Characterizing Sorption and Permeation Properties of Membrane Filters Used for Aquatic Integrative Passive Samplers

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1 Characterizing Sorption and Permeation Properties of
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4

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17 Abstract

18 Aquatic integrative passive sampling is a promising approach to measure the time-weighted average
19 concentration, yet our understanding for the sampling mechanisms of polar organic contaminants should be
20 further advanced to fully exploit the potential of the method for real-world applications. This study aimed to
21 characterize the sorption and permeation properties of polyethersulfone (PES) and poly(tetrafluoroethylene)
22 (PTFE) membrane filters (MFs) used for passive samplers. Batch sorption experiments with 14 probe
23 chemicals showed that the sorption by PES was generally strong, with the respective sorption coefficients
24 greater than the octanol-water partition coefficients by 2–3 log units. In contrast, the PTFE filter exhibited no
25 significant sorption for all tested chemicals, representing a promising candidate MF that avoids lag-times and
26 slow responses to fluctuating concentrations. Permeation experiments in a glass cell system and successive
27 modeling demonstrated that, if no sorption to the MF occurs, the MF permeation of a chemical can be fully
28 described with a first-order model that considers the transfer through the aqueous boundary layers and the
29 diffusion in water-filled MF pores. Significant sorption to the MF coincided with substantial delay of
30 permeation, which was successfully modeled with the local sorption equilibrium assumption. These findings
31 have implications for improved sampler configurations and successful models for the chemical uptake.

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33 Keywords: Integrative passive sampler, membrane filter, permeation, sorption, diffusion

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37 Introduction

38 Aquatic integrative passive sampling methods have received increasing attention from
39 environmental scientists over the last decades.¹⁻⁴ Among strong advantages of integrative passive sampling
40 is its potential to provide time-weighted average (TWA) concentrations at low cost and with a relatively
41 small effort. TWA concentrations are more representative and more relevant for ecotoxicological risks
42 associated with the contaminants of concern than spot concentrations measured by grab sampling. Active
43 research is ongoing to evaluate and improve the accuracy and reliability of the methods^{2,4} and to extend the
44 measurement concept to further chemicals,⁵⁻⁷ sampling environments,⁸ and purposes.⁹⁻¹¹

45 The most widely used integrative samplers today for polar organic contaminants may be Polar
46 Organic Contaminants Integrative Samplers (POCIS)¹² and Chemcatcher.¹³ Both POCIS and Chemcatcher
47 comprise of sorbent, a membrane filters (MF), and a body of the sampler that holds the former two. The
48 sorbent (e.g., OASIS HLB, Empore SDB disk) serves as the sink of monitored chemicals and will be subjected
49 to chemical analysis in the end. The MF (or MFs) physically hold the sorbent and protect it from physical
50 damages, particle adhesion, and biofouling. The MFs also serve to regulate the chemical uptake by the
51 sampler, as chemicals in water have to permeate through the MF(s) before sorbing to the sorbent.

52 In integrative passive sampling, the TWA concentration is derived using the sampling rate (R_s [L/d]).
53 R_s is “the theoretical volume of water sampled by the sorbent per time” and is equal to “the rate of increase
54 in the chemical amount sorbed by the sorbent” divided by “the external aqueous phase concentration”.
55 Thus, in theory, the TWA concentration is calculated as,

56
$$\frac{\int_0^t C_w dt}{t} = \frac{m_s}{tR_s} \quad (1)$$

57 The left-hand side of eq 1 is the TWA concentration, t [d] is the deployment time, m_s [mg] is the measured
58 amount in the sorbent, and C_w [mg/L] is the external aqueous phase concentration. Under constant C_w
59 conditions, eq 1 can be simplified to,

$$m_s = t R_s C_w \quad (2)$$

Thus, m_s should linearly increase with time. Equation 2 is also used to calibrate R_s experimentally, based on data measured in a controlled laboratory condition with known C_w .

For using aquatic integrative samplers to measure a broad range of polar organic contaminants, however, three major obstacles appear to exist. First, the chemical uptake behavior often does not follow eqs 1 and 2. Experimental data show that a slightly curvy uptake can occur even well below the sorption equilibrium.^{14,15} Moreover, chemicals with relatively hydrophobic nature can exhibit substantial lag-times (i.e., delays of increase of m_s in the early time of sampling) because of their significant sorption to the MF.^{9,14,16-19} Indeed, various chemicals have been detected in the MF in substantial amounts, sometimes even more than in the sorbent.^{13,14,18,20} The sorption to the MF can also cause slow responses to fluctuating aqueous phase concentrations,^{21,22} which violates a condition of eq 1. The second issue is that, even if eqs 1 and 2 hold true, the value of R_s has to be known to convert the measured m_s to the TWA concentration. R_s depends on the chemicals and the sampler configurations and is also influenced by the external environmental conditions such as the flow regime around the sampler. Various methods are available for experimental determination of R_s , although all are laborious to varying degrees.² A model to predict R_s for given chemicals, samplers, and environmental conditions does not exist so far, despite the fact that there have been some attempts to predict R_s from empirical correlation approaches.^{23,24} The third problem is the absence of a field-correction method for POCIS and Chemcatcher, such as performance reference compounds for hydrophobic passive samplers, because the uptake and release of chemicals are not simply isotropic in many cases.^{14,25,26} Clearly, better understanding is needed for the sampling mechanisms to achieve linear uptake, avoid significant lag-times, establish general R_s prediction models, and develop field-correction methods for a wider range of chemicals.

