

Sorption of polycyclic aromatic hydrocarbons (PAHs) to low and high density polyethylene (PE)

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Abstract

Background, aim, and scope According to their high sorption capacity polyethylene (PE) passive samplers are often used for the analysis of polycyclic aromatic hydrocarbons (PAHs) in the aquatic environment. PE is also one of the primary synthetic polymers found in oceans, and sorption of PAHs to marine PE debris may determine PAH exposure and therefore hazards in marine ecosystems. Thus, an understanding of the sorption process is of great importance. In the present study, the sorption of several PAHs with different polarities to low density polyethylene (LDPE) and high density polyethylene (HDPE) was studied in order to improve our understanding of the influence of material properties on the Fickian diffusion of PAHs into PE.

Materials and methods Batch sorption experiments were performed with aqueous solutions containing acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and LPDE or HDPE pellets. Samples were shaken in the dark at $20 \pm 1^\circ\text{C}$ for 16 time intervals within one week. Concentrations of PAHs were determined in the

aqueous samples using solid-phase microextraction coupled with gas chromatography–mass spectrometry. The distribution coefficients (K_{PE}) between PE and water were estimated from different models reported in the literature. Kinetic sorption of the PAHs into the plastic pellets was described by a diffusion model based on Fick's second law in spherical coordinates.

Results and discussion A comparison between different models describing the equilibrium distribution of PAHs between PE and water revealed that the sorption equilibrium seemed to be driven by parameters other than, or in addition to, organic carbon. For both plastic types, diffusion coefficients decreased while the molecular weight of the PAHs increased which indicates a hindered diffusion through the matrix as a result of a larger molecule size. Higher diffusion coefficients were derived for LPDE than for HDPE indicating a greater sorption velocity for LPDE according to the lower polymer density.

Conclusions Our results revealed that equilibrium time could be shortened during passive sampling as polymer membranes of lower density are used. In some areas, marine ecosystems may not be in equilibrium with respect to concentrations of organic contaminants and abundance of marine plastic debris. In such cases, different polymer densities should be taken into account in risk assessments.

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1 Background, aim, and scope

Plastics have benefits in a wide range of areas including technology, energy savings and improved consumer health.

The packaging industry uses the most plastic, 18 million tons corresponding to 40.1% (Plastics Europe 2010). Polyethylene (PE) is about one third of the Europe plastics demand among other resin types (Plastics Europe 2010). Recently, PE devices have been applied for measuring polycyclic aromatic hydrocarbons (PAHs) in aquatic environments (Mueller et al. 2001; Booij et al. 2003; Adams et al. 2007; Cornelissen et al. 2008; Hale et al. 2010; Smedes et al. 2009).

Plastic debris in aquatic ecosystems is a rapidly increasing long-term and widespread threat that represents a great challenge for remediation (Zarfl et al. 2011). Since the early 1970s, plastic debris has become widespread in marine habitats, in sediment and in the surface waters of coastal areas and oceans throughout the world (Goldberg 1997; Mato et al. 2001; Derraik 2002; Rios et al. 2007; Sheavly and Register 2007; Moore 2008; Barnes et al. 2009; Ryan et al. 2009; Browne et al. 2010). PE is one of the primary synthetic polymers found in the oceans (Mato et al. 2001).

PE is classified into several different categories based mostly on its density and branching. In terms of sold volumes, the most economically important grades are high density polyethylene (HDPE) and low density polyethylene (LDPE) that account for 12% and 17%, respectively, of the total European plastic materials demand (Plastics Europe 2010).

PAHs are a class of hydrophobic organic chemicals (HOC) that occur all over the world in seawater (Da Silva et al. 2007; Arias et al. 2009; Ren et al. 2010). It has been reported that pre-processing plastic pellets and fragments of consumer products in ocean environments are contaminated with PAHs (Rios et al. 2007). Organic pollutants associated with plastics have been identified as one of the hazards related to plastic debris in the marine environment (Betts 2008). Zarfl and Matthies (2010) reported that HOC with octanol–water partitioning coefficients ($\log K_{OW}$) >6.5 have an enhanced mobility because of their sorption to buoyant microplastic material. Plastic debris floating on the surface of the ocean can be ingested by seabirds (USEPA 1990; Ryan et al. 1988; Blight and Burger 1997; Moser and Lee 1992; Spear et al. 1995; McCauley and Bjorndal 1999; Provencher et al. 2009) and hazards from a subsequent transfer of sorbed contaminants must be considered.

