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ABSTRACT

The Polar Organic Chemical Integrative Samplers (POCIS) is the most widely used passive sampler for hydrophilic compounds, but unsuitable for certain ionic organic contaminants. The Diffusive Gradient in Thin-Film technique (o-DGT) has shown positive results for both ionic and hydrophilic compounds. However, a calibration step is now needed to evaluate kinetic constant of accumulation for a wide range of molecules.

In this study, o-DGT and POCIS were compared for the sampling of three families of micropollutants of potential risk to aquatic environments: 53 pesticides, 36 pharmaceuticals and 20 hormones. A calibration experiment was conducted to compare the kinetic models and constants from a scientific and practical perspective. The results are discussed in a single table that summarizes the performance of both passive samplers for the 109 compounds of interest. The advantage of o-DGT is that it allows linear accumulation for 72 compounds versus only 33 with POCIS. The mean times to equilibrium obtained with o-DGT are higher than those obtained with POCIS. These results confirm that the presence of a diffusion gel delays the achievement of equilibrium during compound accumulation. Therefore, o-DGT can be considered for situations where POCIS cannot be used due to non-linear accumulation over a typical 14-day deployment period. However, overall sampling rates and mass transfer coefficients also appear reduced with o-DGT, which is explained by the smaller exchange surface area, as well as the consideration of an additional diffusive layer in this device. This paper also showed that the most appropriate membrane to sample polar compounds with o-DGT was a polyethersulfone polymer with a pore size of 5 µm.

INTRODUCTION

Passive sampler devices (PSD) were developed in order to improve sampling and thus the determination of the chemical contamination level in aquatic environments (Huckins et al., 2006; Vrana et al., 2005). These passive sampling tools have several advantages. For example, sampling over a more or less long period of time (a few days to several months) makes it possible to obtain a better temporal representativeness by determining the average micropollutant concentration over the exposure period (TWAC for time-weighted average concentration). Passive sampling also allows the pollutants to be extracted and pre-concentrated in situ, which limits the problems of sample conservation and allows the assessment of the concentration of trace pollutants (< ng L^{-1}). Recently, PSD were officially

adopted in France as possible tools for improving the regulatory monitoring of water quality (introduction of these tools for certain substances in the new French monitoring decree of 2022, establishing the monitoring program for water status, , April 2022, https://www.legifrance.gouv.fr/jorf/id/JORFTEXT000045780020).

For TWAC calculation, kinetic constants for each compound have to be determined in laboratory or *in situ* by achieving calibrations.

Passive sampling of hydrophobic compounds is now well developed but many uncertainties still exist, in particular for the sampling of hydrophilic and ionic compounds (Miège et al., 2015). Currently, the most commonly used passive sampler for hydrophilic compounds is POCIS (Polar Organic Chemical Integrative Sampler). However, POCIS remains unsuitable for sampling some ionic organic contaminants such as acid herbicides. It has been shown that the half time to reach equilibrium ($t_{1/2}$) for ionic compounds was often lower than that observed for neutral compounds and mostly lower than 14 days (Morin et al., 2013). This is a problem given that PSD cannot be placed in the field for a longer time than their $t_{1/2}$, otherwise the linear regime of accumulation is not applicable. In addition, a phenomenon of delayed accumulation (i.e. "lag phase") can be observed, most generally for neutral hydrophobic compounds (log K_{OW} > 4), such as hormones (Morin et al., 2013). On the contrary, a rapid accumulation at the beginning of exposure leading to a biphasic accumulation (i.e. "burst effect") has been observed for anionic compounds (Bäuerlein et al., 2012, Fauvelle et al. 2014; Morin et al. 2013), and less generally for a few neutral compounds with a log K_{OW} < 3 (Morin et al., 2013). This phenomenon may be partly due to the initial wetting of the membrane and/or the adsorbent phase, which would increase accumulation rates (Mazzella et al., 2007). These different phenomena can make kinetic models inapplicable in this case (anisotropic exchanges), making any TWAC estimation difficult.

Given the limitations noted to date, an alternative to POCIS is to adapt the DGT (Diffusive Gradient in Thin film) technique, initially developed for metals in labile form (Davison and Zhang, 1994), to organic compounds (Chen et al., 2012). Nowadays, many compounds are studied with this technique, mainly pharmaceuticals and pesticides (Amato et al., 2018; Chen et al., 2013; Ren et al., 2018; Stroski et al., 2018). Each component of o-DGT can be chosen according to the compounds studied. o-DGT was generally optimized only for fewer than 20 compounds, mainly from the same chemical family or similar structures. Membranes used on o-DGT device have to respect two criteria: (i) to ensure the protection of o-DGT and thus of diffusive gel and resin, (ii) not to interfere with the diffusion of compounds from the sampled

medium to the resin. Polyethersulfone (PES) is the most used and reported membrane for the sampling of many organic compounds (Mechelke et al., 2019) including pharmaceuticals and especially antibiotics (Chen et al., 2015, 2014, 2013, 2012; Ren et al., 2018; Xie et al., 2018; Zhang et al., 2018). This PES material, also used with POCIS, has the advantage of being effective in limiting biofouling (Uher et al., 2012). However, this membrane presents the disadvantage of accumulating some hydrophobic compounds (Challis et al., 2016; Chen et al., 2017; D'Angelo and Starnes, 2016; Xie et al., 2018; Zhang et al., 2019; Zheng et al., 2015). Concerning diffusive gel, agarose gel is mainly used for the sampling of many organic compounds including pharmaceuticals, pesticides, bisphenols, parabens or flame-retardants. Resin is composed of a gel and a receiving phase. The gel used is generally the same as that used as a diffusive gel, while receiving phases are chosen according to their affinity to the compounds studied. For this purpose, the accumulation of compounds in the receiving phases or resins, the elution yield and the maximum capacity of the receiving phases or resin are studied. The Oasis® HLB and XAD-18 phases are the two most used receiving phases (Amato et al., 2018; Challis et al., 2016; Chen et al., 2012; Guo et al., 2017; Zhang et al., 2018; Zou et al., 2018). In the case of o-DGT, the calibration step is not essential, when diffusive constants are available. Indeed, the diffusion of the compounds through the diffusive layer (gel and/or membrane) can be determined using other methods such as the diffusion cell method or slice stacking method (Bonnaud et al., 2021). However, these methods do not provide access to the accumulation kinetics and sampling rates of the entire tool. Consequently, calibration experiments were carried out in few studies for some organic compounds such as pharmaceuticals and pesticides (Belles et al., 2017; Buzier et al., 2019; Challis et al., 2016; Fauvelle et al., 2015; Urík and Vrana, 2019; Xie et al., 2018; Zhang et al., 2019).

