



HAL
open science

First study of passive sampling to monitor short-chain chlorinated paraffins in water: Comparing capabilities of Chemcatcher® and silicone rubber samplers

Mathilde Godere, Stella Mondange, Pierre Doumenq, Catherine Gonzalez,
Laure Malleret

► To cite this version:

Mathilde Godere, Stella Mondange, Pierre Doumenq, Catherine Gonzalez, Laure Malleret. First study of passive sampling to monitor short-chain chlorinated paraffins in water: Comparing capabilities of Chemcatcher® and silicone rubber samplers. *Talanta*, 2021, 224, pp.121920. 10.1016/j.talanta.2020.121920 . hal-03592529

HAL Id: hal-03592529

<https://imt-mines-ales.hal.science/hal-03592529v1>

Submitted on 1 Mar 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Contents lists available at ScienceDirect

Talanta

journal homepage: <http://ees.elsevier.com>

First study of passive sampling to monitor short-chain chlorinated paraffins in water: Comparing capabilities of Chemcatcher® and silicone rubber samplers

Mathilde Godere^a, Stella Mondange^{a,b}, Pierre Doumenq^a, Catherine Gonzalez^b, Laure Malleret^{a,b,*}^a Aix Marseille Université, CNRS, Laboratoire Chimie Environnement, France^b Laboratoire de Génie de L'Environnement Industriel, IMT Mines Alès, 6 Avenue de Clavières, 30319, Alès, France

ARTICLE INFO

Keywords

Chlorinated paraffins
European water framework directive
Chemcatcher®
Silicone rubber
Passive sampling
Complex mixtures

ABSTRACT

Short-chain chlorinated paraffins (SCCPs) are high-volume chemicals raising concerns because of their classification as priority hazardous substances by the European Water Framework Directive (WFD) and their recent inclusion in the persistent organic pollutants' (POPs) list by the Stockholm convention. As this group cover up to 5000 isomers, their measurement is still challenging. Hence the SCCPs occurrence in the environment is poorly documented in comparison with other POPs, especially in matrices where they are present at ultratrace levels such as waters. In the two-past decades, passive sampling has been increasingly used as it overcomes some major drawbacks associated to the conventional grab sampling. This study constitutes the first work aiming to examine the passive sampling's applicability for the monitoring of such complex analytes' mixtures in waters. Optimization and calibration of two proven passive samplers, namely silicone rubbers and Chemcatcher®, were performed through batch and laboratory pilot experiments. Despite the thousands of molecules present in the SCCPs mixture, the resulting global kinetic uptakes fitted well with the theoretical model, for both samplers. Sampling rates of 8.0 L d⁻¹ for silicone rubbers and 0.53 L d⁻¹ for Chemcatcher® were found, and logK_{sw} determined for silicone rubbers equaled 4.24 to 4.95. These values are in complete agreement with published data for other HOCs. A field trial carried out in marine coastal environments provided further evidence to demonstrate the applicability of the passive samplers to measure CPs amounts in water bodies. All these results unveil that passive sampling using silicone rubbers or Chemcatcher® can be a relevant approach to track traces of such complex mixtures in water.

1. Introduction

Chlorinated paraffins (CPs) constitute high-volume chemicals produced by chlorination of the n-alkanes feedstocks under forced conditions (ie. UV and/or pressure) [1]. The low positional selectivity of the reaction leads to the formation of complex mixtures constituted by thousands of isomers and congeners. They are classified into three categories depending on their carbon chain lengths: 10–13, 14–17, 18–30 carbon atoms for respectively the short (SCCPs), the middle (MCCPs) and the long chains (LCCPs). Only the SCCPs are under regulation by the Water Framework Directive (WFD) in which they are listed as priority dangerous substances [2]. They were also included in 2017 in Annex A listing Persistent Organic Pollutants (POPs) of the Stockholm Convention [3]. The WFD has emitted Environmental Quality Standards (EQS) in water for the SCCPs, equaling 0.4 µg L⁻¹ for the annual average concentration and 1.4 µg L⁻¹ for the maximum admissible concentration. Compliance to these requirements is nowadays achieved

through different extraction procedures, like LLE [4] or micro-LLE [5], SPE [6,7], SPME [8–10] and SBSE [11]. Despite these analytical developments, information on the water occurrence of SCCPs is still lacking comparing to other Hydrophobic Organic Compounds (HOCs), like PCBs or PAHs [12]. In this frame, alternatives to conventional grab sampling can be considered, and among them the passive sampling approach seems to be relevant [13–16]. Based on the accumulation of compounds from the targeted matrix to a physical device during a determined exposure period, passive sampling provides an in-situ preconcentration. Moreover, a time weighted average concentration (TWAC) reflecting the whole period of exposure, usually several weeks, or an equilibrium concentration can be obtained, which is helpful in the understanding of the contaminant fluxes with other accumulative matrices in the aquatic compartment [17]. As only the freely dissolved fraction of contaminants is accumulated into the sampler, passive sampling reflects more properly the pressure on organisms in the aquatic compartment [18,19].

* Corresponding author. Aix Marseille Université, CNRS, Laboratoire Chimie Environnement, France.

E-mail address: laure.malleret@univ-amu.fr (L. Malleret)

Among the existing passive samplers applied for HOCs, the Semi-Permeable Membrane Device (SPMD) has been extensively used, but due to laborious extraction and purification protocols, a shift occurred towards monophasic polymers during the last decade, mainly Low-Density Polyethylene (LDPE) and Silicone Rubber samplers [18]. The latter is particularly interesting as having a higher permeability than LDPE, implying an enhanced sampler mass capacity [20,21]. Multiphasic devices, such as Chemcatcher®, composed of a receiving phase and a membrane enclosed into a housing [22], were also applied to several families of nonpolar compounds [23,24]. Nonetheless, passive sampling studies for HOCs in water were mostly performed for PAHs, PCBs or OCPs [25,26], and extended very recently to emerging compounds, such as PBDEs, PFOA and PFOS [17,21,27]. All these studies focused on individual analytes, but the passive sampling approach has never been applied to mixtures composed of a large number of compounds, like SCCPs, as the large range of physicochemical properties associated complicates the understanding of the accumulation mechanisms.

In this frame, the present work aimed to explore the applicability of passive sampling to search for SCCPs in water by studying both silicone rubber and Chemcatcher® samplers. Experiments were performed using a SCCPs technical mixture, instead of individual congeners, as being much more relevant for assessing real-world applicability, since SCCPs are exclusively produced and dispersed into the environment as mixtures. Batch experiments were carried out to optimize the Chemcatcher® configuration. To compare the capabilities of both samplers, kinetic exchanges were studied through two laboratory calibration pilots, using a passive dosing system (implying the use of dosing silicone sheets) [28] for silicone rubber sampler and a continuous water flow through system for Chemcatcher® [29,30]. Both water spiking procedures were discussed and key values governing compound's accumulation into the samplers (i.e. sampling rates and equilibrium partition coefficients) were determined. Benefits of passive sampling for the SCCPs monitoring in water bodies were discussed in the light of these constants, and performance of the calibrated samplers was tested through a field trial.

2. Materials and methods

2.1. Chemicals and materials

All the solvents used were of HPLC grade and obtained from VWR Chemicals (Fontenay-sous-Bois, France), except ethyl acetate, which was of technical grade and supplied by Sigma-Aldrich (Lyon, France). SSP-M823 silicone sheets (250 µm thick) were furnished by Shielding Solutions Limited (Braintree, United Kingdom). The Chemcatcher® comprised a reusable polytetrafluoroethylene (PTFE) housing, constituted by a 20 mm deep cup in front of the device (first design), and provided by Portsmouth University. Diffusion membranes made of PolyEtherSulphone (PES, 150 µm thick) and Low-Density Polyethylene (LDPE, 40 µm thick) were supplied by Merck Millipore and Portsmouth University, respectively. Three receiving phases (Empore™ disks, 47 mm diameter) were tested: C₈ obtained from Agilent Technologies (Montpellier, France), C₁₈, and Grease and Oil from Sigma Aldrich. They consisted in octyl (C₈ disk) or octadecyl (C₁₈ and Grease and Oil disk) carbon chains bonded silica, embedded in a PTFE network. This matrix in the Grease and Oil disk was sandwiched between two films of polypropylene. The technical SCCPs mixture Cloparin 55 was kindly offered by Caffaro Industry (Torviscosa, Italy), and was composed of C₁₀ to C₁₃ chains and an averaged chlorine content of 56% by weight. PCB 54 and SCCPs analytical standard (C₁₀₋₁₃, 63% of chlorine by weight) were purchased from CIL Cluzeau (Courbevoie, France), and ¹³C₆-hexachlorobenzene was obtained from Sigma-Aldrich. For water extraction, C₁₈-bonded silica cartridges (1 g/6 mL) from Supelco (Lyon, France) were used.

2.2. Samplers preparation

Before use, the receiving phases of Chemcatcher® were pre-cleaned and conditioned using protocols adapted from previous works [31,32]. Briefly, the disks were soaked in methanol for 12 h, then 50 mL of methanol followed by 150 mL of ultrapure water were slowly percolated through vacuum filtration. The diffusion membranes were soaked overnight in n-hexane and methanol, respectively for LDPE and PES membranes [32]. The latter were rinsed with ultrapure water [33], and both membranes were dried before use. The Chemcatcher® assembly consisted in placing the disks in the PTFE housing and covering them with the diffusion membranes, gently pressed with a lint-free tissue to remove any air bubble [23]. To prevent from drying out, the device was either immersed directly in the experimental medium or filled with ultrapure water, sealed, and stored at 4 °C.

Concerning the silicone rubber samplers, dosing and uptake sheets were cut into pieces of 15 × 15 cm and 5.5 × 9.5 cm, respectively. They were precleaned and spiked according to protocols adapted from the guidelines provided by the International Council for the Exploration of the Sea (ICES) [34], details can be found in Supplementary Material, S1. A 29-h Soxhlet extraction followed by 2 Soxtherm® (i.e. automated Soxhlet extractor) extraction cycles of 3.5 h each, using ethyl acetate were performed. This step allowed the oligomers present in the original material to be eliminated, as they can notably interfere with the instrumental analysis. The sheets were then stored in methanol until use. For the passive dosing system employed for silicone rubber samplers calibration, dosing sheets were spiked with Cloparin 55 by equilibration in solutions of water and methanol [35].