Environmental hazards associated with sorbed PAHs to microplastics in the aquatic environment were assessed theoretically assuming thermodynamic equilibrium (Gouin et al. 2011). Although results suggested microplastic being of low importance as a vector of substances to aquatic organisms in comparison with other exposure pathways, the authors identified a need to better understand the influence of material properties on the

Fickian diffusion of a chemical through the polymeric material. For instance, a decreased diffusivity for several hydrocarbons was observed with increasing polymer crystallinity (Vittoria 1995; Luetzow et al. 1999). In the study of Karapanagioti and Klontza (2008), a slower diffusion of phenanthrene into plastic-eroded pellets compared to virgin materials was attributed to an increase in crystallinity due to weathering. Although several sorption studies of PAHs were performed with PE passive samplers, powder and pellets (Booij et al. 2003; Adams et al. 2007; Teuten et al. 2007; Cornelissen et al. 2008; Karapanagioti and Klontza 2008; Smedes et al. 2009; Hale et al. 2010), the influence of different types of PE on the sorption behaviour of PAHs has been addressed rarely. In Mueller et al. (2001), the hypothesis that different types of PE passive samplers have different sampling properties was not definitely answered.

The objective of the present study was to investigate the diffusivity of several PAHs in LDPE and HDPE. Batch sorption experiments were performed with acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene and fluoranthene and with LDPE and HDPE pellets, respectively.

2 Materials and methods

2.1 Chemicals and sorbents

A ‘PAH Mix’ standard solution was purchased from Neochema (Bodenheim, Germany), containing acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLN), phenanthrene (PHE), anthracene (ANT) and fluoranthene (FLT) in acetone with a concentration of $50 \text{ ng } \mu\text{L}^{-1}$ of each PAH. Acetone (HPLC grade) was purchased from Sigma Aldrich (Seelze, Germany). Ultrapure water was taken from a Sartorius Arium 611VF water purification system (Goettingen, Germany). PAH stock solutions with final concentrations of each PAH of 60 and 100 ng L^{-1} were produced by adding 3 and $5 \mu\text{L}$, respectively, of the ‘PAH Mix’ standard solution to 2.5 L of ultrapure water. All PAHs were $<0.01\%$ saturation. The stock solution of 100 ng L^{-1} was diluted proportionately with ultrapure water to levels between 1 and 100 ng L^{-1} . A mixture of deuterated PAHs containing D10-ACE and D10-PHE with a concentration of each compound of $500 \text{ ng } \mu\text{L}^{-1}$ was purchased from Dr. Ehrensdoerfer GmbH (Augsburg, Germany). A stock solution with a concentration of $50 \text{ pg } \mu\text{L}^{-1}$ was prepared with acetone and used as an internal standard (IS).

LDPE pellets (Lupolen 1840 D, LyondellBasell) and HDPE pellets (Hostalen ACP 9255 Plus, LyondellBasell) were used as sorbents. The densities of LDPE and HDPE

were given in the product data sheets at 0.919 (LyondellBasell 2007a) and 0.957 g cm⁻³ (LyondellBasell 2007b), respectively. The mean measured mass ($n=10$) was 14±2 mg for LDPE and 34 g±3 mg for HDPE. The measured mean sizes ($n=6$) were 4.0×4.4×2.0 mm (width×length×height) for LDPE and 4.2×4.7×2.8 mm for HDPE.

2.2 Batch experiments

One plastic pellet and 7 mL of the PAH stock solution containing ACY, ACE, FLN, PHE, ANT and FLT (60 ng L⁻¹ of each PAH) were added to a 10-mL glass vial (Gerstel, Muelheim, Germany). The vial was sealed with a magnetic crimp cap equipped with a Teflon-faced silicone septum (Gerstel, Muelheim, Germany) wrapped with aluminium foil. Samples were shaken in the dark at 20±1°C for 16 time intervals within one week in a reciprocating shaker at 300 rpm. After being shaken, the cap was opened, the pellet and the aluminium foil were quickly removed with tweezers, 9 µL of the IS stock solution were added and the caps were closed immediately.

To assess compound loss from additional removal processes, e.g. sorption to the glass wall and/or volatilization, controls (7 mL PAH stock solution, 60 ng L⁻¹) were shaken for similar time periods. The analytical loss was taken into account in the mass balance equation used in the calculation of the diffusion coefficients. For all of the sorption experiments, procedural blanks (ultrapure water, pellet) were shaken daily and weekly, respectively. All samples were performed in triplicates.

