

Research Article

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Sorption of alkylphenols and estrogens on microplastics in marine conditions

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Abstract: In marine ecosystems, living organisms are continuously exposed to a cocktail of anthropogenic contaminants, such as microplastics (MPs) and endocrine disrupting compounds (EDCs). Being able to adsorb organic compounds, MPs would act as an additional contamination vector for aquatic organisms. To support this hypothesis, the sorption of six EDCs on MPs, including 4-*t*-butylphenol, 4-*t*-octylphenol, 4-*n*-octylphenol, 4-*n*-nonylphenol, 17 β -estradiol and its synthetic analog 17 α -ethinylestradiol, has been investigated. These compounds belong to two contaminant families, alkylphenols and estrogens, included in the EU priority and watch lists of the Water Framework Directive. Sorption kinetics were studied onto polyethylene and polypropylene MPs under seawater conditions. MPs at a concentration of 0.400 mg mL⁻¹ were added to a mix of the six EDCs, each at the individual concentration of 100 ng mL⁻¹. The concentrations of contaminants were chosen to be close to environmental ones and comparable with those found in literature. The results demonstrated that the hydrophobicity of the compounds and the MP type are the two factors influencing the sorption capacity. The distribution coefficient (K_d) of each compound was determined and compared to others found in the literature.

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A high affinity was demonstrated between 4-*n*-NP and PE, with a sorption reaching up to 2,200 ng mg⁻¹.

Keywords: distribution coefficient, endocrine disrupting compounds, polyethylene, polypropylene

1 Introduction

Microplastics (MPs) have been defined as plastic items ranging from 1 μ m to 5 mm in size [1]. They are omnipresent and persistent in the environment, from the mountains to the seabed [2–6]. In addition to MPs, aquatic living organisms are continuously exposed to a cocktail of environmental organic contaminants impacting their health. Many deleterious effects of plastic wastes (including MPs) have been reported in animals [7–12]. Besides some physical effects, MPs lead to reproduction and immunological disruptions in some species [13]. Additional effects could also be the result of another organic compound transfer pathway to the organisms, through their sorption onto MPs. The MPs would act as a vector of organic contaminants for organisms. The presence of organic compounds in/onto MPs may have two origins. On the one hand, chemicals have been added during the plastic production as additives, such as phthalates, bisphenols and alkylphenols (APs), in order to adapt the plastic properties to their uses [14]. On the other hand, some environmental contaminants, polycyclic aromatic hydrocarbons (PAHs), polychlorobiphenyls (PCBs) or APs for example, can be sorbed onto MP surface *via* chemical interactions. As a general trend, environmental organic compounds show a high affinity for plastics due to their same hydrophobic characteristics [15–17]. Their sorption capacity also depends on MP characteristics and environmental composition [18,19]. The cocktail of environmental organic contaminants associated with MPs could potentially threaten the health of living organisms and even more, humans through the magnification along the food chain [20].

Different contaminants were measured on MP surfaces collected in aquatic ecosystems [21–23]. For example, some

concentrations up to 14,459 ng g⁻¹ for PAHs, 2,856 ng g⁻¹ for PCBs and 454 ng g⁻¹ for pesticides have been reported on plastic fragments sampled in the North Pacific [24]. Lowest values have been measured on plastics collected near the Vietnam coast: 2,024, 102, 108 and 551 ng g⁻¹ for PAHs, PCBs, dichlorodiphenyltrichloroethane (DDT) and nonylphenol (NP), respectively [21]. The concentrations of PCBs and DDT from MPs collected along the Atlantic coast were, respectively, 7 and 4 ng g⁻¹ [22], while they were found at higher concentration (53 and 27.6 ng g⁻¹, respectively) on Izmir coast, Turkey [23]. Despite these observations, the study of sorption mechanisms was debated latterly and still remains very limited to date [25,26].