2.3. Batch experiments

To optimize the Chemcatcher® configuration, batch experiments were conducted in 600 mL glass beakers filled with ultrapure water, fortified with a solution of Cloparin 55 prepared in methanol. The resulting nominal concentration was equal to 10 µg·L⁻¹. The beakers were agitated using a magnetic bar and placed onto a stirring table and the decrease of SCCPs concentration in the aqueous phase was monitored for 30 h. In a first series of experiments, the Chemcatcher® was equipped with the three selected receiving phases without membrane. The second optimization step consisted in exposing Chemcatcher® equipped with the previously optimized disk (i.e. Empore™ C₁₈) covered by a diffusive membrane. Four configurations were studied, with the disks impregnated either with water or n-octanol according to a protocol described elsewhere [32], and isolated from the exposure medium by PES or LDPE membranes. The tests were carried out in duplicate over a period of 7 days.

2.4. Calibration pilots

The flow-through exposure system employed for the laboratory calibration of Chemcatcher® consisted of a 25 L tank coated with a PTFE film. The system comprised a PTFE carousel with places for 14 samplers, connected to an electronic stirrer to simulate turbulent conditions [29,36]. Tap water was fed to the tank from a 200 L aquarium by a peristaltic pump, with a flow rate of 34 mL min⁻¹. Stock solution of SCCPs in methanol (Cloparin 55 at 0.9 mg·L⁻¹ and 1.5 mg L⁻¹ for configurations with LDPE and PES membranes, respectively) was delivered to the tank by a HPLC pump with a flow rate of 0.2 mL min⁻¹, to maintain a constant concentration of analytes in water. The theoretical nominal concentrations were of 5.3 and 8.8 µg L⁻¹, for respectively the configurations with LDPE and PES membranes. An overflow was put in place to keep the volume of water constant in the tank. The stabiliza-

tion of the concentration in the tank was obtained after three complete renewals of the water in the tank (i.e. after 38 h here).

The laboratory calibration of silicone rubber samplers was based on the work of Rusina et al. and was operated in a stainless-steel tank [28], filled with 35 L of tap water agitated by means of two aquarium pumps (see Supplementary Material, S2). Five dosing sheets were placed at the bottom whereas 26 others were mounted on fixation rods. The water was renewed after two days, followed by another equilibration period of two days. This step allowed the SCCPs to reach partition equilibrium between dosing sheets and water, ensuring stability of concentrations during the exposure [28].

The temperature and water velocity are known influential parameters on analyte uptake by passive samplers thus, they were determined during the experiments. The agitation at 50 rpm in the Chemcatcher® calibration's tank resulted in linear flow velocity of 100 cm s^{-1} . In silicone rubber samplers calibration, velocity measurements were conducted with an electromagnetic current meter (BFM801, Ponsel, France). The associated confidence interval of 95% was comprised between 5.5 and 8.6 cm s^{-1} ($n = 30$ measurements at the sheets' positions). The water temperature in the tank remained stable with a mean value of $21 \pm 0,4 \text{ }^\circ\text{C}$ for Chemcatcher® ($n = 9$), and $25,6 \pm 0,6 \text{ }^\circ\text{C}$ ($n = 14$) for silicone rubber samplers.

2.5. Samplers exposure in calibration pilots

For silicone rubber samplers calibration, the uptake sheets were immersed in water, and collected in duplicate at 8 h, and 1, 3, 5, 7 and 14 days, at different positions in the tank (see Supplementary Material, S2). During the whole exposure period, four sheets were exposed simultaneously, corresponding to an exposed surface area equal to 3% of that of the dosing sheets [28]. Such a low ratio prevents the depletion of SCCPs from the dosing sheets and their direct transfer to the uptake sheets. In addition, the exposure of a limited number of sheets avoids the deployment of a too large quantity of dosing sheets, and therefore a too large quantity of analytes to be spiked. To check the non-depletion criterium, SCCPs concentrations were measured in the dosing sheets, by cutting 6 pieces at different positions in the tank, and in water at the beginning and at 12 days of exposure [27,37].

The Chemcatcher® calibration involved the exposure of 14 devices in the tank, with successive retrieval in duplicate (on each stage of the carousel) at set time intervals (4, 6, 10, 12, 14, 17 and 19 days). They were all replaced by empty Chemcatcher® bodies to avoid any modification of hydrodynamic conditions in the tank. The aqueous concentrations of SCCPs were determined each time the samplers were removed.

Blanks were also performed in both experiments: a Chemcatcher® and silicone rubber sampler were exposed to air each exposure time, then stored at $4 \text{ }^\circ\text{C}$ (Chemcatcher® was filled with ultrapure water) until the next sample was taken. No contamination by SCCPs was noticed for Chemcatcher®, whereas these compounds were detected in silicone rubber samplers, but the associated levels did not exceed 5% of that in the passive samplers.

After the collection of the passive samplers, the water was removed gently with a lint-free tissue for silicone rubber samplers and LDPE membranes whereas the C_{18} disks were dried 30 min on a vacuum filtration ramp. The water samples and the passive samplers were stored in the dark at $4 \text{ }^\circ\text{C}$ in glass jars and extracted within a week.

2.6. Field performance of passive samplers

To perform the field trial, the Gulf of Fos, a semi enclosed bay located in the Mediterranean Sea in the South-East of France, was chosen as it constitutes a heavily industrialized area. Silicone rubber and Chemcatcher® (ie. C_{18} Empore disk impregnated with water and topped by an LDPE membrane) samplers were deployed at five stations.

Four were near petrochemical and metallurgic industries and the fifth in a mussel farming area, as described in Supplementary Material, S3. Grab water samples were collected at the deployment and retrieval of the samplers, at each station. The samplers were transported in amber glass jars stored in cool boxes and were placed in stainless-steel cages (represented in Supplementary Material, S3), in triplicate. Note that according to the ICES guidelines, a silicone rubber sampler consisted of three exposed sheets [34]. The cages were roped to mooring buoys at about 2 m below the surface, and the exposure periods lasted between 3 and 6 weeks (See Supplementary Material, S3). During the deployment and retrieval steps, two samplers were deployed simultaneously to the air and kept as field blanks. After their retrieval, silicone rubber samplers and LDPE membranes were rinsed with distilled water and the eventual bio-fouling was removed using a lint-free tissue. After their transportation to laboratory, both samplers were stored in amber glass jars at $-20 \text{ }^\circ\text{C}$ until extraction and analysis. No contamination was observed in the blank Chemcatcher® but SCCPs were detected in silicone rubber samplers. No correction was performed since the associated levels were always lower than 5% of that in the samplers deployed.

2.7. Extraction of SCCPs from samplers and water

Details on the extraction conditions for both samplers can be found in Supplementary Material, S4. Briefly, Chemcatcher® membranes and disks were extracted separately in two successive ultrasonic baths, 10 min each, using 10 mL of n-hexane/acetone (1:1, v/v). The extracts were then concentrated under a gentle flow of nitrogen at $30 \text{ }^\circ\text{C}$. Validation of the Chemcatcher® extraction was carried out in duplicate, by directly spiking the analytes onto the disks and letting the solvent to evaporate. The associated recovery was equal to $101.5 \pm 1\%$ ($n = 3$). Concerning silicone rubber samplers, a protocol adapted from the ICES guidelines was employed [34], consisting briefly in an automated Soxhlet extraction using a methanol/acetonitrile mixture (1:1, v/v). Before each extraction, 500 ng of recovery standard (PCB 54, prepared in acetone solution) were added to the samplers.

For water extraction, C_{18} -silica cartridges conditioned with 4 mL of methanol followed by 4 mL of Milli-Q water were employed. 500 mL water samples were percolated at approximately 10 mL min^{-1} . After vacuum drying for 2 h, the cartridges were eluted using 6 mL of n-hexane. Validation of the extraction was performed with 1 L of ultrapure water, spiked with a solution of SCCPs in acetone followed by a 30-min equilibration period under orbital agitation at 200 rpm. The obtained recoveries were equal to $80.1 \pm 2.3\%$ ($n = 6$).

All the extracts were concentrated to near dryness under a gentle flow of nitrogen and reconstituted with 0.5 mL of n-hexane. 50 μL of $^{13}\text{C}_6$ -hexachlorobenzene 0.01 ng/ μL was added as internal standard in the extracts before instrumental analysis.

2.8. Instrumental analysis

A gas chromatograph (7890A GC) coupled to a tandem mass spectrometer (Triple quadrupole 3000 A) from Agilent Technologies was employed for the identification and quantification of SCCPs. 1 μL was injected in pulsed splitless mode at $250 \text{ }^\circ\text{C}$ and 10 psi. SCCPs were separated on a HP-5MS column of 30 m long, with a film thickness of $0.25 \text{ } \mu\text{m}$, and an internal diameter of 0.25 mm . The oven was heated at $70 \text{ }^\circ\text{C}$ for 1 min and increased at $15 \text{ }^\circ\text{C}-300 \text{ }^\circ\text{C}$, maintained 5 min. Helium was used as the carrier gas, at 1 mL min^{-1} . Transfer line and ion source (electronic impact at 70 eV) were heated at 250 and $280 \text{ }^\circ\text{C}$, respectively. The detection of SCCPs was achieved using the multiple reaction mode, as detailed in Supplementary Material, S5, adapted from the work of Zencak et al. [38]. The quantification of SCCPs was performed with solutions of Cloparin 55 for all laboratory samples, whereas SCCPs analytical standard (C_{10-13} , 63% of chlorine by weight)

was used for the field samples quantification, as the composition of the environmental mixture was unknown. Calibration curves were established using 6 concentration levels, ranging from 1 to 20 ng μL^{-1} . The associated R^2 was always higher than 0.98 and the accuracy was equal to $100 \pm 7\%$. Solvent blanks and standard controls were respectively injected every 3 and 6 samples. MassHunter Quantitative analysis software was used for the data treatment and quantification of samples.