This study aimed to characterize, quantitatively, the sorption and permeation properties of MFs. To this end, we performed batch sorption experiments and permeation experiments using isolated MFs (not the whole samplers). Poly(ethersulfone) (PES) and poly(tetrafluoroethylene) (PTFE) MFs were used in this work.

85 The former is the current standard MF for POCIS and Chemcatcher when polar contaminants are targeted.^{2,4}
86 Various neutral and ionic chemicals were used as probes. The results of permeation experiments were
87 analyzed using mathematical models. While an ever increasing number of studies report determination of R_s
88 and field applications of aquatic passive samplers, the diffusive permeation behavior of chemicals through
89 isolated MFs has not been investigated in the existing studies. The outcomes of this study should provide
90 useful insights into the sampling mechanisms of POCIS, Chemcatcher, and any analogous sampler.

91 Materials and Methods

92 **Materials.** PES filters (Supor 100 Membrane Disc Filter, 0.1 μm pore size, 132 μm thickness, Pall
93 Corporation, NY, US) pre-cleaned with methanol were obtained from EST-Lab (St. Joseph, MO, US). This
94 specific type is among the most frequently used PES filters in previous studies.^{5,9,12,14,15,18} Hydrophilic PTFE
95 filters (Omnipore, 0.1 μm pore size, 30 μm thickness) were purchased from Millipore. HPLC grade methanol
96 was obtained from Wako Pure Chemicals (Osaka, Japan) and acetonitrile from Sigma-Aldrich Japan (Tokyo).
97 Chemicals that used as solute were purchased from Tokyo Chemical Industry (Tokyo, Japan), Sigma-Aldrich
98 Japan, and Wako Pure Chemicals. Glassware was rinsed with methanol or heated at 450°C for 4 h to remove
99 organic residues.

100 All experiments described in the following were conducted with water purified with a Millipore
101 Direct Q3 Water Purification System. For ionizable chemicals, buffer solution (pH 7.5) containing 5 mM CaCl_2
102 and 2 mM Tris was used instead of pure water for both sorption and permeation experiments to control pH
103 and ionic strength.

104 **Batch sorption experiments.** To investigate the kinetic and equilibrium sorption properties of the
105 MFs, batch sorption experiments were performed using 14 chemicals (Table 1). Out of these, 9 chemicals are
106 >99% neutral, 2 chemicals are >99% anionic, and 2 chemicals are >98% cationic at pH 7.5. Umbelliferone
107 (pK_a , 7.78)²⁷ is partially (33%) anionic at pH 7.5 and is classified into neutral compounds here. Table S1 in the
108 Supporting Information (SI), SI-1, summarizes pK_a , $\log K_{ow}$, and $\log D_{ow}$ calculated for pH 7.5. These probe

chemicals were selected on the basis of functional group diversity, hydrophobicity, and analytical possibilities, but not environmental relevance. Methanolic stock solutions were further diluted with water (or buffer) to make test solutions. The final methanol content was < 0.04 % (v/v). PES and PTFE filters were cut into pieces of 1 × 1 or 1 × 2 cm². One or two pieces (ca 5–20 mg in total) were weighed into 5–20 mL vials and sonicated once in methanol and at least twice in water (or buffer) for 5 min each in order to clean the MF and remove residual air from the pores. After sonication, water was removed from the vial using a Pasteur pipette as much as possible, and 4–20 mL aqueous solution of a test chemical was added. Residual water after pipetting was little (<2%) compared to the volume of the test solution and was thus ignored in the later calculations. The vials were shaken horizontally in an air-conditioned room (25°C) at a speed of 150 rpm. For PES, 24 and 48 h were initially given for equilibration. The aqueous phase concentration was then measured, and the sorbed concentration in the PES filter was derived from the mass balance calculation. The resulting (apparent) PES–water partition coefficients $K_{\text{PES/w}} [L_{\text{water}}/\text{kg}_{\text{PES}}]$ were compared between the 24h and 48h tests to check equilibrium. Note, the measured $K_{\text{PES/w}}$ can be “apparent” because of possible nonequilibrium. If $K_{\text{PES/w}}$ at 48 h > $K_{\text{PES/w}}$ at 24 h by >10%, additional experiments for 96 h (4 d) and 168 h (7 d) were conducted. Duplicate vials were prepared for each sampling time for PES, which mostly resulted in a difference of less than a few percent in $K_{\text{PES/w}}$. For PTFE, only 24h tests were performed, mostly in duplicates but with some compounds tested only once. All these experiments were conducted at a single initial concentration for each chemical and MF. The initial concentration in water spanned over 25–1000 µg/L, depending on the chemicals, but the final concentration was in a relatively narrow range, 3–50 µg/L for PES and 50–100 µg/L for PTFE. Control tests (with chemical, but without MF) confirmed 97–102 % recovery. The analytical method for each chemical is given in SI-2.

