Article

Field Calibration of Semipermeable Membrane Devices (SPMDs) for Persistent Organic Pollutant Monitoring in a Reservoir

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Abstract: Persistent Organic Pollutants (POPs) in water can reach levels below ppt (ng L^{-1}), representing a challenge for risk assessment using long-term exposure. Therefore, sampling devices to monitor trace levels of organic compounds are suitable due to their sensitivity and low detection limits. In this work, the field calibration and monitoring for POPs, such as Polycyclic Aromatic Hydrocarbons (PAHs) and pesticides, in a drinking water reservoir were carried out using semipermeable membrane devices (SPMDs). The SPMDs were spiked with deuterated PCBs used as PRCs, and their dissipation was measured at 5, 10, 15 and 24 days. The SPMDs were dialyzed in hexane twice and the initial amount (N) and final amount (N_o) of PRCs in extracts were estimated by GC/MS to calculate the sampling rate (R_s) for target compounds. The PCBs were dissipated more than 30% at 24 days, and R_s were calculated between 27.8 and 72.7 L day^{-1} for PAHs and 35.8 and 71.3 L day^{-1} for pesticides. Finally, PAH congeners such as Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene and Pyrene were detected at water concentration (C_w) ranges between 0.5 and 2.7 ng L^{-1}, whilst chlorpyrifos was the only pesticide detected at 19.0 ng L^{-1} in the reservoir. This calibration showed that PRCs do not dissipate entirely in 24 days and that dissipation modelling may be applied for C_w estimation of POPs in reservoirs.

Keywords: semipermeable membrane devices; performance reference compounds; polycyclic aromatic hydrocarbons; pesticides and passive samplers

1. Introduction

Semipermeable membrane devices (SPMDs) have been widely used as passive samplers for the monitoring of non-polar pollutants in water [1]. SPMDs are passive samplers applied in the detection and quantification of a wide range of Persistent Organic Pollutants (POPs), including polycyclic aromatic hydrocarbons (PAHs), flame retardants, organochlorines pesticides, etc., at very low water concentration (C_w) levels. These POPs are included in the Stockholm Convention because of their persistence, toxicity and bioaccumulation [2–4].

Non-polar POPs are adsorbed inside SPMDs through lipophilic interactions, which can be extrapolated to the bioaccumulation process due to the similar uptake principle by the biota [1]. Thus, SPMDs are usually applied in bioaccumulation factor estimation.

These membranes include the neutral triglyceride triolein, which mimics the partitioned steps during bioconcentration, providing qualitative and quantitative data for non-polar compounds when Gas Chromatography is coupled with Mass Spectrometry during analytical analyses [5]. Triolein is sealed in a lay-flat, thin-wallet tube of Low-Density Polyethylene (LDPE).

The quantification of POPs in SPMDs is challenging due to the multiple parameters that can affect the process, including fluxes, sampling time, water volume and temperature. Hence, the dissolved levels of POPs in water have been estimated by applying dissipation modelling that follows the kinetics of performance reference compounds (PRCs) which have similar properties to the target compounds [5]. The PRCs are initially spiked in SPMDs, and these substances are dissipated during exposure time in the water. Some deuterated Polychlorinated biphenyls (PCBs) congeners, such as 14, 29 and 50, are selected as PRCs since they do not occur in the environment under natural conditions [6]. The initial amount (N_o) of PRCs decreases during the exposure time in the field according to Fick's law [5]. Then, the PRCs' dissipation can be related to the medium exposition and the flow rate in the water body [7]. The release of PRCs from SPMDs to water is related to the n-octanol-water partition coefficient (*log k_{ow}*). Thus, polar compounds dissipate faster than non-polar ones [8]. However, PRCs should not dissipate completely, allowing one to apply a dissipation modelling which includes the initial and final concentration of these substances. Moreover, field calibration should include studying the dissipation of PRCs to avoid their total loss in the water [9,10].

The use of SPMDs for POP monitoring in Colombian drinking water reservoirs represents a suitable alternative due to their sensitivity and low detection limits. Additionally, field data can be compared with bioaccumulation under natural conditions, which is impossible using conventional methods.

Many reservoir may be affected by antropogenic activities in worldwide [11]. Similarly, La Fe, an important reservoir that supplies drinking water to more than two million people in Medellin, the second largest and most industrialized city in Colombia, is being affected by anthropogenic activities. In a previous contribution, it was shown that pesticides applied during agricultural activities and PAHs from mobile combustion emissions are present in tributaries of the La Fe reservoir [12]. The PAHs represent a risk for human health, wildlife and the environment [13–15].