2.9. Data modeling and calculations

An exponential model describing the accumulation of compound onto silicone rubber samplers was fitted to the experimental data:

$$C_s = K_{sw} C_w (1 - e^{-k_e t}) \quad (1)$$

Where C_s is the concentration of SCCPs in the sampler in $\mu\text{g.kg}^{-1}$ at t time in day, C_w is the concentration of SCCPs in water in $\mu\text{g.L}^{-1}$, determined experimentally, K_{sw} is the silicone-water partition coefficient corresponding to the ratio between the concentrations of SCCPs at equilibrium in the silicone and those in water and k_e is the exchange rate coefficient in day^{-1} and constitute the adjustable parameter of the model [28,37,39]. The sampling rate (R_s , in L.d^{-1}) representing an equivalent volume of water sampled per day was derived from the modeled k_e value according to the following equation:

$$R_s = k_e K_{sw} m_s \quad (2)$$

Where m_s is the mass of the sampler (ie. $1.35.10^{-3} \pm 2.10^{-5}$ kg). For the optimization of the Chemcatcher® receiving phase, the ratio between the initial water concentration and the concentration during the exposure (C_t/C_0) decreased exponentially. Consequently, for better visualization of the differences, we represented the \ln transformed ratio, and performed a linear fitting. For the calibration of Chemcatcher®, as being integrative samplers, the following linear model was fitted to the measured values:

$$N_s = C_w R_s t \quad (3)$$

where N_s is the mass of SCCPs accumulated in the sampler in μg at t time. For the field trial, the freely dissolved water concentrations were calculated as follows for the linear uptake phase:

$$TWAC = \frac{N_s}{R_s t} \quad (4)$$

and for equilibrium sampling the following equation was used:

$$C_{w,eq} = \frac{C_{s,eq}}{K_{sw}} \quad (5)$$

3. Results and discussion

3.1. Spiking procedure and stability of water concentrations in pilots

3.1.1. Continuous water flow-through calibration pilot

For the flow-through pilot, water spiking was performed by pumping the Cloparin 55 stock solution directly into the exposure tank, leading theoretically to the same composition in water. However, the Fig. 1 below reveals that the associated chromatographic patterns are quite different, with a decline of the relative abundances for the later eluted analytes in the fortified water compared to the original spiking mixture. The retention times of a homologs' series on apolar columns increase with the boiling point thus, with the number of carbon and chlorine atoms for SCCPs, which is globally linked with an increase in hydrophobicity [40]. Even if the chlorine atoms can have a slightly different impact on the molecules' polarity [41], the relative abundances found in the SCCPs' pattern in the fortified water tend to globally de-

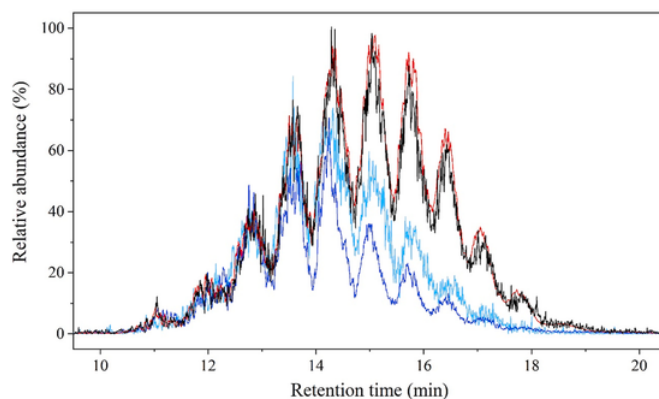


Fig. 1. Overlaid chromatograms acquired by GC/EI-MS/MS (m/z transition: 101 \rightarrow 65) corresponding to the Cloparin 55 technical mixture (red), the fraction spiked onto the dosing sheets (black), the fraction recovered in water during the passive dosing calibration (dark blue) and the flow-through experiment (light blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

crease with analytes hydrophobicity. This discrepancy could be explained by sorptive losses, as the more hydrophobic the molecules are, the more they tend to sorb to solid surfaces. This assumption is also supported by the measured water concentrations, which were systematically lower than the nominal value. When set at $8.8 \mu\text{g L}^{-1}$ for the configuration with PES membrane, the measured value equaled $5.5 \pm 1.0 \mu\text{g L}^{-1}$, and $2.2 \pm 0.4 \mu\text{g L}^{-1}$ for configuration with LDPE membrane instead of a nominal value of $5.3 \mu\text{g L}^{-1}$. These results are in line with other works in which sorptive losses were also suspected, when dealing with HOCs [31,36,42]. Nonetheless, a satisfactory stability of the water concentration was achieved during sampler exposure, with relative standard deviations of 11% ($n = 16$) and 19% ($n = 16$) for the calibration of Chemcatcher® equipped with LDPE membrane and PES membrane, respectively. Thus, the pre-exposure procedure involving a three-times renewing of the water tank and a daily checking of pump flows during exposure enabled to properly stabilize the aqueous concentration.

3.1.2. Passive dosing calibration pilot

The passive dosing calibration pilot implied a first stage consisting in spiking the dosing silicone sheets with the studied compounds. The loading of the SCCPs technical mixture onto the dosing sheets reflected perfectly the composition to the original spiking mixture of Cloparin 55, as shown by the complete superposition of the two chromatographic patterns (see Fig. 1). These observations demonstrated the efficiency of the spiking protocol, involving equilibration in mixtures of methanol and ultrapure water, even for complex HOCs mixtures such as SCCPs.

Conversely, as for Chemcatcher®, discrepancies in chromatographic patterns between the spiking solution and the fortified water were observed and were even larger in case of analytes eluted in the 15–18 min range (Fig. 1). When the passive dosing system is employed, sorptive losses from the freely dissolved fraction must be compensated by a compound's release from the dosing sheets. The observed disparity could result from the non-attainment of the partition equilibrium for the most hydrophobic compounds, thus leading to the underrepresentation of the latest eluted compounds in the fortified water chromatograms. But the complete superposition of the patterns at the beginning of the exposure and at 14 days for mixtures in the dosing sheets on the one's hand and mixtures in water on the other hand (see Supplementary Material, S6) did not support this hypothesis. Moreover, the aqueous concentrations in water remained stable, differing only by about 5% between 0 and 14 days. A more likely assumption would be

linked to a decline in the partition of SCCPs towards water, this effect being increased with hydrophobicity. Similar decline was already shown for the $\log K_{sw}$ of other HOCs families like PCBs, spanning over several orders of magnitude [43].

The water concentrations in the passive dosing experiments ($123.7 \pm 6.4 \mu\text{g L}^{-1}$) were 23–56 times higher than the values found in the flow-through experiments. This concentration is congruent with the very high SCCPs levels in the dosing sheets (ie. $11.2 \pm 0.9 \text{ mg g}^{-1}$), chosen by using K_{sw} values (mandatory when partition-controlled delivery is employed) extrapolated for Cloparin 55 mixture [9]. As the latter were determined through SPME extraction of water at 70 °C, the effect of this high temperature on partition was corrected using factors provided by Jonker et al. for PCB and silicone rubber samplers [44]. As substantial differences in the temperature impact were mentioned in this work, the maximal corrective value (ie. $-0.035 \text{ log unit per } ^\circ\text{C}$) was used to avoid too low a concentration in the water tank. Nonetheless, the measured level in water was much higher than the expected value, implying that the temperature has a weaker influence than expected on the partition coefficients of SCCPs. Furthermore, the different polymers' suppliers in the studies resulted probably in another bias in the calculation of the spiking concentration, as differences in $\log K_{sw}$ up to 0.4 log unit were observed between silicone of different brands [20]. These results point out that accurate K_{sw} values are requisite to properly perform the spiking of dosing sheets and therefore that of the water in passive dosing system.

The concentrations in the fortified water remained stable during the experiments and the corresponding chromatographic patterns were well overlaid at 0 and at 14 days of exposure (see Supplementary Material, S7). These results implied that the pre-exposure protocol to reach partition equilibrium between dosing sheets and water was valuable, i.e. renewing water after two days and waiting for another equilibration period of two days. Furthermore, when applying the passive dosing approach, the non-depletion criterium, evoked in part 2.5, must also be assessed. To this end, the evolution of the SCCPs concentrations in the dosing sheets was studied, and from the beginning to 14 days of exposure, a decrease of 12% was observed. This value is in the high range of the variation observed by Jacquet et al. for PCB (ie. between 3 and 11%) [37]. But as the pollutants' mixture studied here are much complex leading thus to higher analytical uncertainties, the non-depletion criterium was considered as fulfilled with good confidence. To conclude, the partition-controlled delivery system was proven effective for maintaining a stable water concentration of HOCs, even when they represent complex mixtures like SCCPs.

3.2. Uptake kinetics of SCCPs in silicone rubber samplers

The uptake kinetics of SCCPs in silicone rubber samplers are represented in Fig. 2, with a fitting model as follows: $C_s(t) = 2178 (\pm 171) (1 - e^{-0.337 (\pm 0.0702) t})$. The associated R^2 value equaled 0.94, the k_e and the product $K_{sw}C_w$ had respectively relative standard deviation of 20.8 and 7.9%. These satisfying values imply that even if the SCCPs mixture comprises thousands of molecules, the global accumulation model agrees well with the experimental data. This is not surprising since SCCPs constitute a series of homologs and congeners.

