

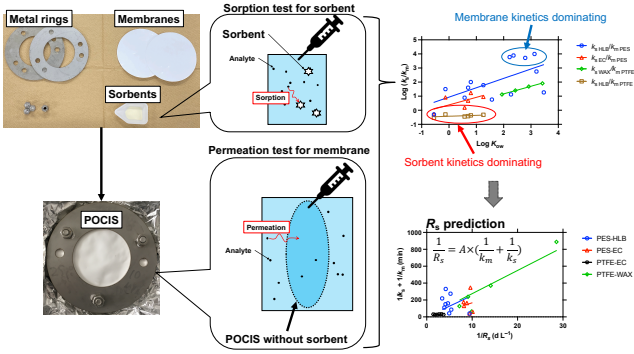
Characterization of the permeation properties of membrane filters and sorption properties of sorbents used for polar organic chemical integrative samplers

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ABSTRACT. Polar organic chemical integrative samplers (POCIS) are promising devices for measuring time-weighted average concentrations of hydrophilic compounds in aquatic environments. However, the mechanism of POCIS uptake remains unclear. This study characterizes the permeation properties of polyethersulfone and polytetrafluoroethylene and the sorption properties of Oasis HLB (Waters), Envi-Carb (Supelco), and Oasis WAX (Waters) under identical conditions via calibration experiments of the POCIS. Plant protection products, neonicotinoid herbicides, and linear alkyl benzene sulfonates (LAS) were tested. The permeation experimental results suggested that the penetration rate constants ( $k_m$ ) with high  $K_{ow}$  values ( $K_{ow}$ : octanol–water partition coefficient) were low, which indicated that the sorption of chemicals on the membrane may constitute a limiting factor for the permeation. The sorption experiments indicated that the sorption rate constants ( $k_s$ ) depended on the type of sorbent instead of the  $K_{ow}$  values. Low  $k_s/k_m$  ratios were obtained for chemicals with low  $K_{ow}$  values, which implied that the POCIS uptake for highly hydrophilic compounds was controlled by both membrane and sorbent kinetics. The  $k_m$  and  $k_s$  values corresponded to the model and predicted the values of the sampling rates ( $R_s$ ) for the LAS. These findings revealed the possibility of using  $k_s$  and  $k_m$  values to predict  $R_s$  values.

22 KEYWORDS. plant protection products, pesticides, surfactant, passive sampling, sampling rate,  
23 POCIS  
24  
25 GRAPHIC FOR TABLE OF CONTENTS (TOC)/ABSTRACT ART.



INTRODUCTION. Polar organic chemical integrative samplers (POCIS) have been used as a passive sampling device for hydrophilic contaminants ( $0 < \log K_{ow} < 4$ ;  $K_{ow}$ : octanol–water partition coefficient) in aquatic environments (1). Sampling using these devices can obtain time-weighted average (TWA) concentrations of contaminants such as pesticides, pharmaceuticals, drugs, and munitions (1–12). TWA concentrations obtained from POCIS sampling were reported as being consistent with the mean concentrations estimated from grab sampling (1).

Sampling rate ( $R_s$ ) values are required to quantify the concentrations of the contaminants for POCIS sampling and must be obtained via time-consuming calibration experiments. Three types of calibration experiments have been conducted in previous laboratory-based studies: static renewal, tank, and static experiments. In previous static renewal experiments, a single POCIS device was deployed for certain periods (typically 1–28 d) in a 1 L glass beaker with solutions containing contaminants, and was refreshed every 1–2 days to avoid changes in contaminant concentrations (1,5,6,8,9,13,14). In tank experiments, POCIS devices were deployed in a tank filled with solution (typically 50–100 L) for certain periods (15–18).  $R_s$  values were also estimated from the collected amount of contaminants on the sorbent in the POCIS devices used in static renewal experiments and tank experiments. Static experiments were conducted in a manner similar to static renewal experiments; however, the solution was not refreshed during the course of the experiment (11,19–24). In these studies, the contaminant concentration decrement in the solution was subsequently monitored to estimate the  $R_s$  values (11,19–24). All calibration experiments for evaluating the  $R_s$  values are time-consuming tasks. For example, at least 28 d is required to estimate the  $R_s$  value for the POCIS devices, which applied to field observations for a 28 d duration. Moreover, POCIS sampling targets several contaminants in aquatic environments. Therefore, prediction methods for  $R_s$  values have been required in previous experiments (25).

The effects of environmental factors on  $R_s$  values have been investigated, such as temperature, flow velocity, exposure scenario, and suspended sediment (9,26–28). However, the kinetics of the POCIS uptake, which should control  $R_s$  values, are not fully understood. Previous studies have reported that POCIS uptakes were controlled by membrane kinetics, thereby implying that the  $R_s$  values may depend on the type of membrane instead of the sorbent type (29). However, recent investigations have reported conflicting data regarding the POCIS uptake model controlled by membrane kinetics. For example, Noro et al. (5) indicated that  $R_s$  changed when different sorbents were used. In addition, Jeong et al. (30) revealed that the  $R_s$  values of POCIS devices containing polyethersulfone (PES) membranes and polytetrafluoroethylene (PTFE) were similar (30). Both investigations implied that sorbent kinetics may affect POCIS uptake. A recent investigation demonstrated that  $R_s$  values may be predicted by a first-order chemical reaction kinetic model with octanol–water dissociation constants and membrane–water distribution coefficients (31). However, these experiments required 28 days to obtain the membrane–water distribution coefficients (31). Thus, this model may not be suitable for predicting  $R_s$  values at low costs.

This study characterizes the permeation properties of membranes and the sorption properties of sorbents. First, a permeation experiment was conducted to estimate the penetration rate constants of contaminants diffusing from the aqueous phase to the inside of a POCIS device through the membrane. POCIS devices with polyethersulfone (PES) and polytetrafluoroethylene (PTFE) membranes were used in this work. Second, the sorption rate constants of the contaminants on the sorbent were estimated for the three studied sorbents; Oasis HLB (Waters), Envi-Carb (Supelco), and Oasis WAX (Waters). Plant protection products (PPPs), neonicotinoid herbicides, and surfactants were used. Then, the penetration rate and adsorption rate were compared to

estimate the rate-limiting step of POCIS uptake. Finally, the applicability of the  $R_s$  prediction model, reported by Morin et al. (31), was evaluated using the penetration rate constants, sorption rate constants, and  $R_s$  values.

## MATERIALS AND METHODS.

### *Materials and chemicals*

Oasis HLB, Oasis WAX (Waters, Milford, MA, USA), and ENVI-Carb (Supelco, Bellefonte, PA, USA) were used as sorbents. Polyethersulfone (PES) microporous (0.1  $\mu\text{m}$  pore size and 102–158  $\mu\text{m}$  thickness) and hydrophilic polytetrafluoroethylene (PTFE) (0.1  $\mu\text{m}$  pore size and 35  $\mu\text{m}$  thickness) membranes were purchased from Nihon Pall Ltd. (Tokyo, Japan) and Advantec Toyo Kaisha, Ltd (Tokyo, Japan), respectively, for the POCIS devices.