This study focused on the field calibration of SPMDs to estimate the levels of pesticides and PAHs to assess their possible impacts on a Colombian water reservoir's quality. In addition, we aim to estimate the range of time at which the dissipation was not complete during the SPMDs' deployment in the drinking water reservoir.

2. Materials and Methods

2.1. Chemicals and Reagents

Organophosphate (OP) Pesticide Mix (Purity > 99.5%), Priority pollutant PAHs in acetonitrile (Sigma-Aldrich, St. Louis, MO, USA) and deuterated PCB 14, PCB 29 and PCB 50 were purchased from Chemservice, West Chester, PA, USA, and used as PRCs. Solvents such as hexane and acetone were supplied by Burdick and Jackson, Morristown, NJ, USA. SPMDs, large canisters and spider holders were all provided by Environmental sampling technologies Laboratory (Est-Lab), St Joseph, MI, USA. The SPMDs used as passive samplers were previously spiked with PCB 14, 29 and 50 at concentrations of 200 ng L^{-1} by the provider.
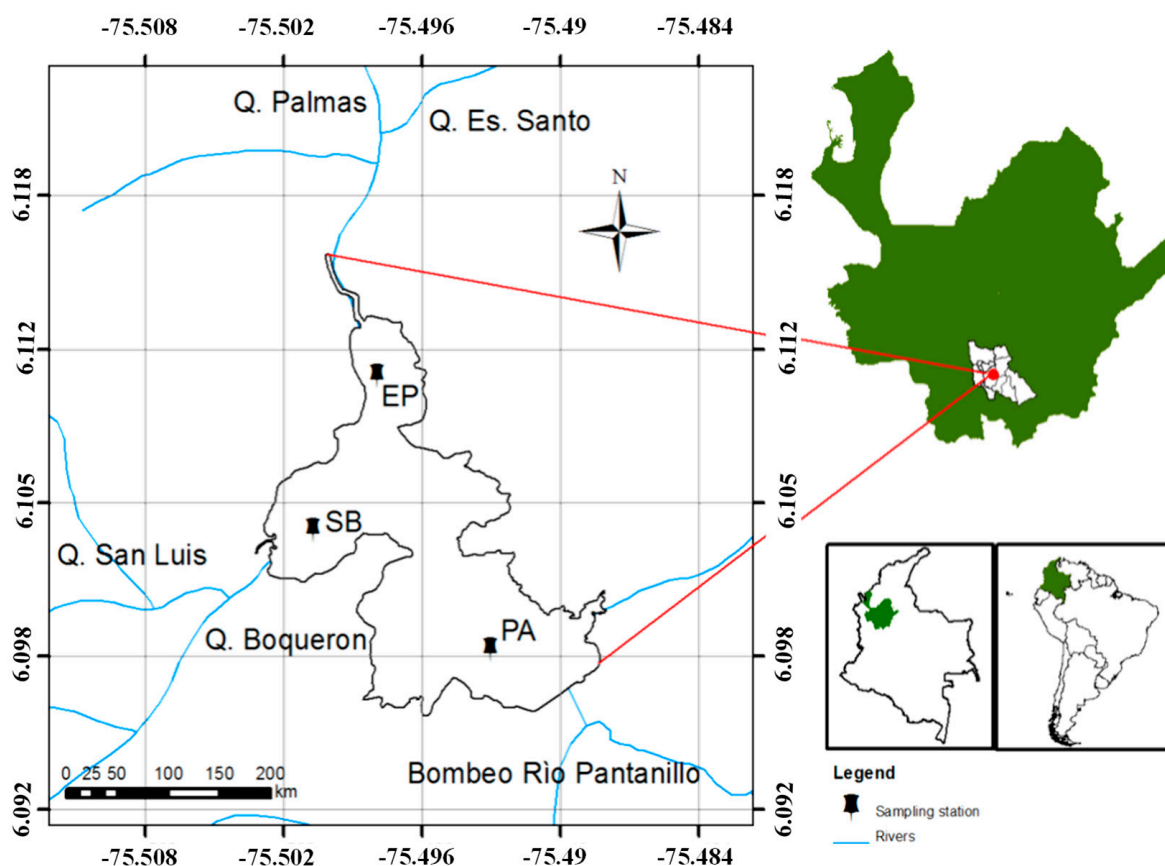
2.2. Gas Chromatography /Mass Spectrometric Analysis