Among aquatic pollutants, endocrine disrupting compounds (EDCs) are of great concern due to their multiple action mechanisms on organisms at low doses. Several observations of adverse effects on reproduction, growth and development of aquatic wildlife species have been reported [27–29]. At a global scale, waste water treatment plant effluents were characterized as one of the major sources of EDC-like molecules in aquatic ecosystems, particularly natural and synthetic steroidal estrogens (17 β -estradiol (E2) and 17 α -ethinylestradiol (EE2)), as well as APs, such as 4-*tert*-octylphenol (4-*t*-OP) or NPs [30–32]. These two classes of substances are included in the EU priority and watch lists of the Water Framework Directive [33]. Environmental concentrations of estrogens were reported in different compartments of aquatic ecosystems. For example, E2 reach 175 ng L⁻¹ in seawater in Italy [34], while EE2 was reported at 134 ng g⁻¹ in sediment collected in Brazil [35] and at 38 ng g⁻¹ of lipids in a marine mollusk (*Mytilus galloprovincialis*) collected in Italy [34]. APs are commonly used as plastic additives for their antioxidant and detergent roles. They were also frequently detected in aquatic environments [36–38].

The aim of this research was to characterize the sorption of 6 EDCs, i.e., four APs (4-*tert*butyl-phenol (4-*t*-BP),

4-*tert*octyl-phenol (4-*t*-OP), 4-*n*-octylphenol (4-*n*-OP) and 4-*n*-nonylphenol (4-*n*-NP)) and two estrogens (E2 and EE2) on polyethylene (PE) MPs. The concentrations of contaminants (0.400 mg mL⁻¹ of MPs and 100 ng mL⁻¹ of each EDC) were chosen considering the marine environmental medium, i.e., being close to environmental ones as well as comparable with those found in literature. The suitable equilibrium time and the distribution coefficients were determined, as well as the EDC recoveries throughout the experiment. Two different types of MPs, PE and polypropylene (PP), corresponding to the two most produced plastics frequently detected in marine environment [39], were then used to evaluate the influence of the polymer nature on the sorption of 4-*n*-NP.

2 Materials and methods

2.1 Chemicals, quality assurance and quality control

Low density MPs made of PE and PP were obtained from household products, a bag and a cable, respectively. After grinding the items (Cryogenic mill, SPEX 6770), particles with a size ranging from 53 to 100 μ m were selected using a metallic sieve.

The suppliers and the chemical properties of the six studied EDCs are presented in Table 1, and their chemical structures are given in Supplementary Information (Figure S1). Cellulose nitrate filters (12 μ m of porosity and 25 mm of diameter) were purchased from Merck-Millipore. All organic solvents were (high performance liquid chromatography (HPLC) grade and purchased from VWR: acetonitrile (ACN), dichloromethane (CH₂Cl₂) and dimethylformamide (DMF).

Table 1: Chemical properties of the six organic compounds used for the sorption study onto microplastics

Properties	APs				Estrogens	
	4- <i>t</i> -BP	4- <i>t</i> -OP	4- <i>n</i> -OP	4- <i>n</i> -NP	E2	EE2
Formula	C ₁₀ H ₁₄ O	C ₁₄ H ₂₂ O	C ₁₄ H ₂₂ O	C ₁₅ H ₂₄ O	C ₁₈ H ₂₄ O ₂	C ₂₀ H ₂₄ O ₂
log K _{ow}	3.29	3.70	4.12	4.48	4.01	3.67
Solubility ^(*) (mg L ⁻¹)	610	12.6	7.0	5.4	11.3	3.9
C.A.S. number	98-54-4	140-66-9	1,806-26-4	104-40-5	50-28-2	57-63-6
Provider	Fluka	Sigma-Aldrich		Alfa-Aesar	Sigma-Aldrich	

^(*): Values measured in water at 25°C.

4-*t*-BP: 4-*t*-butylphenol; 4-*t*-OP: 4-*t*-octylphenol; 4-*n*-OP: 4-*n*-octylphenol; 4-*n*-NP: 4-*n*-nonylphenol; E2: 17 β -estradiol and EE2: 17 α -ethinylestradiol.

All the laboratory material, chemicals and apparatus were pretreated to prevent cross-contaminations. Solvents were directly used after delivery and not reused. All glass materials were washed with Milli-Q water and pyrolyzed (550°C for 4 h) to eliminate all traces of organic compounds. The cellulose nitrate filters were rinsed with MilliQ-Q water before being used to prevent cross-contamination by MPs. The assessment of the absence of organic compound cross-contamination was performed by preparing different blank samples, i.e., without MPs and EDCs, as well as with MPs or EDCs only in seawater. These additional conditions were used for data correction concern.