The equilibrium was attained at 14 days, which is lower than the values reported for calibration experiments involving HOCs (ie. about several weeks to months). The thickness of our polymer, two times lower than in the other studies, thus increasing the transfer rates, can partly explain these results. Other parameters can affect the time to attain equilibrium. To illustrate these, Vrana et al. found for PCB 10 a desorption of 90% at 16 days of exposure, whereas only 20% were dissipated at the same period in Jacquet et al. The two experiments were carried out at similar temperatures, and despite that the silicone-based samplers had different geometries (notably 7-times lower area exposed

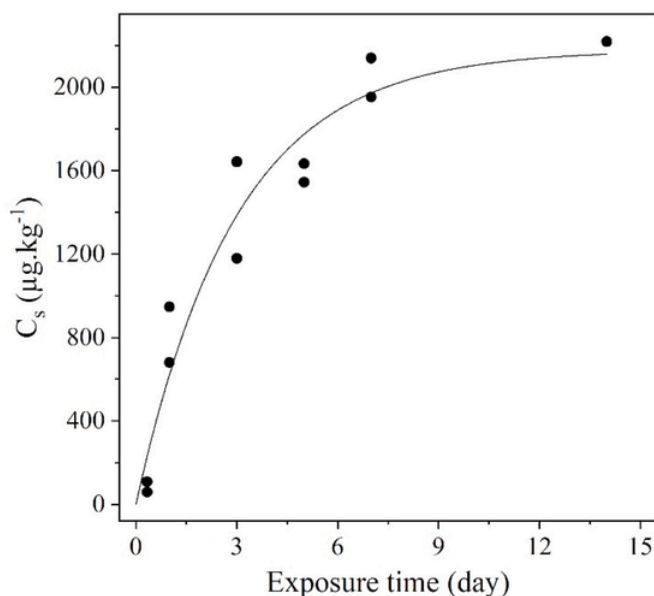


Fig. 2. Uptake kinetics of short-chain chlorinated paraffins (Cloparin 55 technical mixture, C_{10-13} , 56% Cl) in the silicone uptake sheets. The dots represent the experimental SCCPs concentrations in the uptake sheets (C_s), the line shows the fitted model described in equation (1).

in Vrana et al.), the much higher flow velocity in Vrana et al. (300 rpm against 33 rpm in Jacquet et al.) would be the main explaining factor. Overall, this indicates that a comparison is very difficult to make in terms of equilibrium times. All these parameters should be precisely informed to provide elements for comparison between the laboratory exposures.

Among the parameters estimated through the calibration, the R_e calculated from k_e according to the equation (2) equaled $8.0 \pm 2.1 \text{ L d}^{-1}$ and the $\log K_{sw}$ derived from equation (5) was equal to 4.24 ± 0.04 . Nevertheless, this value must be taken with precaution as it describes the fraction of SCCPs adsorbed onto the uptake sheets after partitioning into the water from the preloaded dosing sheets, as described in part 3.1.2. This value is named $\log(K_{sw}^a)$ (for absorption of SCCPs from water to the silicone uptake sheets) in the following discussion. To calculate a K_{sw} value representative of the original Cloparin 55 mixture, the concentration measured in the dosing sheet at equilibrium partition was used instead of that in the uptake sheets. The corresponding partition coefficient was called $\log(K_{sw}^d)$ (for desorption of SCCPs from the silicone dosing sheets to water), and equaled 4.95 ± 0.06 .

The 0.7 log unit increase compared to K_{sw}^a might be likely due to the higher amounts of hydrophobic SCCPs congeners present in the original mixture. This assumption also supports the discussion in part 3.1.2, where differences in the partitioning behavior between silicone and water were suspected. Furthermore, both partition coefficients could have been biased by a possible overestimation of the freely dissolved concentrations. HOCs easily sorb onto particulate matter and organic carbon and can aggregate to each other when transferred to water. This non dissolved fraction could have been coextracted in spot sampling of water performed during the calibration. These phenomena could have been enhanced by the probable exceedance of the water solubilities of some congeners, since estimated values for the most hydrophobic SCCPs may possibly reach a dozen of $\mu\text{g.L}^{-1}$ [41] which is lower than the measured value. Overall, the hereby calculated K_{sw} values are in a range close to the $\log K_{sw}$ of 4.4 reported by Gandolfi et al. for the same mixture and by Castells et al. for a C_{10-13} , 63% Cl standard mixture, through the partitioning between water and a polydimethylsiloxane SPME fiber [8,9]. They are also in line with K_{sw} reported for other SCCPs mixtures like Cereclor 50LV (K_{sw} of 3.6), or Huels 70 (K_{sw}

of 4.2) through partitioning between water and silicone [45]. Nevertheless the discussed values represent averages for mixtures composed of thousands congeners with very different chemical properties and then behaviors, as reflected by the log K_{ow} ranging from 4.5 to 7 for SCCPs [1]. For other HOCs families with K_{ow} also covering several orders of magnitude, the log K_{sw} values spanned also over several log units, equaling for instance 4.0 to 7.6 and 3.0 to 6.8 for PAHs and PCBs, respectively [27,28,37]. It means that the presented curve reflected an average of individual kinetics, in which low hydrophobic congeners reached equilibrium fast, while some other remained probably in the linear phase at the end of the experiment. This average behavior also depends on the weight of the different congeners in the total mixture. Hence, future work is mandatory to give insights in the partition properties of CPs mixtures towards silicone.

3.3. Accumulation of SCCPs in Chemcatcher®

3.3.1. Optimization of the Chemcatcher® configuration

The depletion kinetics of SCCPs in the aqueous phase, in which the three types of Empore™ disk (C_{18} , C_8 and “grease and oil”) were immersed, are represented in Fig. 3. The slopes associated to the linear fits are the lowest for the C_8 phase, which corresponds to the least apolar phase among the three tested, and the highest for the C_{18} receiving phase, which was thus chosen as the best receiving phase. These results are consistent with a fairly general use of this phase for compounds with $\log(K_{ow}) > 4$ [23] and with the use of SPE cartridges comprising C_{18} -silica sorbent for the extraction of SCCPs from water [6,7].

Moreover, the fast depletion highlights that the inclusion of membranes in Chemcatcher® is required to keep the uptake in the integrative stage, in addition to the protection of the receiving phase from degradation and/or biofouling [46]. Two membranes were tested here with the selected C_{18} disks, with or without disk saturation with n-octanol. In both cases, the measured quantities of SCCPs in the receiving phases after seven days were much lower when PES ($< 19 \pm 2$ ng per

disk) was used in comparison with LDPE ($> 1208 \pm 37$ ng per disk). This is not surprising since the latter is particularly well adapted for HOCs, while PES membranes are usually employed for more polar organic pollutants [23]. This is also in good agreement with Kingston et al., showing that LDPE and PolyVinyl Chloride (PVC) membranes were more suitable for PAH and PCB [22].

A layer of n-octanol between the disk and the membrane is widely added in Chemcatcher® for hydrophobic compounds, since it constitutes a high permeability solvent for such compounds, thus increasing the uptake rates [23]. However, with PES membrane, no SCCPs were detected when n-octanol was used whereas when the disks were impregnated with water, the accumulation equaled 19 ± 2 ng per disk. One explanation may rely on the incompatibility of the PES membrane with n-octanol as it has pores of $0.45 \mu\text{m}$, which may have been filled by the solvent and furthermore could have leaked from the Chemcatcher®. Concerning the configuration including LDPE membranes, the amount of SCCPs accumulated onto a C_{18} disk impregnated with octanol (ie. 1474 ± 310 ng per disk) was 1.2 times higher than that observed without n-octanol (1208 ± 37 ng per disk), but this difference was not significant (t-test, p of 0.05). These results are quite contradictory with the observations of Vrana et al. and de la Cal et al., who showed a clear improvement for PAHs and PBDEs accumulation, when n-octanol was used to saturate the disks [31,32]. In our case, SCCPs are linear molecules, which tend to diffuse along their long axis thus faster than aromatics [47,48] and maybe have a higher surface area in contact with the C_{18} chains, favoring their binding. Finally, the viscosity of n-octanol makes it difficult to handle, when mounting the Chemcatcher® device (like phase moving during its positioning in the device). Leaks to the aqueous medium can occur, as well as constrains in GC analysis with a possible decrease in repeatability [32,37]. Hence, for practical reasons, the configuration including water saturated C_{18} disk was chosen for the subsequent experiments.

3.3.2. Uptake kinetics in Chemcatcher®

Uptake kinetics of SCCPs were evaluated for both C_{18} /PES and C_{18} /LDPE Chemcatcher® configuration. When LDPE membranes were used, a small and almost constant amount was accumulated in the C_{18} receiving phase over the first ten days of exposure. This observation probably reflects a lag-time effect, due to accumulation of SCCPs in the LDPE diffusion barrier, as this polymer has high affinity for HOCs, and is even used alone for passive sampling purposes [37]. The coextraction of LDPE membranes supported this assumption as significant quantities of SCCPs were found in these. Long lag phases such as observed here were also reported in other studies focusing on Chemcatcher® [22,49]. Beyond the lag-time period, the accumulated quantity began a linear trend but correlations between the modeled and experimental data were not satisfactory (R^2 of 0.56). When considering the uptake in both membrane and disk, the quantity accumulated much better fitted the model (Fig. 4), with a R^2 of 0.978 and a slope of 1.175 ± 0.048 . By using equation (3), a sampling rate of $0.54 \pm 0.13 \text{ L d}^{-1}$ was determined for the LDPE/ C_{18} configuration.

The same methodology was applied to model the quantity of SCCPs accumulated in the PES/ C_{18} configuration. As no SCCPs were detected in the PES membrane, the fitted data corresponded only to the uptake in the receiving phase, with a corresponding R^2 of 0.82 and a slope of 0.049 ± 0.007 . The latter yielded to a drastically decreased sampling rate of $0.0085 \pm 0.0022 \text{ L d}^{-1}$ in comparison with the configuration with LDPE membrane. This is in line with the polarity of PES and our previous results found in part 3.3.1. The absence of SCCPs' accumulation in the PES membrane and the good linearity of the uptake considering the receiving phase only, indicates that apparently no lag-time effect occurs, contrarily to the configuration including LDPE membrane. This would be advantageous for passive sampling, in particular to avoid delays in the sampler response, which may cause the non-detect-

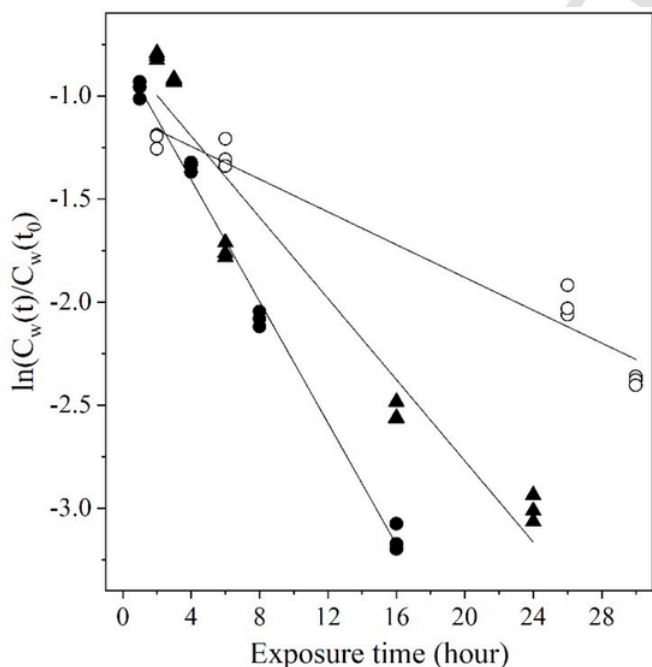


Fig. 3. Depletion kinetics of short-chain chlorinated paraffins (Cloparin 55 technical mixture, C_{10-13} , 56% Cl) in water in contact with naked Chemcatcher® equipped with receiving phases (Empore disks C_{18} (●), C_8 (○) and Grease and Oil (▲)). The depletion is expressed as a ln transformed ratio of the water concentrations at the beginning ($C_w(t_0)$) and at t exposure time ($C_w(t)$).

