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Research Article

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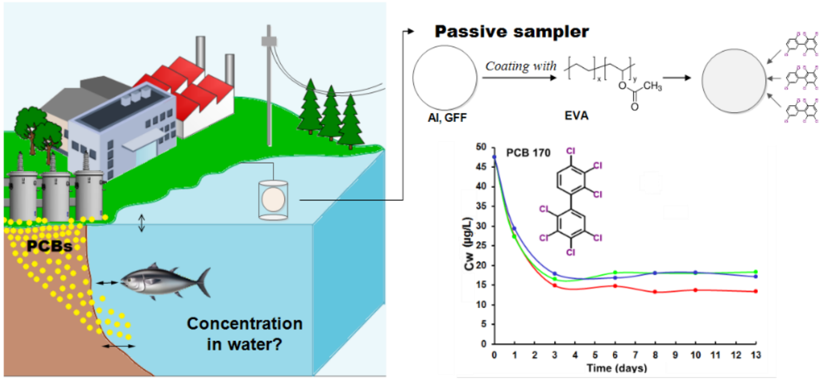
Graphical abstract



Evaluation of poly(ethylene-co-vinylacetate) as polymeric adsorbent of polychlorinated biphenyls in water

Abstract

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Keywords
PCBs
Passive sampler
Polymeric adsorbents
EVA

Evaluación del poli(etilen-co-vinilacetato) como polímero adsorbente de bifenilos policlorados en agua

Resumen
El muestreo pasivo en sistemas acuáticos es una metodología alternativa, económica y de fácil implementación para el monitoreo de compuestos orgánicos, en donde es frecuente el uso de polímeros y resinas como adsorbentes de los analitos. El objetivo de esta investigación fué evaluar el uso del poli(etilen-co-vinilacetato) (EVA) soportado sobre filtros de fibra de vidrio (GF) y láminas de aluminio (Al) como muestreadores pasivos de bifenilos policlorado (PCBs) en agua. Los muestreadores se prepararon por recubrimiento directo del EVA disuelto en diclorometano sobre las superficies de GF y Al. Se realizó una caracterización superficial de los materiales preparados y se determinó la capacidad de adsorción de 19 PCBs a través de experimentos de captación a nivel de laboratorio. Se evidenció que para PCBs de 1 hasta 6 atómos de Cl, a medida que aumentó el número de cloros en el anillo de bifenilo, el tiempo al cual se alcanzó el equilibrio también aumentó (de 4 a 10 días); sin embargo, para los PCBs más pesados (de 6 y 9 Cl), los tiempos de equilibrio no superaron los 6 días. Adicionalmente, se observó una menor disminución en la concentración de estos compuestos en el agua de prueba. Se estimaron coeficientes de reparto EVA-agua (Log $K_{EVA\text{-}W}$) para cada uno de los PCBs como una medida de la afinidad de los analitos por las fases adsorbentes, encontrándose coeficientes entre 4 y 5.4.

Palabras claves
PCBs
Muestreador pasivo
Adsorbente polimérico
EVA

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Evaluation of poly(ethylene-co-vinylacetate) as polymeric adsorbent of polychlorinated biphenyls in water

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Abstract

The passive sampling in aquatic systems is an economical and easy implementation alternative for the monitoring of organic compounds, where the use of polymers and resins as adsorbents of the analytes is frequent. The objective of this research was to evaluate the use of poly(ethylene-co-vinyl acetate) supported on glass fiber filters (GF) and aluminum sheets (Al) as passive samplers of polychlorinated biphenyls (PCBs) in water. A surface characterization of the prepared materials was performed and the adsorption capacity of 19 PCBs was determined through laboratory-level uptake experiments. It was shown that for PCBs from 1 to 6 atoms of Cl, according as the number of chlorines in the biphenyl ring was increased, the time at which the equilibrium was reached also was increased (from 4 to 10 days); however, for the heavier PCBs (6 and 9 Cl), the equilibrium times did not exceed 6 days. In addition, a lower decrease in test water concentration was evidenced. EVA-water partition coefficients (Log $K_{EVA\text{-}W}$) were estimated for each of the PCBs as a measure of the affinity of the analytes for the adsorbent phases, coefficients between 4 and 5.4 were found.

Keywords
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EVA

1. Introduction

Polychlorinated biphenyls (PCBs) are compounds classified as persistent organic pollutants (POPs), these substances until 1975 were widely used in the industry as additives for lubricants, greases, for electrical installations, plastics, among others [1, 2]. Their characteristics of commercial interest were its high thermal, photocatalytic, biological and chemical stability and low electrical conductivity [2]. However, these same properties and their high toxicity were the starting point to classify these compounds as priority pollutants in the Stockholm Convention of the United Nations Environment Program in 2001 [3]. As a result of this, the comercialization and production of PCBs was regulated and its use prohibited.

The general structure of PCBs consists of a biphenyl ring with different degrees of chlorine substitutions, from mono- to deca- substituted (Figure 1), resulting in a total of 209 analogous compounds; PCBs with higher chlorination degree have been identified to be the most toxic [4].

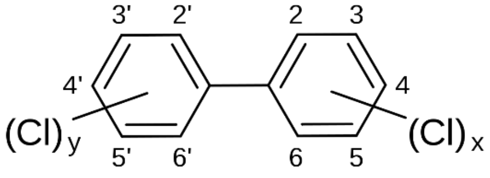

Figure 1. Generalized chemical structure of PCBs

Due to its persistence, despite its prohibition for more than a decade, studies have shown its presence in humans, animals (aquatic and terrestrial), water, air and other environmental matrices [5-9].

Exposure to these compounds has been caused by accidental releases, neglected disposal practices, and leakages from industrial facilities or chemical waste disposal sites. When these substances are released, a recirculation cycle through the environment is initiated [1,10]. Different routes have been identified to understand how PCBs can reach the freshwater sources, being some examples the surface runoff from contaminated soils, dry or wet deposition from the air, deposition of particles on the surface or by exchange of gaseous air to water [10].

