

Article

Laboratory Measurements of Pyrene and Acenaphthene Partition into Microplastics

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Abstract: Microplastics are a major environmental issue. In marine systems, these break down into small fragments that may lodge within organisms, but they behave as vectors for chemicals when pollutants such as metals, polycyclic aromatic hydrocarbons (PAHs), pesticides, and pharmaceuticals are absorbed by the particles. The rate and extent of uptake of organic compounds onto microplastics is dependent on a range of factors such as the sites available on the surface, the type of plastic, and the compound being sorbed, with hydrophobicity an important property. Laboratory experiments determined the uptake of pyrene and acenaphthene (and sometimes phenanthrene) onto pellets of polyvinyl chloride (PVC), polyethylene terephthalate (PET), polyoxymethylene (POM), polypropylene (PP) and polystyrene (PS). The kinetics of uptake in the experiments reveals half-lives ~10 h. The extent of partition onto the plastic pellets was similar for pyrene and phenanthrene, though lower for acenaphthene. This was not surprising because the octanol-water distribution coefficient of acenaphthene is about an order of magnitude smaller than that of pyrene, suggesting it is less hydrophobic. The PAHs are distributed most strongly into PP but only weakly into PVC. The fragmentation and oxidation of microplastics means that they sorb increasing amounts of organic material as they age.

Keywords: phenanthrene; marine plastic waste; distribution coefficient; polycyclic aromatic compounds (PAH); polyvinyl chloride (PVC); polyethylene terephthalate (PET); polyoxymethylene (POM); polypropylene (PP) and polystyrene (PS)



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1. Introduction

Microplastics are widely recognised as an environmental issue and represent a threat to marine life. These small plastic particles can cause problems after lodging within organisms [1–3], but they also behave as vectors for transporting metals or organic compounds bound to their surface [4]. Concern over plastic waste has been notable across recent years, yet there have been warning signs for half a century after Venrick argued that it was likely there were 5.9 million red rubber sandals afloat in the Pacific Ocean [5]. As plastic production has quadrupled since then, we might expect a rising quantity of plastic to be present in the world's oceans, and it is evident that there is an enormous quantity of such marine debris, which is often deposited on beaches and in sediments [6,7]. In the 1950s, an early stage in the growth of the plastics industry, the world produced only two million tonnes per year [8]. However, over the next half-century, with the rapid progress of manufacturing worldwide and the high demand for plastics, global production increased year by year. By 2019, 368 million tonnes of plastics were produced annually [9]. Some 4.8–12.7 million tonnes of plastic are deposited in the sea; this often occurs through stormwater discharge, littering and loss from solid waste disposal sites. Additionally, some plastic is lost during fishing, from sea-going vessels and the offshore oil and gas industry.

Treatment, incineration and recycling represent only a small flux, so only a relatively small fraction of plastic waste is well managed. This is an important issue for the 21st century as most plastic products cannot be readily reused or easily recycled, so much goes to landfill or is simply discarded [10].

Plastics in the environment, especially in marine environments (e.g., beaches and oceans), can be degraded into numerous smaller pieces [11,12]. Microplastics, i.e., pieces of plastic smaller than 5 mm, can be derived from primary (e.g., plastic pellets) or secondary sources (e.g., broken down from larger pieces). Past studies indicate that microplastics in marine organisms cause not only physical but also biochemical damage [2]. The impact of plastic pollution via animal ingestion and entanglement ranges through marine fauna, from zooplankton to organisms at higher trophic levels [13–17]. It is important to consider that microplastics play a role as a vector for environmental pollutants absorbed on their surfaces. Pollutants such as metals, polycyclic aromatic hydrocarbons (PAHs), pesticides and pharmaceuticals have been detected in samples of plastic collected from the environment [18]. Although the fluxes of these adsorbed organic pollutants may be small [19], they can represent a mechanism for the transport of sorbed pollutants within marine ecosystems. In recent years, many laboratory simulations and much fieldwork have assessed the ability of pollutants to be absorbed into microplastics (e.g., [20,21]). Besides, there was also evidence that contaminants could be transferred from plastics to biological tissues [22]. The binding of pollutants to microplastics has become of great concern, along with recent reports of the formation of rock-like materials from waste marine plastic [23].

