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Different partition of polycyclic aromatic hydrocarbon on environmental particulates in freshwater: Microplastics in comparison to natural sediment

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ABSTRACT

Microplastics pollution in the aquatic ecosystems has aroused increasing concerns in recent years. Though microplastics are known to sorb organic contaminants from water, the interaction mechanisms between microplastics and organic chemicals are not yet well understood. Here we investigated the partition characteristics of phenanthrene (Phe) in three mass-produced plastic particles, including polyethylene (PE), polystyrene (PS) and polyvinylchloride (PVC) , and one natural sediment, as a comparison. The sorption kinetics of Phe onto microplastics and natural sediment were successfully described by the pseudo-second-order model ($R^2 > 0.992$), while the equilibrium data were best-fitted to the Langmuir isotherm ($R^2 > 0.995$). Compared with natural sediment, microplastics exhibited higher capacities for Phe which followed an order of PE > PS > PVC. As the aqueous concentration of pyrene (Pyr) increased, both uptakes and distribution coefficients (K_d) of Phe within the solids decreased, with natural sediment giving the largest decline. Although proportions of Phe desorbed from the contaminated microplastics were low, due to the high Phe uptake, microplastics released larger amounts of the sorbed Phe to water than the natural sediment during the desorption process. Given their minimal abundance relative to natural sediment, microplastics may play a less important role in the transport of organic pollutants in a natural aquatic environment.

1. Introduction

Plastics are made from a variety of organic polymers, including polypropylene (PP), polyethylene (PE), polyvinylchloride (PVC), polystyrene (PS), polyester (PET), and so on. Global production of plastics has been continually increasing since 1950s, with 311 million tons generated in 2014 and an estimation of 33 billion tons for 2050 (PlasticsEurope, 2015). Plastics are cheap, lightweight, durable, strong, water and corrosion-resistant, which contribute to their extensive commercial, industrial, and municipal applications (Andrady, 2011). These characteristics also make the degradation process of plastics extremely slow (Barnes et al., 2009). Increasing plastic production and irresponsible waste handling have resulted in a rapid accumulation of plastic waste in both terrestrial and aquatic ecosystems (Barnes et al., 2009; Jambeck et al., 2015). Plastics contamination is emerging as a growing environmental concern (Gregory, 2009; Lönnstedt and Eklöv, 2016).

Microplastics, defined as small plastic particles with a size of < 5 mm (Arthur et al., 2009), can originate from breakdown of larger plastic debris, or may be manufactured plastics with a microscopic size, such as industrial pellets and scrubbers in personal care products (Cole et al., 2011). The small-sized plastic particulates spread globally and become a ubiquitous aquatic contaminant present in oceans, coastlines, freshwater lakes, and rivers all over the world (Barnes et al., 2009; Eerkes-Medrano et al., 2015; Ivar do Sul and Costa, 2014). Due to the large surface area and high fugacity capacity, microplastics can uptake a considerable amount of persistent pollutants, such as heavy metals and especially hydrophobic organic chemicals (HOCs) from ambient water (Holmes et al., 2012; Rios et al., 2007; Wagner et al., 2014), serving as potential sinks and carriers for these pollutants in aquatic ecosystems (Holmes et al., 2012; Rochman et al., 2013; Teuten et al., 2007).

Polycyclic aromatic hydrocarbons (PAHs), such as phenanthrene, are a class of HOCs, characterized by their long environmental persistence and movement (Jaffé, 1991). The wide distribution of PAHs is well-known and has caused growing public concerns on account of their potency as mutagens and carcinogens (Han and Currell, 2017). In the aquatic environment, driven by the high hydrophobicity, these compounds tend to associate with solid phases, such as deposited and suspended natural particles (Bondarenko and Gan, 2009; Pignatello and

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Xing, 1996) and microplastics (O'Connor et al., 2016; Rochman et al., 2013), which would in turn change their mobility (Koelmans et al., 2016) and toxic effect to aquatic organisms (Oliveira et al., 2013; Rochman et al., 2013). A better knowledge of interactions between PAHs and microplastics is indispensable for properly evaluating the contaminant transfer potential of microplastics and their environmental hazards to the aquatic biota.

In recent years, increasing studies have demonstrated that plastic debris recovered globally contained measurable organic pollutants (Fisner et al., 2013; Frias et al., 2010; Hirai et al., 2011; Karapanagioti et al., 2011). However, efforts paid on the partition behavior of organic compounds within plastics are limited to only a few studies (Bakir et al., 2012, 2014; Rochman et al., 2013; Teuten et al., 2007) and current understanding of interactions between organic chemicals and plastic particles is insufficient. The objective of the present study was: to investigate sorption kinetics and isotherms of phenanthrene, a widespread PAH, onto three mass-produced plastic particles (including polyethylene, polystyrene and polyvinylchloride) and the natural sediment as a comparison, since sediment is a natural sorbent for organic pollutants in water (Bondarenko and Gan, 2009; Pignatello and Xing, 1996); to examine the influence caused by addition of pyrene, another frequently encountered PAH, on the sorption properties of phenanthrene within the solid phases; and finally to determine the difference in desorption of phenanthrene from the four kinds of solid particles.

2. Materials and methods

2.1. Materials and chemicals

Phenanthrene (Phe, purity > 99%) and pyrene (Pyr, purity > 98%) were purchased from AccuStandard (USA), and m-terphenyl used as internal standard was obtained from Sigma-Aldrich (USA). Methanol and n-hexane were all of high-performance liquid chromatography (HPLC) grade and purchased from Fisher Scientific (USA). Sodium azide (NaN_3), sulfuric acid (H_2SO_4), potassium dichromate ($K_2Cr_2O_7$), calcium chloride ($CaCl_2$), potassium chloride (KCl), sodium hydrogen carbonate ($NaHCO_3$), magnesium sulfate ($MgSO_4$), sodium hydroxide (NaOH), nitric acid (HNO_3), and anhydrous sodium sulfate (Na_2SO_4) (all analytical grade) were obtained from Shanghai Sinopharm Group (China).