3 Experimental design

3.1 Recovery and distribution coefficient determination

The protocol setup is presented in Figure 1. Experimental concentrations of PE MPs and individual EDCs were fixed at 0.400 mg mL^{-1} and 100 ng mL^{-1} in artificial seawater (salinity of 30 PSU, Aquarium Bulle, Poissy, France), respectively. Triplicates were performed. Practically, 10.0 mg of PE MPs was introduced into a glass tube containing 25 mL of seawater including the six EDCs in solution (100 ng mL^{-1}

each). These concentrations were chosen to be close to those found in the environment as well as to be comparable to previous studies [40,41]. The suspension was kept at 22°C, during 24 h, with agitation (220 rounds per minute) and in dark condition, to enhance contact between MPs and EDCs and to reach the equilibrium.

After 24 h, the solution was filtered using a glass filtration system and a cellulose nitrate filter. As a first step (step 1), the EDCs adsorbed onto the MPs retained on the filter were measured. For that, two successive solid-liquid extractions of the filter with CH_2Cl_2 ($2 \times 5 \text{ mL}$) were performed. Before the evaporation of the organic extract, 200 μL of DMF was added in order to prevent a potential loss of the most volatile compounds during the evaporation. After the evaporation, the remaining DMF volume was adjusted to 1 mL using ACN before the injection in HPLC for the determination of EDC concentrations. As a second step (step 2), the concentrations of EDCs remaining in the filtered seawater solution (the filtrate) were determined by a direct injection in HPLC. When the concentrations were below the detection limits (Table S1), 24 mL of the filtrate was extracted two times with CH_2Cl_2 with the same technique used for extraction of the filter in step 1. Finally, as a third step (step 3) with the aim to calculate the recovery of the EDCs in the experiment, all the glassware used for the filtration, i.e., the tube and the filtration system, were rinsed with 2 mL CH_2Cl_2 and 2 mL ACN. Following the same preparation of sample as explained above for filters (DMF addition, evaporation and volume adjustment with

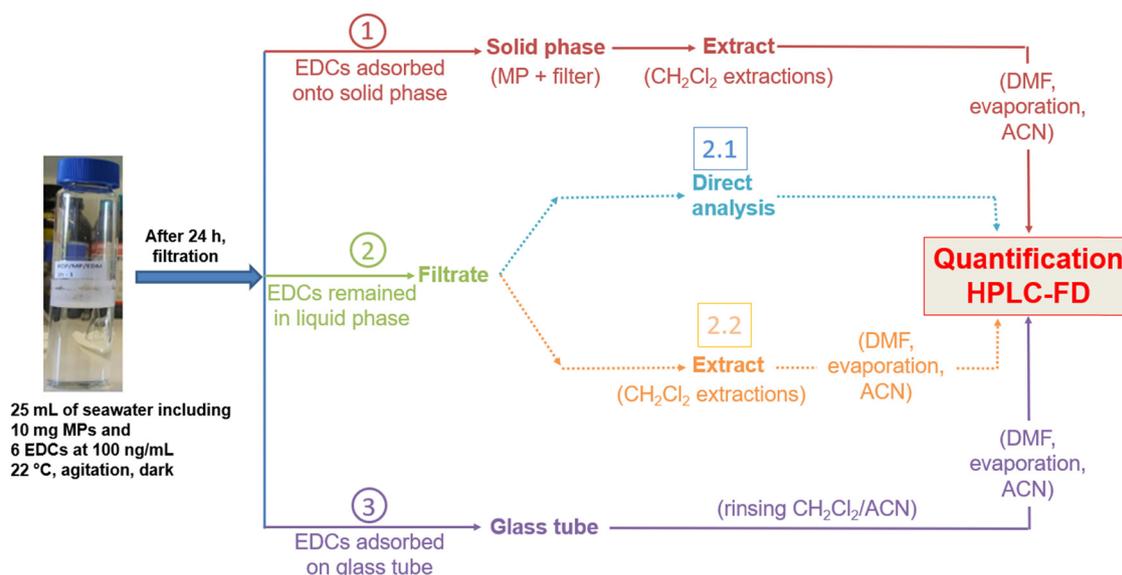


Figure 1: Experimental design for the study of the sorption of six EDCs onto MPs. Three steps were performed: step 1 corresponds to the determination of EDCs adsorbed onto solid phase, step 2 corresponds to the determination of EDCs remained in liquid phase and step 3 corresponds to the determination of EDCs adsorbed on glass tube (EDC: endocrine disrupting compound; MP: microplastic; CH_2Cl_2 : dichloromethane; DMF: dimethylformamide; ACN: acetonitrile; HPLC-FD: high performance liquid chromatography-fluorescence detector).

