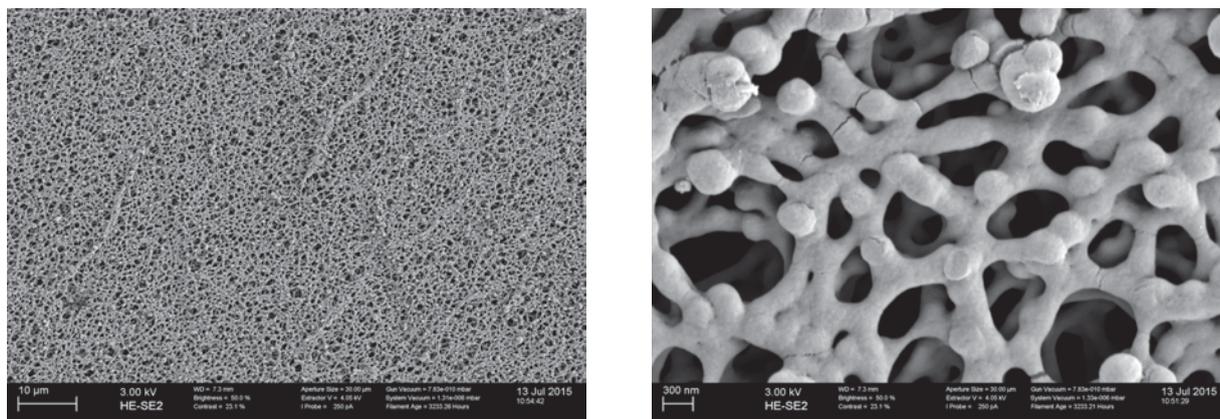


Figure S1: SEM micrographs of plane faces of unused PES membranes (Supor 200) at 10 µm and 300 nm resolution, respectively. The micrographs were produced at ProVIS, UFZ Leipzig.

S5. Uptake and elimination of selected target compounds and PRCs in PES

Table S2: Fractions of remaining PRCs from spiked PES strips that were deployed in the Saale river, Germany during 30 days

Name of PRC	Fractions of remaining	
	PRCs	CV (%)
Acenaphthene-d ₁₀	0.62	4
Fluorene-d ₁₀	0.64	4
Phenanthrene-d ₁₀	0.77	4
Pyrene-d ₁₀	0.81	5
Benzo(a)anthracene-d ₁₂	0.59	9
Chrysene-d ₁₂	0.79	5
PCB 29	0.83	5
PCB 77	0.85	7
PCB 81	0.85	7

CV is the coefficient of variation for n=3.