The influence of time (t) on the ratio between the mean concentrations in the aqueous phase of the sorption samples (C_{aq}) and the controls ($C_{aq,c}$) ($n=3$) was tested by an analysis of variance (ANOVA) with IBM SPSS Statistics 15.0 assuming a significance level (p) of 0.01. A triplicate sample was considered to reach equilibrium when the last two measurements (24 h and one week) were statistically the same.

For determination of sorption distribution coefficients ($K_{PE,24h}$), one LDPE pellet was shaken for 24 h in a reciprocating shaker at 300 rpm in 7 mL of the PAH solution using eight concentrations of PAHs in the initial concentrations range of 1–100 ng L⁻¹. All concentration levels were repeated in triplicates. Controls were also performed at each concentration level in triplicates. Sorption isotherms were generated using a linear model. The slope of the plot $C_{aq,24h}$ against the solid-phase concentration $C_{PE,24h}$ (nanogrammes per kilogramme) represented $K_{PE,24h}$. Therefore, $C_{PE,24h}$ denotes the PAH concentration in the pellet after 24 h calculated from $C_{aq,24h}$ assuming mass balance after correction by the control concentration in solution after 24 h ($C_{aq,c,24h}$) as described in Section 2.4.

2.3 Chemical analysis

The concentrations of PAHs in the aqueous phase were determined by solid-phase microextraction (SPME) using a 65-µm polydimethylsiloxane–divinylbenzene fibre (PDMS/DVB) (Supelco, Seelze, Germany) and gas chromatography–mass spectrometry (GC–MS). The method was described in detail in Kukučka et al. (2010). In brief, extraction temperature and time were 60°C and 60 min, respectively. Agitating speed was 250 rpm. Before extraction, the fibre was pre-baked for 15 min at 270°C in a separate needle heater. Desorption from the fibre was carried out in the GC inlet at 270°C for 5 min in splitless mode. GC analyses were performed on a 6890N GC system coupled with a 5973 inert mass selective detector (Agilent Technologies, Santa Clara, USA). A HP-5MS capillary column (5% diphenyl–95% dimethylpolysiloxane), 30 m×0.25 mm i.d., 0.25 µm film thickness (Agilent Technologies, Santa Clara, USA) was used for chromatographic separation. The GC programme was as follows: 80°C (5 min hold), then at 15°C min⁻¹ to 180°C followed by 5°C min⁻¹ to 310°C (5 min hold). Helium was used as the carrier gas with a flow rate of 1.5 mL min⁻¹. MS with electron impact ionisation (EI) at 70 eV was operated in selected ion monitoring mode. The limits of detection (LODs) were between 0.1 ng L⁻¹ (ANT) and 5.14 ng L⁻¹ (FLT). Values of C_{aq} in blank samples were all below LOD.

2.4 Sorption model

Kinetic sorption of organic substances to plastic pellets can be described by the diffusion model based on Fick's second law in spherical coordinates (Karapanagioti et al. 2010) simulating the change of the solute concentration C_{PE} (in nanogrammes per kilogramme) in the pellet over time t (in seconds) and assuming the pellet to be spherical with a radius r (in centimetres)

$$\frac{\partial C_{PE}}{\partial t} = \frac{D_{PE}}{x^2} \frac{\partial}{\partial x} \left(x^2 \frac{\partial C_{PE}}{\partial x} \right) \quad (1)$$

where D_{PE} (in centimetres per second) is the constant diffusion coefficient in the pellet and x (in centimetres) is the distance from the centre of the plastic pellet with $0 \leq x \leq r$. As described above, sorption experiments were conducted in batches in keeping with tried and tested procedures for batch experiments used to analyse sorption of organic compounds to soil and sediment (OECD 1996).

According to Grathwohl (1998), the following assumptions were made: (1) the solid phase is free of solute at the beginning of the experiment ($C_{PE}=0$ at $t=0$ and for all x with $0 \leq x \leq r$), and (2) in the long run, the concentration in

the solid phase reaches equilibrium (C_{PE}^*) at the surface ($C_{PE} = C_{PE}^*$ at $t = \infty$ and for $x = r$), and (3) in the centre ($x = 0$), the solute concentration does not change in space after the beginning of the experiment ($\frac{\partial C_{PE}}{\partial x} = 0$ for $x = 0$ and $t > 0$).