A electron-impact and single-quadrupole GC–MS from Thermo Scientific Ultra TRACE GC-ISQ (Waltham, MA, USA) was used for pollutant detection and quantification. Organophosphorus (OP) pesticides (parathion, chlorpyrifos and diazinon), PAHs (Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene) and PCBs (14, 29 and 50) were separated on an Rtx 5sil-MS (30 m × 0.25 mm I.D, 0.25 m film thickness) capillary column from Restek (Bellefonte, PA, USA) using helium gas as a carrier at a flow rate of 1 mL min^{-1}. The column was kept for 1 min at 50 °C; then, the temperature was increased to 320 °C at a rate of 25 °C min^{-1} and held for 1 min. The injector and interface temperature were maintained at 270 °C, and the source temperature was held at 250 °C. The injection volume was 1 µL. The instrument was operated in

SCAN mode. Selection Ion Monitoring (SIM) scanning mode was implemented for target compounds. The linearity of the method was evaluated by five-point calibration curves for organophosphate pesticides and PAHs. The C_w of target POPs was determined using PRC dissipation modelling through a five-point PCB calibration curve. This procedure was carried out in triplicate at low and high levels.

2.3. Study Area and Sampling

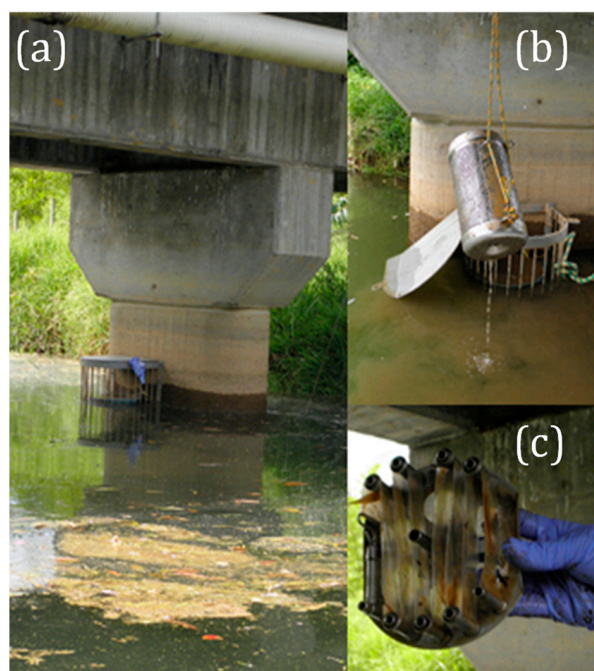The study area is located east of the city of Medellín, Colombia (reservoir). See Figure 1.

Figure 1. Location of reservoir for drinking water supply (Medellín, Colombia).

The sampling place was located at a bridge crossing of an important tributary for the reservoir. A passive sampler protector tube (PSPT) was fastened to the bridge column to avoid damage to the passive samplers (see Figure 2). The sampling was carried out in a low-rainfall dry season.

In the PSPT (Figure 2a), three large canisters containing the SPMDs were deployed (Figure 2b,c). Each canister was collected and analyzed at 5, 10, 15 and 24 days. All samples were stored in the freezer at −20 °C until the extraction and cleanup.

2.4. Extraction and Cleanup of Passive Samplers

A Standard Operating Procedure (SOP) was carried out for handling the SPMDs; blanks were used to estimate the initial concentration of PRCs and contamination during the handling procedure.

Figure 2. (**a**) The PSPT fastened to the bridge column with a protection grill, including a padlock. (**b**) Large deployment canisters. (**c**) SPMDs attached to a spider holder.

SPMDs were extracted following the procedure reported elsewhere [16]. First, the passive samplers were washed with a soft toothbrush and water to remove fouling and dried with a paper tissue. Then, the samplers were dialyzed in hexane for 24 h twice. After this, the hexane fraction was concentrated in a rotary evaporator. The residue was dissolved in 1 mL of acetone before being centrifuged for 5 min at 2500 RPM, and then the sample was injected in GC/MS. The recovery study was based on the extraction of PRCs previously spiked in the SPMDs by the suppliers, which certified the initial concentration. Therefore, four blanks were extracted to estimate the PRC levels of using dialysis extraction. The % of recovery was calculated according to Equation (1):

$$\text{Recovery} = \frac{\text{initial concentration (by suppliers)}}{\text{SPMDs concentration (by Analysis)}} \times 100 \tag{1}$$

2.5. PRC Dissipation Modelling for Calibration and Water Concentration

The PRCs' dissipation was based on the final (N) and initial concentration (N_o) of deuterated PCBs 14, 28 and 50. The N/N_o ratio was applied to estimate the release rate constant (k_e), which includes the initial and final concentration of these substances [9] (see Equation (2)):

$$k_e = -\frac{\ln\left(\frac{N}{N_o}\right)}{t} \tag{2}$$

where t is the field sampling time. k_e was then applied to find the sampling rates (R_s) according to Equation (3):

$$R_s = V_s k_{sw} k_e \tag{3}$$

where k_{sw} is the SPMDs–water partition coefficient and V_s is the triolein volume in the SPMDs. k_{sw} was determined using the Huckins equation [1]:

$$log\, k_{sw} = a_0 + 2.321\, log\, k_{ow} - 0.1618\, (log\, k_{ow})^2. \tag{4}$$

where $a_0 = -2.61$ in PCBs, PAHs and 4,4'-DDE and -3.20 in polar pesticides.