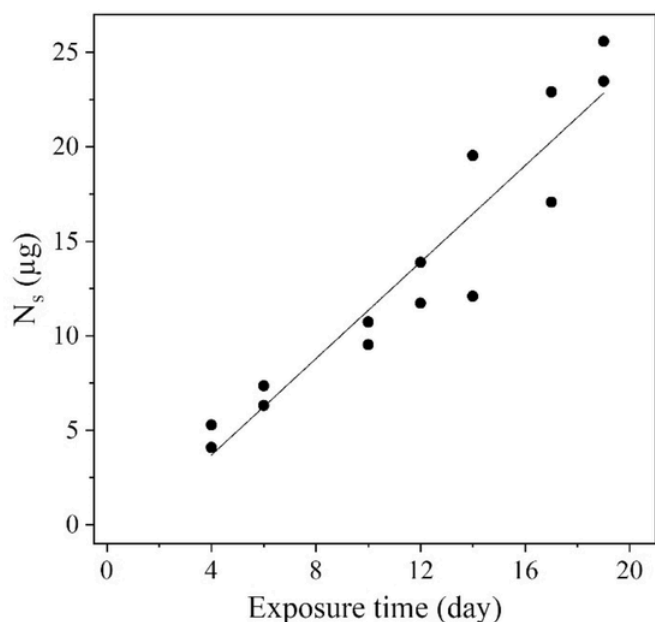


Fig. 4. Uptake kinetics of short-chain chlorinated paraffins (Cloparin 55 technical mixture, C₁₀₋₁₃, 63% Cl) in the Chemcatcher® devices with LDPE membrane and saturated water C₁₈ disk. The dots represent the experimental SCCPs accumulated in the disk and membrane, the line shows the fitted model described in equation (3).

tion of a pollution peak [22]. Nevertheless, the very low sampling rates obtained indicate that the preconcentration power would be too low, which is unfavorable for the sampling of compounds' ultratrace levels.

3.4. Field applicability

3.4.1. Implications relatively to the WFD requirements

To provide a more concrete vision of the potential contributions of both passive samplers in the implementation of the EU WFD, the calculated kinetic parameters were converted into equivalent sampling water volumes for a usual sampling period of 3 weeks. Given a typical GC-MS/MS quantification limit of 0.5 ng µL⁻¹, the quantifiable aqueous concentrations of SCCPs are reported in Table 1 for both samplers in the linear or equilibrium regimes.

Reaching such low levels, in the ng.L⁻¹ with Chemcatcher® and down to the pg.L⁻¹ with silicone rubber samplers, fulfilled the WFD requirements, setting EQS at 0.4 µg L⁻¹ and 1.4 µg L⁻¹ respectively for the Maximum Admissible Concentration (MAC) and the Annual Averaged Concentration (AAC). Only Chemcatcher® with the configuration including PES membrane did hardly reach the AAC, which reinforced

Table 1

Water volumes sampled by Chemcatcher® in both configurations (C₁₈ disk surmounted either by a PES or a LDPE membrane) in linear regime and by silicone rubber sampler in linear or equilibrium regime, for a 3-week exposure time and extrapolated short-chain chlorinated paraffins' freely dissolved concentration (C_{free}) theoretically reachable assuming an instrumental LoQ of 0.5 ng µL⁻¹.

Sampler	Chemcatcher®		Silicone rubber sampler	
	PES membrane C ₁₈ disk	LDPE membrane C ₁₈ disk	Linear	Equilibrium
Accumulation regime	Linear	Linear	Linear	Equilibrium
Equation used	$V_w = R_s t$	$V_w = R_s t$	$V_w = R_s t$	$V_w = m K_{sw}$
Kinetic constant used	$R_s = 0.0085 \text{ L d}^{-1}$	$R_s = 0.54 \text{ L d}^{-1}$	$R_s = 8.0 \text{ L d}^{-1}$	$K_{sw}^a = 4.24^a$ $K_{sw}^b = 4.95^b$
Water volume sampled (L)	0.18	11	504	70
Reachable C _{free} (µg.L ⁻¹)	1.4	0.022	0.0005	0.0036 0.0007

^a Corresponding to the fraction of Cloparin 55 desorbed from the dosing sheets in the water of the passive dosing calibration pilot.

^b Corresponding to the original Cloparin 55 mixture.

the need of a sufficient preconcentration factor and the preference of LDPE diffusive barrier. The WFD compliance requirements can also be reached through the grab sampling approach [5–7,9,11]. But the benefit of passive sampling, with equivalent water volumes filtered amounting to several hundreds of liters, lies undoubtedly in a better representativeness of the water body status.

Recently, EQS values were emitted for SCCPs in biota, precisely because of the lipophilicity of these hydrophobic compounds overcoming then the problematic of ultratrace levels' detection in water [50]. But biota standards raise ethical issues and challenges such as the species selection, the high variability linked to living organisms and extraction of the complex matrices they form. In this line, passive samplers stand as powerful analytical tools since like biota they constitute accumulative matrices for SCCPs, which would be beneficial for assessing water bodies status through WFD implementation.

3.4.2. Field trial

The performance of both passive sampling devices to monitor SCCPs in water were further assessed by carrying a field trial at five stations along the French Mediterranean coastal zone, where CPs were detected in sediments and mussels (unpublished work).

The freely dissolved concentrations of CPs were expressed as TWAC (time weighted average concentration) for Chemcatcher® (see part 3.2.1) and silicone rubber samplers. For the latter, the exposure periods lasting between 25 and 43 days implied a possible attainment of equilibrium for the less hydrophobic CPs congeners. Indeed, the time needed to attain 95% of the equilibrium was calculated according to Booij and Tuca (ie. in which an infinite volume of water is considered, reflecting in-situ deployment conditions): $t_{95\%} = \frac{3 K_{sw} m}{R_s}$ [51]. The associated values were equal to 9 days when using the previously determined log K^a_{sw} of 4.24 but increased to 48 days when employing the K^d_{sw} of 4.95. The chromatographic pattern of the CPs mixture detected in the field was closer to that of the Cloparin 55 original mixture rather than the one of the fractions desorbed into the water in the calibration pilot (see Fig. 1). This implied that the composition of the CPs mixture at field is closer to the one of Cloparin 55. Hence, the value noted K^d_{sw} of 4.95 was used to calculate C_{eq} (equilibrium concentration). TWAC values were also reported for silicone samplers, since exposure periods were lasting between 25 and 43 days (<48 days). Consequently, the most hydrophobic CPs congeners remained probably in the linear phase of accumulation.

C_{free} values were in the ng.L⁻¹ range as presented in Fig. 5-B. It must be noticed that CPs were not detected in any grab water samples. Nevertheless, CPs were present at only 3 stations out of 5 in Chemcatcher® and in only one replicate each, while CPs were detected in all the silicone rubber samplers' replicates.

Several reasons could explain the quasi absence of accumulation in Chemcatcher® devices, neither in the membranes nor the disks. Firstly,

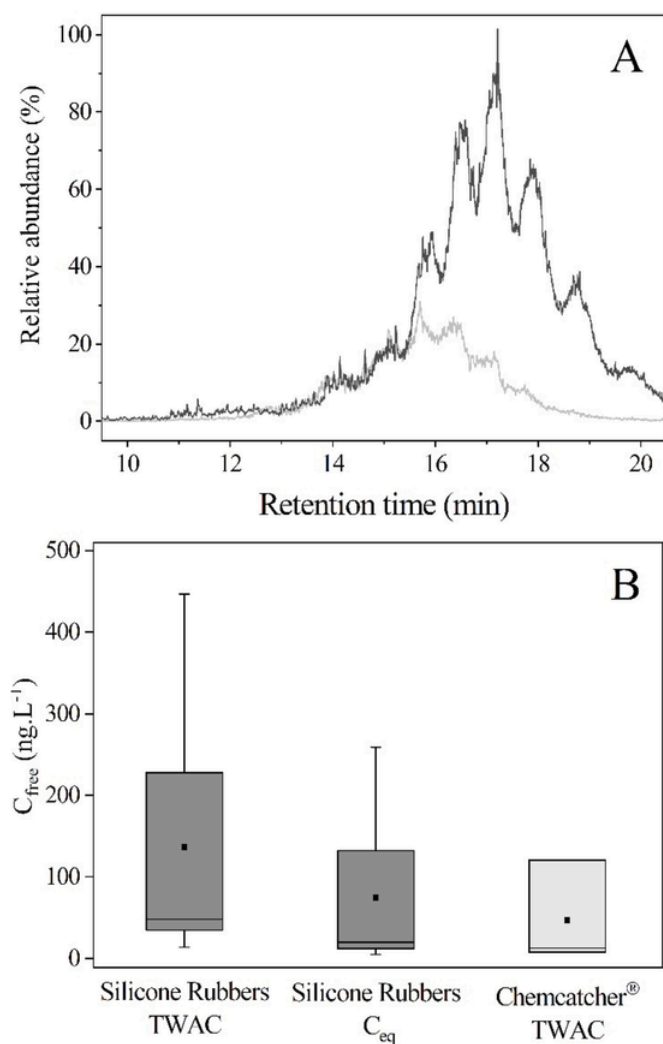


Fig. 5. Chlorinated paraffins (CPs) found during the field application in marine waters, in Chemcatcher® (3 stations, one replicate, light grey) and in silicone rubber samplers (5 stations, 3 replicates, dark grey) passive samplers. The associated reconstructed GC/EI-MS/MS chromatographic patterns (m/z transition: $101 \rightarrow 65$) are represented in part A for Chemcatcher® (light grey) and silicone rubber samplers (dark grey). The part B presents the boxplots of the calculated CPs concentrations in freely dissolved phase (C_{free} , ng.L^{-1}) from the Chemcatcher® (light grey) and silicone rubber samplers (dark grey). The TWAC and C_{eq} are respectively the time-weighted averaged concentration (calculated using equation (4), for silicone rubber and Chemcatcher® samplers) and equilibrium concentration (calculated using equation (5), for silicone rubber samplers). The whiskers on the box plot show the minimum and maximum values. The lines in the boxes represents from the bottom to the top the 25, 50 and 75% percentiles. The mean values are displayed as dots.