ACN, HPLC analysis), the EDC concentrations were then determined. This last step was added to evaluate the fraction of the EDCs adsorbed on glass walls during the experiment. In order to calculate the recovery of the manipulation, this protocol was performed without the addition of MPs in the tubes.

The distribution coefficient (K_d) is the parameter which represents the sorption capacity of the EDCs onto the MPs. This coefficient is known to depend on the MP type, the sorbed compound properties and the experimental conditions. In order to determine the K_d value of each compound, the EDC level sorbed onto the MPs (C_s) was divided by its concentration in the solution (C_w) at the equilibrium and was expressed as $L\ kg^{-1}$.

3.2 Sorption kinetic

To determine the time needed to reach the equilibrium of EDC sorption onto PE MPs, i.e., the equilibrium between the sorption and desorption, the kinetic sorption was determined between 0 and 96 h and involved nine sampling times. Exposure conditions as well as MP and EDC concentrations were similar to those described for K_d determination; four replicates were performed at each sampling time. The concentrations of each EDC sorbed on MPs were determined by solvent extractions involving CH_2Cl_2 , as explained in step 1 of the protocol presented in the latter section. The evolution of the EDC concentrations extracted from PE MPs related to the time allowed to determine the equilibrium time for each compound. Then, the highest equilibration time found for the EDCs was chosen as the duration applied for the determination of both the recoveries and the distribution coefficients.

3.3 Influence of the polymer nature on the sorption of 4-*n*-NP

To highlight the influence of the MP type onto the sorption of organic compounds, the 4-*n*-NP was chosen as a chemical model for experiments, involving PE and PP MPs, with a similar size range, i.e., 53–100 μm . Exposure conditions were the same for both MP types and involved 72 h of contact, 25 mL of seawater at 30 PSU, 22°C, concentrations of 0.800 $mg\ mL^{-1}$ and 10 $\mu g\ mL^{-1}$ for MPs and 4-*n*-NP, respectively. Triplicates were performed. The levels of 4-*n*-NP sorbed onto the MPs were then determined as described in Section 4.2.

3.4 EDC analysis by HPLC-fluorescence detector (FD)

EDCs were analyzed in the different solutions, i.e., MP extracts, in seawater and tube-rinsed solution, using a HPLC system (Dionex Thermo Scientific) equipped with a quaternary pump, a thermally controlled auto-sampler (set at 10°C), a column oven (40°C) and a programmable FD. Chromatographic separation was performed using a C18 column (Kinetex, 150 mm \times 2.1 mm, particle diameter 2.6 μm) and a flow rate of 0.735 $mL\ min^{-1}$. The mobile phase constituted of a mix of ultrapure water (A) and ACN (B). The gradient performed for the analysis was as follows: $t = 0$ –4.2 min: 37% B; $t = 4.2$ –13.8 min: increase of B from 37 to 80%; $t = 13.8$ –14.9 min: increase of % B from 80 to 100% and stays at 100% B until the end of the acquisition time (17.6 min). Excitation and emission wavelengths were 271/334 nm for EE2 and 290/340 nm for the other compounds. Acquisition data treatment was done by Chromeleon 7 software. The quantification of EDCs was performed by external calibration with eight concentration levels from 1 to 200 $ng\ mL^{-1}$ in two different solvents, i.e., ACN and seawater. For each concentration level, six calibration solutions were analyzed. Different parameters of method validation were evaluated, such as the limit of detection (LOD), the limit of quantification (LOQ), the linearity, the accuracy and the repeatability.

3.5 Statistical analysis

Result treatment and graphs were performed using the Microsoft Excel[®] software (version 2019).