The rate of uptake of organic compounds onto microplastics can give clues as to the sorption mechanisms; a first-order uptake onto the surface can suggest that it is largely controlled by physical diffusion from the solution to the plastic. Pseudo-second-order adsorption kinetics can suggest the mechanism may involve the chemisorption of organic compounds [24,25]. Factors relevant to uptake into plastic have been reviewed by O'Connor et al. [26], Liu et al. [27] and Fu et al. [28] and give an outline of the mechanisms of the partitioning of chemicals to different plastics, which can be a function of the strength of the hydrophobic and electrostatic interactions, ageing, crystallinity, functional groups and polarity of microplastics. Particle size is also important as an influence on the number of available adsorption sites on the plastic surface, such that finer-sized microplastics would have a higher number of sites for a given mass [29].

There is considerable interest in the extent to which different plastics vary in terms of the amount of organic compounds that can be sorbed [27]. Rochman et al. [30,31] have examined a range of organic compounds and their absorption on common plastics. After some analytical refinement, they identified a surprising level of uptake of organic pollutants by polystyrene in seawater off the California coast, although the nature of polystyrene would suggest that uptake might be low. The sorption capacity of plastic polymers will depend on the interaction between the polymers and that of the organic contaminants, with hydrophobicity seemingly a key factor. Organic pollutants typically have high-fat solubility and low solubility in water, so they are readily adsorbed onto the surface of the plastic. The octanol/water partition coefficient (K_{ow}) is a useful representation of the hydrophobicity of a substance [28]. Organic pollutants with substituent chlorine atoms are readily adsorbed by polystyrene. While it might be expected there would not be the same attraction for PAHs, the π - π interactions with polystyrene and aromatic compounds can lead to effective binding [29]. Ageing of microplastic particles will cause them to gain more oxidised functional groups; this is likely to increase their adsorption capacity for hydrophobic organic pollutants [32,33], although this is not always observed [34]. Plastic particles with higher crystallinity are likely to result in lower adsorption capacities for organic pollutants [28], such that crystalline plastics such as polyoxymethylene might have lower-than-expected uptake.

Although there are many studies concerning the interaction between contaminants and microplastics, the review by O'Connor et al. [26] shows a rather limited number accounting for the sorption of polycyclic aromatic compounds [35,36], and only a limited number of

studies make laboratory measurements across a range of plastics [37]. Polycyclic aromatic hydrocarbons have been measured in ocean waters [38] and coastal waters [39], with both pyrene and acenaphthene known in aquatic systems [38,40]. Here, we consider pyrene and acenaphthene (and, to a lesser extent, phenanthrene) as probes to explore interaction with different plastics, as it enabled us to explore the differences between a four and three-ring PAH that are widely found in the environment.

2. Materials and Methods

2.1. Materials

This study used pellets of polyvinyl chloride (PVC) and polyoxymethylene (POM) purchased from the Formosa Plastics Corporation in Taiwan, and polypropylene (PP), polyethylene terephthalate (PET) and polystyrene (PS) came from Sigma Aldrich, St. Louis, MO, USA. The properties are listed in Table 1, along with conditions used in the kinetic and isotherm experiments.

Table 1. Properties of the plastics used in the experiments and some of the conditions adopted.

Property	PVC	POM	PET	PP	PS
Density ^a /g cm ⁻³	1.391	1.41	1.68	0.9	1.05
Melting point ^a /°C	212	165	250–255	157	240
Crystallinity ^b	Amph	Cryst	SC	SC	Amph
Water content ^b /mass %	0.04–0.40	0.11–0.50	0.10–0.30	0.01–0.02	0.01–0.04
Global production 2018–2022/Tg a ⁻¹	44	1.4	56	56	4
Experimental conditions					
Plastic in solution/g L ⁻¹	1	5	10	5	10
Pellet diameter/mm	0.1	3	4	5	5

^a Data provided by the pellet manufacturer. ^b Water absorption after 24 h—values from: <https://omnexus.specialchem.com/polymer-properties/properties/water-absorption-24-hours> (accessed on 20 December 2023). Abbreviations SC: Semi-crystalline. Amph: amorphous, and Cryst: Crystalline.