Finally, the C_w was estimated using Equation (5):

$$C_w = \frac{N}{V_s K_{SW}\left(1 - exp\left(-\frac{R_s t}{V_s K_{SW}}\right)\right)} \tag{5}$$

where R_s is the sampling rate calculated according to Equation (3); this value depends on the dissipation of PRCs [6].

3. Results and Discussion

3.1. GC–MS Identification

Retention times (*Rt*) for each analyte, the PCBs used as a PRCs and the ions selected as qualifiers (Q1) and quantitative purposes (Q2) are summarized in Table 1. The ions for the SIM method were selected according to fragment ions with higher molecular weight (HMW), higher abundance and high selectivity.

Table 1. GC–MS SIM mode for identification and quantitation of analytes. N.D., Not detected using SPMDs in SIM mode analysis.

Peak No.	Analytes	*Rt* (min)	Monitor Ions, *m/z* (Intensity %)		
			Target Ion	Q1	Q2
1	Naphthalene (NAPH),	5.81	128	127	129
2	Acenaphthylene (ACEN)	7.37	152	151	153
3	Acenaphthene (ACE)	7.54	154	152	153
4	Fluorene (FL)	7.97	166	165	167
5	PCB-14	8.58	224	152	222
6	Diazinon (DZN)	8.79	137	179	N.D.
7	Phenanthrene (PHE)	8.92	178	176	179
8	Anthracene (ANT)	8.97	178	89	179
9	PCB-29	9.10	256	186	258
10	PCB-50	9.19	292	220	290
11	Chlorpyrifos (CPF)	9.58	314	197	256
12	Parathion (PTN)	9.63	N.D.	N.D.	N.D.
13	Fluoranthene (FLU)	10.20	202	101	203
14	Pyrene (PYR)	10.44	202	101	203

3.2. Quantitative Analysis for Analytes

Quantitative analysis was carried out using PRC dissipation modelling. However, in order to apply the modelling, the masses of different pesticides and PAHs were determined by a calibration curve in hexane following the spiking procedure mentioned above. Correlations (r^2) were found to be higher than 0.950 for all compounds at the concentrations tested, implying good linearity in the MS detector's response. The parameters for quantitative procedures to determine the masses of different analytes and PRCs are shown in Table 2.