Under these initial and boundary conditions and according to Crank (1986), the diffusion equation was solved analytically as formulated by Grathwohl (1998). For the analytical solution, a short-term approximation exists

$$m_{PE}(t) = 6 \cdot m_{PE}^* \cdot \left(\frac{m_{PE}^*}{m_w^*} + 1 \right) \cdot \sqrt{\frac{D_{PE} \cdot t}{\pi \cdot r^2}} \quad (2)$$

where $m_{PE}(t)$ (in milligrammes) is the substance mass in the plastic pellet at time t , and m_{PE}^* and m_w^* (both given in milligrammes) represent the substance mass at equilibrium in the pellet and in solution, respectively.

In order to determine diffusion coefficients by linear regression the short-term approximation was converted to the linear pattern $y = m \cdot x + b$

$$C_{PE}(t) = \sqrt{D_{PE}} \cdot 6 \cdot C_{PE}^* \cdot \left(K_{PE} \cdot \frac{M_{PE}}{V_w} + 1 \right) \cdot \sqrt{\frac{t}{\pi \cdot r^2}} \quad (3)$$

where K_{PE} (in litres per kilogramme) is the equilibrium sorption coefficient, M_{PE} is the mean pellet mass (in milligrammes) and V_w is the volume (in millilitres) of liquid phase in the batches. In this way, $C_{PE}(t)$ are the given y -values, the whole term $6 \cdot C_{PE}^* \cdot \left(K_{PE} \cdot \frac{M_{PE}}{V_w} + 1 \right) \cdot \sqrt{\frac{t}{\pi \cdot r^2}}$ represents the x -values which can be calculated from the given parameters, b is zero, and $\sqrt{D_{PE}}$ is the slope of the line which was determined by linear regression.

Assuming a spherical plastic pellet the radius r was calculated from M_{PE} and pellet density ρ_{PE} (in grammes per centimetre):

$$r = 3 \sqrt{\frac{3 \cdot M_{PE}}{4 \cdot \pi \cdot \rho_{PE}}} \quad (4)$$

$C_{PE}(t)$ denotes the PAH concentration in the pellet at times t calculated from C_{aq} assuming mass balance after correction by $C_{aq,c}$ (derivation of the equation is given in the SI).

$$C_{PE}(t) = (C_{aq,c}(t) - C_{aq}(t)) \cdot \frac{V_w}{M_{PE}} \quad (5)$$

The distribution coefficient K_{PE} between a plastic pellet and water can be estimated in different ways: First of all, the well-established Karickhoff approximation was applied to estimate the distribution coefficient K_{OC} (in litres per kilogramme) between organic carbon and water from the substance's octanol–water distribution coefficient K_{OW} (in

litres per kilogramme) and the organic carbon content (f_{oc}) of the plastic pellet (Karickhoff 1981)

$$K_{OC} = 0.411 \cdot K_{OW} \quad (6)$$

$$\Rightarrow K_{PE-OC} = f_{oc} \cdot 0.411 \cdot K_{OW} \quad (7)$$

Furthermore, regressions have been developed to directly describe PAH partitioning between PE passive samplers and water without explicit relation to the organic carbon content. These are given by Adams et al. (2007)

$$\log K_{PE-OW07} = 1.2 \cdot \log K_{OW} - 0.97 \quad (8)$$

and Smedes et al. (2009)

$$\log K_{PE-OW10} = 1.48 \cdot \log K_{OW} - 2.45 \quad (9)$$

$$\log K_{PE-MW} = 0.0307 \cdot MW - 1.19 \quad (10)$$

where MW is the molecular weight (grammes per mole) of PAHs. Adams et al. (2007) derived their regression equations from eight PAHs at 24°C, and are dependent on the $\log K_{OW}$. Smedes et al. (2009) proposed their estimation method based on sorption investigations on 26 PAHs and finally concluded that correlation of the equilibrium partition coefficient with molecular weight (Eq. 10) might be a more appropriate descriptor for equilibrium sorption than K_{OW} .

Using these estimation methods to calculate K_{PE} , the substance concentration in the plastic particle at equilibrium C_{PE}^* was calculated based on the total substance mass (M_{total} given in milligrammes) admitted to the experimental setup (derivation of the equation is given in the SI):

$$C_{PE}^* = \frac{1}{\frac{V_w}{K_{PE} \cdot M_{PE}} + 1} \cdot \frac{M_{total}}{M_{PE}} \quad (11)$$