the sampling rate calculated was almost 15 times lower than those of silicone rubber samplers, leading probably to insufficient masses accumulated onto the samplers to reach the LoQ. Secondly, the presence of the diffusion limiting membrane lowers the exchange kinetics as well as quieter hydrodynamic conditions due to the use of the first generation's housing (cavity depth of 20 mm) and their deployment in protective cages with small openings limiting the water movements (see Supplementary Material, S3). Conversely, the absence of a surrounding membrane and housing, and the larger exposed area can justify a better detectability of CPs by using silicone rubber samplers. The deployment devices employed for silicone rubber samplers prevent such water flow disturbance, then for a future Chemcatcher® field application, similar cages should be used. The replacement of the old housing design by the new in which the cavity depth has been decreased to 7 mm would be beneficial also to increase the uptake rate [24]. Another option would

imply the deployment of several Chemcatcher® devices pooled at their retrieval to increase both the mass and area exposed, as it is usually done for silicone rubber samplers [34].

Otherwise, the C_{free} for both samplers are in the same range, between less than 50 to about 450 ng L^{-1} , the C_{eq} calculated for silicone rubber samplers being slightly lower than the TWAC. These levels are consistent with the few published data ranging from about dozens to hundreds of ng.L^{-1} [7,9,52]. But the comparison can hardly be made since spot sampling was performed and water bodies were situated in quite distinct environments from ours.

The Fig. 5-A revealed a shift in the chromatographic pattern of CPs accumulated onto silicone rubber samplers towards higher retention times compared to CPs found in Chemcatcher®. These differences are congruent with the variation in the polarities since the $\log K_{\text{ow}}$ covered are up to 6 for Chemcatcher®, and up to 10 for silicone rubber samplers [53] leading probably to the accumulation of different groups of CPs congeners. The chromatographic patterns (Fig. 5-A) were both shifted towards high retention times in comparison with the pattern of the SC-CPs mixture studied in laboratory (see Fig. 1). This illustrates the huge diversity of CPs mixtures in the environment, originating from the numerous mixtures produced and the different fates linked to the biotic or abiotic reactions they can undergo. Further works are needed to evaluate the influence of mixture diversity on key parameters of CPs passive sampling.

3.4.3. Comparison with uptake parameters reported for other HOCs

The passive sampling approach have been successfully applied for a range of HOCs in water. To evaluate the validity of this approach for SCCPs, we compared the uptake constants determined in this work for SCCPs with published data for other HOCs.

R_s is influenced by the samplers' surface area. Silicone-based samplers can be of different shapes and also have different geometry compared to Chemcatcher®. Hence, the values were expressed per 100 cm^2 ($R_{S/A}$) for better comparison of both samplers, and gathered in the Table 2.

$R_{S/A}$ for the two Chemcatcher® configurations and silicone rubber samplers were in the range of the published values. In particular, $R_{S/A}$ for the LDPE/ C_{18} configuration corroborates very well the values calculated for other HOCs by using the same calibration pilot and Chemcatcher® configuration [31].

But globally, strong variations in $R_{S/A}$ values can be noticed from Table 2, firstly linked to the wide range of K_{ow} covered by the studied analytes. On the one hand, variation in $R_{S/A}$ can rely on different geometries and polymer manufacturers for silicone rubber samplers and on different configurations applied for Chemcatcher®. On the other hand, both samplers are affected by the design of the pilot used for the laboratory calibration and also by environmental conditions, such as temperature, water flow velocity, salinity, biofouling, further explaining the differences in the values gathered.

4. Conclusion

This study constitutes the first passive sampling development for the monitoring of SCCPs in waters. The Chemcatcher® configuration was optimized with LDPE membrane and C_{18} disk saturated with water. Both passive dosing and continuous flow-through calibration pilots were implemented and enabled the maintaining of constant SCCPs levels and fulfilled with good confidence the non depletion criterium, although the mixture in the fortified water did not reflect perfectly the composition of the original spiking mixture. Good correlations between modeled and experimental values were found for both samplers. Associated calibration constants values were in the range of those published for other HOCs, and leading to detectable levels of SCCPs up to the

Table 2

Surface area normalized sampling rates $R_{S/A}$ ($L \cdot d^{-1} \cdot 100 \text{ cm}^{-2}$) for several HOCs having $\log K_{ow}$ of 3.4–8.4 through silicone rubber (SR) and Chemcatcher® (CC) samplers of different characteristics, determined in this work and reported elsewhere using diverse laboratory calibration methods.

Sampler	Sampler characteristics	Laboratory calibration method (spiking, agitation)	Analytes	Log K_{ow}	$R_{S/A}$ ($L \cdot d^{-1} \cdot 100 \text{ cm}^{-2}$)	Reference
SR	Sheet; 0.25 mm thick	Passive dosing, agitation pump	SCCPs	4.5–7	8.0 ± 2.1	Present work
SR	Sheet; 0.5 mm thick	Passive dosing, agitation pump	PAHs	3.4–6.8	0.7–25.6	[28]
SR	Sheet; 0.5 mm thick	Passive dosing, stirring blade	PCBs PCBs	5.2–7.4 5.2–7.7	0.6–1.5 3.4 ± 0.6 – 4.2 ± 0.7	[37]
SR	Stir bar; 0.5 mm thick	Single dose, rotating carousel	OCPs	3.7–6.7	3.4 ± 0.7 – 19.1 ± 0.2	[54]
CC	PES membrane Water-saturated C_{18} disk	Flow-through, rotating carousel	PCBs SCCPs	4.6–8.4 4.5–7.0	1.9 ± 0.3 – 12.6 ± 0.4 0.05 ± 0.01	Present work
CC	PES membrane Octanol-saturated C_{18} disk	Single dose, agitation pump	OCPs	3.1–7.0	0.02–0.3	[55]
CC	LDPE membrane Water-saturated C_{18} disk	Flow-through, rotating carousel	SCCPs	4.5–7.0	3.1 ± 0.7	Present work
CC	LDPE membrane Octanol-saturated C_{18} disk	Flow-through, rotating carousel	PAHs	4.0–6.9	0.07 ± 0.04 – 7.9 ± 4.3	[36]
CC	LDPE membrane Octanol-saturated C_{18} disk	Flow-through, overhead stirrer	OCPs CBz PBDEs	3.7–5.4 5.2–5.4 6.8–7.9	0.3 ± 0.08 – 1.8 ± 0.6 0.8 ± 0.2 – 4.9 ± 1.0 1.4 ± 1.8	[31]
CC	LDPE membrane Octanol-saturated C_{18} disk	Passive dosing, stirring blade	OCPs PCBs	5.5–6.5 5.2–7.7	0.006 ± 0.03 1.1 ± 0.2 – 4.0 ± 0.4	[37]
CC	LDPE membrane Octanol-saturated C_{18} disk	Flow-through, rotating carousel	PCBs	5.9–6.6	4.3 ± 2.3 – 5.1 ± 1.2	[42]
			OCPs	5.4–6.4	3.3 ± 0.9 – 4.6 ± 1.0	

Sampler	Sampler characteristics	Laboratory calibration method (spiking, agitation)	Analytes	Log K_{ow}	$R_{S/A}$ ($L \cdot d^{-1} \cdot 100 \text{ cm}^{-2}$)	Reference
			PBDEs	6.8–7.2	1.7 ± 0.6 – 3.3 ± 0.9	

PES: PolyEtherSulfone, LDPE: Low-Density PolyEthylene, PAHs: Polycyclic Aromatic Hydrocarbons, PCBs: PolyChloroBiphenyls, OCPs: OrganoChlorine Pesticides, PBDEs: PolyBro-moDiphenylEthers, CBz: ChloroBenzenes.

$\text{pg} \cdot \text{L}^{-1}$ range. The field trial further established the applicability of both samplers to in-situ deployment.

Some authors have shown that for other HOCs families (ie. PCBs and PAHs) the sampling rate appears to be less sensible than the K_{sw} to molecular properties such as the hydrophobicity. In this frame, Chemcatcher® as being integrative samplers would be more appropriate for estimating a more accurate C_{free} , even if the preconcentrating power is lowered in comparison with silicone rubber samplers. The latter would be powerful for screening ultratracés of SCCPs in unknown environments, pending further studies to give insights into the partitioning behavior of SCCPs. For K_{sw} values less than 5, the time for equilibration at field should remain practicable, the sampling rate being then redundant. But this would require the precise determination of K_{sw} for more mixtures, in order to evaluate the range of variation of this parameter with the type of mixture.

Moreover, as the influencing factors on the constants calculated can be very different between the field and the laboratory, it would be wise to apply corrective approaches. As SCCPs are HOCs, the performance and reference compounds' approach could be considered, especially in the case of silicone samplers, for which this approach is validated. This would enable to provide a more accurate quantification in the field by considering the influence of in-situ conditions. Forthcoming research must focalize on the determination of passive samplers' key parameters for different CPs mixture, aiming to deeper understand the influence of this diversity on R_s and K_{sw} values.