The Phe and Pyr standard stock solutions were prepared in methanol and kept in the dark at 4 °C. The artificial freshwater used as the background solution was prepared as deionized water with $CaCl_2·2H_2O$ (58.5 mg/L), $MgSO_4·7H_2O$ (24.7 mg/L), $NaHCO_3$ (13.0 mg/L), and KCl (1.2 mg/L) (Akkanen and Kukkonen, 2003). The initial pH of artificial freshwater was adjusted to 7 by adding either 0.1 M NaOH or 0.1 M HNO_3 solution.

Microscopic particles of high-density polyethylene (PE), polystyrene (PS), polyvinylchloride (PVC) were purchased from Shanghai Youngling Technology Ltd. (China) and sieved to a size range of 100–150 µm. The natural sediment was collected from the Yangtze River with a pre-cleaned stainless steel grab sampler and transported to the laboratory at 4 °C. The sediment was dried at 150 °C for 5 days in order to eliminate the remaining organic contaminants and other unidentified compounds which might disturb the chromatographic analysis (Cornelissen et al., 1997). After drying, the sediment was sieved into the same size range as the microplastic particles (100–150 µm). The background values of the probe chemicals (Phe and Pyr) in the treated sediment were determined using the method described by Liu et al. (2017) and found to be less than 1% of the laboratory-added concentrations.

The Brunauer, Emmett, and Teller (BET) surface areas of microplastics and natural sediment were determined by the Autosorb 1-MP Surface Area Analyzer (Quantachrome Corp., USA) Briefly, all the test solid samples were pretreated under vacuum conditions at 105 °C for 6 h for degasification. Then the monolayer N_2 sorption capacities of the

Table 1
Basic properties of the solid phases.

Solid phases	Particle size (µm)	Density (g/cm³)	BET surface area (m²/g)	TOC (%)
PE	100–150	0.96[a]	6.91	85.7[c]
PS	100–150	1.05[a]	2.35	92.3[c]
PVC	100–150	1.38[a]	1.87	38.4[c]
Sediment	100–150	na[b]	1.42	10.8 ± 1.3[d]

[a] Provided by the supplier.
[b] na, not analyzed.
[c] Calculated by the chemical formulas.
[d] Mean value ± SD (n = 12).

samples at given relative pressures of N_2 (0.05–0.35) from the N_2-He gas mixture were measured with the surface area analyzer. The vapor uptake process of N_2 occurred at liquid nitrogen temperature and 77 K. Surface areas of the test samples were determined by calculating monolayer coverage of N_2 (molecular surface area 16.2×10^{-20} m²) using the linear BET plot for the N_2 sorption isotherms.

Total organic carbon content (TOC, %) of the natural sediment was analyzed with the Vario TOC Analyzer (Elementar, Germany), while for microplastics, their TOC contents were calculated from the chemical formulas. Basic properties of the solid phases are listed in Table 1. And their surface characteristics were examined with the scanning electron microscopy (SEM) (TM3030, Hitachi, Japan) (Fig. 1).

2.2. Batch experiments

Sorption experiments were conducted in the 60-mL glass centrifuge tubes. 20 mg of solid particles (PE, PS, PVC, or natural sediment) and 50 mL of the prepared artificial freshwater were placed into the glass tube. NaN_3, used as the bio-inhibitor, was added into each tube at a concentration of 25 mg/L. A spike as methanol solution containing a predesigned quantity of Phe was injected into the water. The volume of spiking solvent (methanol) was same for all the samples and less than 0.2% (v/v) in order to minimize co-solvent effects (Cornelissen et al., 1997). The tubes were closed using screw caps with PTFE-lined septa and kept in a state of constant agitation on an orbital shaker (200 rpm) in the dark at 20 °C. Upon equilibration, samples were passed through the 0.45 µm Whatman GF/C glass fiber filters to remove solid particles, and analyzed to determine the residual concentrations of Phe in the liquid phase. All the sorption experiments were conducted in triplicate.

In the sorption kinetics experiment, 50 µL of Phe standard solution (100 mg/L of Phe in methanol) was added to each tube to achieve a concentration of 100 µg/L in water. The tubes were agitated continuously on the shaker for 120 h. At specified time intervals, samples were taken out and filtered, and the aqueous concentrations of Phe were determined. The results of kinetics experiment indicated that sorption equilibriums of Phe within the four kinds of solid phases were reached within 48 h (Fig. 2A).

The sorption isotherm experiment was carried out by varying the initial aqueous concentrations of Phe in the 60-mL glass tubes with 20 mg of solid particles. 50 µL of methanol solution containing an appropriate amount of Phe was injected to each tube. The initial concentrations of Phe in liquid phase were 10, 20, 50, 100 and 200 µg/L respectively. After the samples were equilibrated under continuous agitation for 48 h, solid phases were removed by filtration, and concentrations of Phe in the aqueous phase were measured. Solid particles from samples with the highest initial concentration of Phe (200 µg/L) were collected for the following desorption experiment.

To investigate the effect of presence of Pyr on the sorption of Phe onto the solid particles, an increasing concentration of Pyr (0–100 µg/L) was added into 50 mL of artificial freshwater with a constant initial concentration of Phe (100 µg/L). The total volume of methanol added in each sample was same (50 µL). All samples were treated under same