The calibration curve showed r^2 values higher than 0.980, indicating good linearity for quantification purposes. Additionally, the recoveries after SOPs were between 96% and 103%. The SOP applied here has been previously shown to be adequate for sampling a large range of non-polar compounds using SPMDs [16–18].
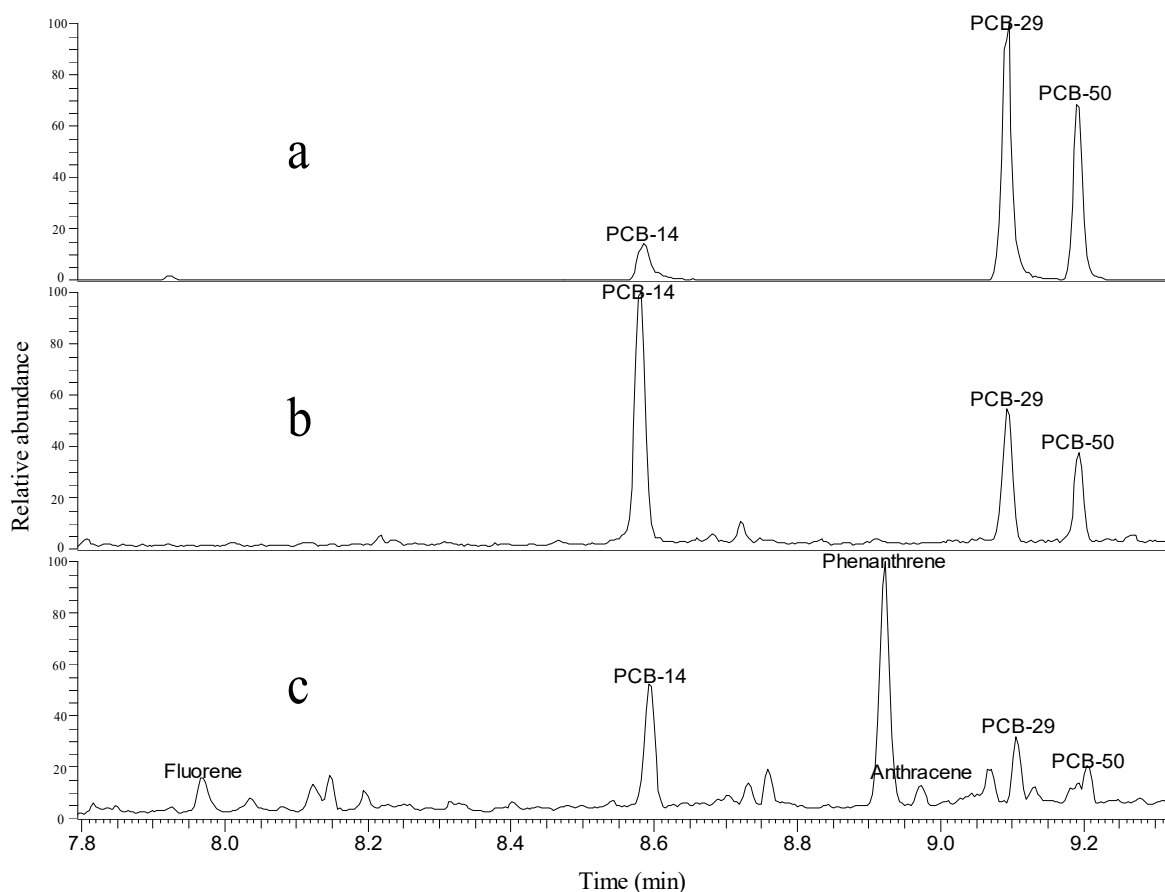
3.3. The Study of Blanks and SPMD Recoveries

All blanks, including field and laboratory blanks, were extracted according to the SOPs. No blank was found to be contaminated with any target compound studied in this paper. Therefore, all detected compounds during the passive sampling were considered waterborne.

The comparison between the deployment of SPMDs in the reservoir, field blank and laboratory blank is presented in Figure 3.

Table 2. R_s estimated at 24 days of sampling deployment. Molecular weight (MW), Linear regression (LR), correlation (r^2). N.D., Not detected using SPMDs in SIM mode analysis.

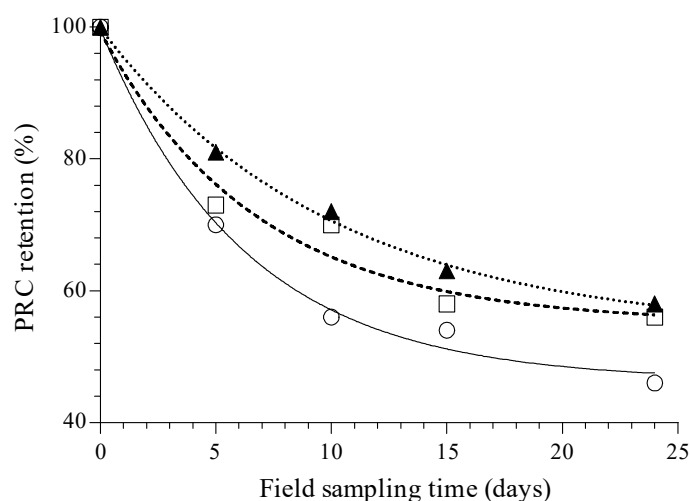| Peak No.	Analyte Names	MW	$log\ k_{ow}$	R_s (L day^{-1})	LR (µg mL^{-1})	r^2
1	NAPH	128.2	3.5	27.8	0.05–1.00	0.982
2	ACEN	152.2	4.1	50.3	0.12–1.00	0.980
3	ACE	154.2	4.2	55.1	0.06–1.20	0.992
4	FL	166.2	4.4	60.1	0.01–1.00	0.989
5	PCB-14	223.1	5.3	72.6	0.002–0.1	0.999
6	DZN (N.D.)	304.3	3.3	35.8	0.01–0.50	0.987
7	PHE	178.2	4.5	62.3	0.09–1.30	0.980
8	ANT	178.2	4.5	64.4	0.02–1.00	0.980
9	PCB-29	257.5	5.6	69.8	0.002–0.1	0.998
10	PCB-50	291.9	5.6	69.3	0.002–0.1	0.992
11	CPF	350.6	4.9	71.0	0.01–0.50	0.987
12	PTN (N.D.)	330.4	3.8	40.1	0.01–0.50	0.987
13	FLU	202.3	5.2	72.7	0.05–0.75	0.980
14	PYR	202.1	5.3	72.5	0.07–1.00	0.987

Figure 3. (**a**) SCAM chromatogram for a typical PCB congener used as a PRC in acetone. (**b**) SCAN chromatogram of the typical SPMD blank at ten days. (**c**) SCAN chromatogram of the SPMD deployment during ten days, including PRCs and some target analytes.