The aim here was to calibrate the assembled o-DGT under controlled flow and temperature conditions, in order to determine its performances (i.e. sampling rates, half time to equilibrium, achievable limits of quantifications, etc.). This calibration was performed with a large panel of 109 compounds covering a wide range of physico-chemical properties. They represent three families of micropollutants (pesticides, pharmaceutical compounds and hormones), occurring in aquatic environments and presenting a potential risk of toxicity. In this study, the more usual POCIS were also studied allowing comparison with o-DGT.

1. EXPERIMENTAL SECTION

1.1. Consumables and standard solutions

Ultrapure water (UPW) was produced by a Synergy UV system from Millipore (Billerica, MA, USA). Methanol (MeOH), acetonitrile (ACN) and ethyl-acetate (EA) were purchased from Biosolve (Dieuze, France). Pharmaceuticals POCIS were purchased from Exposmeter (Tavellsjö, Sweden). o-DGT media were purchased from DGT Research (Lancaster, UK). For o-DGT preparation, PES membranes (both pore sizes) and 0.45 µm nylon membranes (Nylaflo) were purchased from Pall (USA). The 5 µm nylon membranes, were purchased from Fisher Scientific (France) and cellulose membranes (0.45 and 5 µm pore sizes) were purchased from Whatmann (UK). For diffusive gel and resin, agarose powder was purchased from Sigma-Aldrich (Schnelldorf, Germany). Oasis® HLB phase used for resins is packaged in the form of a 6 g polypropylene cartridge (particle size 30 µm, specific surface 810 $m^2\ g^{-1}$, divinylbenzene N-vinyl-pyrrolidone, Waters, France). Suppliers and purity of analytical standards and internal standards are described in Table S2 and Table S3. Associated pesticides and internal standards were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) (purity > 95.5%). Hormones were obtained from Sigma Aldrich (Schnelldorf, Germany) and from LGC Standards (Luckenwalde, Germany) (purity > 95.6%). Internal standards associated to hormones were purchased from CDN isotopes (Sainte-Foy-la-Grande, France), AlsaChim (Illkirch-Graffenstaden, France) and Santa Cruz (Heidelberg, Germany) (purity > 95.1%). Pharmaceuticals were obtained from CIL (Sainte-Foy-la-Grande, France), Sigma Aldrich (Saint-Quentin Fallavier, France), VWR (Fontenay-sous-Bois, France) and CIL (Sainte-Foy-la-Grande, France) (purity > 95%). Internal standards of pharmaceuticals were obtained from CIL (Sainte-Foy-la-Grande, France) (purity > 98%). Stock solution of studied compounds were prepared at 200 mg L^{-1} in ACN or MeOH, which was used to prepare a solution at 5 mg L^{-1}. Internal standard solutions were also prepared in ACN or MeOH at 1 mg L^{-1} for pesticides and hormones and at 200 µg L^{-1} for pharmaceuticals. All working solutions were stored at -18°C for six months at the longest.

1.2. Characteristics of the studied molecules

The 109 studied compounds, as well as their physico-chemical properties, are reported in the supplementary information (SI) (Table S1). The studied compounds were chosen to cover a wide range of physico-chemical properties.

A total of 60 pesticides, 20 hormones and 45 pharmaceutical compounds were studied. Their physico-chemical properties are described in Table S1. The molar masses of the compounds studied ranged from 129 to 749 g mol^{-1}. The log D_{OW} of the compounds studied, taking into account the log K_{OW} (hydrophobicity) and the pKa (ionisation), ranged from - 3.6 to 5.2 at pH 7.4. Insecticides and fungicides studied are all in their neutral form at pH 7, while the herbicides and metabolites studied are, depending on the compound, in anionic or neutral form. The majority of the pesticides are hydrophilic (log K_{OW} < 2) to moderately hydrophilic (log K_{OW} < 3) and only 15 are hydrophobic (log K_{OW} > 4) to moderately hydrophobic (log K_{OW} > 3). Hormones are in their neutral form at pH 7 and are predominantly hydrophobic to moderately hydrophobic. The pharmaceutical compounds studied are predominantly hydrophilic to moderately hydrophilic. They are found in their neutral, anionic or cationic form at pH 7.

1.3. DGT preparation

AG diffusive gels (1.5 % AG) were prepared by placing AG in boiling UPW until dissolution. The mixture was cast between two preheated glass plates separated by Teflon spacers (1 mm thickness) and left to cool down until gelling. For the preparation of resins, 12 mL of mixture AG were mixed with 2 mg of Oasis HLB phase, cast between glass plates separated by Teflon spacers (0.5 mm thickness) and left for polymerization.

All gels and resins were hydrated in UPW for at least 24 hours (UPW was changed 2 times). For all gels and resins, we obtained 1 and 0.5 mm thick gel plates respectively. Indeed, gels and resins do not swell during hydration. Diffusive gels and resins of 2.5 cm diameter were cut out. Gels and resins were stocked in UPW at 4°C before o-DGT preparation. In order to choose the most adapted membrane, several experiments were carried out: protection of diffusion gel and resin by six membranes (PES, cellulose and nylon at two pore size (0.45 µm and 5 µm)) *in situ*, accumulation compounds in the six tested membranes and effect on diffusion compounds of 4 membranes (PES and nylon at both pore size) (see SI for details on experiment procedure). o-DGT were prepared by superposing a resin, an AG diffusive gel and a PES membrane (5 µm) inside a piston type molding (DGT Research, Lancaster, UK). Before exposure, o-DGT were stored at 4°C.

1.4. Calibration setup

The calibration system consisted of two aquariums filled with 50 L of tap water initially spiked at a nominal concentration of 5 µg L^{-1}. In order to prevent concentration variation during the experiment, 15 % of total water volume was renewed every day with freshly spiked tap water using a peristaltic pump (15 L day^{-1} for both aquariums) and overflow. Tap water was spiked using a syringe pump filled with spiking solution (50 $mg.L^{-1}$). The calibration system used in this study was the same as the one used by Morin et al (2013) which provides a water flowof around 10 $cm.s^{-1}$ by a diffusion ramp connected to an immersed pump. The system was maintained at 20°C by a thermostated water-bath. Water concentration was measured twice a week. Triplicates of o-DGT were exposed for 1, 3, 7, 10, 14, 21 and 28 days and triplicates of POCIS were exposed for 1, 2, 6, 12 hours and 1, 3, 7, 10, 14, 21 and 28 days. Temperature and physico-chemical parameters such as pH, conductivity and ionic strength (IS) were followed throughout the entire calibration period in each aquarium. Conductivity was 369.5 ± 12.1 $\mu S.cm^{-1}$ (n=44), pH was 8.2 ± 0.1 (n=44), ionic strength was 1.1 ± $0.003.10^{-2}$ mol L^{-1} (n=10) and temperature was 20.8 ± 0.4 °C (n=4104). For all these parameters, relative standard deviations were inferior to 3 %.