Due to the importance of water as a living resource for ecosystems in all levels, the qualitative and quantitative assessment of their pollution is a priority concern at the global level. In aquatic systems a continuous monitoring of concentration levels is disered in order to assess the ecological risk by the presence of these pollutants [11]. However, nowadays the continuous monitoring of natural sources remains being a challenge, due to the costs of field deployment and the specialized chemical and instrumental analyzes.

Among the methodologies for over time sampling of PCBs from water sources, the passive sampling has become in an attractive option for many researchers because permits the obtaining of information as a function of the time, but also, is a strategy with a low cost-effective, technically simple measurements and reduced detection limits [12, 13]. In general, this type of monitoring technique is based on the free flow of analytes from the sampling medium to a receptor phase arranged in a given device or structure [12-14]. The receptor phase consists of adsorbent or liquid polymeric materials with chemical affinity for the compounds of interest. Different class of devices, mostly based on polymers, have been used for the sampling of organic compounds in water. For example, the so-called passive diffusion bags consist of low density polyethylene (LDPE) membranes sealed and filled with deionized water for the sampling of chlorinated and volatile organic compounds [12,13]. A device similar to the above and more scientifically accepted is known as a semipermeable membrane device (SPMD) consisting of flat polyethylene tubes with a thin film of triolein; The utility of SPMDs has been demonstrated for the monitoring of PCBs, chlorinated pesticides (OCP), polycyclic aromatic compounds (PAHs), among others [12-13,15]. Other polymers used are: films of polyvinyl chloride and polystyrene [1], copolymers of styrene divinylbenzene or polymers of acrylic esters (resins called XAD2, XAD4, XAD7) [15].

Poly(ethylene co-vinylacetate) copolymer or EVA is a polymer recently used in the monitoring of organic pollutants, this has been used for the monitoring of PCBs, PAHs, perfluorinated compounds and pesticides in systems of indoor environments and urban atmosphere [8,9,16,17]; usually, its implementation implies the use of glass surfaces, filters and aluminum as supports. Less frequently, EVA has been used in water sources, however, its application to aquatic environments has been carried out to monitor fungicides, organophosphorus pesticides, carbamates and PCBs (PCB105, PCB3, PCB15 and PCB 18) in estuarine ecosystems [8,19], and also for the capture of freshwater pesticides [14]. Additionally, EVA supported on glass fiber filters (GF) has been used as a cypermethrin uptake device in salmon farms [20].

In the light of the above, the objective of this research was to evaluate the use of EVA supported on GF filters and aluminum sheets as polymeric surfaces for the passive uptake of 19 PCBs in water, as well as, to stablish the analytical and instrumental conditions for the quantitative determination of these compounds in the analysis matrix.

2. Experimental section

2.1. Making of sampler

EVA (Elvax® 40W, Dupont Canada) was used as a coating polymer of circular surfaces of GF filters and aluminum sheets with 4.6 cm in diameter. To carry out the coating, an impregnation solution was prepared using 4.0 g of EVA per 200 mL of dichloromethane [14,19], later, substrates were individually immersed in the solution for 10 seconds, eliminating the remaining solvent by means of an air stream and heating in an oven at 100 °C for 3 h. GF with EVA (GF-EVA) was prepared with different immersion in the solution, one and two, which were identified as GF-EVA-M1 and GF-EVA-M2, respectively. Besides, aluminum sheets were identified as Al-EVA.

2.2. Characterization of passive samplers

In order to identify the surface features, samplers GF-EVA were analyzed by scanning electron microscopy (SEM, Jeol® JSM6490 LV®). Additionally, their hydraulic permeabilities were determined through permeability measurements (L) to obtain information related with hydrpdyamic of catchment process. For the determination of L, an ultrafiltration equipment (Amicon 8050, Millipore) of 44.5 mm diameter operated at 50 kPa pressure was used [14]. Distilled water was passed through the GF-EVA for the collecting of permeate in test tubes. The amount of water and the permeate time were determined in triplicate. Flow values were calculated using Darcy's law:

$$J = LP \tag{1}$$

where J is the flow volume ($Lm^{-2}s^{-1}$), L is the permeability ($ms^{-1}kPa^{-1}$) and P is the applied pressure (kPa). In addition, the relative permeability (L_{rel}) was calculated by:

$$L_{rel} = \frac{L_2}{L_1} \tag{2}$$

where L_1 is the permeability calculated for GF without impregnation and L_2 is the permeability for passive sample (*i.e.*, GF-EVA-M1 and GF-EVA-M2). In addition, the average percentage change in pore radius (Δr_p) was evaluated using the membrane-equivalent concept based on the Hagen-Poiseuille model [21]; thus, the Equation 3 is stablished, being:

$$\Delta r_p = (1 - L_{rel}^{0.5}) \times 100 \tag{3}$$

2.3. Analytical and instrumental methods

2.3.1. PCBs: 19 PCB congeners (PCBs 1, 5, 18, 31, 44, 52, 66, 87, 101, 110, 138, 141, 151, 153, 170, 180, 183, 187, 206) were analyzed. Mixture of congeners from RESTEK (USA) was used (100 µg/mL in iso-octane, Method 8082A).

2.3.2 Extraction of PCBs in GF-EVA and Al-EVA: Three methods were used to extract the adsorbed PCBs on the EVA; in all cases, the efficiency of the chemical extraction of the analytes was tested by the application of 600 µL of a solution of PCBs (300 µg/L) on the surfaces of the materials. After one day of interaction, the materials were cut into small pieces to proceed to the corresponding extractions. The first method evaluated (M1) consisted of two consecutive washes with 15 mL of methanol and vortexing for 1 min between washes, the extracts obtained were filtered, mixed and rotaevaporated to dryness and reconstituted with 2 mL of hexane: acetone (80:20 v/v). Finally, the extracts were filtered using 0.45 µm nylon filters.