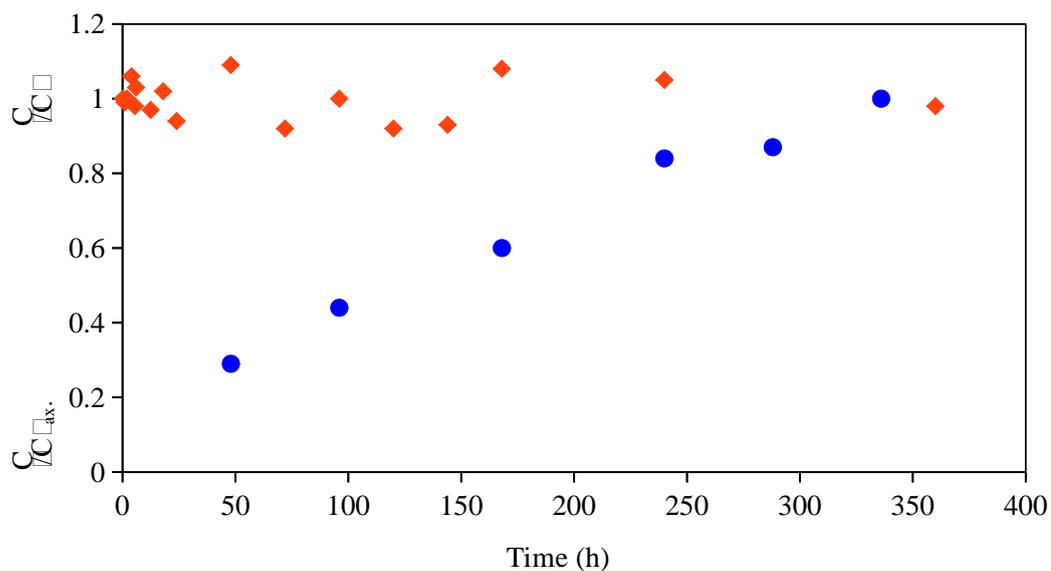


Figure S2a: Plots of uptake (blue circles) vs. release (red diamond) of PCB 28 against time. m_0 and m_{max} are the initial (preloaded) and maximum mass in PES, respectively, and m_t is the mass determined for time t .

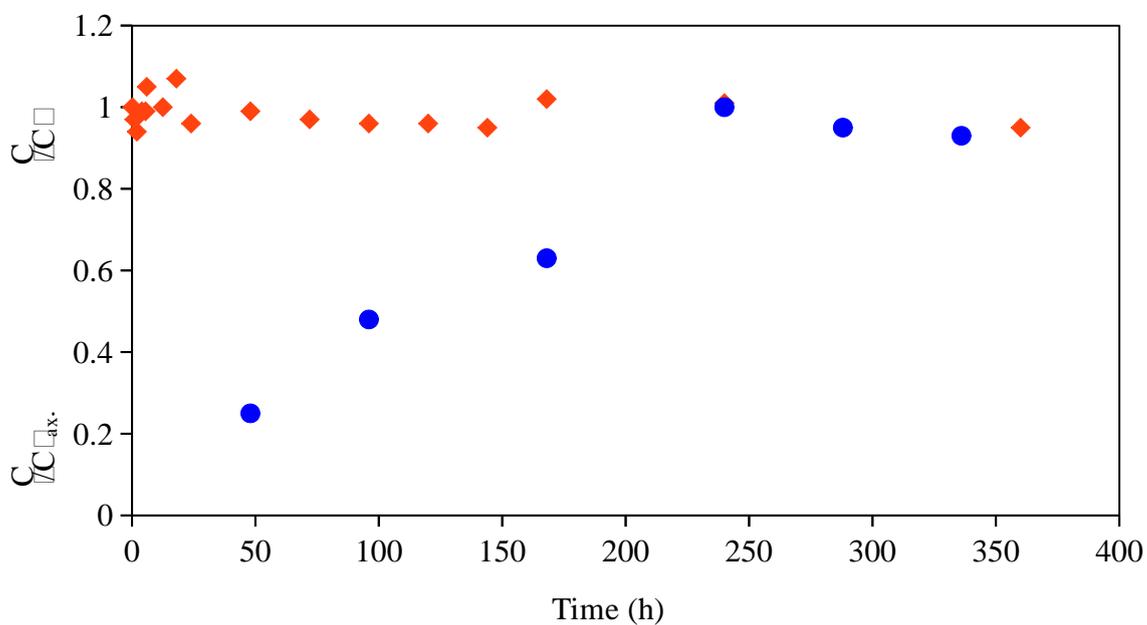


Figure S2b: Plots of uptake (blue circles) vs. release (red diamond) of fluoranthene against time. m_0 and m_{max} are the initial (preloaded) and maximum mass in PES, respectively, and m_t is the mass determined for time t .

S6. PES-water partition coefficients and sampling rates estimated using a LSER model

a) PES-water partition coefficients

In addition to our $\log K_{pw}$ values (Table 1) we used the published experimental data (see legend in Fig. S3 for the sources). The Abraham descriptors of solutes needed for the model were taken from Abraham Absolv database which is integrated in the UFZ-LSER database (Ulrich et al. 2017). The resulting LSER is the following (thereby the values given in parentheses are the standard errors of the parameters):

$$\log K_{pw} = 5.07(0.41) + 0.80(0.13)E - 0.69(0.22)S - 1.46(0.31)A - 2.68(0.21)B + 0.70(0.24)V$$