A neonicotinoid mixture solution (20  $\text{mg L}^{-1}$  each) from FUJIFILM Wako Chemicals, Inc. (Osaka, Japan) was used for the experiments. An acetonitrile solution containing 10  $\text{mg L}^{-1}$  of acetamiprid- $d_3$ , clothianidin- $d_3$ , dinotefuran- $d_3$ , imidacloprid- $d_4$ , nitenpyram- $d_3$ , thiamethoxam- $d_3$ , and thiacloprid- $d_3$  was purchased from Hayashi Pure Chemical, Inc. (Osaka, Japan) and was used as the internal standard for neonicotinoid pesticide analysis. An anionic surfactant mixture (LAS) methanolic standard solution containing sodium decylbenzenesulfonate ( $\text{C}_{10}$ -LAS), sodium undecylbenzenesulfonate ( $\text{C}_{11}$ -LAS), sodium dodecylbenzenesulfonate ( $\text{C}_{12}$ -LAS), sodium tridecylbenzenesulfonate ( $\text{C}_{13}$ -LAS), and sodium tetradecylbenzenesulfonate ( $\text{C}_{14}$ -LAS) at 1 g/L concentration was purchased from FUJIFILM Wako Chemicals Ind. (Osaka, Japan). A sodium 4-dodecylbenzenesulfonate (RING- $^{13}\text{C}_6$ ) 10  $\text{mg L}^{-1}$  methanolic solution was purchased from Cambridge Isotope Laboratories, Inc. (Tewksbury, MA, USA) and used as an internal standard for the LAS analysis. The PPPs standard reagents isoprocarb, fenobucarb, pyroquilon,

bromobutide, cyanazine, S-metolachlor, paclobutrazol, and furametpyr were obtained from Wako Pure Chemical Ind. Methanol, acetone, and dichloromethane of pesticide-analysis grade (FUJIFILM Wako Chemicals Ind.) were used for the experiments and clean-up processes during the analysis.

#### *POCIS devices*

Metal rings (inner diameter: 54 mm, outer diameter: 102 mm) were used in the POCIS devices for this study. Three types of POCIS devices with 220 mg sorbent have been used in previous reports. PES-Oasis HLB (PES-HLB) POCIS (6,9,32,33) as well as a combination of PES-ENVI Carb (PES-EC) POCIS and PTFE-ENVI Carb (PTFE-EC) POCIS (5) have been used for PPPs and neonicotinoid herbicides; whereas, PTFE-Oasis WAX (PTFE-WAX) POCIS has been used for LAS (34). In this study, the same devices have been used.

#### *Permeation experiment*

A permeation experiment was conducted to estimate the penetration rate of contaminants diffusing from the aqueous phase to the inside of the POCIS device. A glass bar (diameter, 5 mm; length, 10 mm) was installed in the POCIS devices instead of the sorbents. POCIS devices with PES and PTFE membranes were tested. Before the permeation experiment, the POCIS devices were deployed in ultrapure water for 1 h placed in glass beakers and agitated at 1500 rpm. Then, the POCIS devices containing the pure water were installed in 1 L glass beakers (HARIO SCIENCE CO., LTD., Tokyo, Japan) containing a solution with 20  $\mu\text{g L}^{-1}$  contaminant concentration for certain periods. The solution was agitated at 18  $\text{cm s}^{-1}$  under darkness at 20 °C (6). This condition was the same as previously reported calibration conditions for POCIS devices (5,6,34). Following deployment, the membranes of the POCIS devices were cut to transfer the

solution from the POCIS device to glass tubes using glass Pasteur pipettes. Additionally, 3 mL of the solution in the beaker was transferred into glass tubes using glass Pasteur pipettes. The obtained samples were then pretreated prior to gas chromatography–triple quadrupole mass spectrometry analysis (GC-MS/MS analysis) and liquid chromatography–triple quadrupole mass spectrometry analysis (LC-MS/MS analysis). POCIS devices with PES membranes have previously been used to detect PPPs and neonicotinoid herbicides (6,9,10); whereas, POCIS devices with PTFE membranes have previously been used to detect neonicotinoid herbicides and LAS (5,34). Thus, PES membranes were tested for and neonicotinoid herbicides. The PTFE membranes were tested for neonicotinoid herbicides and LAS.

#### *Flow velocity measurements in POCIS devices*

The flow velocity in the calibrated POCIS devices was measured using an Alabaster mass transfer sensor (35). Alabaster cubes ( $1 \times 1 \times 1$  cm) were prepared from Alabaster plates obtained from PaSOC (Kimsward, Netherlands). The alabaster cubes were measured using Vernier calipers to calculate their surface areas. They were then dried at 40 °C for 10 min and weighed. An Alabaster cube was then installed in each POCIS device instead of the sorbent. The POCIS devices were deployed for 1 h in a 1 L glass beaker filled with water. The water in the beakers was agitated at  $18 \text{ cm s}^{-1}$  under darkness at 20 °C. This condition was the same as the calibration used in previous studies (5,6,34). Following deployment, the alabaster cubes were collected from the POCIS device. The deployed alabaster cubes were weighed after drying for 15 min at 40 °C. The flow velocities were estimated based on the dissolution rates of the alabaster cubes, as described in a previous study (35).

#### *Sorption experiment*

Sorption experiments were conducted to estimate the adsorption rate of the contaminant onto the sorbent in the POCIS device. First, the agitation rate was determined to replicate the flow conditions in the POCIS devices. The adsorption rates were then estimated using the determined flow conditions.

The agitation rate, which had a flow velocity similar to that inside of the POCIS device in the calibration experiment, was determined via the Alabaster mass transfer sensor (i.e., Alabaster cubes). Briefly, the alabaster cubes were dried at 40 °C for 10 min and then weighed. Alabaster cubes were installed in the center of a glass beaker (diameter: 53 mm; height: 70 mm) with 100 mL of water. The water in the beakers was agitated at several rates of rotation using glass magnetic stir pieces (diameter, 7 mm; length, 20 mm) under darkness at 20 °C. The flow velocities were estimated based on the dissolution rate of the alabaster cubes as detailed in the previous subsection.

The adsorption rate was estimated using the determined agitation rate. Sorbents (50 mg) were weighed into glass beakers (diameter: 53 mm; height: 70 mm) containing 100 mL of contaminant solution (50 µg L<sup>-1</sup> each). The solution was agitated at the determined rate for certain periods using glass magnetic stir bars (diameter, 7 mm; length, 20 mm). The supernatant (1 mL) was next transferred into glass tubes using glass syringes with syringe filters. The obtained samples were pretreated before GC-MS/MS analysis and LCMS/MS analysis as previously noted. POCIS devices with Oasis HLB sorbent have previously been used to detect both PPPs and neonicotinoid herbicides (6,9,10). Devices with ENVI-Carb and Oasis WAX have also been previously used to detect neonicotinoid herbicides and LAS, respectively. Thus, Oasis HLB was evaluated for PPPs and neonicotinoid herbicides. ENVI-Carb and Oasis WAX were evaluated for neonicotinoid herbicides and LAS, respectively.