4 Results and discussion

4.1 Validation of the EDC quantification by HPLC

The EDC quantification by HPLC performed by external calibration, in both ACN and seawater, was first validated for parameters, such as LOD and LOQ, linearity, accuracy and repeatability. The results obtained for the validation are detailed in Tables S1 and S2. All the coefficients of determination (R^2) of the EDC calibration curves were higher than 0.99, except for 4-*n*-NP in seawater (>0.96). This difference could be attributed to the highest hydrophobicity of 4-*n*-NP among the other compounds, leading

to a lower solubility in seawater, as well as the possible adsorption on vials. The detection and quantification limits were calculated for the six EDCs with values ranging from 0.137 to 4.152 ng mL⁻¹ and from 0.471 to 13.701 ng mL⁻¹ ($n = 6$), respectively. After the injection of three solutions of EDCs individually prepared and solubilized in seawater at 100 ng mL⁻¹ each, the accuracy and the repeatability were assessed (Table S2). The results of the analytical method were different according to the compound, probably depending on their polarity. In seawater, the method can be considered as repeatable because the relative standard deviations (RSD) were lower than 2.64% ($n = 3$) for most of the compounds, except for 4-*n*-NP (9.34% [$n = 3$]). Nevertheless, the relative biases (RB) were quite high, with values around or higher than 15% for five out of six compounds. EE2 was the only one showing an acceptable RB (1.5% [$n = 3$]). Better accuracy and repeatability were obtained using ACN as solvent for the solubilization of the six EDCs. The RB ranged from 0.29 to 3.07% ($n = 3$), and the RSD values were less than 2% (excepted for EE2 at 3.92%, $n = 3$) (Table S2). The lack of accuracy of the method observed using seawater solvent, could be attributed to the sorption of the compounds onto the glassware used for the preparation of the solutions, or to their precipitation, due to a lower solubility in seawater compared to ACN.

4.2 Recovery determination

Table 2 presents the recovery of the protocol developed to assess the sorption of the six EDCs onto the MPs. To reach this objective, the protocol was performed without the addition of MPs in the tube, as a first point of protocol validation. As a consequence, Step 1, corresponding to the extraction of the filter containing the MPs, was not performed and is presented as C_s in Table 3. The total recoveries (Step 2 + Step 3) ranged from 59.73 ± 14.265% ($n = 3$) to 90.21 ± 6.33% ($n = 3$) for 4-*n*-NP and E2, respectively. The highest values, higher than 85%, were obtained for the three compounds with the highest solubility in water

among the six studied, i.e., E2, EE2 and 4-*t*-BP. On the contrary, the lowest values, 59.73 ± 14.265% ($n = 3$), 66.53 ± 11.64% ($n = 3$) and 74.77 ± 15.25% ($n = 3$) were obtained for the lowest water-soluble compounds, 4-*t*-OP, 4-*n*-OP and 4-*n*-NP, respectively. The recovery was also calculated for Step 2, which corresponded to the EDC levels in the seawater. It corresponded to the recovery obtained for Step 2.1 or 2.2 when the concentration of EDCs in the liquid phase was lower than LOQ for the direct analysis performed in Step 2.1, requiring Step 2.2. The same trend was observed for the total, with values reaching only 57.74 ± 9.97% ($n = 3$) and 46.23 ± 11.76% ($n = 3$) for 4-*n*-OP and 4-*n*-NP, respectively. Moreover, the loss of compounds due to the sorption onto the glassware can be found in the line “Step 3” of Table 2. Values of 8.79 and 13.50% were found for the highest hydrophobic compounds, 4-*n*-OP and 4-*n*-NP, respectively. The same result was shown by Bakir et al. [16,17] who reported a loss of bis(2-ethylhexyl) phthalate (DEHP) up to 40% on glass system. For the other compounds, their loss by sorption onto glassware can be considered as negligible, reaching 1–4%. The adsorption of the compounds onto the filter could also be an explanation. Besides, the eluent strength of the solvent used for the extraction of the compounds from the glassware was not enough to desorb the most hydrophobic compounds, i.e., 4-*n*-OP and 4-*n*-NP. The hexane would have probably better desorbed 4-*n*-OP and 4-*n*-NP from the glassware, for which the compounds had likely strong interactions. In this case, the recovery of Step 3 would have been higher. Nevertheless, the choice of a more hydrophobic solvent than CH₂Cl₂ could have decreased the extraction of the compounds with lower hydrophobicity. For further experiments, successive extractions with different solvents or the use of mix of solvents could be tested.