1.5. Sample preparation before analysis

Passive sampler. After exposure, o-DGT were disassembled immediately and resins were eluted. The elution procedure consists of leaving resin in 5 mL of MeOH for 24 h, then in 2.5 mL of MeOH twice for 10 min (ultrasonic). Eluents were evaporated under a dry gentle flow of N_2 and reconstituted into 1 mL of ACN. POCIS were disassembled and the sorbent was transferred into an empty solid-phase extraction (SPE) cartridge using ultrapure water and then dried under N_2. Elution of pesticides was performed using 3 mL of MeOH and then 3 mL of MeOH/EA 75/25. After elution, samples in solvents were evaporated under a gentle nitrogen flow and reconstituted with 1 mL of ACN. Elution of pharmaceuticals and hormones was performed using 10 mL of MeOH, then 10 mL of MeOH/DCM 50/50. In order to purify the extracts, they were filtered through an Oasis® HLB (6 mL, 200 mg) cartridge. Extracts obtained were divided into two parts (one part for hormones analysis and the other for pharmaceuticals analysis). After elution, extracts were evaporated under a gentle nitrogen flow at 30 °C (TurboVap, Uppsala, Sweden). For hormones, extracts were reconstituted with 500 µL of UPW/MeOH 65/35 (v/v) and for pharmaceuticals analysis, extracts were reconstituted with 500 µL of UPW/ACN 95/5 (v/v). To stay in analytical calibration range, each PSD extract was diluted, depending on exposure time, to obtain adequate mobile phase

mixtures (65/35 UPW/MeOH for hormones, 95/5 UPW/ACN for pharmaceuticals, 95/10 UPW/ACN for neutral pesticides and 10/90 UPW/ACN for anionic pesticides).

Water. For hormones and pharmaceuticals analysis, water samples were analyzed by direct injection after dilution to obtain the adequate mobile phase mixtures described above. For pesticides analysis, 2 mL of water were evaporated using a Speedvac concentrator SAVANT SPD121P (Thermo Fisher Scientific; Villebon sur Yvette, France) and reconstituted into adequate mobile phase mixture.

1.6. Theory and modelling – determination of sampling rates & accumulation model selection

After the exposure of a passive sampler to an aquatic environment, contaminant transfer occurs from the water to the passive sampler receiving phase. The accumulation of compounds in the receiving phase of the passive sampler can be generally modelled by the following Fickian diffusion relationship:

$$dN/dt = R_s(C_W - (N/(M_S K_{SW}))) \quad \textit{Equation 1}$$

with N being the amount sampled (g), R_s the sampling rate (L d^{-1}), M_S the sorbent mass (g), C_W the concentration in water (g L^{-1}), and K_{SW} the global equilibrium constant between the sampler and aqueous media (L g^{-1}).

$$N = C_W M_S K_{SW}\left(1 - \exp(-R_S t/M_S K_{SW})\right) \quad \textit{Equation 2}$$

By dividing both sides of Equation 2 by the sorbent mass, it allows the use of the concentration in the sampler (C_S) (Equation 3), and thus the determination of the concentration factor (CF) (Equation 4)

$$C_S = C_W K_{SW}\left(1 - \exp(-(R_S\, t)/M_S K_{SW})\right) \quad \textit{Equation 3}$$

$$CF = C_S/C_W = K_{SW}\left(1 - \exp(-(R_S\, t)/M_S K_{SW})\right) \quad \textit{Equation 4}$$

In addition, the elimination rate constant (k_e) can be defined by Equation 5. This constant can also be related to $t_{1/2}$, corresponding to the time it takes to reach 50 % of equilibrium (Equation 6).

$$k_e = R_S/M_S K_{SW} \quad \textit{Equation 5}$$

$$t_{1/2} = \ln 2/k_e \quad \textit{Equation 6}$$

During the linear regime ($t < t_{1/2}$), or when considering $K_{SW} \rightarrow \infty$, Equation 4 can be reduced and expressed with the sampling rate as follows:

$$CF = C_S/C_W = R_s t/M_S \quad \textit{Equation 7}$$

The mass transfer resistance, which is related to sampling rates, depends on thickness, distribution constant and diffusion coefficient between each compartment. For o-DGT, this mass transfer resistance can be described by Equation 8.

$$1/k_0 = A/R_S = 1/k_w + 1/k_m K_{MW} + 1/k_g K_{GM} + 1/k_s K_{SG} \quad \textit{Equation 8}$$

with k_0 being the overall transfer mass coefficient, k_w, the transfer mass coefficient in DBL, k_m, the transfer mass coefficient in membrane, k_g, the transfer mass coefficient in diffusive gel, k_s, the transfer mass coefficient in receiving phase, K_{MW}, the partition coefficient between membrane and water, K_{GM}, the partition coefficient between gel and membrane and K_{SG}, the partition coefficient between gel and receiving phase.

1.7. Analytical methods

Pesticides were analyzed with Dionex Ultimate 3000 HPLC (Thermo Fisher Scientific, Villebon-sur-Yvette, France). An API 2000 tandem mass spectrometer (Sciex, Villebon-sur-Yvette, France) was used for detection. Chromatographic separation of anionic pesticides was performed on Macherey-Nagel zwitterionic Nucleodur HILIC 3 µm, 100 Å, 125 mm × 2 mm while neutral pesticides were separated with a Gemini-NX C18 (3 µm, 100 × 2 mm) column by a SecurityGuard cartridge Gemini-NX C18 (4 × 2.0 mm) (Phenomenex, Le Pecq, France). Pharmaceuticals and hormones were analyzed using Acquity H Class coupled XECO TQ-XS tandem mass spectrometer (Waters, Saint-Quentin-en-Yvelines, France). Chromatographic separation of pharmaceuticals was performed by a C18 HSS T3 column (1.8 µm, 2.1 × 100 mm), while a C18 BEH (1.7 µm, 2.1 × 100 mm) column was used for hormones separation (Waters, Saint-Quentin-en-Yvelines, France). Internal calibration was performed by a linear curve from 0 to 100 µg L^{-1} for pesticides and from 0.01 to 50 µg L^{-1} for pharmaceuticals and hormones. The accuracy of analysis was ensured by quality controls (standards at 0.5 and 25 µg L^{-1} for pesticides and at 0.5 and 10 µg L^{-1} for hormones and pharmaceuticals) and analytical blanks every 10 samples. All mass parameters, elution gradients and chromatographic conditions are described in SI (from Table S4 to Table S10).