Finally, the initial average concentration found in the SPMD blanks for PCB-14, PCB-29 and PCB-50 congeners were applied in the dissipation modelling to estimate the analytes' concentration in the water. The relative standard deviations (% RSD) were 2.1, 1.7 and 4.0 for PCB-14, PCB-29 and PCB-50, respectively, implying a good precision of the sample extraction method, evidenced by the low RSD values.

3.4. Dissipation of PRCs from SPMDs—Calibration Study

Dissipation plots for PCB congeners are shown in Figure 3. The release "half-life" (t_{50} day^{-1}) for each PCB was calculated by applying one phase decay regression ($r^2 > 0.97$) plot as 4.3, 4.7 and 7.0 for PCB-14, PCB-29 and PCB-50, respectively. According to Huckins, this type of exchange kinetics is constant for a set of conditions and chemicals [5]. A characteristic curvilinear kinetics approaching the equilibrium after 10 days was found for the PRC dissipation modelling (see Figure 4).

Figure 4. Dissipation of PCB congeners from SPMDs used as a passive sampler: PCB-14 (open circles), PCB-29 (open squares) and PCB-50 (filled triangles).

Biofouling was observed in the SPMD sampling. However, this did not affect the kinetic dissipation model for PRCs (see Figure 4). Typically, short-term biofouling does not have an important effect on R_s. However, extended periods of biofouling may affect R_s, altering the reservoir's calculated C_w [19]. Extreme biofouling effects should be considered when extended sampling periods are applied.

On the other hand, the reservoirs show lower water flow velocity, which does not affect the R_s (flow velocities below 10 cm s^{-1}). Additionally, it has been found that both values lack correlation [6]. At low flow velocity values, inertial currents originating from the inflow orifices may be much larger than the calculated linear velocities. Then, the flow at the SPMD–water interface controls the exchange rates in the boundary layer [5]. Field calibration using PRCs allows for the reduction of all kinetic phases into one equation based on the dissipation modelling for these substances (Equation (5)). More lipophilic substances were found to have higher R_s values due to their dependence of *log k_{ow}* (see Equations (3) and (4)). Similarly, higher-molecular-weight compounds showed higher R_s, which may be related to mass-resistant processes [20].

To avoid overestimations of target POP levels in water due to different exchange kinetics (linear, curvilinear and equilibrium), Equation (5) was applied to calculate the C_w of PAHs and pesticides. Target POPs' R_s values were estimated using Equations (2) and (3). The results are presented in Table 2. R_s values were found to be higher than those reported in the literature, possibly due to the higher flow rates (8 cm s^{-1}) used here compared to previous studies (0.004–0.006 cm s^{-1}) [21]. Higher flow rates may increase the dissipation of PRCs from SPMDs; thus, release rate constants (k_e) impact the calculated R_s. For instance, reported R_s values for some PAHs such as ACE, PHE, FLU and PYR are 68.0, 104.9, 125.2 and 130.1 L day^{-1}, respectively, at 90 cm s^{-1}, which are closer to the values presented in Table 2 [22].
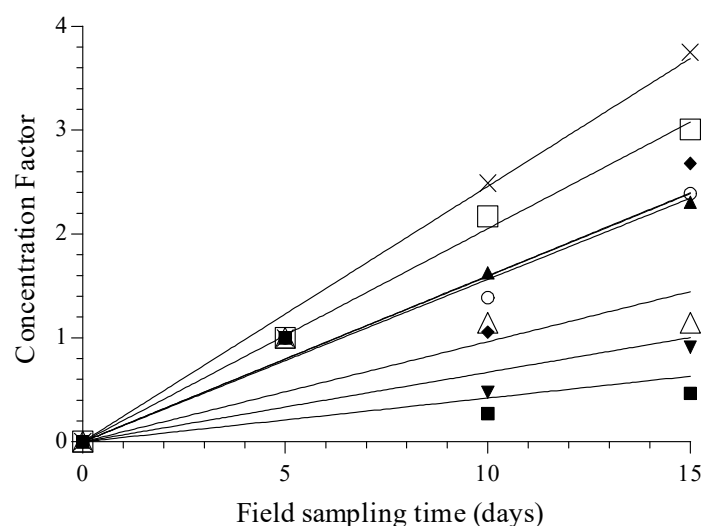
3.5. SPMDs Used for Pesticides and PAH Monitoring

PAHs with low molecular weight were detected in SPMDs during the passive sampling deployment. Initial C_w values are presented in Table 3.

