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Microplastics in the surface sediments from the Beijiang River littoral zone: Composition, abundance, surface textures and interaction with heavy metals

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HIGHLIGHTS

- Occurrence and characteristics of microplastics from Beijiang river sediment were investigated.
- A combination of μ-FTIR and SEM illustrated the chemical degradation of microplastics.
- The content of metals (Ni, Cd, Pb, Cu, Zn and Ti) in microplastics is investigated by ICP-MS.
- We suggested that the majority of heavy metals carried by microplastics were derived from inherent load.

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ABSTRACT

While large quantities of studies on microplastics in the marine environment have been widely carried out, few were available in the freshwater environment. The occurrence and characteristics, including composition, abundance, surface texture and interaction with heavy metals, of microplastics in the surface sediments from Beijiang River littoral zone were investigated. The concentrations of microplastics ranged from 178 ± 69 to 544 ± 107 items/kg sediment. SEM images illustrated that pits, fractures, flakes and adhering particles were the common patterns of degradation. Chemical weathering of microplastics was also observed and confirmed by μ-FTIR. EDS spectra displayed difference in the elemental types of metals on the different surface sites of individual microplastic, indicating that some metals carried by microplastics were not inherent but were derived from the environment. The content of metals (Ni, Cd, Pb, Cu, Zn and Ti) in microplastics after ultrasonic cleaning has been analyzed by ICP-MS. Based on data from the long-term sorption of metals by microplastics and a comparison of metal burden between microplastics, macroplastics and fresh plastic products, we suggested that the majority of heavy metals carried by microplastics were derived from inherent load.

1. Introduction

Microplastics that are less than 5 mm in size (Arthur et al., 2009; Hidalgo-Ruz et al., 2012) have been almost ubiquitous in the global marine environment, including surface waters (Collignon et al., 2012; Frias et al., 2014), beaches (Browne et al., 2011; Claessens et al., 2011; Thompson et al., 2004) and deep sea (Van Cauwenberghe et al., 2013; Woodall et al., 2014). More importantly, plastic debris would continuously degrade into microplastics or nanoplastics (Andrady, 2011; da Costa et al., 2016; Ivar do Sul and Costa, 2014; Wang et al., 2016) as a result of physical, chemical and microbial effects. The majority of marine plastics are considered to originate from land-based source (Allsopp et al., 2006; Andrady, 2011; Wagner et al., 2014), including transport from rivers that may be important pathways (Cheung et al., 2016; Morritt et al., 2014; Rech et al., 2014). Furthermore, one of the few studies focusing on the floating microplastics in the estuary found that the Tamar River could not be identified as a net source or sink, with as many microplastic particles entering the estuary as leaving it (Sadri and Thompson, 2014). Nevertheless, there are very

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few studies on microplastics in freshwater environment (see reviews by Dris et al., 2015; Duis and Coors, 2016; Eerkes-Medrano et al., 2015; Wagner et al., 2014). Some studies not only reported the occurrence of microplastics in freshwater environment (Eriksen et al., 2013; Faure et al., 2012; McCormick et al., 2014; Moore et al., 2011; Morritt et al., 2014), but show that contamination level is as severe as in the marine environment. And fishes in rivers (Sanchez et al., 2014) and birds in terrestrial environment (Zhao et al., 2016) have also been shown to ingest microplastics.

The great concerns about microplastics in the environment are the association with toxic chemicals and subsequent exposure of these chemicals to the multiple kinds of organisms that ingest the debris (Bakir et al., 2014; Bejgarn et al., 2015; Browne et al., 2008, 2013; Rochman et al., 2013b; Van Cauwenberghe and Janssen, 2014). Plastic debris is capable of concentrating hydrophobic organic pollutants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and DDTs (Endo et al., 2005; Gauquie et al., 2015; Hirai et al., 2011; Rochman et al., 2013a; Van et al., 2012), increasing their concentration even up to the order of 10^6 (Mato et al., 2001). Plastic debris could also accumulate metals from the surrounding environment and the accumulation has been demonstrated by laboratory experiments (Holmes et al., 2012, 2014; Turner and Holmes, 2015) and environmental monitoring (Rochman et al., 2014). Metal pollution is common in the environment and is derived from multiple sources such as the industrial and domestic sewage discharges, mining, smelting and e-wastes (Pan and Wang, 2012; Deheyn and Latz, 2006; Wang et al., 2013). However, data on the content of metals accumulation by microplastics in the actual environment is very limited. One of the few studies on the effects of metals interaction with microplastics found a significant decrease of the predatory performance (referred to Artemia franciscana nauplii used as preys) and a significant inhibition of AChE activity under simultaneous exposure to Cr(VI) and microplastics, while fewer inhibition caused by microplastics alone and no observed inhibition caused by Cr(VI) alone (Luís et al., 2015).