1.8. Data processing and procedure

To clarify the results presented and discussed in parts 2.3 to 2.6, the Figure 1 gives an overview on the number of molecules for which it was possible to choose a kinetic model and to calculate kinetic constants, equilibrium constants and limit of quantification (LOQ). A

decision tree representing method used to choose the model is described in Figure S1. Quickly, when CF could be calculated for more than 3 points, CF were fitted with a non-linear (NLS) regression model (i.e. Equation 4) for each compound and each PS. In the case that the non-linear model cannot be fitted for the accumulation of compounds (i.e. either because $t_{1/2}$ > 21 days or no convergence of the K_{SW} variable occurs), then CF were fitted with a linear (LM) regression model (i.e. Equation 7). In order to choose and evaluate the fitting of the regression models, regression characteristics (intercept, p-values and R^2) and standardized residuals were studied. Data processing (choice of kinetic model and kinetic constant determination) and graphical representations were performed with R software (R Core Team, 2018) using the packages "dplyr" (Wickham et al., 2019), "tidyr" (Wickham and Henry, 2019), "tidyverse" (Wickham, 2017), "purr" (Henry and Wickham, 2019), "broom" (Robinson and Hayes, 2019) and "ggplot2" (Wickham, 2016).

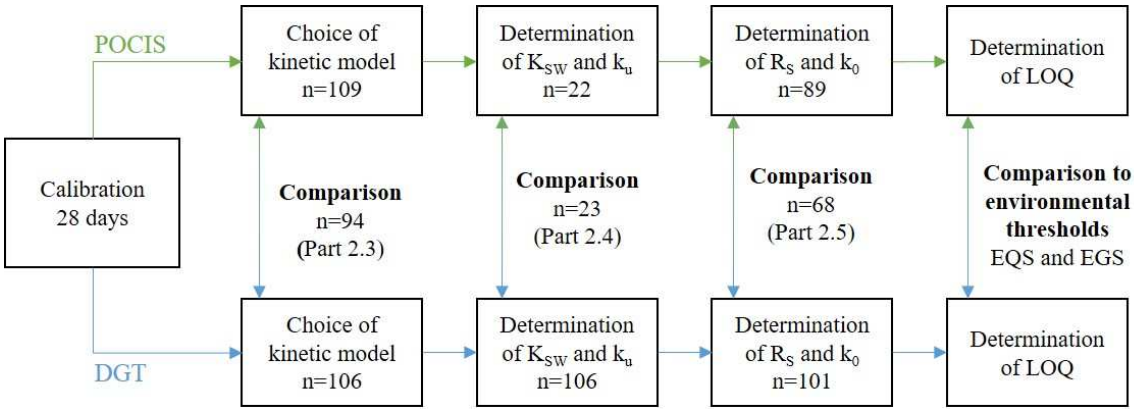

Figure 1: Number of substances with reliable kinetic model and accumulation constants, according to the PSD.

2. RESULTS AND DISCUSSION

2.1. Most adapted membrane for sampling of studied compounds using o-DGT

The following section describes results of the experiment carried out with the aim of choosing a membrane. More details are indicated in SI. The experiment to test protection of the diffusion gel and the resin by membranes showed that the agarose gel not protected by a membrane completely disappeared, contrary to gel protected by a membrane. Membranes were effective in protecting the diffusion gel in the field. Mass loss was higher with cellulose membranes, which can be explained by the fact that cellulose membranes are probably

degraded by microorganisms in the field (Alvarez et al., 2004). Mass loss is lower with PES membranes of both pore sizes. Mass losses seemed to depend mainly on the membrane used and not on pore size. The percentage of accumulated mass in membranes is represented in Figure S4. The number of accumulated compounds decreased with increasing pore size for all membranes tested. Membranes with a pore size of 5 µm therefore appear to be the most suitable for these compounds. Among the 5 µm pore size membranes, the nylon and PES membranes accumulated fewer compounds than the cellulose membrane. As the cellulose membrane accumulates too many compounds, it will not be studied in the following sections. In order to quantify the effect of the membranes on the diffusion coefficients, the ratio of the diffusion coefficients determined in the presence and absence of the membrane were determined and represented in FigureS5. For all tested membranes, diffusion coefficients were less impacted with 5 µm pore size membranes. With PES membrane, a majority of the compounds had similar diffusion coefficients with and without the membrane and consequently did not seem to affect the diffusion of a large proportion of the compounds studied. Based on the results, PES membrane with pore size of 5 µm was chosen for sampling pesticides, pharmaceuticals and hormones using the o-DGT technique. This is a good compromise between compound accumulation, gel protection in the field and the effect on diffusion coefficients.

2.2. The water concentration during calibration

Concentrations determined during the calibration experiment are reported in Table S12 and represented for 4 compounds throughout the calibration experiment in Figure 2. Concentration in water decreased slightly in the beginning of the calibration (6 days) experiment and then remained stable until the end of experiment. This decrease is proportionally linked to hydrophobicity of compounds. Concentration in water ranged from 0.3 to 7.9 µg L^{-1} (median = 3.5 µg.L^{-1}). For 54 compounds, measured concentration was close to the nominal value (5 µg L^{-1}). For 52 compounds, measured concentration was inferior to nominal value (difference > 30 %). Measured concentration was less than 1 µg L^{-1} for 5 compounds (FENO, SPIRO, DPA, MSF and DIES). For FENO, SPIRO and DIES, a 90% decrease in concentration was observed during the 24 hours preceding the start of PSD exposure. FENO and DIES may adsorb onto the calibration system due to their highly hydrophobic nature. Moreover, a diminution of FENO concentration in calibration system was already observed (Morin et al., 2013). The low concentration of these compounds could

be explained by half-life probably lower than the daily turnover rate of the water in the calibration system. To avoid bias in the determination of FC, the water concentrations used were the average ones during the PSD exposure period and not over the whole calibration experiment.

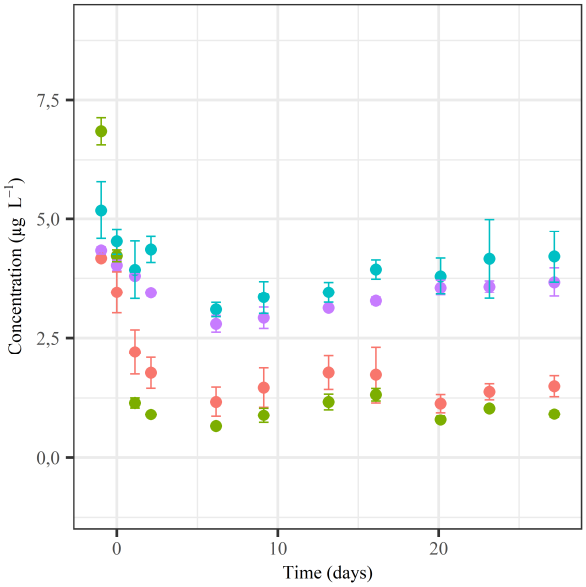

Figure 2: Concentration in water measured during calibration experiment for 4 compounds : CLINDA in red (pharmaceutical, cationic compound), DES in green (hormone, neutral compound), FLM in blue (pesticide, neutral compound) and ISF in purple (pesticide, anionic compound).