163 *Pretreatment and instrumental analysis*

164 The samples obtained in the glass tubes were pretreated prior to the GC-MS/MS and LC-MS/MS  
165 analyses. Three types of pretreatments were used for PPPs, neonicotinoid herbicides, and LAS  
166 analysis.

167 Ultrapure water was added to the glass tubes containing the PPPs samples to maintain a sample  
168 volume of 3 mL. Dichloromethane (2 mL) was added to the glass tubes. The glass tubes were  
169 shaken 50 times. The dichloromethane phases were collected into glass tubes using glass Pasteur  
170 pipettes with 1 g of sodium sulfate in fritted solid phase extraction (SPE) tubes. Then,  
171 dichloromethane (5 mL) was passed through sodium sulfate in the fritted SPE tubes and added to  
172 the dichloromethane phase. The dichloromethane solution was evaporated to dryness using a  
173 gentle nitrogen stream. Acetone (1 mL) containing 0.3% polyethylene glycol was added to the  
174 glass tubes. The acetone solution was then collected in glass vials. The samples were then  
175 analyzed via GC-MS/MS. An Agilent Technologies (Santa Clara, USA) 7890 GC linked to a  
176 7000 mass selective detector was used in the selected ion monitoring mode. The detection limits  
177 of the GC-MS/MS analysis were previously reported (9).

178 The samples (1 mL) of neonicotinoid herbicides and LAS were transferred into glass vials with  
179 internal standards (400 µg L<sup>-1</sup>, 25 µL). Samples were analyzed using LC-MS/MS. The LC-  
180 MS/MS analytical conditions and detection limits have been reported in previous studies (34,36).

181 **RESULTS AND DISCUSSION.**

182 *Penetration rate constants*

183 The penetration rate constants ( $k_m$ ) of PPPs, neonicotinoid herbicides, and LAS were estimated  
 184 via the permeation experiments. PES membranes were tested for PPPs and neonicotinoid  
 185 herbicides. The PTFE membrane was tested for neonicotinoid herbicides and LAS. The  
 186 concentrations of the contaminants gradually increased with time in the POCIS device (Fig. S1).  
 187 The permeation rate of this study should reflect the actual membrane kinetics for the POCIS  
 188 uptake because the permeation experiment was conducted in the same manner as the calibration  
 189 experiments of the POCIS devices (5,6,34).

190  $k_m$  values were obtained by fitting the first-order reaction equation as follows:

$$191 \quad C_p = C_e(1 - e^{-k_m t}) \quad (1)$$

192 where  $C_p$  ( $\mu\text{g L}^{-1}$ ) is the concentration of the contaminants in the POCIS devices,  $C_e$  ( $\mu\text{g L}^{-1}$ ) is  
 193  $C_p$  at 120 min,  $k_m$  ( $\text{min}^{-1}$ ) is the penetration rate constant, and  $t$  (min) is the time. The  $k_m$  values  
 194 are presented in Table 1. The  $k_m$  values of the PES membranes ( $k_{m, \text{PES}}$ ) ranged from  $8.4 \times 10^{-6}$   
 195 (s-metolachlor) to 0.073 (dinotefuran) ( $\text{min}^{-1}$ ) (Table 1). The  $k_m$  values of the PTFE membranes  
 196 ( $k_{m, \text{PTFE}}$ ) ranged from  $1.1 \times 10^{-3}$  (C<sub>14</sub>-LAS) to 0.13 (dinotefuran) ( $\text{min}^{-1}$ ) (Table 1). The  $k_{m, \text{PTFE}}$   
 197 values were higher than the  $k_{m, \text{PES}}$  values because of the difference in the thickness of the  
 198 membranes (PTFE, 35  $\mu\text{m}$ ; PES, 100–150  $\mu\text{m}$ ). This result supports the findings of previous  
 199 investigations (5,37).

Table 1 Log  $K_{ow}$ ,  $k_m$ ,  $k_s$ , and  $R_s$  of plants protection products, neonicotinoid herbicides, and the linear alkylbenzene sulfonates.

Log $K_{ow}$		$k_m$		$k_s$			$R_s$				Referen ce for $R_s$
		$\text{min}^{-1}$		$\text{min}^{-1}$			$\text{L d}^{-1}$				
PES	PTFE	HLB	EC	WAX	PES- HLB	PES- EC	PTFE- EC	PTFE- WAX			

plants protection  
products (PPPs)

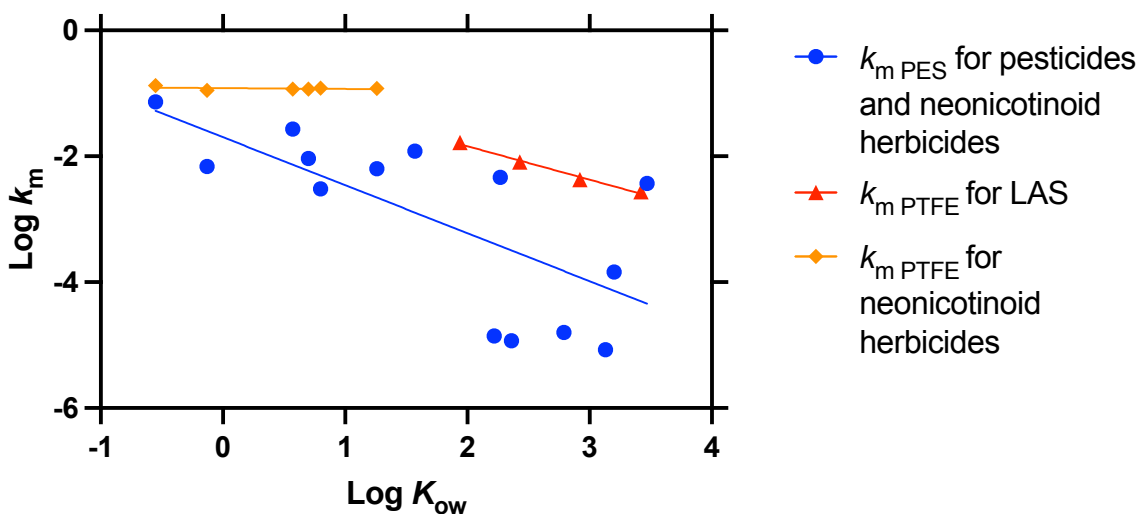
Isoprocab	2.27	$4.6 \times 10^{-3}$	–	0.27	–	–	0.294	–	–	–	Yabuki et al. 2016
Fenobucarb	2.79	$1.6 \times 10^{-5}$	–	0.37	–	–	-	–	–	–	
Pyroquilon	1.57	$1.2 \times 10^{-2}$	–	0.31	–	–	0.185	–	–	–	Yabuki et al. 2016
Bromobutide	3.47	$3.7 \times 10^{-3}$	–	0.30	–	–	0.191	–	–	–	Yabuki et al. 2016
Cyanazine	2.22	$1.4 \times 10^{-5}$	–	0.37	–	–	0.280	–	–	–	Ahrens et al. 2018
s-Metolachlor	3.13	$8.4 \times 10^{-6}$	–	0.37	–	–	0.338	–	–	–	Poulier et al. 2014
Paclobutrazol	3.2	$1.5 \times 10^{-4}$	–	0.36	–	–	-	–	–	–	
Furametpyr	2.36	$1.2 \times 10^{-5}$	–	0.40	–	–	-	–	–	–	
Neonicotinoid herbicides											
Dinotefuran	-0.55	$7.3 \times 10^{-2}$	0.13	0.037	0.039	–	0.106	0.106	0.308	–	Noro et al. 2019, 2020
Clothianidin	-0.13	$6.9 \times 10^{-3}$	0.11	0.22	0.056	–	0.242	0.113	0.27	–	Noro et al. 2019, 2020
Thiamethoxam	0.57	$2.7 \times 10^{-2}$	0.12	0.21	0.042	–	0.202	0.100	0.366	–	Noro et al. 2019, 2020
Imidacloprid	0.70	$9.3 \times 10^{-3}$	0.12	0.37	0.045	–	0.257	0.122	0.686	–	Noro et al. 2019, 2020
Acetamiprid	0.80	$3.1 \times 10^{-3}$	0.12	0.31	0.052	–	0.239	0.104	0.445	–	Noro et al. 2019, 2020
Thiacloprid	1.26	$6.3 \times 10^{-3}$	0.12	0.38	0.057	–	0.214	0.123	0.548	–	Noro et al. 2019, 2020