Table 3. The C_w estimated for each PAH congener after 5 days of SPMDs' exposure in the water body of the reservoir.

PAH Congener	C_w (5 Days Sampling) ng L^{-1}
NAPH	0.7
ACEN	1.2
ACE	0.7
FL	0.8
PHE	2.3
ANT	0.5
FLU	1.8
PYR	1.3

In general, C_w was found to increase linearly with sampling time, except for ACEN and FL; this might be related to their lower molecular weight. The linear regression is presented in Figure 5.

Figure 5. Uptake plot for PAHs. Concentration values estimated for target pollutant compounds in a principal tributary of La Fe reservoir. NAPH (×), ACEN (■), ACE (△), FL (▼), PHE (♦), ANT (○), FLU (□) and PYR (▲). The concentration factor was calculated as the ratio between the minimum concentration value found for each target compound and all estimated concentrations. C_w was calculated by multiplying the initial concentration by the concentration factor.

Detected PAHs in the reservoir arise from high traffic flow and the combustion of carbon-containing fuels. In addition, the water body is navigated frequently, increasing the probability of contamination from combustion byproducts. The increasing level of PAHs may be related to the continuous input of these substances from the watershed and the linear–curvilinear uptake phase estimated using PCB dissipation modelling.

PYR, FLU, NAPH and PHE represented higher percentages of the total PAHs (more than 80%), which is in good agreement with previous reports [12]. High-molecular-weight (HMW) PAHs, such as benzo[b] fluoranthene (BbF), benzo[k] fluoranthene (BkF) and benzo[a] pyrene (BaP), were also detected in SPMDs, which may be related to the low solubility of these congeners in water. These compounds have been previously detected at low levels using SPMD devices. A previous study in the Great Barrier Reef with an extended

SPMD deployment time (50 days) allowed the detection of HMW PAHs > 202 g mol^{-1} at pg L^{-1} [23]. Note that the extension of time could increase the sensitivity for HMW PAHs.

In a previous contribution, PAHs' C_w were found to range between 4.2 and 32.8 ng L^{-1} in an important tributary for the La FE reservoir, using silicon rubber as a passive sampler [12]. Similarly, PHE presented the highest C_w detected (504–3358 pg L^{-1}). PAHs are mainly produced by fossil fuel combustion, and their levels in water may be initially related to atmospheric deposition. PAHs may reach urban stormwater through road runoff, which in turn reaches the water reservoirs [24,25].

It is important to implement advanced technologies, such as advanced oxidation processes, in water treatment plants in order to remove PAHs, since conventional treatment processes cannot remove POPs entirely [26]. We have reported the presence of PAHs and pollutants such as Levonorgestrel in effluents of wastewater treatment plants using conventional removal processes [12,27]. This reveals that complex fractions containing parent compounds and metabolites may reach natural water, posing several risks to ecosystems, including biota and humans [28]. Among the detected PAHs, PYR poses the most significant ecological risk, followed by ANT, FLU, PHE and NAPH [29]. For instance, ANT, FLU and PYR can induce changes in gestational hormone levels in a placental cell line [30]. These PAHs were found to represent the highest percentage of the total PAHs detected in this study.

For pesticides, an initial SCAN mode was performed in order to identify them in the SPMDs' deployment during the sampling time. Additionally, calibration curves were included for all target compounds.

CPF was the only pesticide absorbed by SPMDs. This can be related to the fact that CPF has a *log k_{ow}* > 4.6, enhancing its adsorption in this membrane, while the other pesticides have lower *log k_{ow}* values, increasing their affinity with water. To overcome this, other researchers have applied a balanced hydrophilic–lipophilic sorbent-embedded cellulose acetate membrane (HECAM) to increase the range of organophosphorus monitored by passive sampling [31]. In an earlier report, the C_w of legacy pesticides such as dieldrin were found to be between 401 and 1919 pg L^{-1} in an important tributary using an LDPE polymer membrane deployed for more than 50 days [12]. CPF is widely applied around the reservoir's watershed due to intensive crop farming such as tree tomato (Solanum betaceum), avocado (Persea Americana) and livestock grazing. In Colombia, CPF comprises about 10% of the total sales of pesticides, which can be associated with its occurrence and detection in water [32]. This substance is not strongly adsorbed by the soil, thus favouring the leaching process [33].