2.3. Comparison of kinetic models

This section describes and discusses accumulation kinetics obtained during the calibration experiment for both PS. Concentration factor versus time curves (example represented in Figure 3) allow us to assign an accumulation type to the studied compound (see decision tree illustrated in Figure S1). The type of accumulation attributed to each compound in the function of PSD is indicated in Table 1.

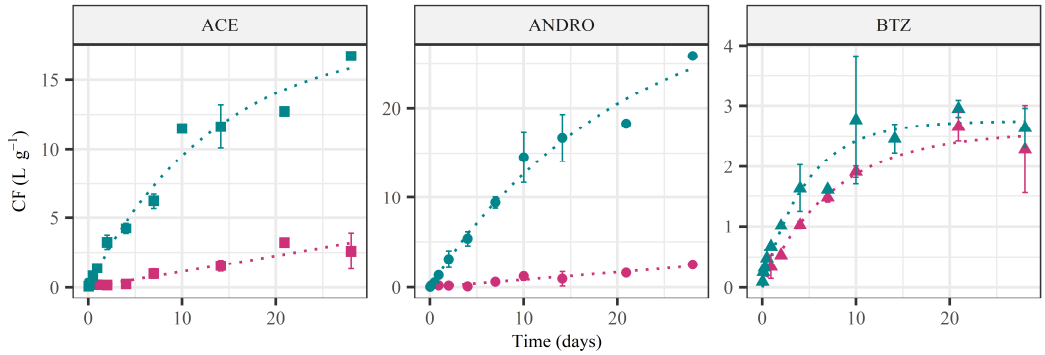

Figure 3 : Concentration factor (CF) throughout the calibration experiment for three organic compounds (acetamiprid (ACE), androstenedione (ANDRO) and bentazone (BTZ)) and associated regressions with POCIS (in green) and o-DGT (in pink).

For some compounds, accumulation kinetics could not be determined due to the very low accumulation of compounds throughout the exposure period (CF < 1). This is the case for dicamba and metformin with both types of PS. Consequently, these compounds were not studied. Moreover, accumulation kinetics of compounds for which the concentration factor was determined for less than 3 exposure times were not studied. This is the case for 9 compounds with o-DGT. Finally, this section describes accumulation kinetic curves obtained for 94 compounds in the case of o-DGT and 107 compounds for POCIS. In the case of o-DGT, 22 compounds followed non-linear accumulation and 72 compounds followed linear accumulation. For POCIS, a linear regression model was selected for 33 compounds while non-linear models provided a better fitting for 74 compounds. Accumulation kinetics determined with POCIS and o-DGT were compared for 94 compounds. For 46 compounds, the kinetic model used was the same between the two PS. However, the use of o-DGT allowed the linear accumulation of 48 compounds that follow a non-linear accumulation with POCIS. The presence of diffusive gel on the DGT delayed equilibrium from being reached during the accumulation of compounds.

*Table 1: Accumulation models, chosen using decision tree (Figure S1), for each compound depending on PS. * : compounds for which a non-linear phase was observed but with $t_{1/2}$ greater than 21 days, thus classified in the group of linear models. The compounds in blue are neutral compounds, the compounds in green are anionic compounds and those in orange are cationic compounds. All kinetic constants are reported in Table S13 for o-DGT and Table S14 for POCIS.*

POCIS (n=109)	**o-DGT (n=106)**
Linear regression (n=33)	**Linear regression (n=72)**
Hormones : DES - MEDROX	Hormones : aE2 - ANDRO - ANDROSTER* - bE2 - CORT - CORT.OH - DES - DEXA - DIES - DROSPI - E1 - E3 - EE2 - EPI-TESTO - LEVO - MEDROX - MEG.AC - NORE - PROG - TESTO
Pesticides : ATC - ATZ - AZS - CTL - CYPRO - DCPMU - DET - DIU - DMM - DTC - DTM - EPOX - FLM - FLZ - IPPMU - IPPU - IPU - IRG - LINU - MTC - MTX - MTZ - NFZ - PIRI* - TBZ - TYZ	Pesticides : ALC - ATC* - ATZ - CBF - CBZ - CTL - CYPRO - DEA - DIA - DIU - DMM - DMO - DPA - DTC - DTM - EPOX - FLM - FLZ - HEXA - IMI - IPPU - IPU - IRG - MCP - MTC - MTX - MTY - MTZ - NFZ - PIRI - TBZ - TYZ
Pharmaceuticals : AMS - CLARI - ERY - FENO - OFLO	Pharmaceuticals : ACE - ACFENO - BEZA - CARBA - CARBAEP* - CEL - CLINDA - CYCLOP - DICLO - FCD - FENO - FURO - GEM - KETO - LAM - MET - NAPROX - NIF - PROP - SOT
Non-linear regression (n=74)	**Non-linear regression (n=22)**
Time necessary to reach half of equilibrium < 14 d	**Time necessary to reach half of equilibrium < 14 d**
Hormones : aE2 - bE2 - CORT - CORT.OH - DEXA - DIES - DROSPI - E1 - E3 - EE2 - EPI-TESTO - LEVO - MEG.AC - NORE - PROG - TESTO	
Pesticides : ATC.OA - BTZ - CBF - DCP - DEA - DIA - DMO - DPA - FNP - IMI - ISF - IXI - MCP - MCPA - MSF - MST - MTC.ESA - MTC.OA - MTY - NSF - SCT - SPIRO	Pesticides : ATC.OA - BTZ - DCP - FNP - MCPA - MSF - MST - MTC.OA - NSF - SCT - SPIRO
Pharmaceuticals : ACE - ACFENO - ACSMX - APZ - ATE - BEZA - CARBA - CARBAEP - CEL - CLINDA - CYCLOP - DIAZ - DICLO - FCD - FURO - GEM - KETO - LAM - MET - METRO - NAPROX - NDZ - NIF - PARA - PROP - SALBU - SMX - SOT - THEO - TRIM	Pharmaceuticals : ACSMX - METRO - PARA - SMX - THEO
Time necessary to reach half of equilibrium > 14 d	**Time necessary to reach half of equilibrium > 14 d**
Hormones : ANDRO - ANDROSTER - DIES	
Pesticides : ALC - CBZ - DCF - HEXA	Pesticides : DCF - ISF - IXI - MTC.ESA