Linear  
alkylbenzene  
sulfonates (LAS)

C <sub>10</sub> -LAS*	1.94	–	$1.7 \times 10^{-2}$	–	–	0.22	–	–	–	0.101	Noro et al. 2021
C <sub>11</sub> -LAS*	2.43	–	$8.1 \times 10^{-3}$	–	–	0.21	–	–	–	0.139	Noro et al. 2021
C <sub>12</sub> -LAS*	2.92	–	$4.3 \times 10^{-3}$	–	–	0.21	–	–	–	0.110	Noro et al. 2021
C <sub>13</sub> -LAS*	3.42	–	$2.7 \times 10^{-3}$	–	–	0.22	–	–	–	0.071	Noro et al. 2021
C <sub>14</sub> -LAS*	–	–	$1.1 \times 10^{-3}$	–	–	0.40	–	–	–	0.035	Noro et al. 2021

200

201 A correlation between the log  $k_m$  values and the log  $K_{ow}$  values ( $K_{ow}$ ; octanol–water partition  
202 coefficient) is shown in Fig. 1. The  $k_{m \text{ PES}}$  values and  $k_{m \text{ PTFE}}$  values for the LAS were negatively  
203 correlated with the  $K_{ow}$  values, thereby implying that sorption of the contaminants on the  
204 membrane interfered with the permeation of the contaminants (37). The neonicotinoid herbicides  
205 did not adsorb on the PTFE membrane, which resulted in constant  $k_{m \text{ PTFE}}$  values for the  
206 neonicotinoid herbicides (Fig. 1 (5)). The mean  $k_{m \text{ PES}}$  values of neonicotinoid herbicides in this  
207 study ( $0.021 \text{ min}^{-1}$ ) were higher than those in a previous study conducted in cells ( $0.0053 \text{ min}^{-1}$ )  
208 (5). Note that the data were taken from Noro et al. (5) (Supplemental Table 4) and calculated  
209 using Eq. (1). Water boundary layers (WBL) on both sides of the membrane in the cells may  
210 have induced low  $k_m$  values in a previous study (28).



**Figure 1.**  $\text{Log } k_m$  vs.  $\text{Log } K_{ow}$ .  $k_m$ : penetration rate constant ( $\text{min}^{-1}$ ),  $K_{ow}$ : octanol–water partition coefficient. The solid lines indicate linear regressions.

No correlation between the  $k_m$  values and  $R_s$  values was observed (Fig. S2). However, diffusion through the membrane may dominate mass transfers and POCIS uptake rates (29). This implies that there may have been a degree of sorbent kinetics in the POCIS uptake.

#### *Flow velocity determination*

The flow velocity data in the POCIS device were required to conduct the sorption experiment because flow velocity can potentially affect the sorption rate. The Alabaster sensor along with the required agitation condition was used to determine the flow velocity in the POCIS device (35). It was calculated to be  $0.06 \text{ cm s}^{-1}$ .

A previous study indicated that WBL exists on the membrane when the flow velocity is above  $6 \text{ cm s}^{-1}$  (28). Thus, WBL was expected to exist and affect the mass transfer in the POCIS devices

in this study. The flow velocity outside the POCIS devices in the calibration experiments (18 cm s<sup>-1</sup>) was above 6 cm s<sup>-1</sup>, thereby implying that there was no WBL outside the POCIS device (6).

The flow velocity in the glass beakers was 0.06 cm s<sup>-1</sup> in the condition described in “*Sorption experiment*”. Thus, we concluded that this agitation condition replicated the flow velocity in the POCIS device.

#### *Adsorption rate constants*

The adsorption rate constants ( $k_s$ ) of the PPPs, neonicotinoid herbicides, and LAS were estimated via the adsorption experiments. Oasis HLB was used for PPPs and neonicotinoid herbicides. ENVI-Carb was used for neonicotinoid herbicides, and Oasis WAX was used for LAS. The concentrations of the contaminants gradually decreased with time in the beaker (Fig. S3). The  $k_s$  values of this study should reflect the actual sorption kinetics for the POCIS uptake because the adsorption experiments were conducted under a similar flow velocity condition as the calibrations of the POCIS devices (5,6,34).

The adsorption rate constants were calculated by fitting the first-order reaction equation as follows:

$$C_b = C_o e^{-k_s' t} \quad (2).$$

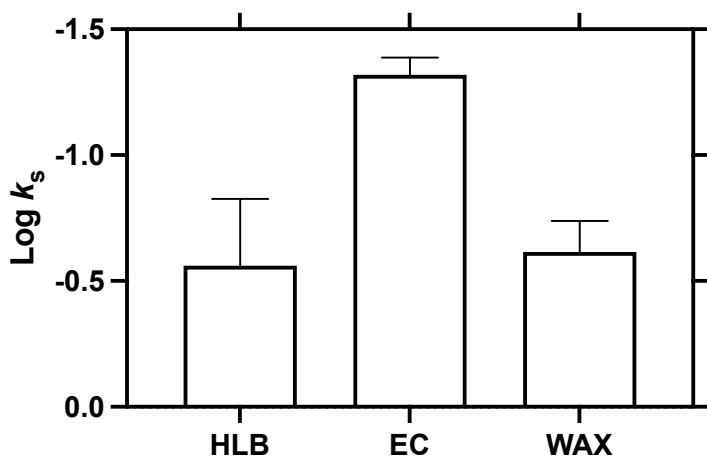
where  $C_b$  (μg L<sup>-1</sup>) is the concentration of the contaminants in the beaker,  $C_o$  (μg L<sup>-1</sup>) is the initial value of  $C_b$ ,  $k_s'$  (min<sup>-1</sup>) is the apparent adsorption rate constant, and  $t$  (min) is the time.