4.3 Sorption kinetic

Figure 2 presents the evolution of the levels of EDCs sorbed onto PE MPs related to the time of contact, to assess the equilibration time of sorption. Two out of the

Table 2: Recovery of the different steps of the protocol for the study of the six EDC sorption (percentages, average ± SD, $n = 3$)

	APs				Estrogens	
	4- <i>t</i> -BP	4- <i>t</i> -OP	4- <i>n</i> -OP	4- <i>n</i> -NP	EE2	E2
Step 2 (% in the filtrate of seawater)	89.08 ± 2.97	71.30 ± 14.79	57.74 ± 9.97	46.23 ± 11.76	83.87 ± 3.28	89.60 ± 6.25
Step 3 (% adsorbed onto the glassware)	0.73 ± 0.08	3.47 ± 0.46	8.79 ± 1.67	13.50 ± 2.50	0.84 ± 0.16	0.61 ± 0.08
Total	89.81 ± 3.05	74.77 ± 15.25	66.53 ± 11.64	59.73 ± 14.265	84.71 ± 3.44	90.21 ± 6.33

4-*t*-BP: 4-*t*-butylphenol; 4-*t*-OP: 4-*t*-octylphenol; 4-*n*-OP: 4-*n*-octylphenol; 4-*n*-NP: 4-*n*-nonylphenol; E2: 17β-estradiol; EE2: 17α-ethiny-lestradiol and MPs: microplastics.

Table 3: Concentrations and distribution coefficient of six EDCs studied after sorption experiment onto PE MPs and distribution coefficients ($n = 4$)

	APs				Estrogens	
	4- <i>t</i> -BP ^(*)	4- <i>t</i> -OP	4- <i>n</i> -OP	4- <i>n</i> -NP ^(*)	E2 ^(*)	EE2
C_s (ng mg ⁻¹)	<LOQ	7.07 ± 3.05	44.9 ± 5.95	77.3 ± 9.18	<LOQ	2.69 ± 1.41
C_w (ng mL ⁻¹)	33.9 ± 19.7	48.1 ± 14.7	34.4 ± 13.8	<LOQ	70.1 ± 33.2	62.3 ± 26.8
K_d (L kg ⁻¹)	12.1 ± 8.30	171 ± 120	1,579 ± 1,004	106 ± 12.6	2.28 ± 0.974	45.3 ± 21.8

(*): Value estimated using the LOD in liquid phase (4-*n*-NP) and solid phase (4-*t*-BP and E2).

4-*t*-OP: 4-*t*-octylphenol; 4-*n*-OP: 4-*n*-octylphenol; EE2: 17 α -ethinylestradiol.

C_s : solid phase concentration; C_w : liquid phase concentration; K_d : distribution coefficient.

six studied compounds were not detected in the extracts of MPs. They corresponded to 4-*t*-BP and E2 which are the two compounds with the lowest hydrophobicity. In the seawater, the recovery of these two compounds during the time were found high but variable (62.8 ± 31 and 72.8 ± 27% for 4-*t*-BP and E2, respectively [$n = 8$]). To enable the assessment of the sorption kinetic of these two compounds, it seems necessary to increase the MP concentration used in the experiment and thus the solid/liquid ratio, in order to reach the analytical requirement for sensitivity. Indeed, in case of low adsorption occurrence, a higher solid/solution ratio is recommended to meet the experimental needs, as described in guidelines of adsorption/desorption of chemicals on soils [42].

The results shown in Figure 2 also highlight that the levels of sorbed compounds onto MPs were stable from

24 h until the end of the experiment. This means that the equilibrium of sorption reached quite rapidly, i.e., before 24 h. Figure 2 also allows comparing the differences of sorption between the four EDCs. The levels of sorption are inversely correlated to the solubility of the studied compounds. The most sorbed compound was 4-*n*-NP, with 80% of the nominal concentration on the MPs.

4.4 Distribution coefficient

The distribution coefficients were calculated in function of the EDC levels in two phases, solid and liquid. After an equilibration time of 24 h, the distribution coefficients of three compounds, 4-*t*-OP, 4-*n*-OP and EE2, were calculated and are presented in Table 3. As the most