The polycyclic aromatic hydrocarbons used in the experiments were:

1. Pyrene (PYR: C₁₆H₁₀) was purchased from Sigma-Aldrich and is a polycyclic aromatic hydrocarbon (PAH) consisting of four fused benzene rings, resulting in a flat aromatic system. Boiling point 394 °C. Solubility in water 0.049 mg L⁻¹ (0 °C), 0.139 mg L⁻¹ (25 °C), and 2.31 mg L⁻¹ (75 °C) [41]. The logarithm of the partition coefficient (n-octanol/water) is 4.88.
2. Acenaphthene (ACE: C₁₂H₁₀) is a polycyclic aromatic hydrocarbon (PAH) consisting of naphthalene with an ethylene bridge connecting positions 1 and 8. Solubility in water is 4 mg L⁻¹, and vapour pressure is 5 mmHg at 115 °C. It was purchased from Supelco. The logarithm of the partition coefficient (n-octanol/water) is 3.92.
3. Phenanthrene (PHE: C₁₄H₁₀) was purchased from Sigma-Aldrich (St. Louis, MO, USA) and is a polycyclic aromatic hydrocarbon (PAH) consisting of three angled fused rings. Solubility in water is 1.6 mg L⁻¹, and the logarithm of the partition coefficient (n-octanol/water) is 4.46.

2.2. Experimental Method

Uptake experiments used PAH solutions in ultra-pure water with no background electrolytes or buffers. In the experiments, it stabilised to ~pH 6. As the compounds are only slightly soluble in water, they were dissolved in small amounts of methanol before being added to the aqueous solution under preparation. In the time-variant experiments, the starting concentrations for pyrene and for acenaphthene were 50 or 150 µg L⁻¹, dependent on the plastic. In the 48 h experiment to establish the variation of uptake with PAH concentration with an isotherm, pyrene and acenaphthene concentrations from 30 to 250 µg L⁻¹ were used.

The PAH solutions (40 mL) with different quantities of microplastic beads were placed in an amber glass bottle with a Teflon cap and stirred in an orbital shaker at 20 revolutions per minute. This rate ensured the particles mixed well with the solution. If the stirring rate is too fast, the centrifugal force causes the pellets to deposit in the bottom of the bottle. At various times up to 120 h, 1 mL samples were removed from the vials, although never more than two samples were taken from any given vial to avoid changes in the amount of material associated with the experiment. The quantities of plastic varied (see Table 1) because of differences in the extent of uptake.

The small quantities of solution extracted from the bottles were analysed for the PAHs using high-performance liquid chromatography coupled with a fluorescence detector (Hitachi L-2130 Pump and Hitachi L-7485 FL detector Merck KGaA, Darmstadt, Germany). The wavelengths for excitation and emission are: Ex/Em for pyrene is 317/406 nm, Ex/Em for phenanthrene is 288/364 nm, and Ex/Em for acenaphthene is 288/337 nm. The mobile phase used was methanol/water with a ratio of 9:1. In this study, all the methanol is the LCMS grade purchased from J.T. Baker.

A set of isotherm experiments was run in much the same way as discussed above, gently agitating the solutions for 48 h, after which time equilibrium was achieved. Three bottles were available for each initial concentration of PAH, which enabled an estimate of the standard deviation for the measured concentrations.