	Pharmaceuticals : ATE - TRIM

2.4. Comparison of distribution and elimination kinetic constants

All kinetic constants are reported in Table S13 for o-DGT and Table S14 for POCIS. In the case of o-DGT, distribution coefficients (K_{SW}), determined by using model, ranged from 0.97 to 22.55 × 10^3 L kg^{-1} (median = 5.27 × 10^3 L kg^{-1}, n = 22) while with POCIS, K_{SW} ranged from 1 to 86 × 10^3 L kg^{-1}. In literature, the K_{SW} for o-DGT were determined in one study on alkylphenols. Values determined in this study were inferior to those determined for alkylphenols (n = 23; 1.51 × 10^3 L kg^{-1} and 295 × 10^3 L kg^{-1}; median = 35 × 10^3 L kg^{-1}) (Urik and Vrana, 2019). The receiving phase was the same between the three PSD and it has been shown that the distribution coefficients were similar when the phase is free or mixed with gel (Urik and Vrana, 2019). Consequently, K_{SW} values determined in this study should be similar between the two passive samplers. K_{SW} determined using o-DGT and POCIS were compared for 23 compounds. They were similar for the majority of compounds (n = 17). However, K_{SW} were different for six compounds. In the case of ISF, IXI, TRIM and SPIRO, the K_{SW} determined with o-DGT were lower than those obtained with POCIS. For ISF and IXI, the concentrations measured with o-DGT after 28 days of exposure appeared to be underestimated, resulting in a non-linear accumulation over the duration of exposure, whereas it appears to be linear for the first 21 days of exposure. In the case of TRIM, the relative standard deviation (RSD) of K_{SW} for o-DGT was greater than 50 %. The difference can then be explained by a poor fit with the kinetic model. In the case of SPIRO, the low value of K_{SW} obtained with o-DGT can be explained by the high uncertainty of samples exposed for more than 14 days. On the contrary, the K_{SW} determined for MCPA with o-DGT was higher than that determined with POCIS. For these compounds, there are still uncertainties regarding kinetic model determination, and the resulting constants. They were removed from the dataset for both the uptake rates k_u (or R_s) and $t_{1/2}$ estimates. The k_u values ranged from 0.03 to 1.05 L d^{-1} g^{-1} (median = 0.25 L d^{-1} g^{-1}, n = 89) for o-DGT and 0.06 to 4.3 L d^{-1} g^{-1} (median = 0.77, n = 101) for POCIS. The time necessary to reach half of equilibrium determined with POCIS and o-DGT were compared for 17 compounds. The $t_{1/2}$ were greater with o-DGTs than with POCIS for all compounds. The use of the o-DGT technique allows an increase in the linear phase compared to POCIS, for the same K_{sw} value.

Figure 4: Comparison of distribution coefficients (K_{SW}) obtained with the two passive sampler: POCIS (in green) and o-DGT (in pink). All kinetic constants are reported in Table S13 for o-DGT and Table S14 for POCIS.

2.5. Comparison of sampling rates and overall mass transfer coefficient

Sampling rates (R_s) obtained with o-DGT were represented in Figure 4 and ranged from 1.2 to 42.8 mL d^{-1} (median = 10.2 mL d^{-1}, n = 89) and those obtained with POCIS ranged from 11.3 to 858 mL d^{-1} (median = 153 mL d^{-1}, n = 101). In addition, the mean for the whole R_s data associated to the o-DGT and the POCIS were 10 ± 7 mL d^{-1} and 190 ± 112 mL d^{-1} respectively, and then used for the further estimates of the limits of quantifications (LOQ) (see Table 2). RSD on the R_S were lower with o-DGT than with POCIS. This can be explained by the fact that a linear model, less complex than a non-linear one, could be used for a majority of compounds with o-DGT, contrary to POCIS.

In the case of o-DGT, R_s of anionic compounds (median = 15 mL d^{-1}, n = 23) were higher than those of neutral compounds (median = 9 mL d^{-1}, n = 59) and cationic compounds (median = 6 mL d^{-1}, n = 7). In the case of POCIS, R_s of neutral compounds (median = 145 mL d^{-1}, n = 67) were lower than R_s of anionic (median = 221 mL d^{-1}, n = 24) and cationic compounds (median = 211 mL d^{-1}, n = 10). With o-DGT, R_s of hormones were lower than those of pharmaceuticals and pesticides. This may be partly explained by a slight delay in accumulation ("lag phase") of one to three days, although the confidence interval of the intercept at baseline contains zero. These low R_s values determined for hormones compared to pharmaceuticals and pesticides have not been observed elsewhere in the literature (Challis et al., 2016; Stroski et al., 2018). This delay in accumulation can be explained either by a significant resistance to mass transfer between the gel and the receiving phase or by a significant resistance to mass transfer between the membrane and the diffusive gel. However, the diffusion coefficients of hormones determined in diffusion cells with and

without membrane are similar (D ratios between 0.7 and 1.3 except for estriol, data not shown). Consequently, the lag phase of hormones would be due to a non-negligible resistance to mass transfer between the gel and the receiving phase. Comparison between sampling rates obtained with POCIS and o-DGT has not been done for hormones, due to the lag phase associated with these ones. As a result, sampling rates obtained with POCIS and o-DGT were compared for 68 compounds. R_s determined with o-DGT (median = 11 mL d^{-1}) were lower than those observed with POCIS (median > 150 mL d^{-1}). These observations could be explained by lower exposure surface and higher diffusive layer thickness, due to the presence of a gel, in the case of o-DGT. In literature, some discrepancies in R_s remains according to calibration systems and operating conditions (Morin et al., 2012). In this study, R_s of the two passive samplers were obtained in the same calibration experiment, and then similar temperatures and flow velocities, thus providing comparisons that are more consistent.

