



# Sorption of non-polar organic compounds by micro-sized plastic particles in aqueous solution<sup>☆</sup>



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## ABSTRACT

The presence of microscale polymer particles (i.e., microplastics) in the environment has become a major concern in recent years. Sorption of organic compounds by microplastics may affect the phase distribution within both sediments and aqueous phases. To investigate this process, isotherms were determined for the sorption of seven aliphatic and aromatic organic probe sorbates by four polymers with different physico-chemical properties. Sorption increased in the order polyamide < polyethylene < polyvinylchloride < polystyrene. This order does not reflect the particle sizes of the investigated microplastics within the aqueous dispersions, indicating the influence of additional factors (e.g.,  $\pi$ - $\pi$ -interactions) on the sorption of aromatic compounds by polystyrene. Linear isotherms by polyethylene suggested that sorbate uptake was due to absorption into the bulk polymer. In contrast, non-linear isotherms for sorption by PS, PA, and PVC suggest a predominance of adsorption onto the polymer surface, which is supported by the best fit of these isotherms using the Polanyi-Manes model. A strong relationship between the sorption coefficients of the microplastics and the hydrophobicity of the sorbates suggests that hydrophobic interactions are of major importance.

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## 1. Introduction

Over recent years the spread of plastic debris has become an issue of increasing concern for both scientists and regulators (Cole et al., 2011). Meanwhile, the production of plastics continues to increase and reached 311 Mt in 2014 (PlasticsEurope, 2015). The input of these materials into natural environments from both single-point and diffuse sources has prompted questions regarding their impact on ecosystems. In this context it has been estimated that 10% of world-wide plastic waste will end-up in the world's oceans (Thompson, 2006) and terrestrial sources account for an estimated 80% of the plastic litter found in marine environments (Andrady, 2011). Research into the impact of plastic debris on marine systems has consequently been increasing steadily. Primary plastic materials that have been introduced into natural environments are highly resistant to mineralization, although larger primary fragments will breakdown into smaller particles known as

microplastics (Thompson et al., 2004). The term “microplastic” was first used by Thompson et al. (2004), but there is to date no consistent (official) definition of the characteristics of microplastics and the variety of plastic debris referred to as microplastics has now broadened to include particles ranging in size between 5 mm and 1  $\mu$ m.

There have been a number of investigations into the occurrence of microplastics in marine systems, with the smallest particle size reported from the world's oceans to date being 1.6  $\mu$ m (Galgani et al., 2010). Research into the distribution of microplastics within natural environments has clearly focused on marine systems and there is little information available on the presence of these materials within terrestrial aquatic systems. There have, however, been a growing number of reports of plastic debris in non-marine (e.g., estuarine (Sadri and Thompson, 2014) and riverine (Lechner et al., 2014)) water samples, and also in sediments (e.g., from Lake Garda in Italy (Imhof et al., 2013)), indicating a quantitatively similar degree of contamination within these systems. The load of plastic debris transported by the Danube River into the Black Sea has recently been estimated to be 4.2 t per day (Lechner et al., 2014).

The input of plastic debris into environmental ecosystems represents a potential hazard due to either entanglement with, or

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ingestion by living organisms (Wright et al., 2013). There is also a growing concern about an “indirect” effect from plastic particles acting as carriers of contaminants (Rochman et al., 2013; Rillig, 2012). Sorption of organic compounds by microplastics is one of the major processes involved; it can affect the distribution of organic compounds, both in sediments and in aqueous phases. Strong sorption of organic compounds by microplastics, even at relatively low sorbent concentrations could, for example, result in a reduction in the available (free) aqueous concentration of these compounds within sediments.

Investigations carried out to date into the sorption by microplastics have been limited to relatively high and to restricted ranges of sorbate concentrations (Guo et al., 2012; Ahn et al., 2005). Furthermore, the range of probe sorbates investigated has been limited to those compounds that have been detected in microplastics, such as polycyclic aromatic hydrocarbons (PAHs) (Guo et al., 2012; Ahn et al., 2005; Teuten et al., 2007) and polychlorinated biphenyls (PCBs) (Pascall et al., 2005; Mato et al., 2001). Both compound-specific factors and polymer properties need to be taken into account in order to achieve a comprehensive understanding of the interactions involved. In this regard, Bakir et al. investigated the sorption of various organic pollutants (i.e., phenanthrene, DDT, PFOA, and DEHP) by polyethylene and polyvinylchloride (Bakir et al., 2014). Both microplastics showed little affinity for PFOA, whereas DEHP interacted strongly with polyethylene, but only weakly with polyvinylchloride.

A detailed knowledge of the sorption properties of microplastics is, among other factors, of crucial importance to our understanding of the possible impacts of microplastics in natural environments. The aim of this study was therefore to achieve a better understanding of the interactions between microplastics and organic compounds. Sorption experiments were conducted using probe sorbates and microplastic sorbent materials that had been carefully selected on the basis of their physico-chemical properties.

