



Sorption of organic compounds by aged polystyrene microplastic particles[☆]

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ABSTRACT

Microplastics that are released into the environment undergo aging and interact with other substances such as organic contaminants. Understanding the sorption interactions between aged microplastics and organic contaminants is therefore essential for evaluating the impact of microplastics on the environment. There is little information available on how the aging of microplastics affects their sorption behavior and other properties. We have therefore investigated the effects of an accelerated UV-aging procedure on polystyrene microplastics, which are used in products such as skin cleaners and foams. Physical and chemical particle characterizations showed that aging led to significant surface oxidation and minor localized microcrack formation. Sorption coefficients of organic compounds by polystyrene microplastics following aging were up to one order of magnitude lower than for pristine particles. Sorption isotherms were experimentally determined using a diverse set of probe sorbates covering a variety of substance classes allowing an in-depth evaluation of the poly-parameter linear free-energy relationship (pPLFER) modelling used to investigate the contribution of individual molecular interactions to overall sorption. The pPLFER modelling was validated using internal cross-validation, which confirmed its robustness. This approach therefore yields improved estimates of the interactions between aged polystyrene microplastics and organic contaminants.

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1. Introduction

The distribution of plastic materials in the environment is becoming of increasing concern over recent years for scientists, the public regulators (Cole et al., 2011), and has led to a marked increase in both public and political awareness. In the “Leaders’ Declaration” from the 2015 G7 Summit in Germany it is stated that marine litter poses a global risk, and in particular plastics are a threat to marine life, ecosystems, and further to human health (G7 Presidency, 2015 Final, 2015). After plastic materials are released into the environment they are highly persistent, although large primary debris breaks down into smaller fragments called microplastics (Thompson et al., 2004). Despite the rapidly increasing research into the impact of microplastics on a variety of ecosystems, the understanding of microplastic aging mechanistics within the environment remains limited.

Microplastic particles are susceptible to different aging

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processes once they enter the environment, while abiotic mechanisms seem to be of major importance for PS due to its durability toward biodegradation (Lambert and Wagner, 2016; Weinstein et al., 2016). The abiotic degradability of polymers has been investigated under a range of different environments (under different temperatures, and in air or in water) and different atmospheric conditions (O₂, N₂, and air) (Lambert and Wagner, 2016; Weinstein et al., 2016; Andrady and Pegram, 1993; Andrady, 1990). The molecular weight of polymers has been found to decrease during the aging process and oxygen-containing functional groups are incorporated into the polymers. In addition to possible photo-induced surface oxidation of the polymers, the morphology of the parent particles also changes with aging; macroscopic networks of microcracks have been observed to form following UV irradiation due to chain scission of the polymer, increasing with the duration of the radiation (Pandey and Singh, 2001). Crosslinking from macro-radical recombination under irradiation in the presence of oxygen has also been observed, as well as important changes in surface mechanical properties (especially hardness) (Larche et al., 2012). Further evidence of the crosslinking process was the loss of the viscous composite components or

plastic deformation and the transition to an almost completely elastic response. Chemical reactions, such as oxidation initiate polymer breakdown and result in embrittlement of the plastic, which makes it susceptible to fragmentation at a low energy level. The combination of UV-induced photo-oxidation, high temperatures and humidity, conditions typically encountered at beaches, has been shown to change microplastics surface properties (Mato et al., 2001; Endo et al., 2005; Karapanagioti and Klontza, 2008).

Microplastics have previously been assumed to provide a vector for the relocation of hydrophobic organic compounds (HOCs) within natural environments through the sorption of these contaminants to the microplastics and, probably even more important, to release additives. Although the impact of microplastics on the global persistent organic pollutant distribution seems to be of minor importance (Koelmans et al., 2016), they become important sorbents at hotspots close to the pollutants' point of discharge. Understanding the interactions between organic compounds and microplastics remains an important aspect of the evaluation of the impact of microplastics on the environment. Despite the number of microplastic sorption studies that have been published, the information available on the effect of microplastic aging on their particle properties, and ultimately their sorption behavior is limited (Karapanagioti and Klontza, 2008; Hüffer et al., 2017a; Fotopoulou and Karapanagioti, 2012; Endo, Koelmans).

While the interpretation of molecular interactions and their prediction are key to understand environmental phase transfer processes, distribution coefficients cannot be determined for all compounds of interest because of the large number of compounds and phases involved. Correlations between compound distribution within natural phases (i.e. free-energy of transfer, Δ_{12G_i} , between water and solid phases) and their specific physico-chemical properties (i.e. one parameter linear free-energy relationships: opLFERs) are therefore commonly used to predict sorption in environmental systems. The disadvantage of using the correlation between phase transfers and hydrophobic parameters (such as the octanol-water partitioning constant, K_{ow} , or the aqueous solubility, S_w) is that the prediction of sorption is limited to the specific compound class and phases that the fitting parameters were determined for (Goss and Schwarzenbach, 2001).