The second method (M2) included the same methodological steps used in M1, however, vortex agitation was elimiated and instead GF-EVA was put in contact with methanol for 24 hours of interaction.

The third method (M3) consisted of two consecutive washes with 15 mL of dichloromethane. Resulting extracts were then rotoevaporated to dryness, later, 2.0 mL of hexane were added and the extracts were transferred to centrifuge tubes and 4.0 mL of methanol was added in order to precipitate the polymer. A 1.0 mL aliquot of the supernatant was transferred to a test tube by a low-pressure stream of nitrogen in a water bath at 70 °C until dry. Finally, solvent was reconstituted with 1.0 mL of hexane:acetone solution (80:20 v/v).

Comparison between methods was carried out by checking of chromatographic areas obtained in each case; additionally, the degree of cleaning of each extract was quantitatively determined. For this purpose, the percentage of coextractives was calculated by determining the mass of residue obtained after evaporating the extracts; with this percentage an estimation of the amount of foreign matter to the analytes that is drawn in each extractive method was obtained. Another methodology used for this purpose consisted in the chromatographic analysis of extracts under the full scan mode of the mass spectrometer.

2.3.3. PCBs extraction from water: The individual concentrations of PCBs in the water samples during the adsorption experiments were determined by liquid-liquid extraction [22]. To 5.0 mL of water sample were added 6.0 g of NaCl followed by vortexing during 1 minute, subsequently 2.0 mL of hexane were added. The extract was shaken and centrifuged for 10 minutes at 3500 rpm. Finally, 1.0 mL of the supernatant was transfered to a vial for its

Table 1. Chromatographic conditions and configuration of the mass spectrometer

Configuration GC

Features capillary column	Column Teknocroma TRB 5MS, (5% Phenil methylpolysiloxane) 30 m x 0.25 mm x 0.25 µm.
Injector temperature (°C)	240
Mode of injection	splitless
Furnace temperature program	80 °C (1 min), from 17 °C/min to 220 °C (4 min), from 4 °C/min to 270 °C (5 min.)

Configuration ITQ

Scan mode	MS/MS (MS^2)
Ionization method	Electron impact, 70 eV
Maximum excitation power	0.45 eV
Collision Energy	1.05 1.30

Precursor ions (PI)

Compound	IP	Compound	PI	Compound	PI
PCB 1	188	PCB 101	240.96	PCB 187	393.84
PCB 5	222.02	PCB 87	325.9	PCB 183	393.81
PCB 18	186.02	PCB 110	325.92	PCB 180	393.83
PCB 31	256.01	PCB 151	359.84	PCB 170	393.82
PCB 52	291.92	PCB 153	359.87	PCB 206	463.73
PCB 44	291.92	PCB 138	359.84		
PCB 66	291.97	PCB 141	359.87		

respective chromatographic analysis.

2.3.3. Instrumental analysis by GC-ITQ-MS/MS: A gas chromatograph (TRACE 1300) coupled to an ITQ 700 quadrupole ion trap mass spectrometer (Thermo Scientific, USA) were used for detection and quantification of analytes. Details of the instrumental configuration are shown in Table 1.

2.4. Analytical quality parameters

Quantitative and instrumental determinations of the PCBs from prepared materials and water samples were performed by external calibration method. In addition, matrix effect (ME%) and linearity of the calibrated curves were analyzed. Accuracy and precision of the extractive methodologies were verified through different fortifications with intra and interday extractions. Sensitivity was assessed by the calculation of detection limit (LD) and quantification limit (LC) based on signal-to-noise ratios (S/N) of 3 and 10, respectively.

2.5. Adsorption experiments

Prepared materials were submerged in water contaminated with PCBs, to observe the decrease of the concentration of the contaminants in the water as a result of the presence of the adsorbents. Contaminated water was prepared by adding of 220 µL of PCBs (100 µg/mL in methanol) to 2 L distilled water; later, the mixture was left under stirring for 3 days. Glass containers with sealed cap and 400 cm^3 of volume were used with 300 mL of the water. After, GF-EVA (arranged in stainless steel meshes) and Al-EVA were immersed in the mixtures. Four GF-EVA-M1, two GF-EVA-M2 y seven Al-EVA were used, corresponding to 66.7 (± 1.2), 66.3 (± 0.8) y 19.0 (± 0.8) mg of total EVA for each adsorption experiment, respectively. Samples of 5 mL of water (in duplicate) were taken over a period of 13 days to determine the concentrations of PCBs in water. Finally, the materials were extracted to determine the concentrations of the analytes in the adsorbent, in this case, extracts after the rotavaporation of the methanol were brought up to 25 mL with hexane: acetone (80:20 v/v).

3. Results and discussion

3.1. Features of passive samplers

The amounts of EVA adsorbed on GF-EVA and Al-EVA are shown in Table 2. These results show that the preparative processes of the materials are reproducible (coefficient of variation was < 7.6%).

Table 2. Amount of EVA (g) in GF-EVA and Al-EVA, permeabilities (*L*), relative permeability (L_{rel}) and pore size variation (Δr_p).