Accordingly, more research efforts should be contributed to investigate the occurrence and characteristics, especially the interaction with heavy metals, of microplastics in the freshwater environment so as to further assess the potential environmental risks. Additionally, shore surface sediment samples could reflect the result of long-term interfacial interaction between waters and land surface (Yu et al., 2016), and thus provide vital information on the transportation and fate of pollutants. And similar types of plastics in the water column as in sedimentary habitats have been previously shown (Thompson et al., 2004), suggesting that density was not a dominant factor influencing distribution of microplastics and sediment samples are good representations for long-term accumulating result of microplastics. In this study, thus, microplastics were retrieved in the surface sediment samples from the Beijiang River littoral zone, and the main objective is to provide data on their characteristics including composition, abundance, surface textures acting as an indicator of degradation and interaction with heavy metals.

2. Methods and materials

2.1. Sampling sites

Sediment samples were collected from 8 sites chosen in the surface layer of Beijiang River littoral zone (shown in Fig. 1). In each site, three sediments were randomly sampled to a depth of 2 cm using a stainless-steel shovel and a 20 × 20 cm wooden frame with a 2-cm height, and then these sediments were transferred into an aluminum foil bag, in which they were mixed together as one single sample. Sample collection was conducted in March 2015. Beijiang River is one of the three main streams of the second river system Pearl River in China, with a length of 573 km and a drainage area of 52,068 km^2. All the selected 8 sampling sites are located in middle and lower reaches of Beijiang River crossing the Qingyuan city with a population of 4,020,000. By 2015, 18 wastewater treatment plants have been available in the city, with a sewage-effluent processing capacity of 425,000 tons/day and a treatment efficiency of 90% municipal sewage. In other words, the other 10% were sources of pollutants (e.g., microplastics and metals) and potentially discharged into the river. For example, illegal discharges of industrial effluent were revealed in 2013.

2.2. Flotation

All sediment samples were dried at 50 °C for at least 48 h. Triplicate 30 g dried sediments in each site were investigated. Microplastics were extracted from each sediment replicate based on a density separation method (Thompson et al., 2004). Sediments were mixed with 200 mL of saturated NaCl solution in a glass beaker for 2 min by stirring with a glass rod. After 2 h of settlement, the microplastics floating in the supernatant of the glass beaker were cleaned in an ultrasonic bath for 5 min in order to remove surface sand and loosely adhered materials (Ashton et al., 2010; Corcoran et al., 2015; Turner and Holmes, 2015; Zbyszewski et al., 2014). The mixture was left standing overnight and the resulting supernatant was filtrated through a glass microfiber filter (Whatman GF/B, diameter 47 mm, pore size 1 μm) with a vacuum pump. The wall of the filtering device was washed with deionized water multiple times and the washing solutions were also filtered. All the components on the filters were dried at 50 °C for 48 h and then stored in Petri dishes.

2.3. Microscopic imaging and μ-FTIR analysis

Microplastics on the filters were optically analyzed and imaged (30–50 magnification) using a digital handheld microscope (Dino-lite, AM3011T) that is equipped with a software program Dino-Capture 2.0. The photographs of suspected particles were directly taken on the filters. The initial visual inspection separated natural debris from material suspected to be plastic according to the most commonly used criteria of visual observation elsewhere (Hidalgo-Ruz et al., 2012; Norén, 2007).

All the suspected particles were further identified by μ-FTIR (Nicolet iN10, Thermo Fisher, USA) (Qiu et al., 2015; Vianello et al., 2013) equipped with a Deuterated Triglycine Sulfate (DTGS) detector. After being identified, macroplastics that >5 mm could be selectively separated from microplastics by fast measurement with a ruler for 5 mm is an apparent size. Samples could be non-destructively detected at room temperature without liquid nitrogen. Spectra were collected in reflectance mode and their ranges were set at 4000-400 cm^{-1} with a collection time of 16 s for each measurement. Samples were placed on copper-coated microscope slide by using long-pointed and non-magnetic tweezers. The resulting spectra need no transformation or post-processing (Frias et al., 2014; Li et al., 2016) and were directly compared with the reference library databases provided by Thermo Fisher Scientific in OMNIC software. At least two different surface sites of each sample were detected (Qiu et al., 2015) in order to obtain higher match degrees of resulting spectra and the absorption peaks of developed functional groups. For example, ester carbonyl and ketone indicating oxidative degradation could be found in the repeated analysis after the suspected particles were identified.

The abundance of microplastics in the sediments of each site was calculated with the number of identified microplastics in the