Linear regressions with Eq. 3 and K_{PE-MW} as a reference scenario but also with alternative K_{PE} estimates (K_{PE-OC} , $K_{PE-OW07}$, $K_{PE-OW10}$) to consider the possible range were finally conducted using the least squares method and resulted in diffusion coefficients D_{PE} . According to Tinsley (1979), diffusion coefficients of the investigated PAHs i were normalised arbitrarily to FLT by the normalisation factor $(MW_i/MW_{FLT})^{0.5}$. Based on the derived values D_{PE} , the time t_{90} to reach 90% of equilibrium was calculated by Eq. 12 (derivation of the equation is given in the SI):

$$t_{90} = \frac{\pi \cdot r^2}{D_{PE}} \cdot \left(\frac{0.9}{6 \cdot \left(K_{PE} \cdot \frac{M_{PE}}{V_w} + 1 \right)} \right)^2 \quad (12)$$

The period t_{90} was calculated from the deduced diffusion coefficients. These values are helpful for the future design

of equilibrium batch experiments of PAH sorption into different plastic particles.

3 Results and discussion

3.1 Sorption kinetics

Mean values of $C_{aq} C_{aq,c}^{-1}$ with minimum and maximum values obtained from batch experiments with LDPE and HDPE pellets and different PAHs were plotted versus time t (Fig. 1). Values of $C_{aq} C_{aq,c}^{-1}$ decreased with time for both pellet types indicating sorption of all investigated PAHs.

The physicochemical properties of PAHs are shown in Table SI-1 in the [Electronic supplementary material](#). Values of $C_{aq} C_{aq,c}^{-1}$ fell more quickly as $\log K_{OW}$ values of PAHs increased. Results of the ANOVA demonstrated that a triplicate did not reach equilibrium for all PAHs after 24 h under the experimental conditions because the last two measurements (24 h and one week) were not statistically the same ($0.014 \leq p \leq 0.320$). In Fig. 2, the values of $K_{PE,24h}$ obtained from the sorption isotherms using a linear model were compared to the K_{PE-MW} values calculated from Eq. 10. The lower values of measured $K_{PE,24h}$ than of calculated K_{PE-MW} verified the fact that equilibrium was not reached in batches under the experimental conditions.