2.3. Data Analysis

Both kinetic rate constants and equilibrium partition or distribution constants are frequently reported in studies of the binding of organic materials to plastics. The rate of approach to equilibrium has been treated as both a first and second-order process, but here, we adopt a first-order process as our results suggest the kinetics for equilibrium was relatively constant among the plastics. This may reflect what might be expected from a transport-driven process where reactions at the surface are rather fast, but we did not examine this process over a wide range of concentrations. The partition or distribution coefficient K_d is the ratio of the concentration of a compound in a mixture of two immiscible solvents at equilibrium, but it is adopted here to describe uptake from a solution onto particles. It is, for example, an important parameter for understanding the partition of a compound between water and the solid phase and its mobility in the environment. In this study, K_d (L g^{-1}) was used as the key parameter, a partition or distribution coefficient, to represent the affinity for distinct plastics:

$$K_d = q_e / c_e \quad (1)$$

where q_e is the amount of compound ($\mu\text{g g}^{-1}$) adsorbed on microplastics at equilibrium and c_e is the concentration of the compound ($\mu\text{g L}^{-1}$) in the liquid phase at equilibrium.

The amount of a compound sorbed on the microplastics was determined from the experiments as follows:

$$q_e = (c_0 - c_e)V/m \quad (2)$$

where c_0 is the initial concentration of the compound ($\mu\text{g L}^{-1}$) in the liquid phase, c_e compound concentration ($\mu\text{g L}^{-1}$) in the liquid phase at equilibrium, V is the volume of solution (L), and m is the mass of the microplastic (g).

Uptake isotherms can also be interpreted in terms of Freundlich, linear, and Langmuir sorption isotherms [37]. The Freundlich isotherm takes the form:

$$K_d = q_e / (c_e)^{1/n} \quad (3)$$

where n is typically close to unity and accounts for saturation to the uptake at high concentrations. However, as PAH concentrations in environmental systems would typically be small, such saturation might not be realised. The Langmuir isotherm [37], which imagines a continuous monolayer of adsorbate molecules covering the sites on a homogeneous

surface, has also been used by some studies and as with the Freundlich isotherm it leads to saturation (q_{max}) at high concentrations.

3. Results

Smaller particles, which have a higher specific surface area, were usually considered to adsorb more pollutants [42]. The solid-to-liquid ratio defines the mass of the microplastic in the volume of the liquid phase.

3.1. Setting Concentrations

Initial partition experiments established suitable amounts of plastic for the study. In these, the solutions of both pyrene and phenanthrene (initial concentration $50 \mu\text{g L}^{-1}$) had different amounts of plastic in suspension in the apparatus to establish the solution concentrations after 48 h. As expected, greater concentrations of suspended plastic pellets led to more PAH being removed from the solution (Figure 1). It is also evident that there are substantial reductions in the concentrations of PAH by polyvinyl chloride at 10 g L^{-1} of plastic. This was greater than that for other plastics, which tend to have less site to bind the organic compounds. The differences between the binding of pyrene and phenanthrene are relatively small. Phenanthrene binds a little more strongly to polyvinyl chloride and polyethylene terephthalate than pyrene, though the results for other plastics are less clear (Figure 2). However, as the differences between phenanthrene and pyrene were relatively small and not in the same direction (Wilcoxon signed-rank test, $p_2 \sim 0.13$), so subsequent experiments replaced phenanthrene with acenaphthene, which has a lower K_{OW} .

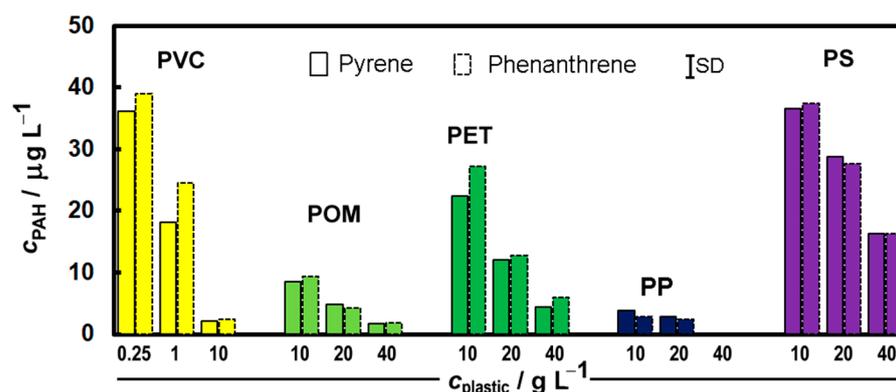


Figure 1. The concentrations of pyrene (solid outline) and phenanthrene (dashed outline) after 48 h exposure to suspensions of various types of plastic pellets in solution. SD shows the standard deviation of the concentration measurements. Note polypropylene samples at 40 g L^{-1} were lost.