Material	EVA mass (g)	CV (%)	L x10^{-7} ($ms^{-1}kPa^{-1}$)	L_{rel} (%)	Δr_p (%)
GF-EVA M1	0.0167	7.6	4.78	24	51.0
GF-EVA M2	0.0326	4.1	2.35	12	65.7
Al-EVA	0.0027	4.9	-	-	-
GF	-	-	20.1	100	-

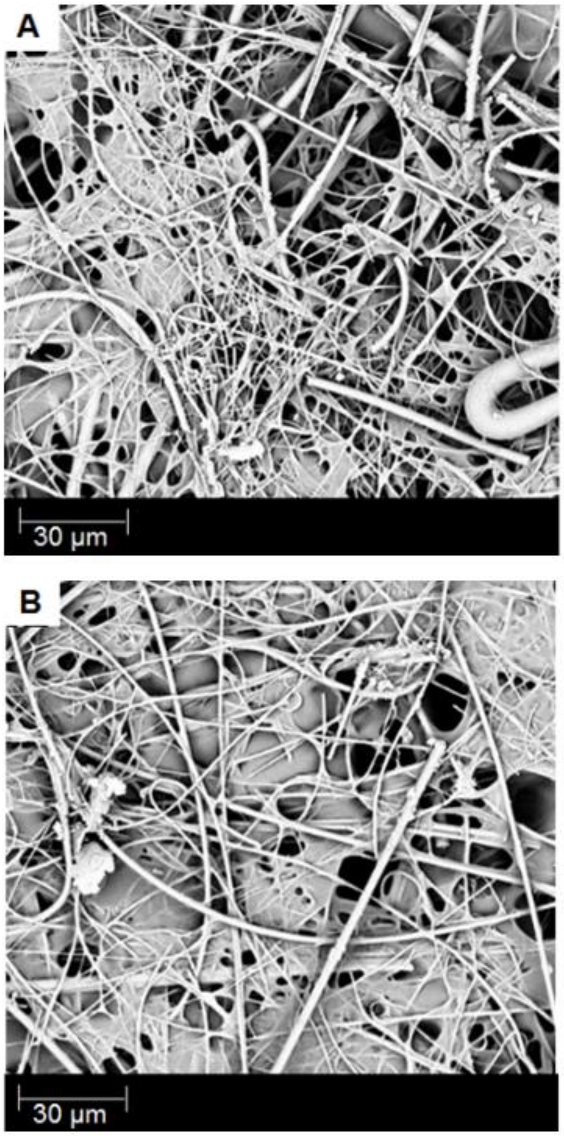

Figure 2. Images of SEM for A) GF-EVA-M1 and B) GF-EVA-M2.

At superficial level, a significant visual difference between GF-EVA and GF is not identified. However, a microscopical level, from SEM images can be observed that EVA is adsorbed in the inside of GF filters occuping the interstices of the pores instead to be deposited on the surface (see Figure 2), this is congruent with the increase in mass observed for each filter (~13 and ~26 % for GF-EVA-M1 and GF-EVA-M2, respectively). In addition, values of permeability decreased 76 and 88 % in the same order (see Table 2, values of L_{rel}). According to Hagen-Poiseuille model permeability is strongly affected by the decrease of pore radious (L depends on pore radius by a r_p^4 factor. Other factors are the viscosity of fluid, surface porosity and thickness of the filter. However, only it was observed a change in the pores and surface porosity (*i.e.*, $\varepsilon = 4\pi r_p^2$). Relative changes in the porous ratio for Hagen-Poiseuille membranes are shown in the Table 1.

Our data suggest that flow rate of water should influence the adsorption of compounds by changes in the residence times in the inside of the filter. Thus, for high flow rate, small residence times should be expected and retention should be decreased. GF-EVA should be considered as an active porous material instead of a dense surface coated with active film. For Al-EVA is not a porous material and in consequence transport through material not ocuur.

3.2 Extractive method selection of PCBs in EVA

Figure 3 shows the chromatographic areas obtained for two of the PCBs evaluated (PCB 44 and PCB 110). In general, regarding the comparison between the areas obtained for each extractive method, there was no significant difference between methods ($p < 0.3$). Due to the above, the method selection was based mainly on the cleaning of the extracts, through the coextractive percentages and chromatograms in full scan mode.

For GF-EVA-M1, GF-EVA-M2 and Al-EVA, the chromatographic profiles and coextractive percentages showed the same trend. A comparison of the chromatograms obtained for each extractive method in GF-EVA-M2 is shown in Figure 4A. Two major peaks were identified by the database (NIST MS

Search 2.0) as di-6-methylheptyl phthalate, which is compound used as an additive to increase the flexibility of the polymers and butylhydroxytoluene, a synthetic antioxidant.

As can be seen in Figure 4b, for the M1 method which included vortex agitation, the percentage of coextractives calculated was higher than the percentages obtained for M2 and M3 treatments. Results agreeing with the chromatograms showing for M1 a slightly larger area for BHT and greater background noise in the area between 14.0 and 20.6 min. The M3 method presented a lower percentage of coextractives and chromatograms with lower noise, however, the use of a more toxic solvent and a greater number of steps in the extractive process were criteria for the selection of method M2 as extraction method.

3.3 Analytical quality parameters

3.3.1 Matrix effect (ME): The effect of the matrix on the chromatographic peaks for each of the analytes was evaluated by Equation 4. For this, the analyte areas were compared in hexane: acetone (A1), with the areas obtained in matrix (A2).