$$(n = 92, R^2 = 0.85, R^2_{adj} = 0.84, SD = 0.77, F = 94).$$

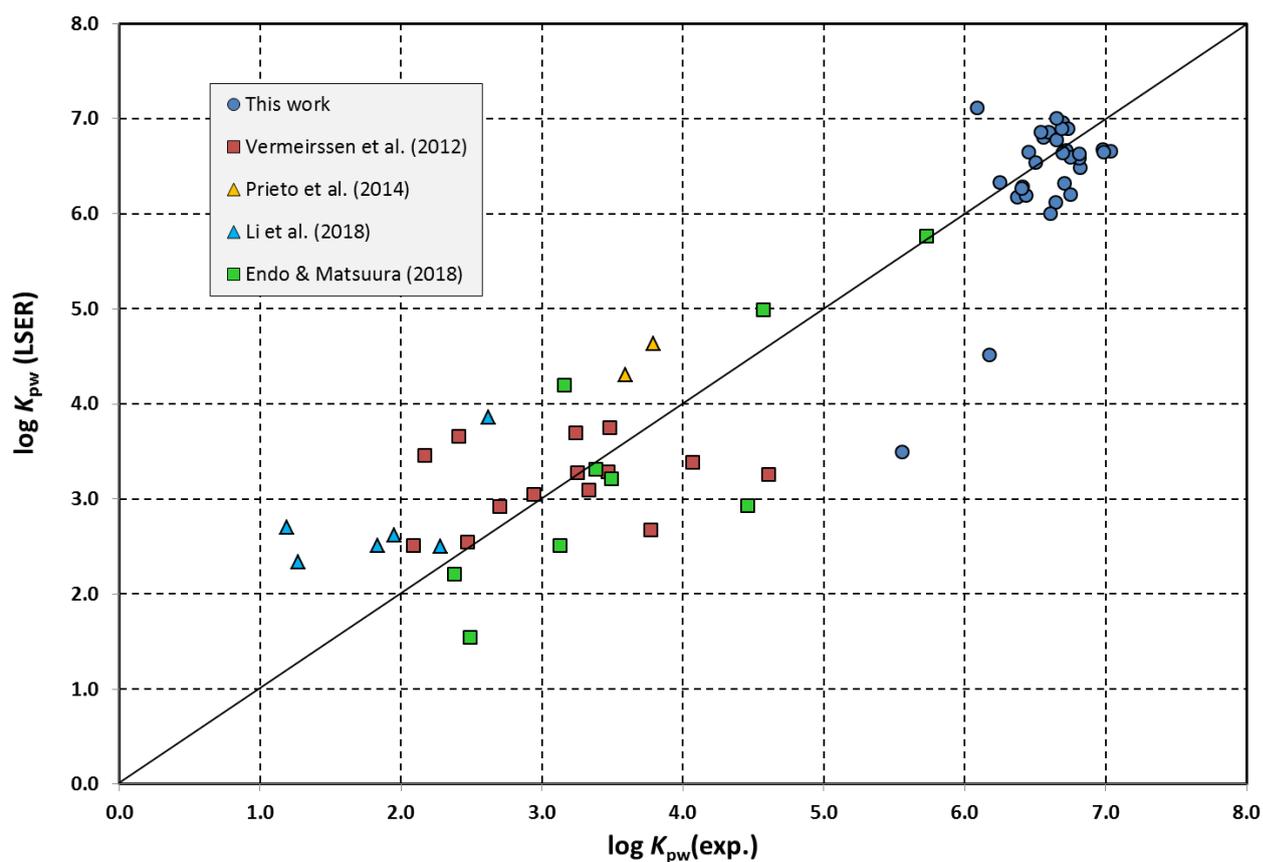


Figure S3. Comparison of $\log K_{pw}$ values estimated using a LSER with those from experiments.

b) PES sampling rates

From Vermeirssen et al. (2012) we took the uptake parameters k_{wPES} , multiplied by the area of the PES membrane ($= 0.159 \text{ dm}^2$) as sampling rates for all test substances which show considerable uptake in PES in the 6 days trial (*ibid.* Table S1 and Fig. S1; in detail we excluded hydroxyatrazine, diclofenac, mecoprop sulfamethazole and sulcotrione). From Morin et al.(2018) we calculated the sampling rate by multiplying the k_e value for the CRK1 model (*ibid.*Table S2) with the 28-day concentration factor CF_{membrane} (*ibid.*Table 2; CF_{membrane} assumed as apparent K_{pw}) and the volume of the two 90-mm \emptyset PES membranes used in their study ($V_{\text{membrane}} \approx 0.35 \text{ cm}^3$).