Abraham's linear solvation-energy relationships (LSERs) offer a promising approach for overcoming these limitations as they break down Δ_{12G_i} of organic compounds between two phases, into all relevant interaction-representing terms within a single equation (Abraham, 1993; Abraham et al., 2004). For sorption of non-ionic organic compounds the relevant interactions are non-specific van-der-Waals and specific electron-donor-acceptor (EDA) interactions (such as hydrogen bonding). Each LSER term reflects the contribution made by the individual interactions to the sorbate properties (solute descriptors) and to the properties of the sorbent (phase descriptors) (Abraham et al., 2004, 1994a, 1994b). The solute descriptors can be obtained from literature for many thousands of organic compounds. Most previous investigations have fitted two types of poly-parameter linear free-energy relationship (ppLFER) to the experimental sorption data, as follows:

$$\log K_{i,12} = eE + sS + aA + bB + vV + c \quad (1)$$

$$\log K_{i,12} = eE + sS + aA + bB + lL + c \quad (2)$$

where $\log K_{i,12}$ represent the logarithmic distribution coefficient of a sorbate (i) between phases 1 and 2, E , S , A , B , V , and L represent excess molar refraction, dipolarity/polarizability, solute hydrogen (H)-bond acidity, solute H-bond basicity, molar volume, and the logarithmic hexadecane-air partitioning constant, respectively.

Another combination of descriptors has also been proposed as a ppLFER equation (Goss, 2005):

$$\log K_{i,12} = sS + aA + bB + vV + lL + c \quad (3)$$

The phase descriptors e , s , a , b , v , l in equations (1)–(3) are obtained as regression coefficients from linear multiple regression analysis (MRA), using experimentally determined distribution coefficients. To date, ppLFERs models have been successfully used to provide both qualitative and quantitative descriptions of the sorption of organic compounds by activated carbon (Shih and Gschwend, 2009), solid-phase microextraction (SPME) fibers (Endo et al., 2011), carbon nanotubes (Hüffer et al., 2014) and many more.

The objective of our research was to investigate the sorption properties of aged polystyrene microplastic (PSMP) particles by characterizing their physical and chemical properties and determining experimental sorption data using a probe sorbate set of a variety of substance classes. A ppLFER model was derived from sorption isotherms data of aged PSMP particles, to investigate the individual molecular interactions and their contribution to overall sorption.

2. Materials and methods

Materials. Non-porous PSMP powder was purchased from Goodfellow Cambridge Ltd. (Huntingdon, UK.) and sieved to a size fraction between 125 and 250 μm prior to aging. The twenty-one probe sorbates selected covered substance classes including apolar aliphatics, monopolar aliphatics, bipolar aliphatics, non-polar aromatics, monopolar aromatics, and bipolar aromatics. Selected physico-chemical properties and ppLFER descriptors for the sorbates used can be found (Table 1 in ref (Hüffer, Weniger, Hofmann)). Sorbate stock solutions dissolving the pure compound in methanol were prepared weekly and stored in the dark at 4 °C.

Aging and characterization of PSMP particles. PSMP particles were artificially aged in a custom-made aging chamber. The particles were weighed into quartz glass petri dishes and 50 mL of H_2O_2 (10 vol-%) added to each of the dishes, which were then covered with quartz glass lids. H_2O_2 was added for hydroxyl radical formation to enhance surface oxidation of the sorbent. The samples were then exposed to UV light (4*15W UVC-bulbs, max. wavelength at 254 nm) for 96 h. The aged samples were then washed with deionized water, dried, and characterized prior to their use in sorption batch experiments. This approach of particle aging was chosen to mimic the effect of surface functionalization of PSMP on sorption and obtain PSMP commonly encountered in environmental samples. Polymer degradation by surface oxidation is an important aspect but particles can also undergo other degradation pathways like fouling or mechanical abrasion leading to a large variety of degree of microplastic aging and surface properties (Endo et al., 2005; Rochman et al., 2013; Turner and Holmes, 2011). The latter processes however were beyond the scope of this study. Further, biotic degradation of PS is considered less important contrary to abiotic mechanisms due to durability of PS toward biodegradation (Gewert et al., 2015). The surface functionalization of the aged PSMP was determined using attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR), using a Tensor 27 FTIR spectrometer (Bruker, Germany). From FTIR spectra, the carbonyl index was calculated as a measure of the photo-oxidation of PSMS from the absorbance ratio between the reference bands maximum carbonyl band and the symmetric CH_2 stretching band at 2851 cm^{-1} (Myllari et al., 2015). For scanning electron microscopy (SEM), PSMPs were placed on a sticky sample holder and coated with a layer of gold using a sputter coater (Bio-Rad, USA). The

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