For seven compounds, additional batch sorption experiments were conducted with multiple initial concentrations to draw sorption isotherms. The resulting data were fitted to the log-transformed Freundlich equation,

$$\log C_{\text{MF}} = n_{\text{Fr}} \log C_{\text{w}} + \log K_{\text{Fr}} \quad (3)$$

134 where C_{MF} [mg/kg] and C_w [mg/L] are the measured concentrations in the MF and water, respectively, and n_{Fr}
135 [-] and K_{Fr} [(mg/kg)/(mg/L) ^{n_{Fr}}] are the Freundlich exponent and coefficient, respectively. These isotherm
136 experiments were performed with a fixed shaking time of 24 h.

137 **Permeation experiments.** Permeation experiments were conducted using a custom-made glass
138 permeation cell unit (see the graphical abstract of this article). The permeation cell unit consists of two half-
139 cells that are identical in shape and have a large opening (30 mm i.d.) on the side. The MF was cut into a
140 round piece slightly larger than the opening size, conditioned with methanol and water, and was sandwiched
141 with the two half-cells. Each half-cell received 28.8 mL of water (or buffer) and a stirrer bar. The whole cell
142 unit was placed on the magnetic stirrer (Cimarec i Poly 15, Thermo Scientific) at room temperature (25°C),
143 and 20 min were given for equilibration of the water levels in case of any difference. The stirrer was turned
144 on at the maximum speed. Then, 3.2 mL aqueous solution of the test chemical was added to one side of the
145 cell (hereafter referred to as the “donor” side) and the identical volume of water (or buffer) was
146 simultaneously added to the other side (“acceptor”). About 30 s after the addition, 200 μ L of solution was
147 taken from each half-cell and considered as the samples for time 0. The experiment was run over 4 or 6 h,
148 during which time the solutions were sampled up to four more times. At least duplicate experiments were
149 conducted. The small volume reduction due to sampling was ignored in the later modeling.

150 The permeation experiments described above were performed with four “nonsorptive chemicals”
151 and four “sorptive chemicals”. The former were thiourea, glucose, 1,2-propylene glycol, and γ -cyclodextrin,
152 all highly hydrophilic and not expected to show any significant sorption. The latter were taken out of the 14
153 chemicals used for the batch experiments, namely benzimidazole, indole, 2-methoxynaphthalene, and 2-
154 naphthalene sulfonate, having varying sorption properties. The initial donor concentration was 0.05–0.5
155 mg/L, except for the three chemicals analyzed with the total organic carbon (TOC) analyzer (glucose, 1,2-
156 propylene glycol, γ -cyclodextrin). For these chemicals, the initial concentration was raised up to 200 mg/L,
157 because of the low sensitivity of the instrument. In addition, for the TOC-measured chemicals, each cell had
158 to be sacrificed at the sampling because the TOC analyzer needed a sample volume of ca 10 mL. Therefore,

three replicate cell units were prepared for a single run, and at least two runs were performed, which resulted in at least 6 data points in total for each chemical and MF. A longer-term permeation experiment up to 36 h was additionally conducted for indole permeating through the PES filter.

We note that the system of the permeation experiment is not intended to mimic real environmental conditions. In fact, the donor phase concentration in our system decreases throughout as the result of the mass transfer toward the acceptor. We however stress that, by analyzing the data using mechanistically-based models, it is possible to achieve general conclusions regarding permeation of chemicals through MFs, as shown below.

Modeling the results of permeation experiments. The permeation experiments were simulated with two mathematical models. Both models consider the transfer of chemicals through the two aqueous boundary layers (ABLs) in the direct vicinity of the MF and the diffusion through the water-filled pores of the MF. Model details are provided in the SI (SI-3), and thus the description here is only brief.