3.2. Uptake onto Pellets

The experimental results from the uptake of pyrene and acenaphthene onto the five plastic pellets over time are shown in Figure 2a–f. As seen in these experiments, the PAHs are gradually removed from the solution by the pellets and seem to be reaching an equilibrium value towards the end of the 120 h experiments. The uptake of the particles is reflected in the mirror image curves that show the increase in concentrations on the plastic pellets (Figure 2g,h).

3.3. Kinetics

These experiments were primarily designed to determine the rate of partitioning of PAHs to the plastics. Figure 2 shows a typical exponential change with time as the PAHs deposit onto the pellets and are lost from the solution. It seems to follow a curve expected from first-order kinetics:

$$c_t = c_0 \exp(-k/t) + c_e \quad (4)$$

where k is the first-order rate constant, t is the elapsed time, and c_t is the aqueous concentration after the elapsed time. The equation was solved for the experiments shown in Figure 2a–f. The first-order rate constants for the uptake of pyrene and acenaphthene onto the pellets are given in Table 2 as reciprocal seconds. A second-order fit to the experimental data gives slightly better agreement but is not necessarily a large improvement, given the small number of measurement points. The half-lives for uptake are shown in Figure 3. The rate constants for uptake of PAH on the pellets are all rather similar and remain almost the same ($\sim 0.06\text{--}0.1\text{ h}^{-1}$, i.e., $\sim 17\text{--}28 \times 10^{-6}\text{ s}^{-1}$) for both pyrene and acenaphthene. However, it should be noticed that polypropylene seems different because the uptake of acenaphthene is slower, with a longer half-life of almost 15 h.