For the modelling we used the substance descriptors from the Abraham Absolv database downloaded from the UFZ-LSER database (Ulrich et al. 2017).

The LSER model describes the 71 data insufficiently as can be seen in Fig. S4. ($R^2 = 0.63$; $SD = 0.68$).

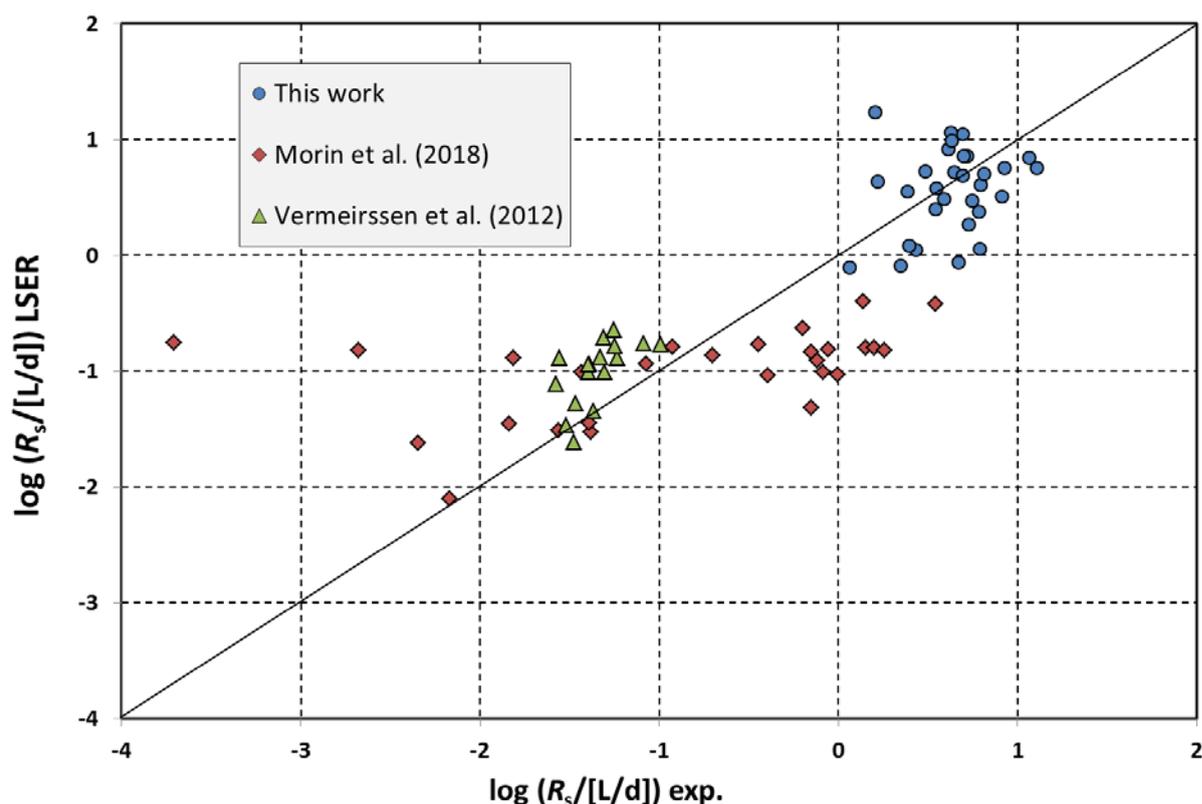


Figure S4. Comparison of R_s values estimated using a LSER with R_s from laboratory experiments.