$$ME(\%) = \frac{A_1}{A_2}\times 100 \tag{4}$$

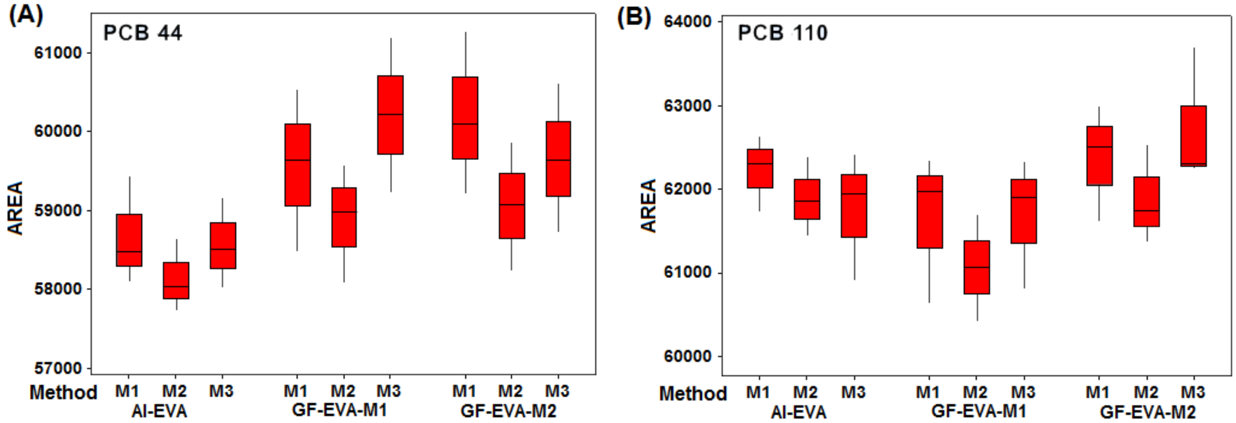

Figure 3. Comparison of chromatographic areas obtained for PCB 44 and PCB 110 for each extractive method (M1, M2, M3) in the three materials evaluated (GF-EVA-M1, GF-EVA-M2, Al-EVA).

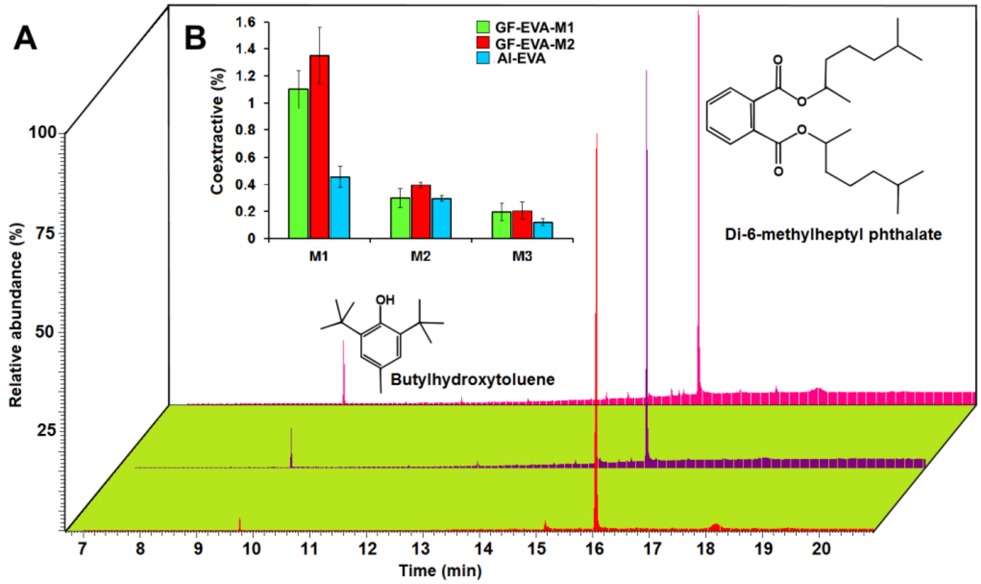

Figure 4. (A) Full scan mode chromatograms for GF-EVA-M2 obtained for the three extractive methods (M1, M2, M3), (B) Calculated co-extractive percentages.

Table 3. Mean matrix effect EM and its corresponding CV calculated for each PCB.

Compound	EM (%)	CV (%)	Compound	EM (%)	CV (%)
PCB 1	98.1	10.5	PCB 151	128.2	18.9
PCB 5	104.4	12.5	PCB 153	132.3	19.4
PCB 18	121.3	16.5	PCB 138	135.8	18.5
PCB 31	122.2	15.1	PCB 141	135.9	18.4
PCB 52	120.3	14.1	PCB 187	131.6	21.4
PCB 44	115.4	13.2	PCB 183	128.3	19.9
PCB 66	125.2	13.6	PCB 180	137.7	20.3
PCB 101	126.1	10.6	PCB 170	135.6	19.6
PCB 87	123.9	19.5	PCB 206	115.7	18.9
PCB 110	128.1	22.5			