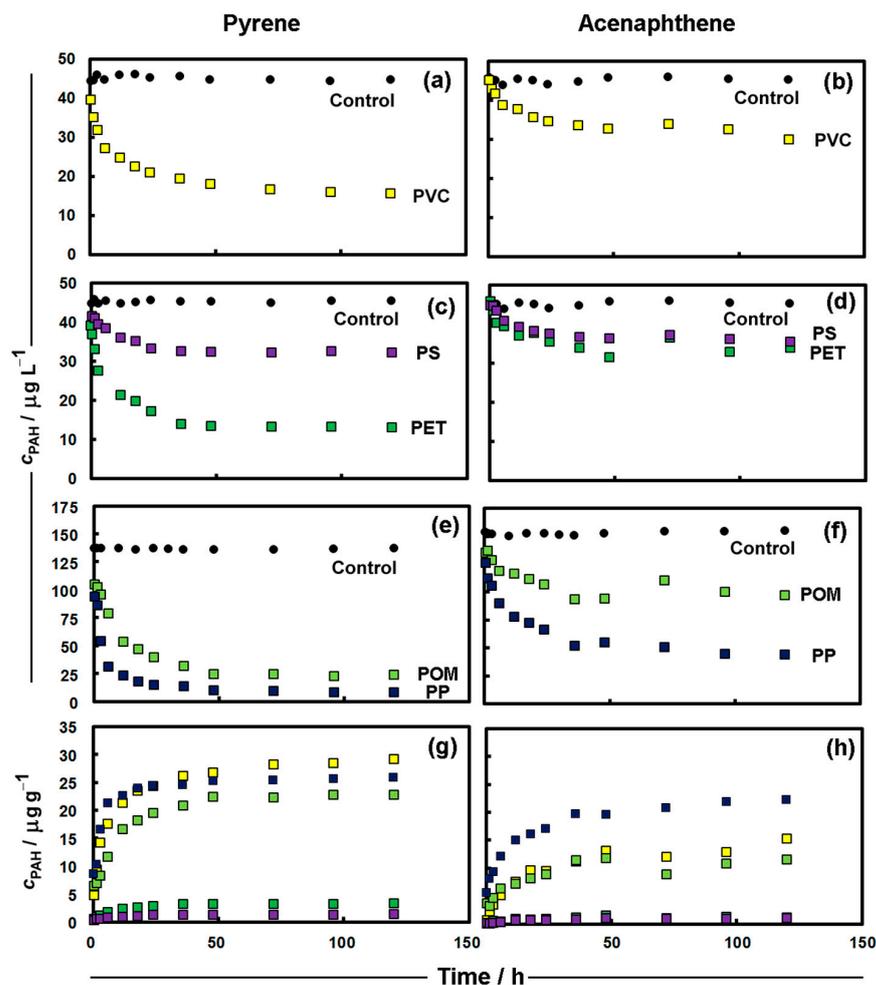


Figure 2. (a–f) Measurements of the concentration of pyrene and acenaphthene in the solutions as a function of time as it is taken up by five types of plastic pellets over a period of 120 h. (g,h) The amount of pyrene and acenaphthene present on five types of plastic pellets over a period of 120 h. Colours follow scheme of (a–f).

Table 2. Rate constants for uptake of pyrene and acenaphthene onto the plastic pellets.

Plastic	$k_{PYR}/10^{-6}\text{ s}^{-1}$	$k_{ACE}/10^{-6}\text{ s}^{-1}$
PVC	23.44 ± 0.06	21.11 ± 0.07
POM	15.06 ± 0.005	17.62 ± 0.13
PET	25.55 ± 0.014	27.20 ± 0.31
PP	45.59 ± 0.25	13.65 ± 0.01
PS	21.98 ± 0.01	26.11 ± 0.04

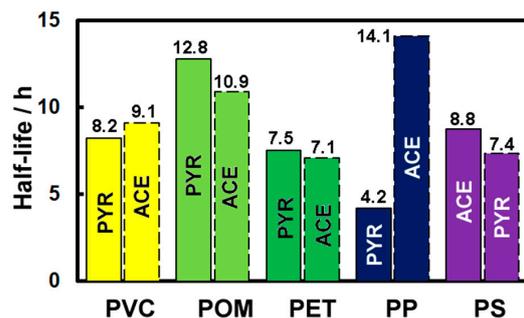


Figure 3. The half-life (hours) for the uptake of pyrene (solid outline) and acenaphthene (dashed outline) onto the plastic pellets. Note: values are listed as numbers by each bar.

3.4. Estimating K_d

The values of K_d were estimated by linear least squares fits to the data from the isotherm experiments shown in Figure 4. Non-linear fits reflecting a Freundlich isotherm were slightly better, but given the small number of points and the limited range of concentrations, it was hard to be certain that the non-linear fit was more appropriate as the linear correlation coefficients often exceeded 0.9. The calculated results would suggest that pyrene and acenaphthene partition most strongly to polyvinyl chloride (Figure 5a), but the polyvinyl chloride particles are very much smaller and, therefore, would have more adsorption sites for a given mass of pellets [43,44]. The uptake values have been adjusted by the particle area, assuming the pellets are spherical, and recalculated to represent uptake to an area of a particle 1 mm in diameter, as shown in Figure 5b, using the sizes listed in Table 1. It is clear that all the pyrene experiments show PAHs to be more strongly partitioned to the plastic pellets than acenaphthene, much in line with its higher octanol-water distribution. As there are only five plastics, the Wilcoxon signed-rank test can suggest only that $p_2 < 0.1$.