S7. *In situ* sampling rates and partition coefficients for PAHs to SR

Table S3. Partition coefficients for PAHs between water and SR and the *in situ* sampling rates determined using PRCs (for calculation details see Chepchirchir et al. 2017)

Name of chemical	<i>In situ</i> R_s /[L/d] \pm SD		K_{pw} /[L/kg] ^a
	Station 1	Station 2	
Naphthalene	70.7 \pm 0.9	31.3 \pm 1.8	3.03
Acenaphthylene	65.2 \pm 0.8	28.9 \pm 1.7	3.26
Acenaphthene	64.8 \pm 0.8	28.7 \pm 1.7	3.92
Fluorene	62.6 \pm 0.8	27.7 \pm 1.6	3.79
Phenanthrene	60.6 \pm 0.7	26.8 \pm 1.6	4.11
Anthracene	60.6 \pm 0.7	26.8 \pm 1.6	4.21
Fluoranthene	57.1 \pm 0.7	25.3 \pm 1.5	4.62
Pyrene	57.1 \pm 0.7	25.3 \pm 1.5	4.68
Benzo[a]anthracene	53.9 \pm 0.7	23.9 \pm 1.4	5.32
Chrysene	53.9 \pm 0.7	23.9 \pm 1.4	5.25
Benzo[b+k]fluoranthene	51.4 \pm 0.6	22.8 \pm 1.3	5.74
Benzo[e]pyrene	51.4 \pm 0.6	22.8 \pm 1.3	5.64 ^b
Benz[a]pyrene	51.4 \pm 0.6	22.8 \pm 1.3	5.69
Perylene	51.4 \pm 0.6	22.8 \pm 1.3	5.64 ^b
Indeno[1,2,3-cd]pyrene	49.3 \pm 0.6	21.8 \pm 1.3	6.06
Dibenzo[a,h]anthracene	49.1 \pm 0.6	21.7 \pm 1.3	6.24
Benzo[ghi]perylene	49.3 \pm 0.6	21.8 \pm 1.3	6.02
1-Methylnaphthalene	67.4 \pm 0.8	29.8 \pm 1.8	3.39 ^b
2-Methylnaphthalene	67.4 \pm 0.8	29.8 \pm 1.8	3.39 ^b
2,7-Dimethylnaphthalene	64.4 \pm 0.8	28.5 \pm 1.7	3.67 ^b
1,6,7-Trimethylnaphthalene	61.9 \pm 0.8	27.4 \pm 1.6	3.96 ^b

^a K_{pw} values were obtained from Smedes et al. (2009); K_{pw} s were estimated by linear interpolation using the formula $\log K_{pw} = 0.99 \log K_{ow} - 0.42$ (Smedes et al., 2009).

S8. Comparison of field concentration based on PES and SR

Table S4. TWA concentrations determined from the parallel exposed PES and SR sheets at the two sampling sides in the Sosiani river near Eldoret in Kenya