The first model simulates the cases where the sorption of the chemical to the MF is negligible. Assuming the steady-state mass transfer through the two ABLs and the MF, the concentration change in the donor side solution can be described by the following first-order equation,

$$V \frac{dC_{don}}{dt} = -k(C_{don} - C_{acc}) \quad (4)$$

where V [m³] is the volume of the solution in the donor cell, which is equal to that in the acceptor cell, C_{don} and C_{acc} [mg/L] are the concentrations in aqueous solution of the donor and acceptor half-cells, respectively, and k [m³/s] is the overall mass transfer coefficient. From the mass conservation, " $C_{don} + C_{acc}$ " is equal to the initial donor concentration $C_{don,0}$ at any time. Hence, by solving eq 4, we obtain,

$$C_{don} = \frac{C_{don,0}}{2} \left(1 + e^{-\frac{2k}{V}t} \right), C_{acc} = \frac{C_{don,0}}{2} \left(1 - e^{-\frac{2k}{V}t} \right) \quad (5)$$

Equation 5 can be fitted to the results of permeation experiments with k being the adjustable parameter. As k is the reciprocal of the sum of mass transfer resistances posed by the two ABLs and the MF, it can be

related to the aqueous diffusion coefficient (D_w [m^2/s]), the area of the opening of the half-cells (A [m^2]), the thickness of the ABLs (d_{ABL} [m]), and the porosity (ϵ [-]), the tortuosity (τ [-]) and the thickness (d_{MF} [m]) of the MF (see SI-3). Of these parameters, D_w , A , ϵ , and d_{MF} are known or can reasonably be estimated. τ is difficult to estimate and was set to 1.3 here as an initial guess for both MFs. The validity of this will be discussed below. d_{ABL} was estimated with permeation data, as shown later.

The second model additionally considers the sorption to the MF. The model calculates the transient concentrations in MF porewater (C_{mw}) along the normal axis to the MF surface using a second-order differential equation (see SI-3 for details). The assumptions here are a linear sorption isotherm and local sorption equilibrium between MF solid and porewater at any position in the MF. No surface diffusion or matrix diffusion is assumed. The fluxes of mass from the donor cell to the MF and from the MF to the acceptor cell are calculated at each time step by assuming the steady-state flux through the ABLs. In this work, the differential equation was numerically solved by the finite difference method using *R* software.

Results and Discussion

Equilibrium times for PES filter. Out of the 14 chemicals tested in the batch sorption experiments, 8 appear to have reached apparent equilibrium within 24 h (i.e., apparent $K_{\text{PES/w}}$ at 48 h = apparent $K_{\text{PES/w}}$ at 24 h within 10 % difference, as defined in the method section). The other six chemicals, namely 2-methoxynaphthalene, 1-cyanonaphthalene, 1-naphthaleneacetamide, caffeine, propranolol, and tryptamine showed a gradual decrease in the aqueous phase concentration (i.e., increase in apparent $K_{\text{PES/w}}$) over 7 d (Figures S1, S2). In the Supporting Information SI-4, we explain our modeling efforts to reproduce and understand this slow equilibration. In brief, the slow equilibration of two chemicals with the highest $K_{\text{PES/w}}$ (2-methoxynaphthalene, 1-cyanonaphthalene) can be well explained by the diffusion in filter pores that is strongly retarded by the sorption to PES matrix. For the other four chemicals, however, it is not clear why the equilibration needs > 7 d. Particularly, the slow sorption behavior of caffeine, a relatively hydrophilic neutral chemical, cannot be explained by our model. We extracted the PES filters after the 7 d sorption experiment (duplicate) with acetonitrile and obtained 99 and 101 % recovery, indicating reversible sorption

207 of caffeine by PES. We speculate that slow absorption (diffusion) into the PES polymer matrix occurs and
 208 becomes rate-limiting for relatively large chemicals, causing slow equilibration in batch experiments. That
 209 said, more work is clearly necessary for elucidating the actual mechanisms.

210 **Sorption isotherms for PES filter.** The sorption isotherms to the PES filter were measured for 4
 211 neutral, 2 anionic, and 2 cationic organic chemicals with a sorption time of 24 h (Figure 1). Note that, as
 212 shown above, 24 h was not sufficient to reach equilibrium for some chemicals (2-methoxynaphthalene,
 213 propranolol, tryptamine here), but we still show the results of these chemicals in Figure 1 as additional
 214 information. All measured isotherms follow the Freundlich model (eq 3). The Freundlich exponent (n_{Fr}) was
 215 from 0.74 to 0.95 (Table 1), indicating moderately nonlinear to linear isotherms. To our knowledge,
 216 nonlinear sorption isotherms from water to PES filters have not been shown before. Isotherm nonlinearity
 217 suggests that $K_{PES/w}$ should be measured at a field-relevant concentration to obtain useful results. Moreover,
 218 since nonlinear sorption is nothing but occurrence of self-competition at sorption sites (i.e., molecules of the
 219 single chemical compete with each other), it is expected that competitive sorption between multiple solutes
 220 could also occur.