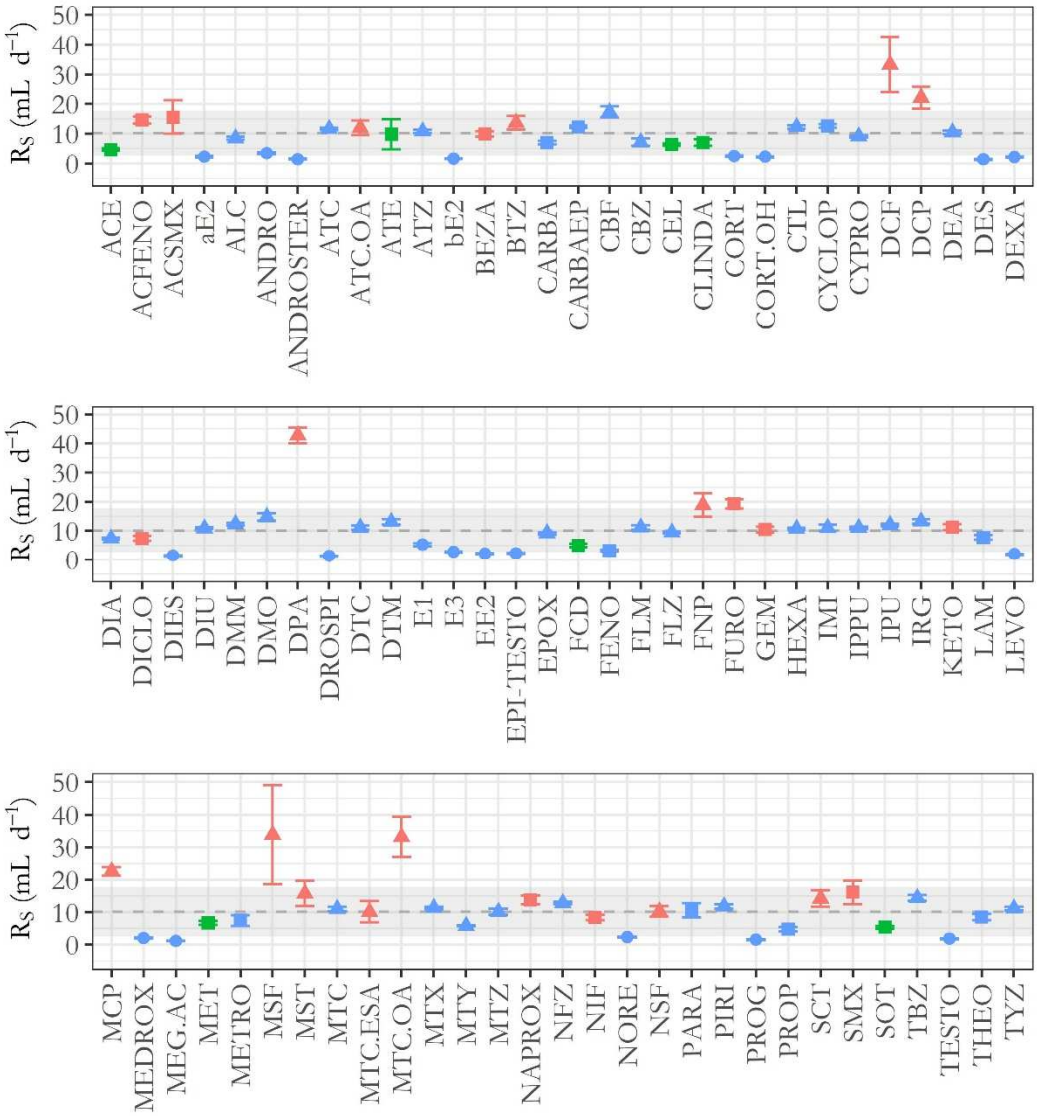

Figure 5 : Sampling rates (R_s) obtained with o-DGT for each compound (anionic compounds in red, cationic compounds in green and neutral compounds in blue). The grey area corresponds to the 95 % confidence interval around the mean of R_s. All kinetic constants are reported in Table S13 for o-DGT..

In order to compare overall mass transfer coefficients k_0, sampling rates have been normalized by the area of exposure (see Equation 8). The k_0 values, represented in Figure 6, were higher with POCIS (median at 167 cm d^{-1}) than with o-DGT (median at 11 cm d^{-1}).

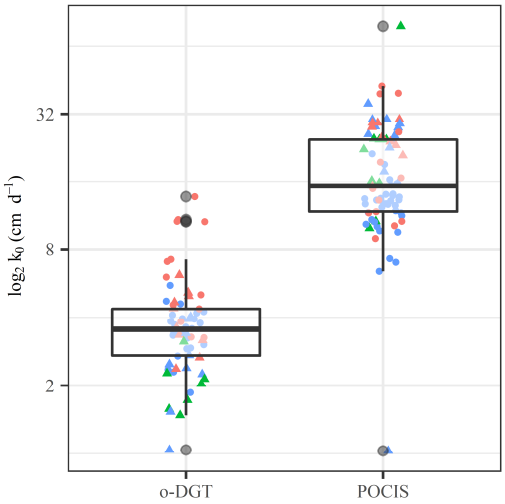

Figure 6: Overall resistance transfer mass coefficients obtained with the two passive samplers for hormones (square), pharmaceuticals (triangle) and pesticides (circle) (anionic compounds in red, cationic compounds in green and neutral compounds in blue). All kinetic constants are reported in Table S13 for o-DGT and Table S14 for POCIS.

In literature, k_0 were comparable between the POCIS and o-DGT tested (using POCIS exposure surface area of 45.8 cm²) (Chen et al., 2018; Guibal et al., 2017). For this calibration, the exposure surface area value used for calculation of k_0 was approximately 11 cm², corresponding to the actual exposure surface of the receiving phase for POCIS (membrane surface area of 45.8 cm², 200 mg of phase) because of sedimentation of receiving phase between the membranes when the POCIS is placed vertically, which reduces the effective exchange surface (Fauvelle et al., 2014). Besides, the resistance transfer mass coefficient related to the receiving phase (i.e. K_{SW}) can be neglected for pesticides and pharmaceuticals. In our case, the difference between k_0 can more probably be explained by the resistance transfer mass coefficient related to gel occurring in the o-DGT only. For this purpose, the resistance transfer mass coefficient related to membrane could be described by Equation 9. Diffusion coefficient (D) were determined using Equation 10 for compounds which follow linear accumulation. K_{GM} ranged from 7.0 to 12.4 (n=71) except for fenofibrate (0.2). Consequently, resistance transfer mass coefficient related to gel is due to gel thickness.

$$1/k_g K_{GM} = \delta/K_{GM} \times D \qquad \textit{Equation 9}$$

$$D = (\delta \times R_S)/A \qquad \textit{Equation 10}$$

2.6. Limits of quantification reached with POCIS and o-DGT versus environmental threshold required for regulatory water monitoring programs