Name of chemical	TWA concentrations [ng/L] ^d			
	Station 1 - PES	Station 1 - SR	Station 2 - PES	Station 2 - SR
Naphthalene	5.62 ± 1.65	16.13 ± 4.30	20.22 ± 2.55	25.95 ± 9.38
Acenaphthylene	3.29 ± 0.16	6.03 ± 0.32	7.38 ± 0.90	8.09 ± 1.94
Acenaphthene	0.93 ± 0.02	0.84 ± 0.11	1.56 ± 0.12	0.92 ± 0.27
Fluorene	3.54 ± 0.16 ^a	6.32 ± 0.18	6.82 ± 0.86 ^a	7.84 ± 0.96
Phenanthrene	7.21 ± 0.30	8.60 ± 0.29	14.81 ± 1.91	10.80 ± 0.41
Anthracene	0.39 ± 0.01	0.65 ± 0.13	0.82 ± 0.03	0.91 ± 0.01
Fluoranthene	2.91 ± 0.16	1.89 ± 0.07	4.78 ± 0.53	3.51 ± 0.14
Pyrene	4.24 ± 0.19	1.77 ± 0.06	6.09 ± 0.64	3.92 ± 0.16
Benz[a]anthracene	0.23 ± 0.01	0.09 ± 0.01	0.28 ± 0.02	0.30 ± 0.02
Chrysene	0.45 ± 0.01	0.20 ± 0.01	0.62 ± 0.06	0.62 ± 0.04
Benzo[b+k]fluoranthene	0.24 ± 0.01	0.07 ± 0.01	0.24 ± 0.01	0.21 ± 0.02
Benzo[e]pyrene	< SL	0.05 ± 0.01	< SL	0.13 ± 0.01
Benzo[a]pyrene	< SL	0.02 ± 0.00	< SL	0.06 ± 0.01
Perylene	n.d.	< SL	n.d.	< SL
Indeno[1,2,3-cd]pyrene	n.d.	< SL	n.d.	< SL
Dibenz[a,h]anthracene	n.d.	n.d.	n.d.	n.d.
Benzo[ghi]perylene	n.d.	< SL	n.d.	< SL
1-Methylnaphthalene	2.31 ± 0.04 ^b	3.50 ± 0.79	4.33 ± 0.55 ^b	5.35 ± 2.88
2-Methylnaphthalene	2.79 ± 0.12	4.07 ± 0.88	4.33 ± 0.69	6.20 ± 3.36
2,7-Dimethylnaphthalene	2.33 ± 0.01	3.08 ± 0.38	2.88 ± 0.39	3.33 ± 1.47
1,6,7-Trimethylnaphthalene	1.87 ± 0.04 ^c	4.09 ± 0.27	2.39 ± 0.29 ^c	5.45 ± 1.71

n.d., not detected; SL = TWA sampling limit (values given in Table S7). R_s for some compounds were estimated as follows: a- average of values from 3- ringed members; b- equal to R_s of 2-Methylnaphthalene; c- average of values of all alkyl naphthalenes; d- error sign (\pm) represent standard deviations ($n = 3$).

