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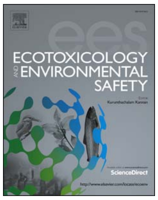

The implications of water extractable organic matter (WEOM) on the sorption of typical parent, alkyl and N/O/S-containing polycyclic aromatic hydrocarbons (PAHs) by microplastics

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ABSTRACT

Microplastics sorption of persistent organic pollutants (POPs) was the core processes that cause negative effects to biota, and their influencing factors and related mechanisms are poorly understood. In this study, we explored the impacts of water extractable organic matter (WEOM), an important source of endogenous dissolved organic matter in mangrove sediment, on the sorption coefficients of typical parent, alkyl and N/O/S-containing polycyclic aromatic hydrocarbons (PAHs) by microplastics. The presence of L-WEOM (D) impeded the PAHs sorption as the coefficients (K_f) decreased to 10.17 (μg/kg)/(μg/L)^n and to 8.39 (μg/kg)/(μg/L)^n for fluorene (Flu) and 1-methyl-fluorene (1-M-Flu), respectively. The K_f exhibited good linear relationships with the aliphaticity of L-WEOM ($p < 0.05$) rather than the aromatic carbon/alkyl carbon content ($p > 0.05$). Under the presences of L-WEOM (D), (S) and (K), the lone pair electrons of N/O/S-containing PAHs was the dominant factor contributing to the obvious difference of the K_f values from the other groups. Moreover, the largest impact of L-WEOM (D) on the Flu sorption was in the case of PVC microplastics, while almost no effect was in the case of PS microplastics. The findings of our work may be helpful in improving our understanding of the role of WEOM on the sorption of PAHs to microplastics in the field mangrove sediment.

1. Introduction

The global production of plastics has increased significantly over the past decades from 1.7 million tonnes in the 1950s to 299 million tonnes in 2013 (Weinstein et al., 2016; Erni-Cassola et al.,; Auta et al., 2017). Due to their chemical inertness, the plastics are generally resistant to complete degradation in the environment (Bouwmeester et al., 2015; Zhang et al., 2017), but most of them will experience fragmentation into small particles under the action of sunlight and tidal, namely microplastics. Microplastics are considered to be one of the persistent environmental contaminanted it is estimated that the microplastics particles cannot be degraded within a decade (Frere et al., 2017; McCormick et al., 2014). Recent studies showed that the microplastic fragments and fibres were widespread in terrestrial and oceans including the metropolis, remote/pelagic zones and reservoirs (Thompson et al., 2004). For example, the abundance of microplastics (< 5 mm), reported by Cauwenberghe et al. (2013). and Fok and Cheung (2015), can reach up to 1 items/25 cm^3 even in deep marine sediment and 5595 items/m^2 in Hong Kong at the Pearl River Estuary.

The persistent, high occurrence and wide distribution of microplastics in the environment constitutes a potential hazard for their ingestion by living organisms (Besseling et al., 2017). Using the coherent anti-stokes Raman scattering microscopy, Cole et al. (2013) observed that the zooplankton taxa (*Oxyrrhis marina*) had the capacity to ingest 1.7–30.6 μm microplastics. Moreover, the microplastics accumulated by marine planktonic can transfer from one tropic level (mesozooplankton) to a higher level (macrozooplankton) (Setälä et al., 2014).

Except for the direct route for biota exposure, some recent studies confirmed that these particles always acted as the vector of persistent organic pollutants (POPs) and threatened the biota health indirectly (Hüffer and Hofmann, 2016). Chua et al. (2014) and Batel et al. (2016) observed that the POPs adsorbed on the microplastics could transfer

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into marine Amphipod (*Allorchestes compressa*) and the microplastics associated with benzo[a]pyrene (B[a]P) desorbed from the intestine of the zebrafish (*Danio rerio*) using epi-fluorescence microscopy. More serious was that, the microplastics carried two typical kinds of POPs ((polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs)) and were detected in many kinds of marine organisms in the human food chain, such as the common goby (*Pomatoschistus microps*) and lugworms (*Arenicola marina*) (Oliveira et al., 2013; Koelmans et al., 2013).

Further studies demonstrated that the sorption of POPs to microplastics were the core processes that induced the transportation of organic contaminants and had negative effects (Bakir et al., 2014). Therefore, many studies focused on investigating the mechanisms and influences factors of PAHs sorbed onto microplastics using kinetic (Pseudo-second-order model) or isotherms models (Langmuir model, Freundlich model and so on) (Teuten et al., 2007; Wang and Wang, 2018a). Recent studies confirmed that the sorption/partition coefficients of POPs (K_d) were dependent upon not only the polymer type of the microplastics but also the lg K_{ow} values of the adsorbate (Lee et al., 2014). Aside from the above intrinsic factors, the external conditions (e.g. pH, salinity and temperature), widely existing in various environmental media, have also been confirmed to significantly influence the adsorption of different kinds of non-polar organic compounds to microplastics (Wang et al., 2015).

The dissolved organic matter (DOM) fractions were widespread in the aquatic environment and known to largely influence the transportation (including sorption) and transformations of POPs. Different from the commonly external conditions and intrinsic factors, the corresponding impacts of DOM on the sorption of POPs to microplastics may be determined by the binding affinity of POPs-DOM complexes (Akkanen et al., 2012; Chen et al., 2017). Better knowledge was indispensable for investigating the influences of DOM to microplastics sorption POPs.