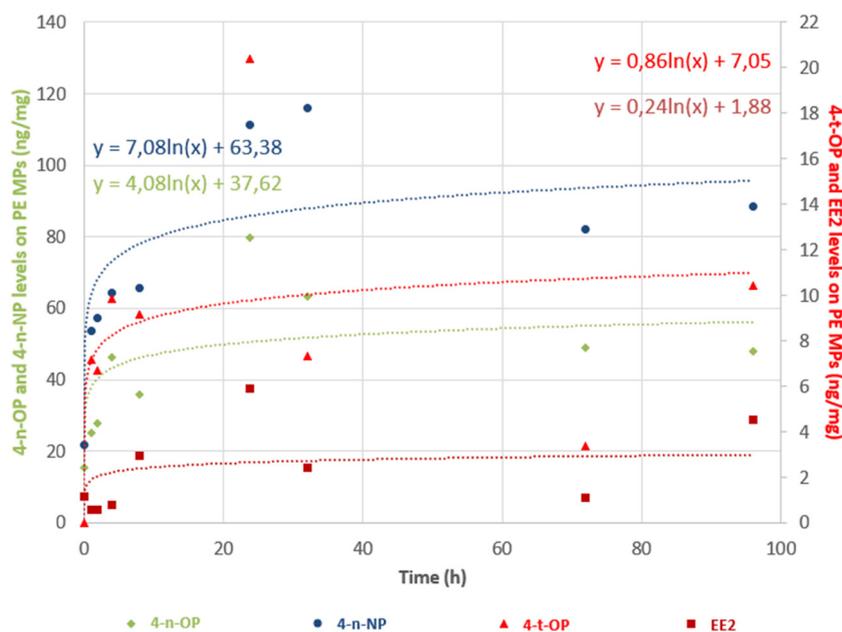


Figure 2: Sorption kinetics of four EDCs onto MPs of PE. The kinetic curve was based on logarithmic model. 4-*n*-OP: 4-*n*-octylphenol (green); 4-*n*-NP: 4-*n*-nonylphenol (blue); 4-*t*-OP: 4-*t*-octylphenol (red); EE2: 17 α -ethinylestradiol (purple).

hydrophobic compound, 4-*n*-NP, was not detected in the liquid phase. Its distribution coefficient has been determined using the LOD value as the C_w ; its K_d can be thus estimated to be $106.423 (\pm 12.649, n = 4) \text{ L kg}^{-1}$. Concerning 4-*t*-BP and E2, their K_d could be estimated to be $12.141 (\pm 8.303, n = 4)$ and $2.276 (\pm 0.974, n = 4) \text{ L kg}^{-1}$, respectively, using the LOD values as C_s .

Other results of distribution coefficients of organic contaminants onto MPs are reported in Table 4, for both types of MPs and equilibrium times. To the best of our knowledge, the present study is the first one investigating the K_d values of APs onto MP surfaces in marine conditions. Mean values were 170.914 ± 119.784 and $1579.478 \pm 1003.520 \text{ L kg}^{-1}$ ($n = 4$) for 4-*t*-OP and 4-*n*-OP, respectively. Compared to other organic compounds, they are relatively low. For example, the K_d of 4-methylbenzylidene camphor (4-MBC) onto PE particle reached more than 50.000 L kg^{-1} [40]. For the estrogen compounds, EE2, the K_d was lower than the value reported by Wu et al. [40], 45.286 vs 312 L kg^{-1} . On the contrary, similar K_d value (2.5 L kg^{-1}) was reported for E2 onto PE MPs in another recent studies [41] after 24 h of equilibrium time. Recently, Hu et al. [47] demonstrated that

the adsorption capacity of MPs (PS, PE and PVC) to E2 is stronger than the capacity of the soil. Regarding the equilibrium time, most of the studies reported that it is reached between 24 and 48 h. Karapanagioti and Klontza found an equilibrium time of many days [44]. This difference can be notably explained by larger MPs used (size ranging from 2 to 3 mm), presenting a lower active surface. Llorca et al. [45] also reported an equilibrium time of 7 days for the acid perfluoro-octanoic (PFOA) on PE MPs (3–16 μm) and up to 7 days for PS MPs (10 μm).

4.5 Influence of MP type on NP sorption

The levels of 4-*n*-NP sorbed onto two types of MPs were determined after 72 h of equilibrium. They reached 2260.08 ± 198.67 and $200.12 \pm 25.26 \text{ ng mg}^{-1}$ ($n = 3$) for MPs made of PE and PP, respectively. These results demonstrated that the levels of 4-*n*-NP sorbed onto MPs of PE were ten times higher than PP MPs. Hence, the polymer nature plays an important role in the sorption mechanisms. The time of contact was increased to 72 h in

Table 4: Distribution coefficients and equilibration time of different organic contaminants sorbed onto MP surface