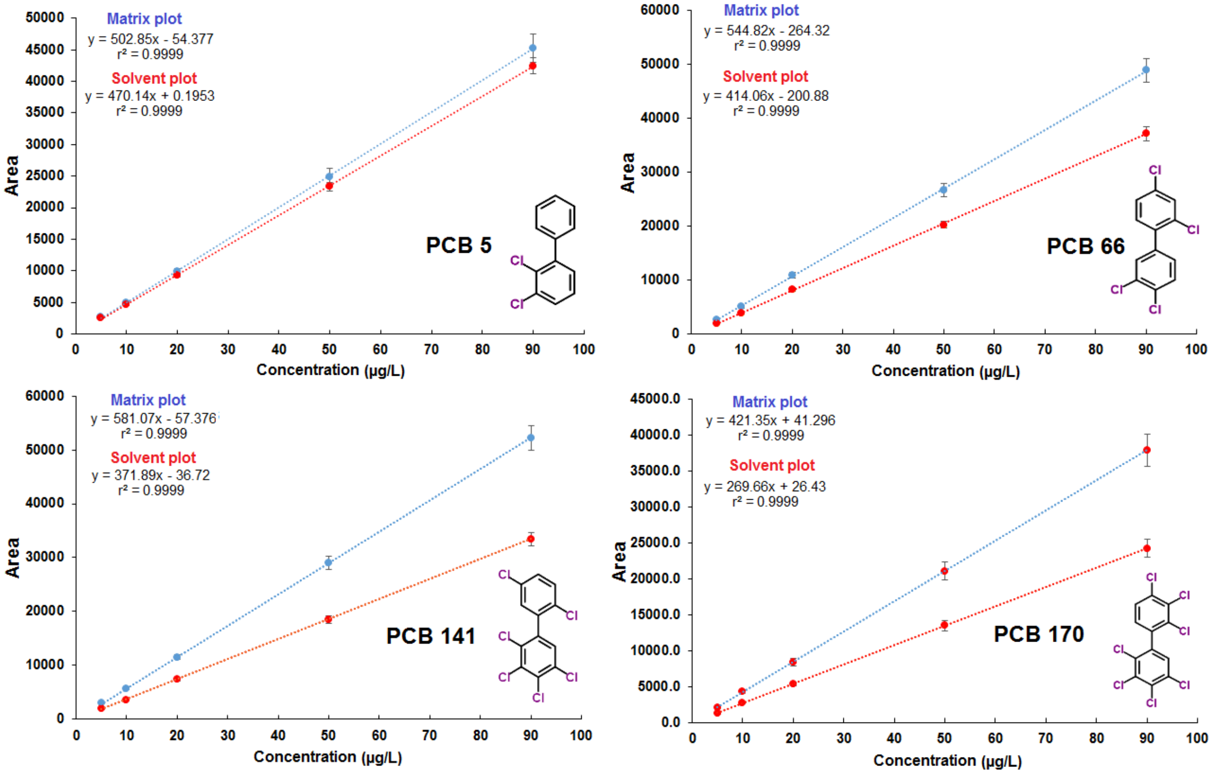

Figure 5. Evidence of matrix effect on PCBs analyzed (PCBs 5, 66, 141, 170). Comparison of calibration curves prepared using as solvent a hexane:acetone mixture (80:20 v/v) and matrix.

It should be mentioned that values of positive ME are stronger for molecules with particular functional groups such as alkylphosphate, carbamates, amine, imidazol, hydroxyl and urea derivatives [23].

Compounds such as hydrophobic and nonpolar PCBs should be less affected by matrix effects because these are thermally stable and less adsorbed on the surface of the inlet to the chromato-graphic system [23,24]. However, as it is shown into the Table 3, although ME was not as marked for these compounds, values of ME (%) were between 98.1 and 135.9 %. Several of the PCBs exceeded 120 %, which is the value typically considered as the upper limit for ME in the analysis of pollutant residues [25]. In addition, in Figure 5 are shown comparative cali-bration curves for 4 of the PCBs evaluated. These were prepared with solvent and with matrix extracts. It can be seen that according as the chlorination degree and molecular weight of the PCB increase, the difference between the areas is more evident at higher concentrations (*i.e.*, between 50 and 90 µg/L).

Table 4. Analytical quality parameters (%R, CV, LOD, LOQ), partition coefficients K_{OW} and $K_{EVA\text{-}W}$

Compounds	No. Cl	PM (g/mol)	Log K_{OW}	Log $K_{EVA\text{-}W}$	% R* (n=12)	CV (%)	LOD	LOQ
PCB-1	1	188.9	4.5	5.1	81.3	5.7	0.5	3.0
PCB-5	2	223.1	5.0	5.4	103.2	5.8	1.0	3.0
PCB-18	3	257.6	5.6	5.2	100.5	5.1	1.0	3.0
PCB-31	3	257.6	5.8	5.4	106.5	2.7	1.0	3.0
PCB-52	4	291.9	6.1	5.4	107.2	2.3	0.5	3.0
PCB-44	4	291.9	5.8	5.0	104.7	3.5	3.0	5.0
PCB-66	4	291.9	6.3	5.1	109.5	2.5	1.0	3.0
PCB-101	5	326.4	6.8	4.5	102.1	3.9	3.0	5.0
PCB-87	5	326.4	6.9	4.5	104.1	3.3	3.0	5.0
PCB-110	5	326.4	6.2	4.6	108.3	1.8	3.0	5.0
PCB-151	6	360.9	7.6	4.3	101.2	2.6	1.0	3.0
PCB-153	6	360.9	7.8	4.1	111.3	2.0	3.0	5.0
PCB-138	6	360.9	7.4	4.2	107.2	2.3	3.0	5.0
PCB-141	6	360.9	7.2	4.4	102.9	1.8	3.0	5.0
PCB-187	7	395.3	8.3	4.1	100.8	1.0	3.0	5.0
PCB-183	7	395.3	8.3	4.1	107.1	1.2	1.0	3.0
PCB-180	7	395.3	8.3	4.2	101.2	1.8	3.0	5.0
PCB-170	7	395.3	8.3	4.0	105.9	2.7	3.0	5.0
PCB-206	9	464.2	9.1	4.0	119.3	2.0	4.0	5.0

* Average recovery percentages obtained for GF-EVA and Al-EVA at 20 and 90 μg/L

In addition, slopes of the curves were significantly different ($p < 0.0007$). Therefore, to avoid over-estimation of concentrations, matrix calibration became necessary.

3.3.2 Accuracy, precision and sensitivity of analytical and instrumental methods: The validity of extractive method (M2) was evaluated from recovery experiments in which the prepared surfaces (GF-EVA-M1, GF-EVA-M2, Al-EVA) were carefully doped under two concentration levels (20 and 90 μg/L). In the Table 4 shows the values of efficiency in the extraction of the analytes by the selected method, these values are considered to be appropriated with recovery rates between 81.3 and 119.3 % and precisions, in terms of CV, less than 5.8 %. Two calibration curves were used, one to low concen-trations (from 3 to 120 μg/L) and another to high concentrations (from 0.1 to 1.0 mg/L). For all PCBs in both curves the quadratic correlation coefficients were larger than 0.9977. In addition, instrumental LOD and LOQ were between 0.5-4.0 and 3.0-5.0 μg/L, respectively.