Then, the  $k_s$  (min<sup>-1</sup>) values were calculated from the  $k_s'$  values to correct for the influence of the sorbent mass as follows:

245 
$$k_s = \frac{m_p}{m} \times k_s' \quad (3)$$

246 where  $m_p$  (mg) is the mass of the sorbent in the POCIS devices (220 mg) and  $m$  (mg) is the mass  
 247 of the sorbent weighed in the glass beakers (50 mg).

248 The results of the adsorption experiments and  $k_s$  values are shown in Fig. 2 and Table 1,  
 249 respectively. The  $k_{s\text{ HLB}}$ ,  $k_{s\text{ EC}}$ , and  $k_{s\text{ WAX}}$  values indicate the  $k_s$  values for the Oasis HLB, Envi-  
 250 Carb, and Oasis WAX, respectively.



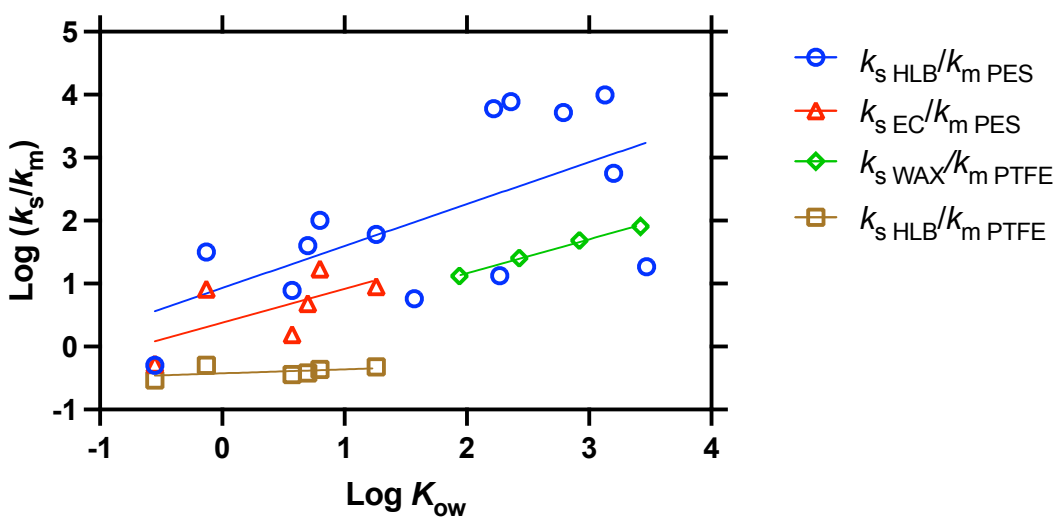
251 **Figure 2.** Log  $k_s$  values for each sorbent.  $k_s$ : sorption rate constant ( $\text{min}^{-1}$ ). Oasis HLB (HLB) was  
 252 evaluated for PPPs and neonicotinoid herbicides. Envi-Carb (EC) was evaluated for neonicotinoid  
 253 herbicides. Oasis WAX (WAX) was evaluated for the linear alkylbenzene sulfonates. Error bars  
 254 show 1  $\sigma$ .

255 The  $k_{s\text{ HLB}}$ ,  $k_{s\text{ EC}}$ , and  $k_{s\text{ WAX}}$  values ranged from 0.037 (dinotefuran) to 0.40 (furametpyr), from  
 256 0.039 (dinotefuran) to 0.57 (thiacloprid), and from 0.21 ( $\text{C}_{11}$ -LAS,  $\text{C}_{12}$ -LAS) to 0.40 ( $\text{C}_{14}$ -LAS)  
 257 ( $\text{min}^{-1}$ ), respectively (Table 1). The  $k_{s\text{ HLB}}$  values of the neonicotinoid herbicides (0.039  
 258 (dinotefuran) – 0.38 (thiacloprid)) were higher than those of the  $k_{s\text{ EC}}$  values (0.037 (dinotefuran)  
 259 – 0.057 (thiacloprid)), whereas the sorption coefficients ( $K_d$ ; L/kg) of the neonicotinoid

herbicides with Oasis HLB were lower than those with ENVI-Carb (5). This implies that the adsorption rate may depend on other characteristics (i.e., particle size) of the sorbent besides the capacity. The elevated  $k_s$  values of Oasis HLB may have resulted in the high  $R_s$  values for neonicotinoid herbicides compared to ENVI-Carb (Table 1) (5,6). Therefore, the sorption rate can be a parameter to predict the  $R_s$  values of highly hydrophilic compounds ( $\log K_{ow} < 2$ ) such as neonicotinoid herbicides.

#### *Relationship of $K_{ow}$ and $k_m/k_s$ ratio*

The correlation between the  $K_{ow}$  values and  $k_s/k_m$  ratios was obtained to investigate the kinetics of the POCIS uptake (Fig. 3). The  $k_{s\text{ HLB}}/k_{m\text{ PES}}$ ,  $k_{s\text{ EC}}/k_{m\text{ PES}}$ , and  $k_{s\text{ WAX}}/k_{m\text{ PTFE}}$  ratios were positively correlated with the  $K_{ow}$  values, whereas  $k_{s,\text{EC}}/k_{m,\text{PES}}$  and PTFE ratios were constant. The high  $k_s/k_m$  ratios indicated that the adsorption rate was higher than the penetration rate. In short, permeation is the rate-limiting step for the POCIS uptake of contaminants with a high  $k_s/k_m$  ratio. Thus, the POCIS uptake kinetics of contaminants with high  $\log K_{ow}$  values should be controlled by the membrane.





**Figure 3.** Log ( $k_s/k_m$ ) vs. log  $K_{ow}$ .  $k_m$ : penetration rate constant ( $\text{min}^{-1}$ ),  $k_s$ : sorption rate constant ( $\text{min}^{-1}$ ),  $K_{ow}$ : octanol–water partition coefficient. Solid lines indicate linear regressions. The  $k_{s_{HLB}}$  values are the sorption coefficients of Oasis HLB for PPPs and neonicotinoid herbicides. The  $k_{s_{EC}}$  values are the sorption coefficients of Envi-Carb for neonicotinoid herbicides. The  $k_{s_{WAX}}$  values are the sorption coefficients of Oasis WAX for linear alkylbenzene sulfonates. The  $k_{m_{PES}}$  values are the permeation coefficients of polyethersulfonate (PES) membranes for PPPs and neonicotinoid herbicides. The  $k_{m_{PTFE}}$  values are the permeation coefficients of polytetrafluoroethylene (PTFE) membranes for the neonicotinoid herbicides and the linear alkylbenzene sulfonates.