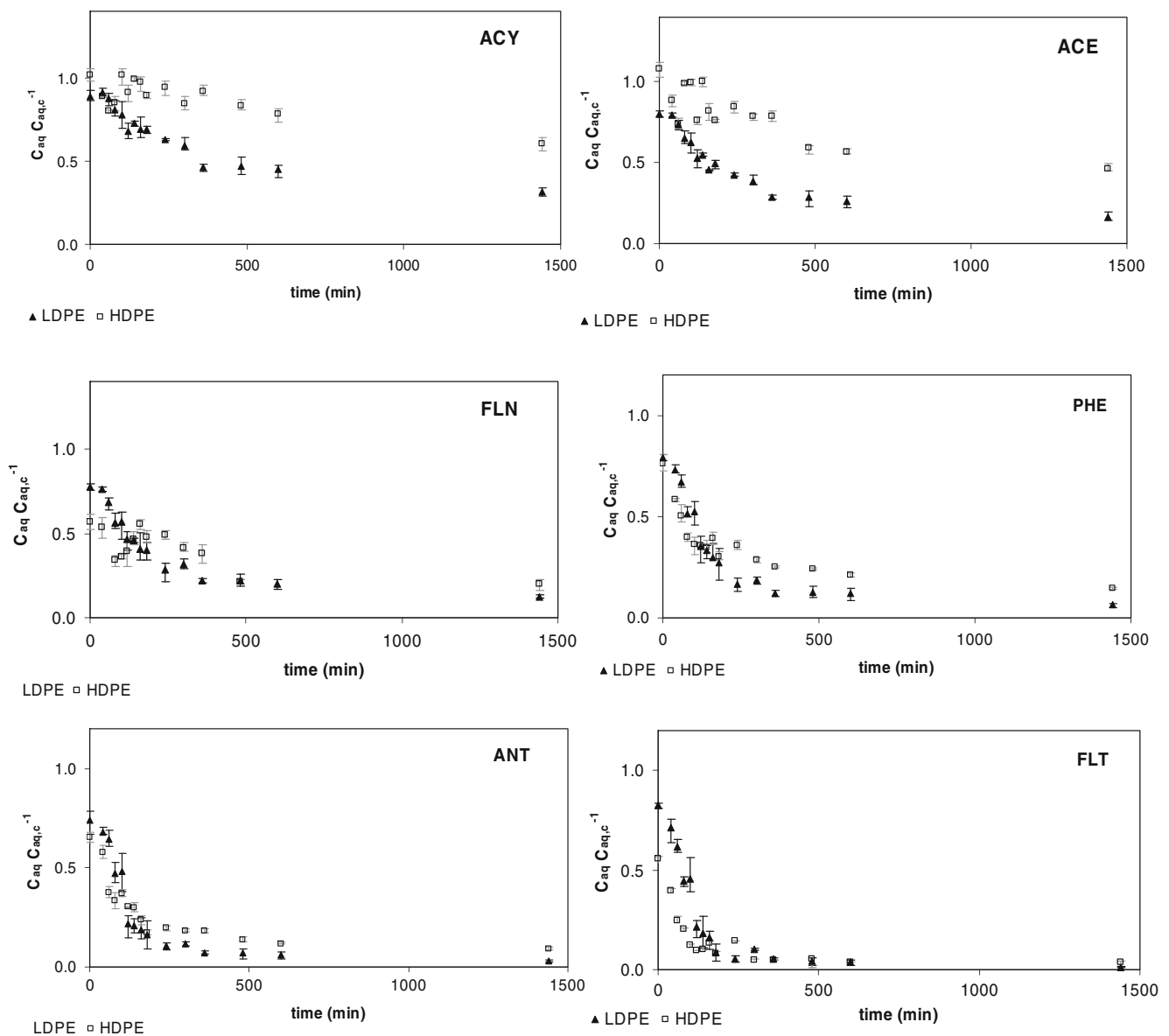


Fig. 1 Plots of mean values of $C_{aq} C_{aq,c}^{-1}$ versus time for LDPE and HDPE (error bars reflect minimum and maximum values)

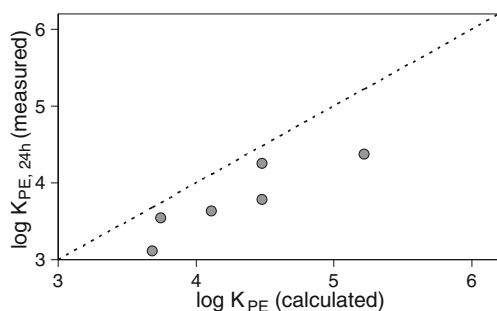


Fig. 2 Comparison of values of $K_{PE,24h}$ for ACY, ACE, FLN, PHE, ANT and FLT obtained from the sorption isotherms using a linear model with K_{PE-MW} values calculated from the regression given by Smedes et al. (2009)

3.2 Equilibrium sorption coefficients

Since sorption equilibrium was not achieved in the kinetic batch experiments, the equilibrium sorption coefficients K_{PE} were estimated as reported above. Calculated K_{PE} values ranged from 382 Lkg^{-1} (NAP) to $12\text{E}+06 \text{ Lkg}^{-1}$ (BEP). Since K_{OW} increased by raising the molecular weight of the PAH (except for ACY), equilibrium sorption described by K_{PE} simultaneously indicated this positive correlation, which was represented by all of the four proposed regressions (Fig. 3). Figure 3 also displays measured K_{PE} values available from the literature for sorption of PAHs to PE passive samplers with mean and minimum–maximum ranges (Mueller et al. 2001; Booi et al. 2003; Adams et al. 2007; Cornelissen et al. 2008; Hale et al. 2010; Smedes et al. 2009). The regression assuming the K_{OC} concept (K_{PE-OC} , Eq. 7) represented a lower boundary for all predicted K_{PE} of most of the PAHs ($\log K_{OW} > 4.1$). Moreover, measured K_{PE}

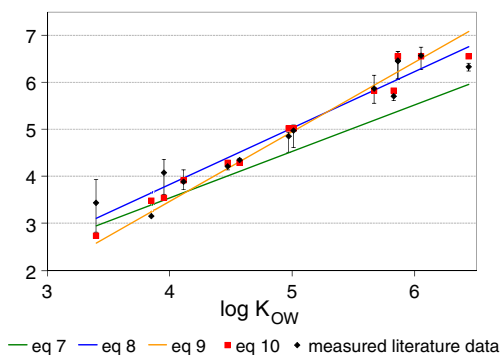


Fig. 3 Measured literature data (black diamonds mean and minimum–maximum range) (Mueller et al. 2001; Booi et al. 2003; Adams et al. 2007; Cornelissen et al. 2008; Hale et al. 2010; Smedes et al. 2009) and regression results for equilibrium sorption coefficient $\log K_{PE}$ of PAHs with different $\log K_{OW}$. Lines represent regressions based on a correlation between K_{PE} and K_{OW} both given in litres per kilogramme [eq 7 K_{PE-OC} (Karickhoff 1981), eq 8 $K_{PE-OW07}$ (Adams et al. 2007), eq 9 $K_{PE-OW07}$ (Smedes et al. 2009)]. Black squares indicate regression results derived from molecular weight (K_{PE-MW} , Smedes et al. 2009) of those PAHs which can also be characterised by available measured data (black diamonds) for K_{PE}