Mangrove ecosystems located at intertidal estuarine wetlands may become the habitats for both the POPs (PAHs, PCBs, PFOS and so on), which are of particular concern to their carcinogenicity, mutagenicity and toxicity to biota, and the microplastics with the development of the coastal economy (62.7 ± 27.2 particles/kg (dry sediment) in the zones of Lim Chu Kang of Singapore) (Nor and Obbard, 2014), increasing the possibility of POPs sorption onto microplastics. Besides, water extractable organic matter (WEOM) is widely recognized as an important source of endogenous DOM in mangrove sediment for the flooding, a unique factor of the mangrove ecosystem, promoting the transformations of soil organic matter to WEOM (Li et al., 2016). Therefore, the investigation into the impacts of WEOM on the sorption of POPs to microplastics was critical important, but few research has focused on exploring the mechanisms at presents.

PAHs are a group of POPs that are ubiquitous in nearly all the environment media (e.g. soil/sediment, water and air). They have been of particular concern and need special attention due to their carcinogenicity, mutagenicity and toxicity to biota. In this study, the implications WEOM/L-WEOM to the sorption of PAHs by microplastics and its corresponding mechanisms were explored in combination with the chemical compositions of WEOM/L-WEOM samples (the results comes from ^{13}C NMR and ICP-MS). The high-density polyethylene (PE), polystyrene (PS) and polyvinylchloride (PVC), three commonly used plastics with different physicochemical properties, were selected as model microplastics.

2. Materials and methods

2.1. Chemicals

The PE, PS and PVC were purchased from Suzhou SmartyNano Technology Co., Ltd. (China) and used as model microplastics particles (sieved to a size ranges of 63–250 μm). The Fluorene (Flu), 1-methylfluorene (1-methyl-Flu), dibenzothiophene (DBT), carbazole (CAR) and dibenzofuran (DBF) with a purity of 99% were obtained from J&K Co., Ltd. (USA). All of the other reagents used in this study were analytical reagents (A.R.) purchased from Aladdin Co., Ltd. (China).

2.2. Sampling

Three types of field contaminated mangrove sediment were used for this research. Field mangrove sediment collected from the Daoshuiao Mangrove Swamp (21°40′ N, 108°21′ E), the Kangxiling Mangrove Swamp (21°52′ N, 108°30′ E) and the Shajing Mangrove Swamp (21°51′ N, 108°35′ E) in Guangxi, South China were labelled mangrove sediment (D), mangrove sediment (K) and mangrove sediment (S), respectively. The sediment was air-dried, ground, sieved (1.0–2.0 mm) and stored in a closed container.

2.3. Extraction of the WEOM and loosely attached water extractable organic matter (L-WEOM) samples from the mangrove sediment

The WEOM samples of mangrove sediments were obtained using the method described by Guigue et al. Guigue et al. (2014). First, 50 g mangrove sediment samples with 200 mL Milli-Q water were shaken at 120 rpm for 60 min at a temperature of 298.15 ± 3 K. Then, the extraction solutions were centrifuged for 10 min at 4600*g* and filtered through 0.45 μm pore size cellulose acetate filters. Lastly, the aqueous solutions of WEOM were dried in an oven at 333.15 ± 3 K for about 12 h.

Another 100 g of mangrove sediment samples were placed in columns with inner diameter 54 mm to extract the L-WEOM fractions of mangrove sediment. To avoid the loss of sediment particles, the sand with acid-washed sand was placed at the bottom of the column. Approximately 400 mL Milli-Q water were used to extract L-WEOM fractions of mangrove sediment with a flow rate of 1.5 mL/min. Then, similar to the procedures for WEOM, the extraction solutions were filtered through 0.45 μm pore size cellulose acetate filters and dried in the oven at 333.15 ± 3 K for 12 h.

2.4. Characteristics of the WEOM/L-WEOM samples

To obtain the bulk composition information of WEOM and L-WEOM, the technique of solid-state ^{13}C CP-MAS NMR was used. Prior to NMR analysis, the WEOM/L-WEOM samples were treated repeatedly with 10% hydrofluoric acid to concentrate the WEOM and L-WEOM and remove the iron oxide mineral. After hydrofluoric treatment, the samples were rinsed with Mill-Q water, air dried and ground to particles less than 100 μm. Solid-state ^{13}C NMR spectra were obtained using an Advance III 400 MHz spectrometer (Bruker, Germany) operating at a ^{13}C frequency of 100 MHz. Total concentrations of metal in WEOM/L-WEOM samples were determined by ICP-MS instruments (Thermo Fisher, US) using indium as an internal standard. Prior to ICP-MS analysis, to avoid interference with organic matter during analysis, samples were digested with 14 mol/L HNO_3 at 100 °C and then taken up again in 0.4 mol/L HNO_3 after complete evaporation (Grybos et al., 2007).

2.5. The implications of WEOM on the sorption of PAHs to microplastics

The sorption of PAHs on microplastics with and without the WEOM was conducted by batch experiment in 50 mL screw cap vials. Prior to the study, the vials were pre-combusted at 450 °C for 24 h, rinsed with Milli-Q water three times. A certain amount (0.5 g) of microplastics and 25 mL of background solutions (0.01 mol/L $CaCl_2$ and 0.2 mg/L NaN_3) and three different concentrations of WEOM (TOC content: 100 mg C/L) were first added into the vials, followed by the injection of seven content of PAHs ethanol stock solution. The ethanol concentrations of both groups were lower than 0.25%, a level at which the ethanol has no