The log  $k_{s_{EC}}/k_{m_{PES}}$  ratios and the log  $k_{s_{WAX}}/k_{m_{PTFE}}$  ratios were relatively low and ranged from –0.27 to 1.9, resulting from the low  $k_{s_{EC}}$  values and the high  $k_{m_{PTFE}}$  values. Therefore, the uptakes of PES-EC POCIS and PTFE-WAX POCIS may be controlled by both the membranes and sorbents. The log  $k_{s_{HLB}}/k_{m_{PTFE}}$  ratios were the lowest group in study, ranging from –0.53 to –0.30, thereby implying that the sorbent kinetics may have dominated the uptake of the POCIS device with the PTFE membrane and the Oasis HLB for the neonicotinoid herbicides.

#### *Implications for $R_s$ predictions*

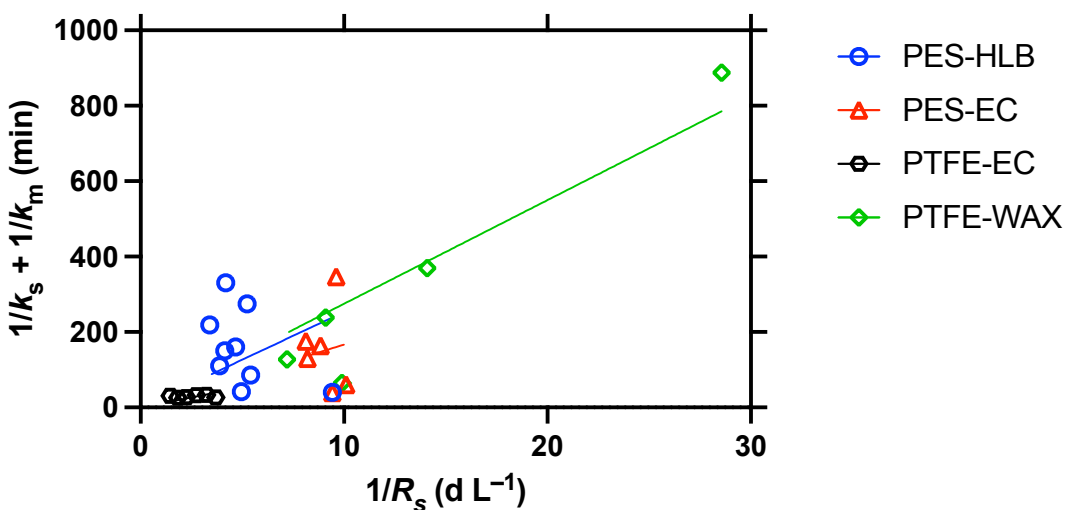
The aforementioned experimental results have important implications for  $R_s$  predictions. Low  $k_m$  values were obtained for chemicals with low  $K_{ow}$  values, thereby indicating that the sorption of chemicals on the membrane may constitute a limiting factor for permeation (37). The  $k_s$  values depended on the types of sorbents instead of the  $K_{ow}$  values. Low  $k_s/k_m$  ratios were obtained for chemicals with low  $K_{ow}$  values, which implied that the POCIS uptake for the hydrophilic compounds was controlled by both membrane and sorbent kinetics.

$k_s$  and  $k_m$  values may be helpful in selecting combination of membranes and sorbents for the POCIS device. High  $k_s$  and  $k_m$  values may result in high  $R_s$  values. Accordingly, the  $R_s$  values of the POCIS device with the PTFE membrane and Envi-Carb were higher than those of the device containing the PES membrane and Envi-Carb (5). Therefore, a suitable combination of the membrane and sorbent can be selected based on the  $k_m$  values,  $k_s$  values, and the adsorption capacity for the duration and concentration of the contaminants in the sampling campaigns.

Additionally,  $R_s$  values may be predicted based on the modified first-order chemical reaction model reported by Morin et al. (31) as follows:

$$\frac{1}{R_s} = A \times \left( \frac{1}{k_m} + \frac{1}{k_s} \right) \quad (4)$$

where  $A$  ( $L^{-1}$ ) is the proportionality coefficient. The  $1/R_s$  values and  $(1/k_m + 1/k_s)$  were compared to validate the model (Fig. 4). The  $A$  value and the coefficient of determination ( $R^2$ ) for the regression line were 0.036 L and 0.94, respectively, for the PTFE-WAX POCIS measuring LAS (Fig. 4). This implies that the model can be used as a potential  $R_s$  prediction tool. However, the model did not fit the PPPs and neonicotinoid herbicides (Fig. 4). The difference in the molecular structures among LAS is the length of the alkyl chain. The simple difference in the molecular structure may induce a correspondence to the model with the experimental values obtained in this study. This implies that the  $R_s$  prediction model can be applied to other families of molecules with simple differences in their molecular structures, such as perfluorooctanates and perfluorooctane sulfonates. We are currently working on comprehensively predicting the  $R_s$  values of a wide variety of contaminants, which will be detailed in a future study



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## Author Contributions

K. Noro, Y. Yabuki, and S. Nakamura conceived and designed the experiments. K. Noro, A. Banno, J. Ono, and Y. Yabuki performed the experiments and chemical analysis. K. Noro wrote the manuscript. Y. Yabuki, A. Banno, J. Ono, and S. Nakamura provided editorial assistance.

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## Notes

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Data availability statement: The datasets generated during and/or analyzed during the current study are shown in the supplemental material as figures.

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## REFERENCES

1. Alvarez, D. A.; Petty, J. D.; Huckins, J. N.; Jones-Lepp, T. L.; Getting, D. T.; Goddard, J. P.; Manahan, S. E. Development of a passive, in situ, integrative sampler for hydrophilic organic

- 352 contaminants in aquatic environments. *Environ. Toxicol. Chem.* **2004**, 23 (7), 1640–1648.  
353 [10.1897/03-603](https://doi.org/10.1897/03-603).
- 354 2. Dalton, R. L.; Pick, F. R.; Boutin, C.; Saleem, A. Atrazine contamination at the  
355 watershed scale and environmental factors affecting sampling rates of the polar organic chemical  
356 integrative sampler (POCIS). *Environ. Pollut.* **2014**, 189, 134–142.  
357 <https://doi.org/10.1016/j.envpol.2014.02.028>.
- 358 3. Kaserzon, S. L.; Kennedy, K.; Hawker, D. W.; Thompson, J.; Carter, S.; Roach, A. C.;  
359 Booij, K.; Mueller, J. F. Development and calibration of a passive sampler for perfluorinated  
360 alkyl carboxylates and sulfonates in water. *Environ. Sci. Technol.* **2012**, 46 (9), 4985–4993.  
361 [10.1021/es300593a](https://doi.org/10.1021/es300593a).
- 362 4. Lissalde, S.; Mazzella, N.; Mazellier, P. Polar organic chemical integrative samplers for  
363 pesticides monitoring: Impacts of field exposure conditions. *Sci. Total Environ.* **2014**, 488–489,  
364 188–196. <https://doi.org/10.1016/j.scitotenv.2014.04.069>.
- 365 5. Noro, K.; Endo, S.; Shikano, Y.; Banno, A.; Yabuki, Y. Development and calibration of  
366 the polar organic chemical integrative sampler (POCIS) for neonicotinoid pesticides. *Environ.*  
367 *Toxicol. Chem.* **2020**, 39 (7), 1325–1333. [10.1002/etc.4729](https://doi.org/10.1002/etc.4729).
- 368 6. Noro, K.; Yabuki, Y.; Banno, A.; Tawa, Y.; Nakamura, S. Validation of the application  
369 of a polar organic chemical integrative sampler (POCIS) in non-steady-state conditions in  
370 aquatic environments. *J. Water Environ. Technol.* **2019**, 17 (6), 432–447. [10.2965/jwet.19-057](https://doi.org/10.2965/jwet.19-057).