221

222 Figure 1. Sorption isotherms for PES filter. Solid lines indicate the Freundlich model fit. Dashed lines
 223 indicate a slope of 1 (i.e., linear isotherms). (+) and (-) are cationic and anionic chemicals, respectively. The
 224 sorption time was 24 h.

225

226 **$K_{\text{PES/w}}$ for neutral chemicals.** To compare the sorption strength of the PES filter across chemicals,
 227 $K_{\text{PES/w}}$ values were plotted against K_{ow} (Figure 2). For the six chemicals that showed slow equilibration, the
 228 apparent $K_{\text{PES/w}}$ values measured at 7 d were used. All values used are given in Table 1. Values of $K_{\text{PES/w}}$ for
 229 neutral chemicals are ~2.5 log units larger than those of K_{ow} , showing strong sorption properties of the PES
 230 filter. Although significant sorption by the PES filter has been noted before with, e.g., pesticides,^{14,16}
 231 alkylphenols,¹⁸ and estrogens,²⁰ such strong sorption by PES in comparison to K_{ow} has not been pointed out.
 232 Interestingly, some researchers in another research field do recognize the strong sorption by PES and even
 233 advocated a deliberate use of PES filters for removal of organic contaminants from water.^{28,29}

234

235

Figure 2. Log $K_{\text{PES/w}}$ vs log K_{ow} . Literature data are from ref 14. The unit of original $K_{\text{PES/w}}$ data from ref 14 was $\text{L}_{\text{water}}/\text{L}_{\text{bulk PES}}$, which was converted to $\text{L}_{\text{water}}/\text{kg}_{\text{PES}}$. The solid lines indicate the linear regressions for neutral chemicals using the data from this work only ($\log K_{\text{PES/w}} = 0.87 \log K_{\text{ow}} + 2.71$; partially ionic umbelliferone was removed from the regression) and using the combined data from this work and ref 14 ($\log K_{\text{PES/w}} = 0.49 \log K_{\text{ow}} + 2.66$). The dashed line shows the 1:1 relationship.

Table 1. Freundlich parameters and $K_{\text{PES/w}}$ for the PES filter.^a

	$\log K_{\text{Fr}}$	n_{Fr}	$\log K_{\text{PES/w}}$	$\log K_{\text{ow}}^e$
<i>neutral chemicals</i>				
indole	4.35	0.89	4.57 ^b	2.14
benzimidazole	2.85	0.74	3.38 ^b	1.32
2-methoxynaphthalene	4.92	0.79	5.73 ^c	3.47
1-cyanonaphthalene	na	na	5.48 ^c	2.72*
1-naphthaleneacetamide	na	na	4.46 ^c	1.72*
phenol	na	na	3.16 ^d	1.46
caffeine	na	na	3.13 ^c	-0.07
acetanilide	na	na	3.49 ^d	1.16
4-nitroaniline	na	na	4.23 ^d	1.39
umbelliferone ^f	3.70	0.87	3.96 ^b	1.58
<i>ionic chemicals</i>				
2-naphthoic acid	2.45	0.96	2.52 ^b	3.28
2-naphthalene sulfonate	1.82	0.90	2.03 ^b	0.63
tryptamine	2.04	0.76	3.08 ^c	1.55
propranolol	2.94	0.75	3.92 ^c	3.48

^aUnits: K_{Fr} [(mg/kg)/(mg/L) ^{n_{Fr}}], n_{Fr} [-], $K_{\text{PES/w}}$ [L/kg], K_{ow} [L/L]. Ionic chemicals, benzimidazole, and umbelliferone were measured with buffer (2 mM Tris, 5 mM CaCl₂) at pH 7.5 and the others with pure water. ^bInterpolated for 10 µg/L using the Freundlich parameters (24 h). ^cApparent $K_{\text{PES/w}}$ measured at 7 d (single concentration, 3–14 µg/L at 7 d). ^dEquilibrium values measured at a single concentration (9–20 µg/L at equilibrium). ^eExperimental values for neutral species from EPISuite 4.1. Asterisk values were predicted by KOWWIN. ^fpK_a 7.78, thus partially ionic at pH 7.5.

243 A high $K_{\text{PES/w}}$ value implies the possible occurrence of significant lag phases when the PES filter is
244 used for aquatic integrative passive samplers. According to ref 14, a substantial lag-time (>5 d) can occur
245 when $\log K_{\text{PES/w}} > 3$. As shown, the measured $\log K_{\text{PES/w}}$ for all 10 neutral chemicals in this work are > 3. While
246 the actual lag-time depends also on the other sampling conditions, generally high $K_{\text{PES/w}}$ values suggest that
247 lag-times can occur to many chemicals.