data of the PAHs were generally higher than was estimated by the K_{OC} concept. Thus, equilibrium sorption of PAHs seemed to be driven by parameters other than, or in addition to, organic carbon. In comparison with the measured K_{PE} data, the correlation with molecular weight actually seemed to be the most appropriate one and was therefore used for the diffusion model as a benchmark. Nevertheless, the alternative estimates for K_{PE} (K_{PE-OC} , $K_{PE-OW07}$, $K_{PE-OW10}$, see Eq. 7–9) were also applied to identify the sensitivity of the diffusion coefficient on the equilibrium constant.

3.3 Diffusion coefficients

For the investigated time periods, the condition given by Grathwohl (1998) was confirmed, i.e. values of the mass Fourier number $D_{PE} \cdot t / r^2$ were smaller than 0.01, and the short-term approximation (Eq. 2) could be applied. Estimated diffusion coefficients of PAHs into LDPE and HDPE investigated in our experiments are summarised in Table 1. For comparison of our diffusion coefficients with already existing data, a review of the literature revealed only a few diffusion coefficients for PAHs and PE. Karapanagioti et al. (2010) observed diffusion of PHE into PE pellets with a radius of 0.14 cm and a respective logarithmic diffusion coefficient of $-11 \text{ cm}^2 \text{ s}^{-1}$ which corresponds to our result of $-11 \text{ cm}^2 \text{ s}^{-1}$ (within a range of -11.22 to $10.45 \text{ cm}^2 \text{ s}^{-1}$) for PHE diffusion into HDPE. Hale et al. (2010) reported logarithmic diffusion coefficients for PHE and ANT of -9.10 and $-8.73 \text{ cm}^2 \text{ s}^{-1}$ into PE membranes of 26 and 51 μm thicknesses, respectively. Simko et al. (1999) calculated a $\log D_{PE}$ of $-10.85 \text{ cm}^2 \text{ s}^{-1}$ for the diffusion of FLT into PE sheets. These values are higher than diffusion coefficients in this study which may be attributable to the difference in the size of sorbents (pellets versus membranes or sheets).

In Table 1, benchmark values are supplied, which were based on equilibrium sorption coefficients K_{PE-MW} calculated from molecular weight (Eq. 10) as well as the respective range of diffusion coefficients resulting from simulations with alternative K_{PE} estimates (K_{PE-OC} , $K_{PE-OW07}$, $K_{PE-OW10}$). In general, for both plastic types, LDPE and HDPE, diffusion coefficients decreased by about a hundred times, while MW of the PAHs increased by 50% (152.2 – 202.3 g mol^{-1}) which indicates a hindered diffusion through the matrix as a result of a larger molecule size. This correlation has also been observed by Hale et al. (2010) and Simko et al. (1999) for diffusion of organochlorine pesticides and PAHs into PE membranes and for PAHs into PE sheets, respectively.

Normalised diffusion coefficients should be equal for all PAHs in the same medium (i.e. LDPE or HDPE, respectively) (Tinsley 1979). Diffusion coefficients still differed within 1 to 2 orders of magnitude since the normalisation factor based on the molecular weight ranges from 0.867 for

Table 1 Log D_{PE} and t_{90} (reference scenario, range given in brackets and resulting from alternative K_{PE} estimations (K_{PE-OC} , $K_{PE-OW07}$, $K_{PE-OW10}$, K_{PE-MW})) for investigated PAHs

	LDPE		HDPE	
	log D_{PE} ($\text{cm}^2 \text{s}^{-1}$)	t_{90} (h)	log D_{PE} ($\text{cm}^2 \text{s}^{-1}$)	t_{90} (h)
ACY	-9.33 [-9.67, -8.86]	20.0 [16.5–21.9]	-10.71 [-11.04, -10.24]	168.3 [154.0–175.3]
ACE	-9.16 [-9.61, -8.86]	10.5 [9.5–11.6]	-10.35 [-10.80, -10.06]	56.6 [54.1–59.2]
FLN	-9.80 [-9.90, -9.24]	9.8 [8.8–9.9]	-10.63 [-10.73, -10.07]	21.1 [20.2–21.2]
PHE	-10.43 [-10.66, -9.89]	8.2 [7.8–8.3]	-11.00 [-11.22, -10.45]	9.2 [9.0–9.2]
ANT	-10.33 [-10.79, -9.98]	6.4 [6.2–6.5]	-10.87 [-11.34, -10.53]	6.9 [6.9–7.0]
FLT	-11.80 [-11.75, -10.77]	6.7 [6.5–6.7]	-12.26 [-12.21, -11.22]	5.7 [5.66–5.71]

ACY to 0.939 for ANT and is not able to cut all diffusion coefficients down to the same order of magnitude. Nevertheless, the uncertainty range also covers about one order of magnitude for most of the PAHs (Table 1).