- 371 7. Rosen, G.; Lotufo, G. R.; George, R. D.; Wild, B.; Rabalais, L. K.; Morrison, S.; Belden,  
372 J. B. Field validation of POCIS for monitoring at underwater munitions sites. *Environ. Toxicol.*  
373 *Chem.* **2018**, 37 (8), 2257–2267. [10.1002/etc.4159](https://doi.org/10.1002/etc.4159).
- 374 8. Thomatou, A. A.; Zacharias, I.; Hela, D.; Konstantinou, I. Passive sampling of selected  
375 pesticides in aquatic environment using polar organic chemical integrative samplers. *Environ.*  
376 *Sci. Pollut. Res. Int.* **2011**, 18 (7), 1222–1233. [10.1007/s11356-010-0436-6](https://doi.org/10.1007/s11356-010-0436-6).
- 377 9. Yabuki, Y.; Nagai, T.; Inao, K.; Ono, J.; Aiko, N.; Ohtsuka, N.; Tanaka, H.; Tanimori, S.  
378 Temperature dependence on the pesticide sampling rate of polar organic chemical integrative  
379 samplers (POCIS). *Biosci. Biotechnol. Biochem.* **2016**, 80 (10), 2069–2075.  
380 [10.1080/09168451.2016.1191329](https://doi.org/10.1080/09168451.2016.1191329).
- 381 10. Yabuki, Y.; Ono, J.; Nagai, T.; Inao, K.; Tanimori, S. Determining the suitability of a  
382 polar organic chemical integrated sampler (POCIS) for the detection of pesticide residue in the  
383 Ishikawa River and its tributary in Osaka, Japan. *J. Pestic. Sci.* **2018**, 43 (1), 18–23.  
384 [10.1584/jpestics.D17-063](https://doi.org/10.1584/jpestics.D17-063).
- 385 11. Yargeau, V.; Taylor, B.; Li, H.; Rodayan, A.; Metcalfe, C. D. Analysis of drugs of abuse  
386 in wastewater from two Canadian Cities. *Sci. Total Environ.* **2014**, 487, 722–730.  
387 <https://doi.org/10.1016/j.scitotenv.2013.11.094>.
- 388 12. Zhang, Z.; Trolldborg, M.; Yates, K.; Osprey, M.; Kerr, C.; Hallett, P. D.; Baggaley, N.;  
389 Rhind, S. M.; Dawson, J. J. C.; Hough, R. L. Evaluation of spot and passive sampling for  
390 monitoring, flux estimation and risk assessment of pesticides within the constraints of a typical

391 regulatory monitoring scheme. *Sci. Total Environ.* **2016**, 569–570, 1369–1379.  
 392 <https://doi.org/10.1016/j.scitotenv.2016.06.219>.

393 13. Arditsoglou, A.; Voutsas, D. Passive sampling of selected endocrine disrupting  
 394 compounds using polar organic chemical integrative samplers. *Environ. Pollut.* **2008**, 156 (2),  
 395 316–324. <https://doi.org/10.1016/j.envpol.2008.02.007>.

396 14. Charlestra, L.; Amirbahman, A.; Courtemanch, D. L.; Alvarez, D. A.; Patterson, H.  
 397 Estimating pesticide sampling rates by the polar organic chemical integrative sampler (POCIS)  
 398 in the presence of natural organic matter and varying hydrodynamic conditions. *Environ. Pollut.*  
 399 **2012**, 169, 98–104. <https://doi.org/10.1016/j.envpol.2012.05.001>.

400 15. Fauvelle, V.; Mazzella, N.; Delmas, F.; Madarassou, K.; Eon, M.; Budzinski, H. Use of  
 401 mixed-mode ion exchange sorbent for the passive sampling of organic acids by polar organic  
 402 chemical integrative sampler (POCIS). *Environ. Sci. Technol.* **2012**, 46 (24), 13344–13353.  
 403 [10.1021/es3035279](https://doi.org/10.1021/es3035279).

404 16. Ibrahim, I.; Togola, A.; Gonzalez, C. Polar organic chemical integrative sampler (POCIS)  
 405 uptake rates for 17 polar pesticides and degradation products: Laboratory calibration. *Environ.*  
 406 *Sci. Pollut. Res. Int.* **2013**, 20 (6), 3679–3687. [10.1007/s11356-012-1284-3](https://doi.org/10.1007/s11356-012-1284-3).

407 17. Lissalde, S.; Mazzella, N.; Fauvelle, V.; Delmas, F.; Mazellier, P.; Legube, B. Liquid  
 408 chromatography coupled with tandem mass spectrometry method for thirty-three pesticides in  
 409 natural water and comparison of performance between classical solid phase extraction and  
 410 passive sampling approaches. *J. Chromatogr. A* **2011**, 1218 (11), 1492–1502.  
 411 <https://doi.org/10.1016/j.chroma.2011.01.040>.