248 The correlation between $\log K_{\text{PES/w}}$ and $\log K_{\text{ow}}$ is high for the neutral chemicals measured in this
249 work (Figure 2). However, the correlation becomes substantially poorer if the data from Vermeirssen et al.¹⁴
250 are combined. The $\log K_{\text{PES/w}}$ values from this work tend to be higher than those from the literature¹⁴ in the
251 $\log K_{\text{PES/w}}-\log K_{\text{ow}}$ plot. Three possible reasons for the observed differences can be offered. First and most
252 importantly, PES and octanol have totally different molecular structures, and they may well undergo
253 substantially different intermolecular interactions with solutes, resulting in a poor correlation between $\log$
254 $K_{\text{PES/w}}$ and $\log K_{\text{ow}}$. Thus, the choice of chemicals largely influences the $\log K_{\text{PES/w}}-\log K_{\text{ow}}$ plot. There is only
255 one chemical common in both studies (caffeine), and the reported $\log K_{\text{PES/w}}$ is only minorly (0.6 log units)
256 higher in this work than the literature. Second, the sorption isotherm nonlinearity and competition might
257 explain the observations, yet only to a minor extent, because the observed isotherm nonlinearity by the PES
258 filter is only moderate (Figure 1). Third, many chemicals used in ref 14 are pesticides and pharmaceuticals
259 and are larger in molecular size than the chemicals used in this work. Possibly, an equilibration time of one
260 week adopted in ref 14 was not long enough to closely approach the true equilibrium $K_{\text{PES/w}}$ for some of their
261 chemicals. In any case, the results shown in Figure 2 clearly tell us that estimation of $K_{\text{PES/w}}$ via K_{ow} can cause
262 substantial errors.

263 We attempted to fit the polyparameter linear free energy relationships (PP-LFERs) with Abraham's
264 descriptors^{30,31} to the $K_{\text{PES/w}}$ data for neutral compounds, which resulted in a relatively poor fit (R^2 , 0.69; SD,
265 0.54; see SI-5 for details). Possible reasons for this result include nonattainment of equilibrium, a mixed
266 mode of adsorption and absorption, and nonlinear sorption isotherms.³¹

267 The strong sorption by PES for a range of compounds may be explained by its molecular structure
268 with phenyl and sulfonate groups. The former offers a desirable hydrophobic molecular environment to the
269 sorbing chemicals, while the latter can undergo strong polar interactions. In addition, a high surface area of
270 the porous filter may be a contributing reason for high $K_{\text{PES/w}}$, provided that the mode of sorption is surface
271 adsorption.

272 **$K_{\text{PES/w}}$ for ionic chemicals.** The sorption of ionic chemicals to the PES filter was generally weaker than
273 that of neutral chemicals (Figure 2). Nevertheless, it is notable that the sorption was always significant and
274 measurable, and that the values of $K_{\text{PES/w}}$ for ionic chemicals are comparable to K_{ow} of their neutral species.
275 $K_{\text{PES/w}}$ was measurable even for 2-naphthalene sulfonate, which is present entirely as ion at around neutral
276 pH. These results further demonstrate the relatively strong sorption properties of the PES filter. In the SI, a
277 plot for $\log K_{\text{PES/w}}$ against $\log D_{\text{ow}}$ is provided as additional information (Figure S3).

278 **No sorption to PTFE filter.** In contrast to the PES filter, the sorption by the PTFE filter was negligibly
279 weak for all chemicals we studied; that is, the final aqueous phase concentration in the batch with the PTFE
280 filter was 94–101% of the initial concentrations. These percentages were just similar to those of the controls
281 without filter (Table S5). From these results and the solid-to-liquid ratio adapted in the experiments, the
282 PTFE–water partition coefficients ($K_{\text{PTFE/water}}$) should be $< 45 \text{ L}_{\text{water}}/\text{kg}_{\text{PTFE}}$ (< 1.65 on the log scale) for all studied
283 chemicals. These results were obtained only in a single experimental condition (one concentration level, 24h
284 equilibration time), but we did not make a further attempt to measure $K_{\text{PTFE/water}}$ accurately, as the sorption is
285 evidently weak. Considering the fact that the sorption to the MF is generally an undesirable feature that can
286 cause a lag-time and/or a slow response to the fluctuating concentration in the field applications, we
287 conclude that PTFE is a more advantageous filter material than PES for aquatic integrative passive samplers.
288 According to the recent comprehensive reviews for POCIS² and Chemcatcher,⁴ vast majority of the previous
289 studies used PES filters, and these reviews even do not mention the use of an inert filter such as PTFE. To our
290 knowledge, only one study in the literature has attempted to use a PTFE filter as the diffusion-limiting
291 membrane for aquatic integrative passive samplers.¹³