Regarding the extractions of PCBs in water, the extractive process used showed excellent recoveries (between 90-101 %) with CVs lower than 3 %. The LOD and LOQ of the method were between 0.2 -1.6 and 1.2-2 μg/L.

3.4 Uptake of PCBs from water

Uptake of PCBs from water is summarized in the Table 5 and examplified in Figure 6 for different PCBs. The concentration change profiles of PCBs in water during the evaluation along the time showed similar behaviors; however, some differ-rences were found depending on the degree of chlorination of the PCBs. The main observations are shown below:

For PCBs lighter with 1 and 2 chlorines (see Table 4), such as PCB 1 and PCB 5, profiles obtained for GF-EVA-M1 and GF-EVA-M2 were found to be similar, but for Al-EVA, concentrations in water were higher between the first and sixth day. On the other hand, for the compounds of up to 4 Cl atoms did not present important differences. According as the number of chlorines increased from 5 to 7, the water concentrations for GF-EVA-M2 and Al-EVA tended to be higher, indicating a lower adsorption by the respective materials.

According as the number of Cl atoms in the biphenyl ring increased (from 1 to 5 Cl atoms), the equilibrium time (t_{eq}) was increased. For example, for PCBs with 1 and 2 Cl atoms (PCB 1 and 5), t_{eq} was reached after 4 days; For PCBs with 3 Cl atoms (PCB 18 and 31) t_{eq} was reached between 6 and 7 days. For PCBs with 4 and 5 Cl atoms (PCBs 44, 66

Table 5. Initial and final concentrations of PCBs in water (Cw_i and Cw_f, respectively) and in the evaluated materials (C_{EVA})

Compounds	Cw_i (µg/L)	GF-EVA-M1		GF-EVA-M2		Al-EVA	
		Cw_f (µg/L)	C_{EVA} (µg/g)	Cw_f (µg/L)	C_{EVA} (µg/g)	Cw_f (µg/L)	C_{EVA} (µg/g)
PCB 1	74.1	2.6	257.3	2.9	256.2	4.2	903.2
PCB 5	51.7	1.5	180.6	0.8	183.1	1.0	634.1
PCB 18	82.9	2.1	290.7	1.8	291.8	3.8	1020.6
PCB 31	51.6	0.9	182.5	0.8	182.8	1.3	640.6
PCB 52	55.2	0.9	195.3	1.0	195.1	1.7	685.5
PCB 44	75.3	3.4	258.7	3.2	259.4	3.5	908.2
PCB 66	53.7	2.5	184.2	2.4	184.6	1.6	646.7
PCB 101	56.8	8.5	173.7	9.9	168.7	6.0	609.8
PCB 87	56.9	8.4	174.5	7.5	177.8	8.3	612.6
PCB 110	75.7	8.9	240.4	8.1	243.2	8.4	843.8
PCB 151	63.5	11.5	187.2	18.1	163.2	11.6	657.2
PCB 153	75.6	19.6	201.5	27.2	174.2	19.9	707.4
PCB 138	62.9	13.3	178.5	13.7	177.0	17.3	626.5
PCB 141	62.4	13.4	176.3	13.5	176.0	7.2	618.9
PCB 187	73.6	18.5	198.3	19.9	193.2	22.1	696.0
PCB 183	74.8	21.2	192.9	19.9	197.5	24.1	677.1
PCB 180	56.9	11.1	164.8	15.2	150.0	19.3	578.5
PCB 170	47.6	13.4	123.1	18.4	105.2	17.2	432.0
PCB 206	50.1	17.6	116.9	16.9	119.5	17.9	410.5

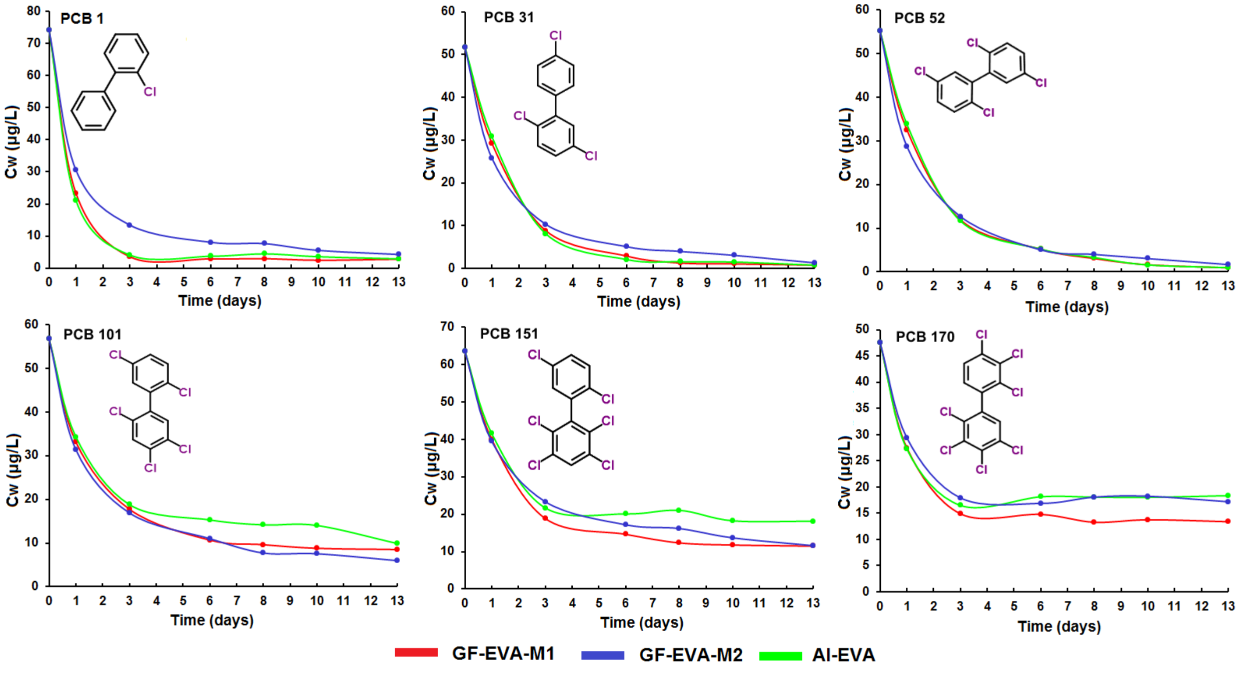

Figure 6. Change in the concentration of PCBs in water (*Cw*) by adsorption on GF-EVA and Al-EVA.