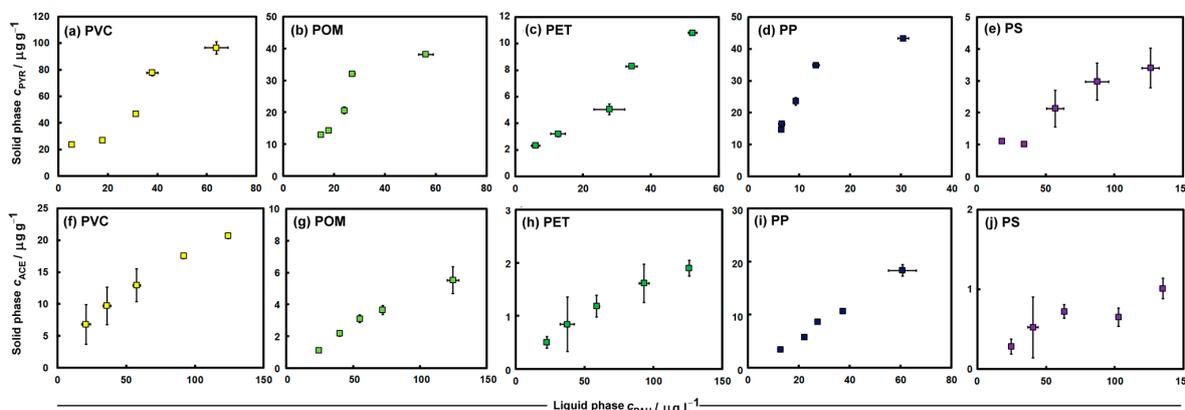


Figure 4. Concentration of pyrene (a–e) and acenaphthene (f–j) on plastic pellets and in the suspending solutions after 48 h.

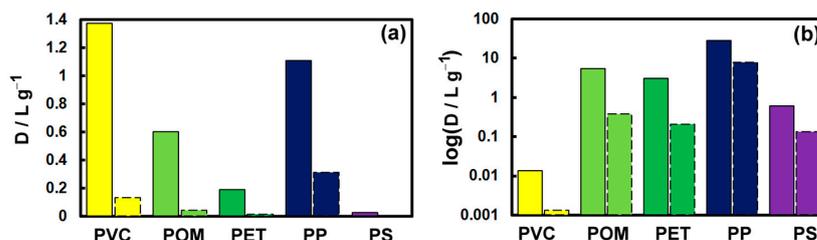


Figure 5. (a) The partition coefficient for the uptake of pyrene (solid outline) and acenaphthene (dashed outline) onto the plastic pellets. (b) The partition coefficients were adjusted to spherical particles of 1 mm diameter and plotted on a logarithmic scale.

It was also possible to estimate values of K_d for pyrene and acenaphthene from the kinetic experiments (Figure 2), along with values of K_d for pyrene and phenanthrene from the initial test experiments (Figure 1). As seen in Table 3, there is a satisfying agreement between the values of K_d determined from each of the methods.

Table 3. The experimental partition coefficients ($L g^{-1}$) of pyrene, acenaphthene, and phenanthrene in plastics assume a linear model (Equation (2)). Note: these are not corrected for particle size.

Plastic	D_{PYR}	D_{ACE}	D_{PHE}	Method
PVC	1.35 ± 0.18	0.13 ± 0.001		isotherm
	1.71 ± 0.17	0.41 ± 0.07		kinetic
	1.83 ± 0.35		1.36 ± 0.48	partition
POM	0.6 ± 0.008	0.016 ± 0.0001		isotherm
	0.96 ± 0.03	0.11 ± 0.02		kinetic
	0.55 ± 0.12		0.53 ± 0.08	partition
PET	0.19 ± 0.0002	0.013 ± 0.0001		isotherm
	0.24 ± 0.006	0.036 ± 0.008		kinetic
	0.18 ± 0.07		0.14 ± 0.05	partition
PP	1.11 ± 0.02	0.31 ± 0.0003		isotherm
	3.00 ± 0.30	0.44 ± 0.07		kinetic
	1.02 ± 0.27		1.33 ± 0.5	partition
PS	0.025 ± 0.0001	0.005 ± 0.0001		isotherm
	0.04 ± 0.01	0.04 ± 0.01		kinetic
	0.04 ± 0.01		0.04 ± 0.01	partition