292 **Permeation of nonsorptive chemicals.** In permeation experiments with the nonsorptive tracers, the
293 decrease in concentration in the donor cell corresponded well to the increase in concentration in the
294 acceptor cell (Figure 3A, B). The sum of the solute masses in donor and acceptor cells at each sampling time
295 was $98 \pm 5 \%$ (mean $\pm$ SD, range: 84–112%) of the initial mass added to the donor cell, indicating no
296 significant loss process including sorption to the MF. The first-order mass transfer model was fitted to the
297 results with k being the fitting parameter. The obtained values of k for both PES and PTFE were in the order
298 of thiourea > 1,2-propylene glycol > glucose > γ -cyclodextrin and were correlated with D_w of these chemicals
299 (Figure 4; see Table S6 for k and D_w values). These correlations suggest that the mass transfer through the
300 MFs is governed by aqueous diffusion. The k values for PTFE are higher than those for PES, agreeing with the
301 fact that the used PTFE filter is thinner than the PES filter (30 vs 132 μm , respectively).

Nonsorptive chemicals

Sorptive chemicals

Figure 3. Results of permeation experiments for nonsorptive chemicals (A, B) and sorptive chemicals (C, D) through PES and PTFE filters. Panel E shows the permeation of indole through the PES filter over 36 d. The vertical axis indicates the concentration relative to the initial concentration in the donor cell. Symbols are explained in the figure. In panels A, B, and D, lines show the fitted first-order mass transfer model. In panels C and E, lines indicate the results of numerical modeling (see text).

Figure 4. Mass transfer coefficients (k) for MF permeation vs aqueous diffusion coefficients (D_w) for sorptive and nonsorptive chemicals. The lines show the linear regressions for the nonsorptive chemicals. The error bars indicate the standard errors (not shown if smaller than the symbols).

Using the permeation data for the nonsorptive chemicals, d_{ABL} was estimated (see eqs S3 and S4 in the SI). The best estimate that minimizes the sum of the squared residuals was 88 μm for PES and 122 μm for PTFE on each side of the filter. These values are well in line with typical ABL thickness in flowing water (ref 32, p 277; refs 1,33). Using these d_{ABL} , the contributions of the ABLs and the MF to the overall mass transfer resistance can be estimated (eq S3 in the SI); they were 35% by the ABLs and 65% by the MF for PES and 79% by the ABLs and 21% by the MF for PTFE. Here, three additional remarks should be stated. First, the obtained values for d_{ABL} are not independent of the other membrane-related parameters used. Particularly uncertain is the tortuosity τ . Use of a higher value for τ would result in a lower value for d_{ABL} , and vice versa. For PES, additional support for $d_{\text{ABL}} = 88 \mu\text{m}$ and $\tau = 1.3$ will be provided below. Second, it is known that the mass transfer through an ABL is actually proportional to $D_w^{2/3}$ instead of D_w .³² Indeed, the k values obtained in this work correlate slightly better with $D_w^{2/3}$ than with D_w ($R^2 = 0.9995$ for PES and 0.97 for PTFE when $D_w^{2/3}$ is used; Figure S4 in the SI). The fixed ABL thickness for all chemicals is an approximation following the film theory,³² but our data do suggest that this simple model can sufficiently well describe the mass transfer through the MFs for chemicals with D_w of $0.3\text{--}1.3 \times 10^{-9} \text{ m}^2/\text{s}$, covering most of the organic contaminants of concern. Third, we used a TOC analyzer, a chemically nonspecific instrument for quantification of three

328 tracer chemicals. Hence, although a good mass balance was obtained and the results are reasonable, we
329 cannot totally exclude the possibility that these chemicals partially transformed to other chemicals during
330 the experiment.

331 **Permeation of sorptive chemicals.** The permeation behavior of the sorptive chemicals through the
332 PES filter was considerably different from that of the nonsorptive chemicals (Figure 3C, E). The concentration
333 in the donor cell decreased faster and that in the acceptor cell increased slower, as compared to the
334 nonsorptive chemicals. The mass balance was not maintained, indicating the significance of the sorption to
335 the PES filter. The rate of concentration decrease/increase appears to be related to $K_{\text{PES/w}}$; that is, the higher
336 the $K_{\text{PES/w}}$ value, the faster the concentration decrease in the donor, and the slower the concentration
337 increase in the acceptor. Particularly, indole and 2-methoxynaphthalene, the two strongly sorbing chemicals
338 tested in this permeation experiment, were not detectable in the acceptor cell within 4 h. The longer term
339 experiment conducted with indole did show the appearance of this chemical in the acceptor cell after 12 h,
340 demonstrating a breakthrough of this chemical (Figure 3E).