Credit author statement

Mathilde GODERE, Methodology, Formal analysis, Data curation, Investigation, Conceptualization, Writing – original draft, Visualization. Stella MONDANGE, Methodology, Formal analysis, Data curation, Investigation. Pierre DOUMENQ, Supervision, Conceptualization, Project administration, Funding acquisition. Catherine GONZALEZ, Supervision, Validation, Visualization, Reviewing and editing, Project administration, Funding acquisition. Laure MALLERET, Supervision, Conceptualization, Validation, Visualization, Writing – original draft, Writing reviewing and editing, Project administration, Funding acquisition

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research was supported by Agence de l'Eau Rhône Méditerranée Corse and was performed thanks to the funding of a delegation as researcher at the National Center for Scientific Research. We thank Max Bresson and Jean-François Barbion from LCE, for their help in the design and construction of the passive dosing exposure pilot and Laurence Asia and Clementine Côte for assistance in GC-MS/MS analyses. Sylvie Spinelli and Murielle Avezac from IMT Mines Alès are acknowledged for their technical support for the calibration of Chemcatcher®.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.talanta.2020.121920>.

References

- [1] D. Muir, G. Stern, G. Tomy, Chlorinated paraffins, *Anthropog. Compd. Part K*, 3, Springer, Berlin, Heidelberg, 2000, pp. 203–236, doi:10.1007/3-540-48915-0_8.
- [2] Off. J. Eur. Union, EU Directive 2013/39/EU of the European Parliament and of the council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy (2013) accessed <https://www.legifrance.gouv.fr/affichTexte.do?cidTexte=JORFTEXT000028022376&categorieLien=id>. (Accessed 21 February 2017).
- [3] United nations environment programme, Stockholm Convention on Persistent Organic Pollutants (2017).
- [4] S. Geiß, N. Lettmann, A. Rey, H. Lepper, B. Körner, S. Mais, T. Prey, B. Hilger, M. Engelke, S. Lebertz, C. Chatellier, G. Sawal, D. Löffler, T. Schillings, Preliminary interlaboratory trial for ISO/DIS 12010: determination of short chain polychlorinated alkanes (SCCP) in water, *Clean* 39 (2011) 537–542, doi:10.1002/clen.201000384.
- [5] C.-Y. Chang, W.-H. Chung, W.-H. Ding, Vortex-assisted liquid–liquid microextraction for the rapid screening of short-chain chlorinated paraffins in water, *J. Separ. Sci.* 39 (2016) 427–432, doi:10.1002/jssc.201500991.
- [6] P. Castells, F.J. Santos, M.T. Galceran, Solid-phase extraction versus solid-phase microextraction for the determination of chlorinated paraffins in water using gas chromatography-negative chemical ionisation mass spectrometry, *J. Chromatogr., A* 1025 (2004) 157–162.
- [7] Y.-J. Wang, Y.-W. Wang, G.-B. Jiang, Solid-phase extraction for analysis of short-chain chlorinated paraffins in water samples, *Chin. J. Anal. Chem.* 46 (2018) 1102–1108, doi:10.1016/S1872-2040(18)61097-7.
- [8] P. Castells, F.J. Santos, M.T. Galceran, Solid-phase microextraction for the analysis of short-chain chlorinated paraffins in water samples, *J. Chromatogr., A* 984 (2003) 1–8, doi:10.1016/S0021-9673(02)01772-7.
- [9] F. Gandolfi, L. Malleret, M. Sergent, P. Doumenq, Parameters optimization using experimental design for headspace solid phase micro-extraction analysis of short-chain chlorinated paraffins in waters under the European water framework directive, *J. Chromatogr., A* 1406 (2015) 59–67, doi:10.1016/j.chroma.2015.06.030.
- [10] N. Zhan, F. Guo, S. Zhu, Z. Rao, Headspace solid-phase microextraction coupled to comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry for the determination of short-chain chlorinated paraffins in water samples, *J. Anal. Methods Chem.* (2018) 2768547, doi:10.1155/2018/2768547.
- [11] P. Tölgyessy, S. Nagyová, M. Sládkovičová, Determination of short chain chlorinated paraffins in water by stir bar sorptive extraction–thermal desorption–gas chromatography–triple quadrupole tandem mass spectrometry, *J. Chromatogr., A* 1494 (2017) 77–80, doi:10.1016/j.chroma.2017.03.012.
- [12] G.-L. Wei, X.-L. Liang, D.-Q. Li, M.-N. Zhuo, S.-Y. Zhang, Q.-X. Huang, Y.-S. Liao, Z.-Y. Xie, T.-L. Guo, Z.-J. Yuan, Occurrence, fate and ecological risk of chlorinated paraffins in Asia: a review, *Environ. Int.* 92 (2016) 373–387, doi:10.1016/j.envint.2016.04.002.
- [13] K. Booiij, C.D. Robinson, R.M. Burgess, P. Mayer, C.A. Roberts, L. Ahrens, I.J. Allan, J. Brant, L. Jones, U.R. Kraus, M.M. Larsen, P. Lepom, J. Petersen, D. Profrock, P. Roose, S. Schäfer, F. Smedes, C. Tixier, K. Vorkamp, P. Whitehouse, Passive sampling in regulatory chemical monitoring of nonpolar organic compounds in the aquatic environment, *Environ. Sci. Technol.* 50 (2016) 3–17, doi:10.1021/acs.est.5b04050.
- [14] W. Brack, V. Dulio, M. Ågerstrand, I. Allan, R. Altenburger, M. Brinkmann, D. Bunke, R.M. Burgess, I. Cousins, B.I. Escher, F.J. Hernández, L.M. Hewitt, K. Hilscherová, J. Hollender, H. Hottler, R. Kase, B. Klauer, C. Lindim, D.L. Herráez, C. Miège, J. Munthe, S. O'Toole, L. Posthuma, H. Rüdél, R.B. Schäfer, M. Sengl, F. Smedes, D. van de Meent, P.J. van den Brink, J. van Gils, A.P. van Wezel, A.D. Vethaak, E. Vermeirssen, P.C. von der Ohe, B. Vrana, Towards the review of the European Union Water Framework Directive: recommendations for more efficient assessment and management of chemical contamination in European surface water resources, *Sci. Total Environ.* 576 (2017) 720–737, doi:10.1016/j.scitotenv.2016.10.104.
- [15] R. Lohmann, D. Muir, E.Y. Zeng, L.-J. Bao, I.J. Allan, K. Arinaitwe, K. Booiij, P. Helm, S. Kaserzon, J.F. Mueller, Y. Shibata, F. Smedes, M. Tsapakis, C.S. Wong, J.

