



# The effect of polymer aging on the uptake of fuel aromatics and ethers by microplastics<sup>☆</sup>

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## ABSTRACT

Microplastics are increasingly entering marine, limnic and terrestrial ecosystems worldwide, where they sorb hydrophobic organic contaminants. Here, the sorption behavior of the fuel-related water contaminants benzene, toluene, ethyl benzene and xylene (BTEX) and four tertiary butyl ethers to virgin and via UV radiation aged polypropylene (PP) and polystyrene (PS) pellets was investigated. Changes in material properties due to aging were recorded using appropriate polymer characterization methods, such as differential scanning calorimetry, Fourier transform infrared spectroscopy, gel permeation chromatography, X-ray photoelectron spectroscopy, and microscopy.

Pellets were exposed to water containing BTEX and the ethers at  $130\text{--}190\ \mu\text{g L}^{-1}$  for up to two weeks. Aqueous sorbate concentrations were determined by headspace gas chromatography. Sorption to the polymers was correlated with the sorbate's  $K_{ow}$  and was significant for BTEX and marginal for the ethers. Due to substantially lower glass transition temperatures, PP showed higher sorption than PS. Aging had no effect on the sorption behavior of PP. PS sorbed less BTEX after aging due to an oxidized surface layer.

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## 1. Introduction

Microplastic particles (MP) or microplastics (MPs), defined as polymer particles  $< 5\text{ mm}$  in size, are found in marine and freshwater ecosystems worldwide (Andrady, 2011; Eerkes-Medrano et al., 2015). MPs can be ingested by several biotas such as various fish, mussels and invertebrates (Lusher et al., 2013; Murray and Cowie, 2011; Van Cauwenberghe et al., 2015). Furthermore, MPs are known to accumulate hydrophobic organic contaminants. The uptake of ubiquitously occurring, persistent, organic pollutants (POPs) has been observed, such as chlorinated biphenyls, organochlorine pesticides or polycyclic aromatic hydrocarbons (Antunes et al., 2013; Endo et al., 2005; Mato et al., 2001; Rochman et al., 2013c; Teuten et al., 2009). POP desorption after ingestion may pose a threat to wildlife (Rochman et al., 2013b). A correlation between plastic particle ingestion and the uptake of chemicals by seabirds and lugworms has been reported (Besseling et al., 2013; Tanaka et al., 2013). Additionally, desorption of POPs under gut conditions is likely to be higher than under seawater conditions

(Bakir et al., 2014).

In general, the sorption of POPs by MPs is determined by the properties of the basis polymer, which have often been neglected in previous studies (Andrady, 2017), and by the properties of the contaminant. Sorption to MP is positively correlated with contaminant hydrophobicity (Hüffer and Hofmann, 2016; Lee et al., 2014) as described by the octanol/water partitioning coefficient  $K_{ow}$ . Previous studies on sorption by polymers relevant as MPs sources focused on nonpolar organic compounds, with log  $K_{ow}$  ranging from 2.08 to 7.88 (O'Connor et al., 2016), and POP concentrations in marine MPs that were up to  $10^6$  times higher than in the surrounding seawater (Mato et al., 2001). Nevertheless, the importance of MPs as a vector for POP bioaccumulation was recently questioned and found to be negligible compared to food intake (Bakir et al., 2016; Koelmans et al., 2016). Furthermore, their role as transport vector for POPs in aquatic ecosystems was found to be unimportant compared to natural sediments (Wang and Wang, 2018). In general, the mass of MPs in the environment is too low to outcompete the distribution of POPs by water and natural organic matter (Lohmann, 2017).

Previous sorption studies used either virgin polymer material (Guo et al., 2012; Hüffer and Hofmann, 2016; Rochman et al., 2013a) or investigated samples of unknown age from the marine environment (Antunes et al., 2013; Endo et al., 2005; Karapanagioti and

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Klontza, 2008). Consequently, a knowledge gap exists with regard to freshwater ecosystems (Horton et al., 2017) and the impact of polymer aging status on sorption behavior (Hartmann et al., 2017). In the present paper, the meaning of sorption behavior includes the sorption capacity (amount of uptake) and as well as the sorption velocity (time depended uptake).

MPs are subject to chemical, physical, mechanical or even biological processes in the environment. The exposure to solar radiation is the most significant mechanism in environment, resulting in fast aging of polymers. Solar UV radiation initiates autocatalytic oxidation, especially at the exposed surface of the particles (Andrady, 2017). Dependent on the polymer type, this oxidation process results in the formation of functional groups, such as ketones, esters, carboxylates or hydroxyl groups. This yields more hydrophilic properties and might reduce the sorption of hydrophobic organic compounds (Mato et al., 2001). Furthermore, under oxidative conditions, polyolefines undergo chain scissions that lead to reduced molecular weight (Celina, 2013). This process can change the relative content of the crystalline phase (as long as the polymer is semi-crystalline), and liberates more flexible chain segments (Fayolle et al., 2008). This in turn might change the sorption at the polymer particle, because predominantly the amorphous fraction of a semi-crystalline polymer is able to dissolve POPs (Andrady, 2017). These effects of aging on sorption behavior have received minor attention in previous studies (Jahnke et al., 2017; O'Connor et al., 2016).

The present study aimed at a better understanding of the sorption behavior of different pollutants to two different polymer types, polypropylene (PP) and polystyrene (PS) as virgin and aged pellets. Pellets are typical primary MP found in the environment. Furthermore, the use of pellets ensures a high reproducibility of the experiment due to their uniform shape. Special attention is given to the characterization of relevant polymer properties. Surface oxidation was recorded with Fourier-Transform Infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). While XPS was used to determine elemental concentrations of oxygen, carbon and nitrogen on the pellet surface, the chemical bond structure, namely the formation of carbonyl groups, was measured via FTIR, which is commonly used as an indicator for the grade of aging. Changes in phase morphology were determined by differential scanning calorimetry (DSC). Molar weight distribution was characterized by gel permeation chromatography (GPC), to draw conclusions about aging-related chain degradation.