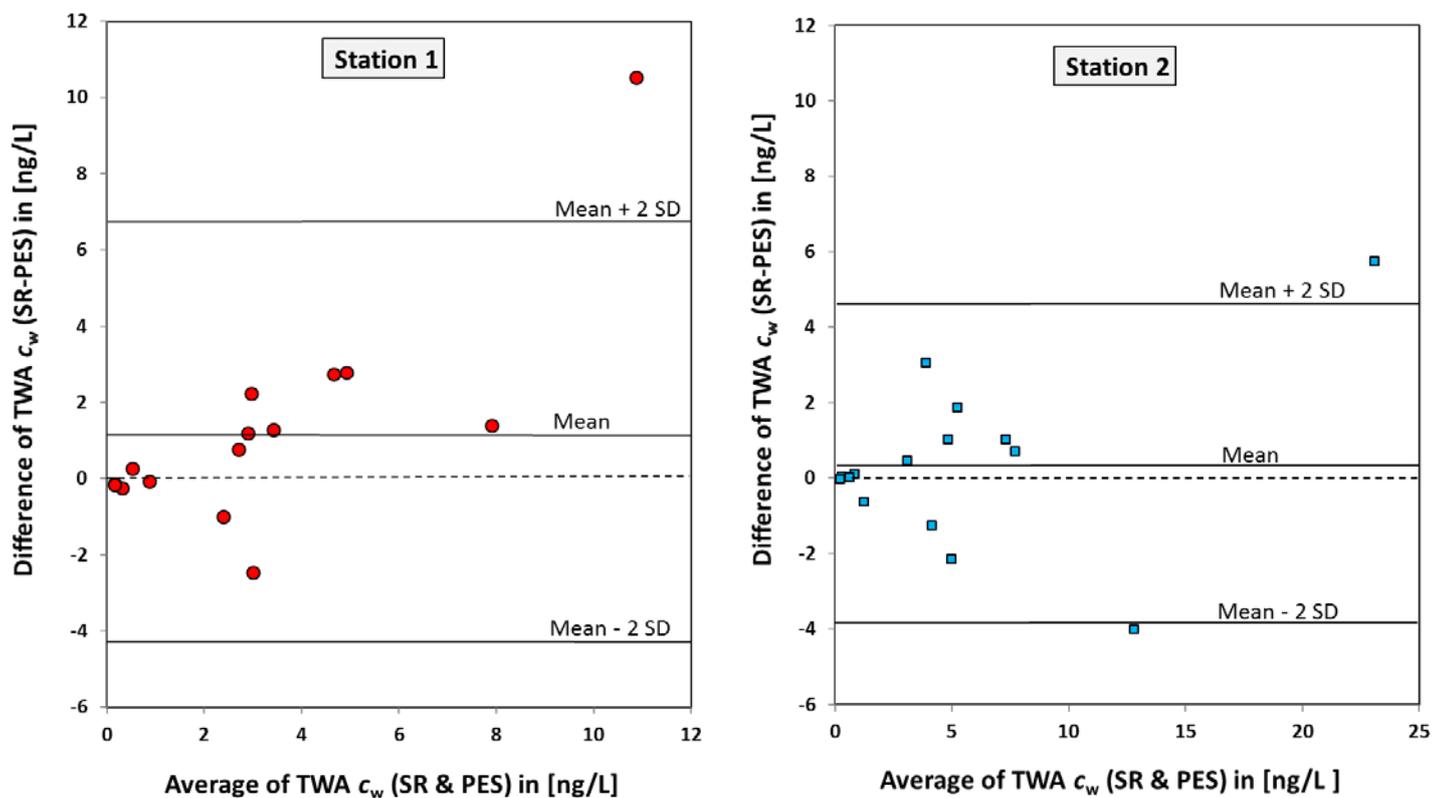


Fig. S5: Bland-Altman plots with the TWA water concentrations obtained based on the two sampler formats (separately for each station) to assess the agreement of the two passive sampling method (see text for interpretation)

The bias between SR- and PES-based results is small at both stations as the means do not differ much from 0. The lines $\langle \text{Mean} \pm 2 \text{ SD} \rangle$ in Fig. S5 indicate the range within 95% of the differences will lie. These are the so-called limits of agreement. The point above the upper limit in both plots is for naphthalene, the compound with the highest analytical uncertainty due to possible background and trip blank contamination.

Table S5. LOQ values and TWA sampling limits (SL)* of the two field-tested passive sampler formats

Name of chemical	LOQ [ng] (for SR & PES)	TWA sampling limit [pg/L]	
		SR**	PES
Naphthalene	0.02	0.022	0.032
Acenaphthylene	0.02	0.023	0.026
Acenaphthene	0.02	0.023	0.029
Fluorene	0.02	0.024	0.017
Phenanthrene	0.02	0.025	0.013
Anthracene	0.02	0.025	0.012
Fluoranthene	0.02	0.026	0.009
Pyrene	0.02	0.026	0.012
Benzo[a]anthracene	0.02	0.028	0.008
Chrysene	0.02	0.028	0.006
Benzo[b+k]fluoranthene	0.05	0.073	0.044
Benzo[e]pyrene	0.05	0.073	0.036
Benz[a]pyrene	0.05	0.073	0.036
Perylene	0.05	0.073	0.036
Indeno[1,2,3-cd]pyrene	0.10	0.153	0.084
Dibenzo[a,h]anthracene	0.10	0.154	0.123
Benzo[ghi]perylene	0.20	0.307	0.445
1-Methylnaphthalene	0.02	0.023	0.015
2-Methylnaphthalene	0.02	0.023	0.015
2,7-Dimethylnaphthalene	0.02	0.023	0.012
1,6,7-Trimethylnaphthalene	0.02	0.024	0.013

* This minimal water concentration that is quantifiable by the sampler was calculated by inserting the instrumental LOQ (per sampler unit) instead of the analyte mass into Eq.1 (for SR) or rearranged Eq. 2 (for PES). - Such SL values are valid only for the samplers of the described material characteristics, sizes and field exposure times as well as for the actual analytical sensitivity because K_{pw} , R_s (see Table S3 for SR and Table 1 for PES), m_p (9.4 g for SR and 1.3 g for PES), t (30 d) and also LOQs are input parameters for SL calculation.

** SL values listed here are for station 2 (with the lower *in situ* R_s values compared to station 1; yielding slightly higher SL)

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