441 The European Water Framework Directive (WFD) was adopted in 2000 by the European
442 Union in order to reach good ecological and chemical status of aquatic environment by 2015,
443 extended to 2027. In this context, environmental quality standards (EQS) have been set as a
444 threshold not to be exceeded for a list of priority substances. In France, Environmental
445 Guideline values (EGV), fixed by INERIS (https://substances.ineris.fr/fr/), are also used as
446 thresholds with regulatory value. The criterion for chemical monitoring is that limits of
447 quantification (LOQ) must be lower than one-third of the EQS (or EGV, when EQS are not
448 available). Values of EGV and EQS were found for 19 chemicals calibrated with both o-DGT
449 and POCIS in this paper, mainly corresponding to pesticides. These values of EGV and EQS
450 range from 13 to 2500 ng L^{-1} (n=8) and from 19 to 1000 ng L^{-1} (n=11), respectively (see
451 Table S15). Other threshold values defined by European commission (Commission
452 Implementing Decision (EU) 2018/840) were found for three hormones (ethinylestradiol,
453 estradiol, and estrone) and were inferior to 0.5 ng L^{-1}.
454 While spot water sampling is widely performed to determine water concentration, it remains
455 some limitations like a lack of temporal representativeness and the need to extract large
456 volume of water to reach the required LOQ. The use of passive samplers generally allows to
457 improve the LOQ compared to those obtained with spot water sampling. For both POCIS and
458 o-DGT, the LOQ were estimated from the average R_s (available in Tables S13 for o-DGT and
459 S14 for POCIS) and considering an exposure durations of 14 days in aqueous media. Besides,
460 the same instrumental limits of quantification (LOQ_i) were considered for the calculation of
461 LOQ after spot water sampling (LOQ_w) and after passive sampling with o-DGT or POCIS
462 (LOQ_{PSD}). Finally, LOQ_{PSD} were compared to LOQ_w, considering either medium (250 mL) or
463 large (1 L) water volumes (see Table 2). Because of lower values of R_s for o-DGT, the LOQ_{o-DGT}
464 are higher than LOQ_{POCIS}. Moreover, the LOQ_{o-DGT} are close to LOQ_w obtained with a
465 250-mL water sample. In this case, the advantage to use o-DGT is limited to the obtaining of
466 time-weighted average concentrations.
467 LOQ of pesticides and pharmaceuticals obtained in this study for both PSD and spot water
468 samples were satisfying, *i.e.* lower to EQS/3 or EGV/3. Consequently, performances of both
469 passive samplers and spot water sampling for these compounds were satisfying for chemical
470 water monitoring, in agreement with regulatory requirements, as it is already shown with
471 POCIS and spot water sampling (Mathon et al., 2022).
472 However, LOQ were not satisfying for the 3 hormones with o-DGT and also for spot water
473 sampling (250 mL extract); for 1 hormone (ethinylestradiol) with POCIS and also for spot

sampling (1 L extract). Such limitations of the actual o-DGT, regarding the hormones only, could be further improved by increasing the surface areas, as recently proposed by Urik et al. (2019) for PFAS or Martins de Barros et al. (2021) for some pesticides.

Actually, a 5-fold improvement of the LOQ can be expected with the use of the Chemcatcher housing for o-DGT technique (15.9 cm² *vs* 3.14 cm² with o-DGT housing) (Martins de Barros et al. 2022), for instance, allowing to reach LOQ up to 0.07 ng L^{-1}, and then compatible with the challenging EQS to reach for both estradiol and estrone.

Table 2: Limits of quantification determined for either POCIS or o-DGT (LOQ_{PSD}) compared to that for spot water sampling (LOQ_w), with a same LOQ_i.

		LOQ_i (ng mL^{-1})	**Mean R_s** (mL day^{-1})	**LOQ_{PSD}** (ng L^{-1})	**LOQ_w** (ng L^{-1})	
					For 1 L	**For 250 mL**
POCIS	Pesticides	0.5	190	0.2	-	-
	Hormones and pharmaceuticals	0.05	190	0.02	-	-
DGT	Pesticides	0.5	10.4	3.4	-	-
	Hormones and pharmaceuticals	0.05	10.4	0.34	-	-
Spot sample	Pesticides	0.5	-	-	0.5	2
	Hormones and pharmaceuticals	0.05	-	-	0.05	0.2

3. CONCLUSION

In this paper, it was shown that membranes with a pore size of 5 µm allow the protection of the diffusive gel in the field while accumulating less compounds than membranes with a pore size of 0.45 µm. In general, the diffusion coefficients were slightly impacted by the presence of the membrane, as already shown in the case of metals. In the end, it was shown that the PES membrane with a pore size of 5 µm is the most suitable for sampling the target compounds.

The calibration experiment showed that o-DGT slows down the compounds accumulation and thus extends the duration of the linear accumulation phase. Consequently, o-DGT can be used for some compounds, for which it is not possible to use POCIS because of too short $t_{1/2}$ (< 4 d).

Contrary to POCIS, the influence of the environmental conditions on compounds accumulation in o-DGT can be neglected or corrected. Actually, the effect of temperature on

compounds accumulation can be corrected using the Stokes-Einstein relation (Zhang and Davison, 1999). Moreover, the presence of a diffusive gel in o-DGT allows decreasing the effect of hydrodynamic condition. If the aquatic environment is sufficiently agitated (from 20 to 150 cm s^{-1} (Belles et al., 2017), the effect of diffusive boundary layer can be neglected with o-DGT. In the case of diffusive boundary layer cannot be neglected, its thickness can be determined by exposing DGT with different thickness gel diffusion (Challis et al., 2016) and taken into account in concentration determination.

With o-DGT, the sampling rates are significantly reduced because of the presence of the diffusive gel. If needed to decrease and improve the LOQ (as for hormones), the solution would be to increase the exposure area as done elsewhere in the literature (Belles et al., 2017; Martins de Barros et al., 2022; Mechelke et al., 2019; Urík and Vrana, 2019).

However, pre-concentration using o-DGT is sufficient to detect them at concentration under EQS or EGS for pesticides and pharmaceuticals (as well as POCIS and spot water sampling). At this stage, the use of PS for hydrophilic to moderately hydrophobic substances in the dissolved water column, is relevant for compliance checking with EQS in water.

Concerning sustainability and greenness, the difference between the 2 PSD is limited. Indeed, volume and type of organic solvents for PSD extraction, the use of which pollutes the environment, were similar. Considering the reusability, rings (inox) of POCIS can be sent back to suppliers for reuse, contrary to DGT (plastic holders).

Lastly, the large dataset presented and discussed in this paper for such a wide range of hydrophilic molecules should contribute to improve PS for regulatory water monitoring of hydrophilic substances (extension to new substances, optimization of accumulation models and of TWA concentrations calculation).

Acknowledgments

The authors gratefully acknowledge Sebastian Lee from Carleton College (Northfield, MN, USA) for English revision.

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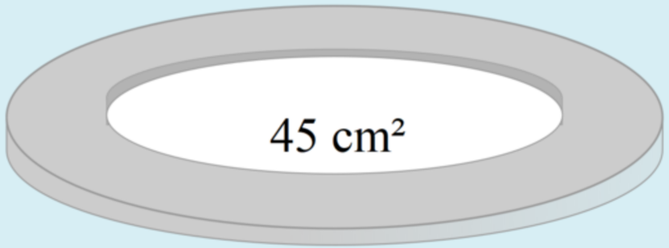
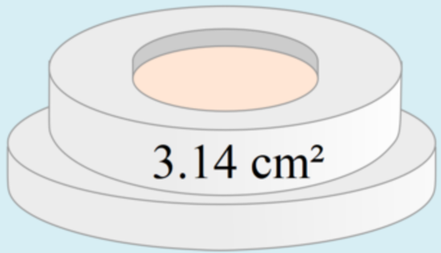
Calibration of passive samplers

Hormones

Pesticides

Pharmaceuticals





POCIS

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