341 In contrast to the PES filter, the permeation behavior of the four sorptive chemicals through the
342 PTFE filter was similar to that of the nonsorptive chemicals (Figure 3D). This result can be expected, as the
343 batch sorption experiments showed that the sorption of all test chemicals to PTFE was negligibly weak.
344 Moreover, the good mass balance obtained indicates that the glass cells used do not significantly sorb the
345 four test chemicals. By fitting eq 5, k was obtained for the sorptive chemicals through PTFE. The resulting k
346 values fall around the k vs D_w regression obtained with the nonsorptive chemicals (Figure 4), which indicates
347 that the overall rate of mass transfer through the PTFE filter is determined by the diffusive mass transfer
348 through the ABLs and the membrane pores for all tested chemicals.

349 **Numerical modeling for PES filter permeation.** The numerical model used in this study considers the
350 steady-state mass transfer through the two ABLs, the diffusion through water-filled membrane pores, and
351 the sorption to the MF polymer matrix. A linear sorption isotherm and local sorption equilibrium were
352 assumed. The $K_{\text{PES/w}}$ value at the estimated final equilibrium concentration in the permeation experiment

353 was interpolated with the Freundlich model (Table 1) and used as an input parameter for modeling. d_{ABL} was
354 set to 88 μm .

355 Figure 3C and 3E show that the model well approximates the results of the permeation experiments
356 for the sorptive chemicals. Assuming linear and equilibrium sorption is a simplification, contradicting the
357 results of batch sorption experiments (i.e., nonlinear isotherms, slow equilibration) in a strict sense. The
358 good model performance suggests that such simplifications do not cause large errors at least in short-term
359 modeling. It is encouraging that the decreasing donor concentrations for strongly sorbing indole and 2-
360 methoxynaphthalene are well predicted by the model. As the PES filter sorbs these chemicals strongly, the
361 bulk surface of the MF (i.e., the first layer that faces the donor solution) serves as an effective sink, and as
362 such, the rate of decrease in the donor concentration is largely determined by the ABL transfer (and not by
363 diffusion in MF pores). Thus, the good agreement between model results and data for the strongly sorbing
364 chemicals suggests that the value used for d_{ABL} is reasonable, and our a priori estimate for tortuosity τ (1.3) is
365 also adequate.

366 A noticeable discrepancy between the model and data is some underestimation of the measured
367 acceptor side concentrations for indole in the 36h experiment (Figure 3E). Incorporating the Freundlich
368 equation in the numerical model (see SI-3) resulted in no difference from the linear sorption isotherm
369 (Figure S5). A possible explanation for the observed underestimation is that the instantaneous sorption
370 assumption is not strictly valid for indole in a longer term.

371 **Implications for passive sampling practices.** The experimental and modeling results shown above
372 has important implications for practices of aqueous passive sampling. The commonly used PES filter is a
373 rather strong sorbent and can cause delayed permeation for many chemicals. The permeation behavior
374 through the PES filter is well approximated by a combination of the ABL transfer, the diffusion through
375 water-filled pores, and the local equilibrium sorption to the PES matrix from porewater, at least for modeling
376 of the short-term permeation behavior. This knowledge should be useful to develop a mathematical model
377 for the sampling behavior by POCIS and Chemcatcher. Minor but significant isotherm nonlinearity of the

sorption by PES suggests that laboratory calibration experiments should be conducted in the field-relevant concentration range. Moreover, some chemicals including highly hydrophilic ones undergo slow, long-lasting sorption by PES. Influences of sorption kinetics to PES on the permeation behavior in a longer term (i.e., weeks) were not studied in this work and could be a topic of future research.

That being said, all these complicated issues related to the sorption to PES can be avoided by simply replacing the PES with the PTFE filter. The sorption of organic chemicals to PTFE is generally weak, as is well-known and was also demonstrated in this work. With the PTFE filter, the permeation behavior is simply determined by the ABL transfer and the membrane pore diffusion. In this case, the simple first-order steady-state diffusion model can be used to calculate the flux through the MF. Also to avoid lag-times and slow responses to fluctuating concentrations, we recommend the PTFE filter for aquatic integrative passive sampling in future work. Disadvantages of the used PTFE filter may be its somewhat higher price, smaller thickness (i.e., R_s more susceptible to the ABL thickness), and far less accumulation of data and experience than PES. However, the cost for MFs should be rather small compared to that of the whole monitoring campaign.¹⁹ Small thickness can be overcome by stacking multiple filters or using a thicker filter. Data and experience should be collected and shared from now on to exploit the full potential of PTFE filters. To establish a mechanistic model for the whole POCIS and Chemcatcher devices, we additionally need to know the sorption and permeation behavior in the sorbent layer. The same applies to developing R_s prediction models. We are currently working on characterizing the properties of sorbent materials, which will hopefully elucidate the full picture of the chemical uptake and release by aquatic passive samplers.

Associated content

Supporting Information

Properties of test chemicals, analytical methods, extended model descriptions, modeling of sorption kinetics, PP-LFER analysis, six tables and five figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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