As sorbates we chose typical freshwater pollutants: the fuel-based aromatics benzene, toluene, ethyl benzene and xylene (BTEX), and four fuel ethers. BTEX is a group of priority water pollutants, that occur together at contaminated sites. Similar concentration levels ( $\sim 100 \mu\text{g L}^{-1}$ ), as used in this study, can be found in contaminated rivers (Lin et al., 2017). As BTEX are often investigated as a group in environmental analysis, they are used as group in this study as well.

The sorption behavior of benzene and toluene to virgin PE and PS has already been investigated (Hüffer and Hofmann, 2016), but studies on xylene, ethyl benzene and the tertiary butyl ethers are lacking. These sorbates are critical in the environment due to their mass production, high water solubility and low biodegradability (Schwarzenbach et al., 2017), and their high presence in surface waters and groundwater used to supply drinking water (Rosell et al., 2006; Williams and Pierce, 2009). Furthermore, their relatively small molecular size, compared to other well-established pollutants like polycyclic aromatic hydrocarbons, predestinates these molecules to diffuse even better through polymers. It should be emphasized that the present study is a lab experiment with tab water and specific pollutants in high concentrations and virgin and artificially aged pellets. The main objective was the connection

between ageing related polymer properties, and the observed sorption to gain a better understanding of the underlying sorption mechanisms, which are contradictorily discussed in the literature.

## 2. Experimental

### 2.1. Materials and chemicals

The PS pellets were of cylindrical shape, 3.5 mm in length and 2.2 mm wide, and weighed an average of 18.3 mg. PP pellets were of spherical shape and 3–5 mm in size with an average weight of 22.3 mg. Both polymers were provided by partners of *PlasticEurope Deutschland* and Partners and contained no UV stabilizers. The chosen materials own low loadings of additives, as it is expected for materials in packings, which represent a relevant class of plastic products or fragments, found in the environment.

Methyl *tert*-butyl ether (MTBE), *tert*-amyl ethyl ether (TAME), benzene, toluene, ethyl benzene, *o*-xylene and *p*-xylene, were >99% pure and were purchased from Merck-Schuchardt (Hohenbrunn, Germany). Ethyl *tert*-butyl ether (ETBE, >99%) was from Sigma-Aldrich (Taufkirchen, Germany) and *tert*-amyl ethyl ether (TAE >98%) was from abcr GmbH (Karlsruhe, Germany).

### 2.2. Aging and characterization of polymers

Pellets were weathered in a Global UV 200 aging test chamber (Weiss Umwelttechnik GmbH, Reiskirchen, Germany) by exposure to UV radiation in a mono granular layer at 60 °C for four weeks. UVA-340 nm fluorescent lamps were installed with orthogonal deflection mirrors, and the UV irradiance applied to the pellets was  $26 \text{ W m}^{-2}$ . The irradiation corresponds to a natural solar radiation of 16 weeks, the increased temperature accelerated the degradation effects. PP and PS pellets were analyzed before and after batch experiments in virgin and weathered conditions, respectively.

A VHX-1000 digital microscope (Keyence Deutschland GmbH, Berlin, Germany) was used to visualize pellet surfaces. Surface photooxidation was measured with a Perkin Elmer 2000 FT-IR system equipped with a diamond crystal, using attenuated total reflection (ATR). The measurement range was  $4000\text{--}400 \text{ cm}^{-1}$  with a resolution of  $1 \text{ cm}^{-1}$  and a penetration depth of about  $1 \mu\text{m}$  depending on the spectral range. Ten individual pellets were analyzed, resulting in an average spectrum. Carbonyl absorbance was measured as band area between  $1700$  and  $1740 \text{ cm}^{-1}$ .

X-ray photoelectron spectroscopy (XPS) was performed on a Sage 100 XPS apparatus (Specs GmbH, Berlin, Germany) with non-monochromatic  $\text{AlK}_{\alpha}$  radiation under a pressure lower than  $3 \cdot 10^{-7}$  mbar as the X-ray source, and was used for elemental analysis of carbon, oxygen and nitrogen in the uppermost surface layer of the pellets. Spectra were recorded with 16 mA, 12.5 kV and were normalized to 285.0 eV (C-C). The scanned area was  $1 \times 3 \text{ mm}$ . An average spectrum of nine pellets was recorded. The typical measurement depth is in the range of tens of nanometers and allows the identification of all interesting elements except hydrogen (Wei, 2004).

Differential scanning calorimetry (DSC) was performed on a Perkin Elmer STA 6000 apparatus equipped with a simultaneous thermal analyzer (Rodgau-Jügesheim, Germany). Heating cycles were applied to samples of about 10 mg under nitrogen protection gas, at a heating rate of  $10 \text{ °C min}^{-1}$  up to a maximum temperature of 190 °C. The expected phase transition signal of PP between  $-20 \text{ °C}$  and  $20 \text{ °C}$  is not covered in this temperature program, because it is usually too small for detection in DSC.

Gel permeation chromatography (GPC) was performed on a SECurity GPC system, equipped with three columns (PL gel,  $30 \times 0.8 \text{ cm}$ ,  $10 \mu\text{m}$ ,  $10^5$ ; PSS SDV gel,  $30 \times 0.8 \text{ cm}$ ,  $5 \mu\text{m}$ , 1000 Å; PL

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