Organic contaminant	$\log K_{ow}$	MP type	MP size (μm)	Equilibrium time (h)	$K_d (\text{L kg}^{-1})$	References	
Phenanthrene	4.5	PE	200–250	24	38,100	[43]	
		PP		24	2,190		
		PVC		24	1,650–1,690		
		PE	2,000–3,000	200–250	24	51,532	[15]
		PVC		24	2,285		
		PE		>80 days	13,000	[44]	
		PP		20–40 days	380		
		POM		>80 days	7,400		
PEP	>80 days	>12,000					
DDT	6.36	PE	200–250	48	96,892	[16,17]	
		PVC		24	104,785		
PFOA	0.7	PE	200–250	24	496		
		PVC		24	7		
DEHP	7.5	PE	200–250	24	98,494		
		PVC		24	11,917		
PFOA	0.7	PE	3–16	7 days	64	[45]	
		PS	10	>7 days			
PCB 77	6.72	PP	>180	8	1,183	[46]	
Carbamazepine	2.45	PE	250–280	48	191	[40]	
4-MBC	5.1	PE		48	53,225		
Triclosan	4.76	PE		48	5,140		
EE2	3.67	PE		48	312		
E2	4.01	PE	250–300	48	2,5	[41]	
4- <i>t</i> -OP	3.70	PE	53–100	24	1,580	This study	
4- <i>t</i> -OP	4.12				171		
EE2	3.67				45		

this experimentation, instead of 24 h for the other experiments. Nevertheless, 72 h was not sufficient to reach equilibrium for distribution of 4-*n*-NP on PP MPs, since some equilibrium times were determined as higher than 20–40 days in some studies, e.g., for phenanthrene sorbed onto PP particles [43]. Second, the size of the MPs was similar for both PE and PP types but other physical properties could be determined, such as the surface area and the crystalline level, to highlight their influences on sorption mechanism [18,48]. Considering the role of the polymer type on the adsorption process, Teuten *et al.* [43] demonstrated a K_d value for PE 20 times higher than for PP for the same size of particles (200–250 μm). These authors also reported that the Brunauer–Emmett–Teller surface of PE is three times higher than for PP polymers. Moreover, the difference of sorption mechanism onto PE and PP MPs was also reported by Karapanagioti and Klontza [44]. Accordingly, PE had a higher affinity for organic compounds than PP (around 40 times). These authors also reported that the sorption onto PP polymer was faster but strongly affected by the physico-chemical conditions of the solution, such as the salinity, which increased the sorption behavior. Hu *et al.* [47] found the sorption capacity of PS > PE > PVC MPs to E2.

5 Conclusion

The present study aimed at assessing the sorption of six EDCs onto MPs in marine conditions. The chosen compounds were four APs, including 4-*t*-BP, 4-*t*-OP, 4-*n*-OP and 4-*n*-NP, as well as two estrogens, E2 and EE2. To the best of our knowledge, the distribution coefficients of NPs on PE MPs have never been determined before. Regarding estrogens, the results on EE2 (equilibrium time and distribution coefficient) were in the same order of magnitude than others found in the literature. Moreover, estimates of 4-*t*-BP, E2, 4-*n*-NP distribution coefficients were made. Then, the sorption mechanisms were found strongly dependent on the hydrophobicity of the studied compounds (4-*n*-NP > 4-*n*-OP > 4-*t*-OP > EE2 > 4-*t*-BP > E2), as well as the type of MPs. Indeed, the sorption of 4-*n*-NP onto PE MPs was found to be ten times higher than onto PP MPs.

Due to the hydrophobicity of the compounds, the analytical method used, i.e., HPLC-FD, showed a lack of accuracy for their direct quantification in seawater. Moreover, working with environmental concentrations of the EDCs was difficult since they were very close to the quantification limits. Concerning the protocol developed for the sorption determination, the main critical

point was the low procedure recoveries, lower than 70% for most of the hydrophobic compounds, i.e., 4-*n*-OP and 4-*n*-NP. In addition, the choice of compounds with a wide range of hydrophobicity was challenging from an analytical and methodological point of view. To study the sorption of individual compound onto MPs could also be interesting, to determine if the behavior would be the same than in a mix. Finally, the assessment of the sorption of environmental organic contaminants onto the wide types of existing MPs remains a large investigation field, considering the diversity of polymers and other MP characteristics, such as the size, the additives, the crystallinity, the surface area and the ageing.

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