## 2. Materials and methods

### 2.1. Materials

Medium-density polyethylene (PE), polystyrene (PS), polyvinylchloride (PVC), and polyamide (PA) were purchased as powders from Goodfellow Cambridge Ltd. (Huntingdon, UK). These model polymers were chosen as they represent the globally reported microplastics (Thompson et al., 2004; Klein et al., 2015) and they were applied previously (Bakir et al., 2012). The polymers were sieved to <250  $\mu\text{m}$  and used without any further treatment. Selected properties of the microplastics are listed in Table 1.

n-Hexane, cyclohexane, benzene, toluene, chlorobenzene, ethylbenzoate, and naphthalene were chosen as molecular probe sorbates (physico-chemical properties of the sorbates are listed in Table S2). All sorbate compounds were purchased from Sigma-Aldrich, with >99% purity. Stock solutions of the sorbates were freshly prepared in methanol (residual analysis grade; Acros

Organic, Geel Belgium) and kept in the dark at 4 °C for no longer than two weeks.

### 2.2. Sorption batch experiments

Weighed portions of microplastics (between 20 and 60 mg) were placed into 20 mL amber headspace screw vials and 10 mL of background solution (containing 10 mM  $\text{CaCl}_2$  and 3.08 mM  $\text{NaN}_3$ ) added into the vials (MacKenzie et al., 2002; Kah et al., 2011; Hüffer et al., 2014; Xing and Pignatello, 1997), which were then closed using screw caps with butyl/PTFE-lined septa. The samples were spiked with methanolic sorbate working solutions in single-sorbate concentrations that ranged over 3 or 4 orders of magnitude. The methanol content in water did not exceed 0.25% (v/v) in order to minimize co-solvent effects. Duplicates of all samples were analyzed to ensure that results were reproducible. All samples were shaken at 10 rpm on an overhead shaker (Heidolph, Reax 20/4, Schwabach, Germany) at 25 °C until equilibrium was reached (17 days for PS and 5 days for PE, PA, and PVC). Equilibration was pre-determined using naphthalene as probe sorbate (Fig. S1 in the Supplement Material). For the quantification, vials were placed in the tray of the autosampler at least two hours prior to analysis in order to allow equilibrium to be reached between liquid and gaseous phases (Endo et al., 2008a). Sorbate concentrations in the gaseous phase were then determined either by direct injection of 500  $\mu\text{L}$  of the vial headspace into a GC-MS system using the autosampler, or by in-tube microextraction (ITEX2). Details of the ITEX2 method have been published elsewhere (Hüffer et al., 2013a, 2014). Quantification was achieved using external calibration. Twelve calibration standards were prepared in 10 mL of background solution one day prior to analysis by GC-MS (Agilent 7890A gas chromatograph coupled 5975C mass spectrometer). An HP-5 ms column (30 m  $\times$  250  $\mu\text{m}$   $\times$  0.25  $\mu\text{m}$ ; J & W Scientific) was used and isothermal oven temperatures of between 70 and 150 °C, depending on the analyte retention. Loss of analytes during the experimental procedure was monitored by preparing spiked samples with no sorbent and incorporating them in the mass balance in order to calculate the concentrations sorbed by microplastics. Air-water partitioning constants were used (Table 2) to calculate the according phase distribution of the probe sorbates.

### 2.3. Sorbent characterization

The particle size distributions of the sorbent dispersions were determined using a particle size and shape analyzer based on laser light shading (time of transition principle, TOT) and simultaneous microscopy (EyeTech, Ankersmid Lab, Nijverdal, The Netherlands). The TOT method uses the laser obscuration time on the detector and a pulse-length analysis to determine particle size and diameter distributions (with a 95% number and volume based confidence level). For TOT analyses, 2 mL of the sorbent dispersions were

**Table 1**

Density, glass transition temperature ( $T_g$ ), surface area ( $A_{\text{surf}}$ ), and number-based diameter of sorbent particles in aqueous dispersion ( $D[4,3]$ ) for selected polymers.

Polymer	Density <sup>a</sup> [g/cm <sup>3</sup> ]	$T_g$ <sup>a</sup> [°C]	$A_{\text{surf}}$ [m <sup>2</sup> g <sup>-1</sup> ]	$D[4,3]$ [ $\mu\text{m}$ ]
PE	0.93	-120	0.308	152.53 $\pm$ 57.92
PS	1.05	100	0.338	168.55 $\pm$ 57.50
PA	1.40	50	0.156	109.44 $\pm$ 44.53
PVC	1.13	85	0.317	57.64 $\pm$ 26.50

<sup>a</sup> Provided by the supplier.

**Table 2**

Physico-chemical properties of sorbates used in this study.

Compound	MW	MV	Log $K_{\text{aw}}$	$S_w$	Log $K_{\text{ow}}$
n-Hexane	86.2	127.6	1.73	9.5	3.90
Cyclohexane	84.2	106.45	0.78	55	3.44
Benzene	78.1	89.4	-0.65	1790	2.18
Toluene	92.1	105.7	-0.60	526	2.72
Chlorobenzene	112.5	101.4	-0.80	498	2.84
Ethylbenzoate	150.17	143.8	-2.38	720	2.64
Naphthalene	128.2	123.5	-1.74	32	3.36

$K_{\text{aw}}$ : air-water partitioning constant [-] from (Schwarzenbach et al., 2003) unless otherwise noted;  $S_w$ : aqueous solubility [mg/L] at 25 °C from Corporation; log  $K_{\text{ow}}$ : octanol-water partitioning constant [-] from Corporation.

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