Diffusion coefficients of PAHs into LDPE were larger than respective coefficients in HDPE (Table 1) indicating that material properties of PE play a role in the velocity of the uptake of PAHs. The difference in the individual compounds' diffusion velocity, however, decreased with increasing MW indicating that the negative influence of the density on sorption became less important.

It took longer to reach 90% of equilibrium concentration in HDPE pellets than in LDPE pellets for all investigated PAHs apart from FLT, which was already implied by the deduced diffusion coefficients. The difference between the diffusion coefficients of FLT in the two plastic types was the smallest while the estimated K_{PE-MW} was ten times higher than even for ANT (Table 2). Thus, the higher radius of the HDPE pellet gained importance in Eq. 12 and led to a shorter t_{90} in HDPE than in LDPE.

Finally, 90% of equilibrium was attained in 24 h for sorption of all of the investigated PAHs in LDPE and of FLN, PHE, ANT and FLT in HDPE. Therefore, we calculated the ratio between PAH concentration in the pellet (C_{PE}) and in the solution (C_{aq}) at 90% of the equilibrium which could be expected to be close to the equilibrium concentration ratio K_{PE-MW} . However, this ratio

was still far from the equilibrium ratio K_{PE-MW} (Table 2). This was also stated by Ahn et al. (2005) who reported results of batch experiments investigating diffusion of PHE into polyoxymethylene (POM) pellets, a rubbery polymer, with 2.0 to 2.8 mm diameters. After 10 weeks, the concentration profile of PHE determined by microscope laser-desorption laser ionisation mass spectroscopy revealed that the diffusion front had not yet reached the centre of the pellet and still remained in the outer 0.6 mm of the POM. This is in the same order of magnitude as the diffusion distances of 0.15–0.68 mm calculated with the Einstein–Smoluchowski equation assuming the diffusion coefficients deduced for PHE in LDPE and HDPE. This means that the time between 90% of equilibrium and equilibrium is long enough to alter the concentration ratio C_{PE}/C_{aq} significantly. Thus, experiments reaching 90% of equilibrium are not sufficient to determine equilibrium distribution coefficients. Consequently, batch sorption experiments aiming to describe equilibrium partitioning of organic compounds into polymer material should adjust their equilibration time and the ratio of sorbent mass to solution volume in order to obtain measurable differences in sorbent concentration between the time only 90% of equilibrium concentration is reached and equilibrium itself.

4 Conclusions

A comparison of predicted and measured equilibrium distribution coefficients between PE and water reported in the literature indicate that equilibrium sorption of PAHs seemed to be driven by parameters other than, or in addition to, organic carbon. Our findings demonstrated that the diffusion coefficients for PAHs are different for LDPE and HDPE. The lower the density of the PE, the higher was the diffusivity. According to our results, equilibrium time could be shortened during passive sampling by using a polymer with a lower density. In some areas, marine ecosystems may not be in equilibrium with respect to concentrations of organic contaminants and abundance of marine plastic debris. In such cases, various densities of

Table 2 K_{PE-MW} values for the reference scenario estimated by Eq. 12 for investigated PAHs and ratio between C_{PE} and C_{aq} at t_{90}

	K_{PE} (L kg^{-1})	$C_{PE} C_{aq}^{-1}$ (L kg^{-1})	
		LDPE	HDPE
		ACY	3,038
ACE	3,501	1,85	1,167
FLN	8,184	2,793	1,480
PHE	19,128	3,567	1,673
ANT	19,087	3,566	1,637
FLT	104,564	4,295	1,817

polymers must be considered in risk assessments. Considering the variety of polymer types, the polymer density should be taken into account when assessing the hazard of PAHs in marine environments. Further studies are needed to investigate the influence of other polymer characteristics, e.g. crystallinity on the sorption behaviour of PAHs to PE.

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Supporting information available

Table with physicochemical properties of PAHs and derivations of selected equations. This material is available free of charge online