- 412 18. Mazzella, N.; Dubernet, J. F.; Delmas, F. Determination of kinetic and equilibrium  
413 regimes in the operation of polar organic chemical integrative samplers: Application to the  
414 passive sampling of the polar herbicides in aquatic environments. *J. Chromatogr. A* **2007**, *1154*  
415 (1–2), 42–51. <https://doi.org/10.1016/j.chroma.2007.03.087>.
- 416 19. Bartelt-Hunt, S. L.; Snow, D. D.; Damon-Powell, T.; Brown, D. L.; Prasai, G.; Schwarz,  
417 M.; Kolok, A. S. Quantitative evaluation of laboratory uptake rates for pesticides,  
418 pharmaceuticals, and steroid hormones using pocis. *Environ. Toxicol. Chem.* **2011**, *30* (6), 1412–  
419 1420. <https://doi.org/10.1002/etc.514>.
- 420 20. Li, H.; Helm, P. A.; Metcalfe, C. D. Sampling in the great lakes for pharmaceuticals,  
421 personal care products, and endocrine-disrupting substances using the passive polar organic  
422 chemical integrative sampler. *Environ. Toxicol. Chem.* **2010**, *29* (4), 751–762. [10.1002/etc.104](https://doi.org/10.1002/etc.104).
- 423 21. Li, H.; Helm, P. A.; Paterson, G.; Metcalfe, C. D. The effects of dissolved organic matter  
424 and pH on sampling rates for polar organic chemical integrative samplers (POCIS).  
425 *Chemosphere* **2011**, *83* (3), 271–280. <https://doi.org/10.1016/j.chemosphere.2010.12.071>.
- 426 22. MacLeod, S. L.; McClure, E. L.; Wong, C. S. Laboratory calibration and field  
427 deployment of the polar organic chemical integrative sampler for pharmaceuticals and personal  
428 care products in wastewater and surface water. *Environ. Toxicol. Chem.* **2007**, *26* (12), 2517–  
429 2529. [10.1897/07-238.1](https://doi.org/10.1897/07-238.1).
- 430 23. Metcalfe, C. D.; Sultana, T.; Li, H.; Helm, P. A. Current-use pesticides in urban  
431 watersheds and receiving waters of Western Lake Ontario measured using polar organic



432 chemical integrative samplers (POCIS). *J. Gr. Lakes Res.* **2016**, 42 (6), 1432–1442.  
 433 <https://doi.org/10.1016/j.jglr.2016.08.004>.

434 24. Snow, D. D.; Chakraborty, P.; Uralbekov, B.; Satybaldiev, B.; Sallach, J. B.; Thornton  
 435 Hampton, L. M.; Jeffries, M.; Kolok, A. S.; Bartelt-Hunt, S. B. Legacy and current pesticide  
 436 residues in Syr Darya, Kazakhstan: Contamination status, seasonal variation and preliminary  
 437 ecological risk assessment. *Water Res.* **2020**, 184, 116141.  
 438 <https://doi.org/10.1016/j.watres.2020.116141>.

439 25. Miller, T. H.; Baz-Lomba, J. A.; Harman, C.; Reid, M. J.; Owen, S. F.; Bury, N. R.;  
 440 Thomas, K. V.; Barron, L. P. The first attempt at non-linear in silico prediction of sampling rates  
 441 for polar organic chemical integrative samplers (POCIS). *Environ. Sci. Technol.* **2016**, 50 (15),  
 442 7973–7981. [10.1021/acs.est.6b01407](https://doi.org/10.1021/acs.est.6b01407).

443 26. Taylor, R. B.; Toteu Djomte, V.; Bobbitt, J. M.; Hering, A. S.; Chen, S.; Chambliss, C.  
 444 K. Effects of environmentally relevant concentration exposure profiles on polar organic chemical  
 445 integrative sampler (POCIS) sampling rates. *Environ. Sci. Technol.* **2020**, 54 (14), 8848–8856.  
 446 [10.1021/acs.est.0c02601](https://doi.org/10.1021/acs.est.0c02601).

447 27. Djomte, V. T.; Chen, S.; Chambliss, C. K. Effects of suspended sediment on pocis  
 448 sampling rates. *Chemosphere* **2020**, 241, 124972.  
 449 <https://doi.org/10.1016/j.chemosphere.2019.124972>.

450 28. Djomte, V. T.; Taylor, R. B.; Chen, S.; Booij, K.; Chambliss, C. K. Effects of  
 451 hydrodynamic conditions and temperature on polar organic chemical integrative sampling rates.  
 452 *Environ. Toxicol. Chem.* **2018**, 37 (9), 2331–2339. [10.1002/etc.4225](https://doi.org/10.1002/etc.4225).

- 453 29. International Organization for Standardization Water quality–sampling–. *Part 23:*  
454 *Guidance on passive sampling in surface waters* **2011**, 23.
- 455 30. Jeong, Y.; Kwon, H. A.; Jeon, H. P.; Schäffer, A.; Smith, K. . Quantitative evaluation of  
456 polyethersulfone and polytetrafluoroethylene membrane sorption in a polar organic chemical  
457 integrative sampler (POCIS). *Environ Pollut.* **2020** 266 (2), 115224.  
458 <https://doi.org/10.1016/j.envpol.2020.115224>.
- 459 31. Morin, N. A. O.; Mazzella, N.; Arp, H. P. H.; Randon, J.; Camilleri, J.; Wiest, L.;  
460 Coquery, M.; Miège, C. Kinetic accumulation processes and models for 43 micropollutants in  
461 “pharmaceutical” POCIS. *Sci. Total Environ.* **2018**, 615, 197–207.  
462 <https://doi.org/10.1016/j.scitotenv.2017.08.311>.
- 463 32. Ahrens, L.; Daneshvar, A.; Lau, A. E.; Kreuger, J. Concentrations, fluxes and field  
464 calibration of passive water samplers for pesticides and hazard-based risk assessment. *Sci. Total*  
465 *Environ.* **2018**, 637–638, 835–843. <https://doi.org/10.1016/j.scitotenv.2018.05.039>.
- 466 33. Poulier, G.; Lissalde, S.; Charriau, A.; Buzier, R.; Delmas, F.; Gery, K.; Moreira, A.;  
467 Guibaud, G.; Mazzella, N. Can pocis be used in water framework directive (2000/60/ec)  
468 monitoring networks? A study focusing on pesticides in a French agricultural watershed. *Sci.*  
469 *Total Environ.* **2014**, 497–498, 282–292. <https://doi.org/10.1016/j.scitotenv.2014.08.001>.
- 470 34. Noro, K.; Yabuki, Y.; Ono, J.; Nakamura, S. Development and evaluation of polar  
471 organic chemical integrative sampler (POCIS) for linear alkylbenzene sulfonate. *ChemRxiv*.  
472 2021. <https://doi.org/10.26434/chemrxiv.14608164.v2>

- 473 35. Booij, K.; Maarsen, N. L.; Theeuwen, M.; van Bommel, R. A method to account for the  
474 effect of hydrodynamics on polar organic compound uptake by passive samplers. *Environ.*  
475 *Toxicol. Chem.* **2017**, *36* (6), 1517–1524. [10.1002/etc.3700](https://doi.org/10.1002/etc.3700).
- 476 36. Banno, A.; Yabuki, Y. Simultaneous analysis of seven neonicotinoid pesticides in  
477 agricultural products involving solid-phase extraction and surrogate compensation using liquid  
478 chromatography-tandem mass spectrometry. *J. Pestic. Sci.* **2020**, *45* (1), 29–38.  
479 [10.1584/jpestics.D19-055](https://doi.org/10.1584/jpestics.D19-055).
- 480 37. Endo, S.; Matsuura, Y. Characterizing sorption and permeation properties of membrane  
481 filters used for aquatic integrative passive samplers. *Environ. Sci. Technol.* **2018**, *52* (4), 2118–  
482 2125. [10.1021/acs.est.7b05144](https://doi.org/10.1021/acs.est.7b05144).