- You, Aquatic global passive sampling (AQUA-GAPS) revisited: first steps toward a network of networks for monitoring organic contaminants in the aquatic environment, *Environ. Sci. Technol.* 51 (2017) 1060–1067, doi:10.1021/acs.est.6b05159.
- [16] C. Miège, N. Mazzella, I. Allan, V. Dulio, F. Smedes, C. Tixier, E. Vermeirssen, J. Brant, S. O'Toole, H. Budzinski, J.-P. Ghestem, P.-F. Staub, S. Lardy-Fontan, J.-L. Gonzalez, M. Coquery, B. Vrana, Position paper on passive sampling techniques for the monitoring of contaminants in the aquatic environment – achievements to date and perspectives, *Trends Environ. Anal. Chem.* 8 (2015) 20–26, doi:10.1016/j.teac.2015.07.001.
- [17] B. Vrana, T. Rusina, K. Okonski, R. Prokeš, P. Carlsson, R. Kopp, F. Smedes, Chasing equilibrium passive sampling of hydrophobic organic compounds in water, *Sci. Total Environ.* 664 (2019) 424–435, doi:10.1016/j.scitotenv.2019.01.242.
- [18] G.A. Mills, A. Gravell, B. Vrana, C. Harman, H. Budzinski, N. Mazzella, T. Ocelka, Measurement of environmental pollutants using passive sampling devices – an updated commentary on the current state of the art, *Environ. Sci. Process. Impacts.* 16 (2014) 369–373, doi:10.1039/C3EM00585B.
- [19] F. Reichenberg, P. Mayer, Two complementary sides of bioavailability: accessibility and chemical activity of organic contaminants in sediments and soils, *Environ. Toxicol. Chem. SETAC.* 25 (2006) 1239–1245, doi:10.1897/05-458R.1.
- [20] T.P. Rusina, F. Smedes, J. Klanova, K. Booi, I. Holoubek, Polymer selection for passive sampling: a comparison of critical properties, *Chemosphere* 68 (2007) 1344–1351, doi:10.1016/j.chemosphere.2007.01.025.
- [21] J.F.N. Valderrama, K. Baek, F.J. Molina, I.J. Allan, Implications of observed PBDE diffusion coefficients in low density polyethylene and silicone rubber, *Environ. Sci. Process. Impacts.* 18 (2016) 87–94, doi:10.1039/C5EM00507H.
- [22] J.K. Kingston, R. Greenwood, G.A. Mills, G.M. Morrison, L.B. Persson, Development of a novel passive sampling system for the time-averaged measurement of a range of organic pollutants in aquatic environments, *J. Environ. Monit. JEM.* 2 (2000) 487–495.
- [23] A. Charriau, S. Lissalde, G. Poulter, N. Mazzella, R. Buzier, G. Guibaud, Overview of the Chemcatcher® for the passive sampling of various pollutants in aquatic environments Part A: principles, calibration, preparation and analysis of the sampler, *Talanta* 148 (2016) 556–571, doi:10.1016/j.talanta.2015.06.064.
- [24] S. Lissalde, A. Charriau, G. Poulter, N. Mazzella, R. Buzier, G. Guibaud, Overview of the Chemcatcher® for the passive sampling of various pollutants in aquatic environments Part B: field handling and environmental applications for the monitoring of pollutants and their biological effects, *Talanta* 148 (2016) 572–582, doi:10.1016/j.talanta.2015.06.076.
- [25] C. Miège, S. Schiavone, A. Dabrin, M. Coquery, N. Mazzella, C. Berho, J.-P. Ghestem, A. Togola, C. Gonzalez, J.-L. Gonzalez, B. Lalere, S. Lardy-Fontan, B. Lepot, D. Munaron, C. Tixier, An in situ intercomparison exercise on passive samplers for monitoring metals, polycyclic aromatic hydrocarbons and pesticides in surface waters, *TrAC Trends Anal. Chem. (Reference Ed.)* 36 (2012) 128–143, doi:10.1016/j.trac.2012.01.009.
- [26] F. Smedes, Chapter 19 Monitoring of chlorinated biphenyls and polycyclic aromatic hydrocarbons by passive sampling in concert with deployed mussels, in: B.V.R. Greenwood (Ed.), *Compr. Anal. Chem.*, Elsevier, 2007, pp. 407–448 accessed <http://www.sciencedirect.com/science/article/pii/S0166526X06480193>. (Accessed 7 March 2017).
- [27] B. Vrana, F. Smedes, R. Prokeš, R. Loos, N. Mazzella, C. Miège, H. Budzinski, E. Vermeirssen, T. Ocelka, A. Gravell, S. Kaserzon, An interlaboratory study on passive sampling of emerging water pollutants, *TrAC Trends Anal. Chem. (Reference Ed.)* 76 (2016) 153–165, doi:10.1016/j.trac.2015.10.013.
- [28] T.P. Rusina, F. Smedes, M. Koblikova, J. Klanova, Calibration of silicone rubber passive samplers: experimental and modeled relations between sampling rate and compound properties, *Environ. Sci. Technol.* 44 (2010) 362–367, doi:10.1021/es900938r.
- [29] A. Garnier, C. Bancon-Montigny, S. Delpoux, S. Spinelli, M. Avezac, C. Gonzalez, Study of passive sampler calibration (Chemcatcher®) for environmental monitoring of organotin compounds: matrix effect, concentration levels and laboratory vs in situ calibration, *Talanta* 219 (2020) 121316, doi:10.1016/j.talanta.2020.121316.
- [30] B. Vrana, G.A. Mills, E. Dominiak, R. Greenwood, Calibration of the Chemcatcher passive sampler for the monitoring of priority organic pollutants in water, *Environ. Pollut.* 142 (2006) 333–343, doi:10.1016/j.envpol.2005.10.033.
- [31] A. de la Cal, M. Kuster, M.L. de Alda, E. Eljarrat, D. Barceló, Evaluation of the aquatic passive sampler Chemcatcher for the monitoring of highly hydrophobic compounds in water, *Talanta* 76 (2008) 327–332, doi:10.1016/j.talanta.2008.02.049.
- [32] B. Vrana, G. Mills, R. Greenwood, J. Knutsson, K. Svensson, G. Morrison, Performance optimisation of a passive sampler for monitoring hydrophobic organic pollutants in water, *J. Environ. Monit.* 7 (2005) 612–620, doi:10.1039/B419070J.
- [33] M. Shaw, G. Eaglesham, J.F. Mueller, Uptake and release of polar compounds in SDB-RPS Empore™ disks; implications for their use as passive samplers, *Chemosphere* 75 (2009) 1–7, doi:10.1016/j.chemosphere.2008.11.072.
- [34] F. Smedes, K. Booi, International Council for the Exploration of the Sea, Guidelines for Passive Sampling of Hydrophobic Contaminants in Water Using Silicone Rubber Samplers, International Council for the Exploration of the Sea, Copenhagen, 2012 accessed <http://bibpurl.oclc.org/web/47286/times52/120621%20TIMES%2052%20Final.pdf> <http://www.ices.dk/pubs/times/times52/120621%20TIMES%2052%20Final.pdf>. (Accessed 3 March 2017).
- [35] K. Booi, F. Smedes, E.M. van Weerlee, Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers, *Chemosphere* 46 (2002) 1157–1161, doi:10.1016/S0045-6535(01)00200-4.
- [36] B. Vrana, A. Paschke, P. Popp, Calibration and field performance of membrane-enclosed sorptive coating for integrative passive sampling of persistent organic pollutants in water, *Environ. Pollut.* 144 (2006) 296–307, doi:10.1016/j.envpol.2005.11.046.
- [37] R. Jacquet, C. Miège, F. Smedes, C. Tixier, J. Tronczynski, A. Togola, C. Berho, I. Valor, J. Llorca, B. Barillon, P. Marchand, M. Coquery, Comparison of five integrative samplers in laboratory for the monitoring of indicator and dioxin-like polychlorinated biphenyls in water, *Chemosphere* 98 (2014) 18–27, doi:10.1016/j.chemosphere.2013.09.011.
- [38] Z. Zencak, M. Reth, M. Oehme, Determination of total polychlorinated n-alkane concentration in biota by electron ionization-MS/MS, *Anal. Chem.* 76 (2004) 1957–1962, doi:10.1021/ac0353381.
- [39] J.N. Huckins, J.D. Petty, K. Booi, Monitors of Organic Chemicals in the Environment : Semipermeable Membrane Devices, Springer, 2006 accessed <http://www.springer.com/la/book/9780387290775>. (Accessed 1 March 2017).
- [40] P. Korytár, P.E.G. Leonards, J. de Boer, U.A.Th Brinkman, Group separation of organohalogenated compounds by means of comprehensive two-dimensional gas chromatography, *J. Chromatogr., A* 1086 (2005) 29–44, doi:10.1016/j.chroma.2005.05.087.
- [41] J. Glüge, C. Bogdal, M. Scheringer, A.M. Buser, K. Hungerbühler, Calculation of physicochemical properties for short- and medium-chain chlorinated paraffins, *J. Phys. Chem. Ref. Data* 42 (2013) 023103, doi:10.1063/1.4802693.
- [42] J. Petersen, A. Paschke, R. Gunold, G. Schüttmann, Calibration of Chemcatcher® passive sampler for selected highly hydrophobic organic substances under fresh and sea water conditions, *Environ. Sci.: Water Res. Technol.* 1 (2015) 218–226, doi:10.1039/C4EW00043A.
- [43] F. Smedes, Silicone-water partition coefficients determined by cosolvent method for chlorinated pesticides, musks, organo phosphates, phthalates and more, *Chemosphere* 210 (2018) 662–671, doi:10.1016/j.chemosphere.2018.07.054.
- [44] M.T.O. Jonker, S.A. van der Heijden, M. Kotte, F. Smedes, Quantifying the effects of temperature and salinity on partitioning of hydrophobic organic chemicals to silicone rubber passive samplers, *Environ. Sci. Technol.* 49 (2015) 6791–6799, doi:10.1021/acs.est.5b00286.
- [45] M. Castro, M. Breitholtz, B. Yuan, I. Athanassiadis, L. Asplund, A. Sobek, Partitioning of chlorinated paraffins (CPs) to *Daphnia magna* overlaps between restricted and in-use categories, *Environ. Sci. Technol.* 52 (2018) 9713–9721, doi:10.1021/acs.est.8b00865.
- [46] R. Greenwood, G.A. Mills, B. Vrana, I. Allan, R. Aguilar-Martínez, G. Morrison, Chapter 9 Monitoring of priority pollutants in water using chemcatcher passive sampling devices, in: B.V.R. Greenwood (Ed.), *Compr. Anal. Chem.*, Elsevier, 2007, pp. 199–229 accessed <http://www.sciencedirect.com/science/article/pii/S0166526X06480090>. (Accessed 21 February 2017).
- [47] A. Reynier, P. Dole, S. Humbel, A. Feigenbaum, Diffusion coefficients of additives in polymers. I. Correlation with geometric parameters, *J. Appl. Polym. Sci.* 82 (2001) 2422–2433, doi:10.1002/app.2093.
- [48] K.S.J. Kwan The role of penetrant structure on the transport and mechanical properties of a thermoset adhesive <https://vtechworks.lib.vt.edu/handle/10919/306661998>
- [49] N. Estoppey, J. Mathieu, E. Gascon Diez, E. Sapin, O. Delémont, P. Esseiva, L.F. de Alencastro, S. Coudret, P. Folly, Monitoring of explosive residues in lake-bottom water using Polar Organic Chemical Integrative Sampler (POCIS) and chemcatcher: determination of transfer kinetics through Polyethersulfone (PES) membrane is crucial, *Environ. Pollut.* 252 (2019) 767–776, doi:10.1016/j.envpol.2019.04.087.
- [50] French Official Journal, National decree of 27 July 2018 about methods and criteria for the assessment of the ecological status, chemical status and ecological potential of surface waters, 2018.
- [51] K. Booi, F. Tucça, Passive samplers of hydrophobic organic chemicals reach equilibrium faster in the laboratory than in the field, *Mar. Pollut. Bull.* 98 (2015) 365–367, doi:10.1016/j.marpolbul.2015.07.007.
- [52] A. Rubirola, F.J. Santos, M.R. Boleda, M.T. Galceran, Routine method for the analysis of short-chain chlorinated paraffins in surface water and wastewater, *Clean* 46 (2018) 1600151, doi:10.1002/clean.201600151.
- [53] B. Vrana, I.J. Allan, R. Greenwood, G.A. Mills, E. Dominiak, K. Svensson, J. Knutsson, G. Morrison, Passive sampling techniques for monitoring pollutants in water, *TrAC Trends Anal. Chem. (Reference Ed.)* 24 (2005) 845–868, doi:10.1016/j.trac.2005.06.006.
- [54] O. Posada-Ureta, M. Olivares, A. Delgado, A. Prieto, A. Vallejo, M. Irazola, A. Paschke, N. Etxebarria, Applicability of polydimethylsiloxane (PDMS) and polyethersulfone (PES) as passive samplers of more hydrophobic organic compounds in intertidal estuarine environments, *Sci. Total Environ.* 578 (2017) 392–398, doi:10.1016/j.scitotenv.2016.10.194.
- [55] L. Ahrens, A. Daneshvar, A.E. Lau, J. Kreuger, Characterization of five passive sampling devices for monitoring of pesticides in water, *J. Chromatogr., A* 1405 (2015) 1–11, doi:10.1016/j.chroma.2015.05.044.