The CPF uptake process was found to fit an exponential curve (r^2 = 0.992) in contrast to the PCBs' dissipation process. While dissipation may show the existence of the elimination process, CPF monitoring exhibits the uptake process (see Figure 6).
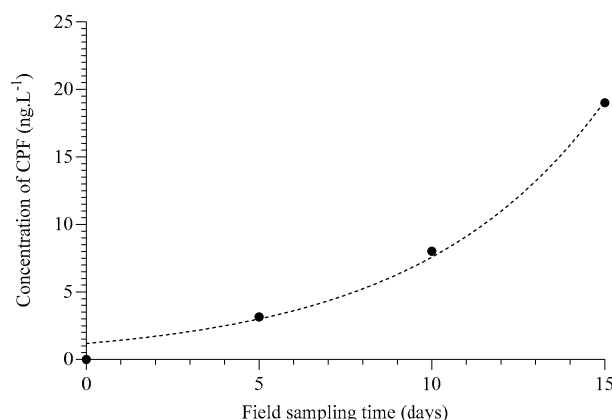

Figure 6. CPF SPMDs uptake process.

The CPF may be adsorbed into SPMDs to reach the equilibrium, and Figure 6 shows a faster uptake in the passive sampler. However, this pesticide may be transformed under natural conditions to 3,5,6-trichloro-2-pyridinol (TCP). A previous report found that CPF is hydrolyzed to TCP at pH values higher than 9.0, showing a half-life close to 12.45 h, indicating the faster transformation and release of TCP in water [34]. TCP's solubility in water increases, and thus its distribution may be higher. However, this substance is not monitored by SPMDs. Although the environmental effects of CPF and TCP are not entirely understood, CPF has been reported as a breast cancer risk factor at low levels [35]. Additionally, the mixture of CPF/TCP induces acute toxicity in Dapnia pulex [34]. Therefore, no conventional water treatment processes such as AOPs are suitable for CPF/TCP removal or elimination.

Although DZN, PTN and organochlorine (OC) pesticides were considered in the monitoring, they were not detected. OC pesticides were banned 30 years ago in Colombia; however, these pesticides are persistent and can remain in the environment for a long time. In this research, no OC pesticides were detected. However, their metabolites should be considered in future studies. Although some analytes were not detected, the R_s for some of them were estimated by applying the PRC dissipation modelling using the Estimated Water Concentration Calculator from SPMD data using PRCs from USGS (Excel file Version 5.1) [36]. Colombia does not have traditional seasons (i.e., winter/summer); we have dry or rainy seasons. Passive sampling was carried out during the dry season. Although the stational variation was not evaluated in this study, no differences in POPs levels during different seasons (dry or rainy season) have been found previously [12]. However, climatic events such as La Niña or El Niño might affect pollutant concentrations, and the differences in dry or rainy seasons are especially quite pronounced.

Similarly, OCs have been widely detected in USA, China and other countries in water bodies using SPMDs [37,38]. The sensitivity of this method can be improved by deploying several SPMDs. In this paper, only three SPMDs were deployed in the field. Some disadvantages of pollutant monitoring using SPMDs have been reported in the literature. For instance, SPMD preparation involves the addition of triolein inside the polyethylene tube, which increases difficulties in lab handling. In addition, after deployment, the extract purification should include the removal of triolein because traces can increase the background noise, affecting the baseline during chromatographic analysis [39].

4. Conclusions

PRC dissipation was carried out under one-phase decay regression. The dissipation modelling showed that all PRCs were not dissipated completely. The appropriate sampling time was estimated to be between 15 and 30 days. Although biofouling may be present in SPMD membranes, the field calibration showed that biofouling is quantitatively reflected by the dissipation. A directly proportional relation between R_s molecular weight and *log k_{ow}* was found, which can be explained by mass-resistance processes and lipophilic affinity.

Pollutant monitoring after calibration allowed the detection of PAHs at levels higher than 0.5 ng L^{-1}, while the CPF was detected at levels close to 20 ng L^{-1}, showing the anthropic influence on the reservoir via the watershed. These results highlight the impact of the widespread use of pesticides and combustion of fossil fuels by cars on water quality. The use of SPMDs allowed us to infer that bioaccumulation processes might occur in this reservoir because of the similarity of triolein with the organism's lipidic tissue. Therefore, future studies should include the analysis of autochthonous biota in the reservoir.

Finally, it is recommended to use SPMDs for non-polar pollutants in a reservoir. However, cleaning steps should be performed to remove triolein to avoid background noise during chromatographic analysis.

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