52, 110, 101, 87) t_{eq} was reached between 8 and 10 days. For the other chlorinated PCBs, the t_{eq} did not follow the behavior described above, for these compounds the variation was identified between 5 and 6 days. Similarly, the difference between Cw_i and Cw_f in water were higher for lighter compounds than for heavier ones, this can be explained by the greater diffusion capacity and permeability of PCBs at the substrate-water mass transfer interface. In addition, the number of PCBs adsorbed on the GF-EVA were similar, for Al-EVA surfaces these concentrations were above (± 300% difference), results could be a consequence of a greater mass transfer from the water to the EVA.

With the final concentrations obtained in the water, for each PCB and each type of sampler, the EVA-water partition coefficients (K_{EVA-W}) were estimated as a measure of the affinity of the compounds for the adsorbent phase. The average log(K_{EVA-W}) was ranged from 4.0 to 5.4 (see Table 4). It was observed that for PCBs with 1 and 4 Cl atoms, more hydrophilic with log(K_{ow}) between 4.5 and 6.3, showed the highest K_{EVA-W} values (between 5.0 - 5.4). On the contrary, for the PCBs with low polarity, these coefficients were between 4.0 and 4.5. This would indicate a greater affinity of the EVA for the more polar PCBs, possibly due to the polar contribution of the carbonyl oxygen of its structure. As it is shown in Table 5, values of log(K_{EVA-W}) have been obtained for organic contaminants such as pesticides, fungicides and some PCBs. S. George (2010) reports for compounds with values of log(K_{ow}) between 2.2 - 5.6 and values of log(K_{EVA-W}) between 2.5-6.3. On the other hand, Martínez *et al*., (2017) reports for organochlorine pesticides and organophosphates values between 1.0 - 4.5 for log(K_{EVA-W}).

3.5 Limits of detection of samplers

Concentration limits of PCBs in water (C_w) capable to be detected by the prepared samplers can be estimated from the following equation 5 [8]:

$$LOD \times \frac{f}{M_{EVA}} \times \rho = C_W \times K_{EVA-W} \tag{5}$$

where *LOD* is the detection limit of the instrument (in µg/L), *f* is the volume in liters of the total extract of EVA obtained after the extractive process (in this study was 0.002 L), M_{EVA} is the amount of EVA in the sampler), ρ is the EVA density (0.93 g/cm^3) and C_w the analyte concentration in water (µg/cm^3).

Table 6 shows the estimated concentrations of PCBs in water that would be able to be determined with the prepared GF-EVA and Al-EVA. For these configurations, the evaluated PCBs can be detected at environmental level in concentrations of the order of ng/L. These limits can be improved by area modifying of exposure or the mass of EVA in the substrates.

Table 5. Reported values of log(K_{EVA-W}) for different organic contaminants [8, 14]

Analytes	Log(K_{EVA-W})
Simazine, Carbofuran, Atrazine, Metolachlor, Alachlor, Format, a-HCH, Diazinon, Disulfoton, Terbufos, Trifluralin, Chlorothalonil Metribuzin, Malathion, Chlorpyrifos, PCB 3, PCB 15, PCB 18	2.5 - 6.3
Profins, α-BHC, β-BHC, Dimethoate, Heptachlor, Aldrin, Chlorpyrifos, 4,4'-DDE, Endrin, 4,4'-DDD, DDT, Famfur, Methoxychlor	1.0 - 4.5

Table 6. Limits of detection of GF-EVA and Al-EVA prepared

Compound	Concentration (ng/L)		
	GF-EVA M1	GF-EVA M2	Al-EVA
PCB-1	4.4	2.3	27.4
PCB-5	2.2	1.1	13.7
PCB-18	3.5	1.8	21.7
PCB-31	2.2	1.1	13.7
PCB-52	2.2	1.1	13.7
PCB-44	5.6	2.9	34.4
PCB-66	4.4	2.3	27.4
PCB-101	17.6	9.0	108.9
PCB-87	17.6	9.0	108.9
PCB-110	14.0	7.2	86.5
PCB-151	27.9	14.3	172.6
PCB-153	44.2	22.7	273.6
PCB-138	35.1	18.0	217.3
PCB-141	22.2	11.4	137.1
PCB-187	44.2	22.7	273.6
PCB-183	44.2	22.7	273.6
PCB-180	35.1	18.0	217.3
PCB-170	55.7	28.5	344.4
PCB-206	55.7	28.5	344.4

4. Conclusions

Sampler prepared from EVA using Al sheets and glass fiber filters as supports proved to be useful tools for the adsorption and estimation of PCB concen-trations in water. In general, lighter PCBs (between 1 to 4 Cl atoms) had a higher affinity for EVA with log(K_{EVA-W}) between 5.0 and 5.4.

Results evidence that EVA amount deposited on the glass fiber changes depending on inmerssion stage. In addition, for times of 24 hours and 1 or 2 inmmersion the EVA is adsorbed mainly in the inside of pores. It was noted that a significant decrease of permeability is obtained to conditions evaluated. EVA retention ocurrs by water flow transport through the filter suggesting that rate flow can affect the retention by changes in the residence times in the inside of the filter.

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Conflict of interests

The authors declare no conflict of interest.

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