4. Discussion

In laboratory experiments, the rate of uptake of PAH onto particles is typically in agreement with the measurements here, suggesting half-lives of a few hours, which tend to be in agreement with measurements of the rate of pyrene uptake onto polyethylene, polystyrene and PVC [43], where the rate constants are in the range $25\text{--}28 \times 10^{-6} s^{-1}$, while the measurements made in the current study were, excluding polypropylene, $15\text{--}26 \times 10^{-6} s^{-1}$. The rate of pyrene uptake to styrene was measured as $63 \times 10^{-6} s^{-1}$ [44], again in reasonable agreement with the measurements made here. Our rate constants for acenaphthene $17\text{--}27 \times 10^{-6} s^{-1}$ are not too different to those for pyrene. Such agreement between different measurements, while satisfying, reflects the immediate uptake of PAHs onto plastic pellets, although it may not reflect longer-term processes in the environment. Year-long observations of exposure of particles in the marine environment would suggest that concentrations of PAH on the microplastic pellets can increase slowly over many months [30,31]. This hints at a difference between rather rapid uptake in laboratory exposures and those that take place more slowly in coastal waters.

Although there are many measurements of the amount of organic materials transferred into plastic [26,45] that are measured for differing ranges of organic compounds and types of plastics, they are hard to compare. The plastic may be in different forms (pellets, fibres, fragments, etc.) and in different solution conditions in terms of salinity and pH; some may be exposed under laboratory conditions, while field experiments can take place in riverine or marine environments.

These difficulties mean that our comparisons with other measurements from the literature are largely in terms of the order of the uptake of plastics. O'Connor et al. [26] suggest that, in general, the partitioning of chemicals likely follows the order $LDPE \approx HDPE \geq PP > PVC \approx PS$, where HDPE and LDPE are high- and low-density polyethylene. The order for partition in the current study for pyrene, acenaphthene and phenanthrene normalised for pellet size follows the order $PP > POM > PET > PS > PVC$. Rochman et al. [31] examined the overall uptake of PAHs onto plastics in two coastal exposures after 12 months as $HDPE > LDPE > PS > PP > PET > PVC$ in one case and in another and $PS > LDPE > HDPE > PP > PET > PVC$. Although these orders seem to give different sequences for two nearby sites, the first three plastics are not very different in terms of the concentrations found to

be present on the particles. Also, as these samples are exposed in situ to coastal waters, it is likely that the concentrations of PAH in the water are a little different at the sites. The observations of Rochman et al. [31] show a similar order PP > PET > PVC that is found in our work, but we did not find polystyrene the most effective plastic for sorbing the PAHs. Teuten et al. [46] measured the uptake of phenanthrene onto plastics and found that the value for polypropylene was greater than polyvinyl chloride, which is in agreement with our work. Unfortunately, phenanthrene uptake, when measured in freshwater during a study of Greek beaches (on Levos), showed polyoxymethylene uptake was actually greater than for polypropylene [33], in disagreement with our work.

Such disagreements seem common, and for example, the study of the antibiotic sulfamethoxazole by Guo et al. [37] on six types of microplastic showed the linear K_d to follow the order: PA > PP > PE > PS > PVC > PET (where PA is polyamide and PE polyethylene). However, the work of Li et al. [47] on the sorption of antibiotics (sulfadiazine, amoxicillin, tetracycline, ciprofloxacin and trimethoprim) onto polyethylene, polystyrene, polypropylene, polyamide and polyvinyl chloride gave ordered sequences that were highly variable. It suggests that even the order of uptake is very sensitive to the organic compounds involved.

5. Conclusions

Our understanding of the partition of organic pollutants to microplastics, though much studied, is nevertheless limited because of the wide range of plastic materials and organic pollutants. The current work revealed half-lives of ~10 h for uptake onto the plastic pellets, with little difference between the pyrene and acenaphthene, and largely independent of the type of plastic. The extent of partition onto plastic pellets was similar for pyrene and phenanthrene, though lower for acenaphthene. The fragmentation of plastics into smaller particles with a higher specific surface area, the role of ageing of the surface and the potential interaction among organic materials at the surface means that such particles are likely to sorb increasing amounts of organic material as they age. The work presented here illustrates that uptake is a relatively rapid process (10 h half-life) in transferring organic materials to particles and that hydrophobicity is a guide to the uptake of PAHs. However, there are multiple factors that affect the sorption of organic compounds by a very wide range of microplastic particles, so much remains to be explored, especially research which considers weathered or photodegraded particles or those coated with a biofilm in the environment.

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