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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 (Dinolite, AM3011T) that is equipped with a software program DinoCapture 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

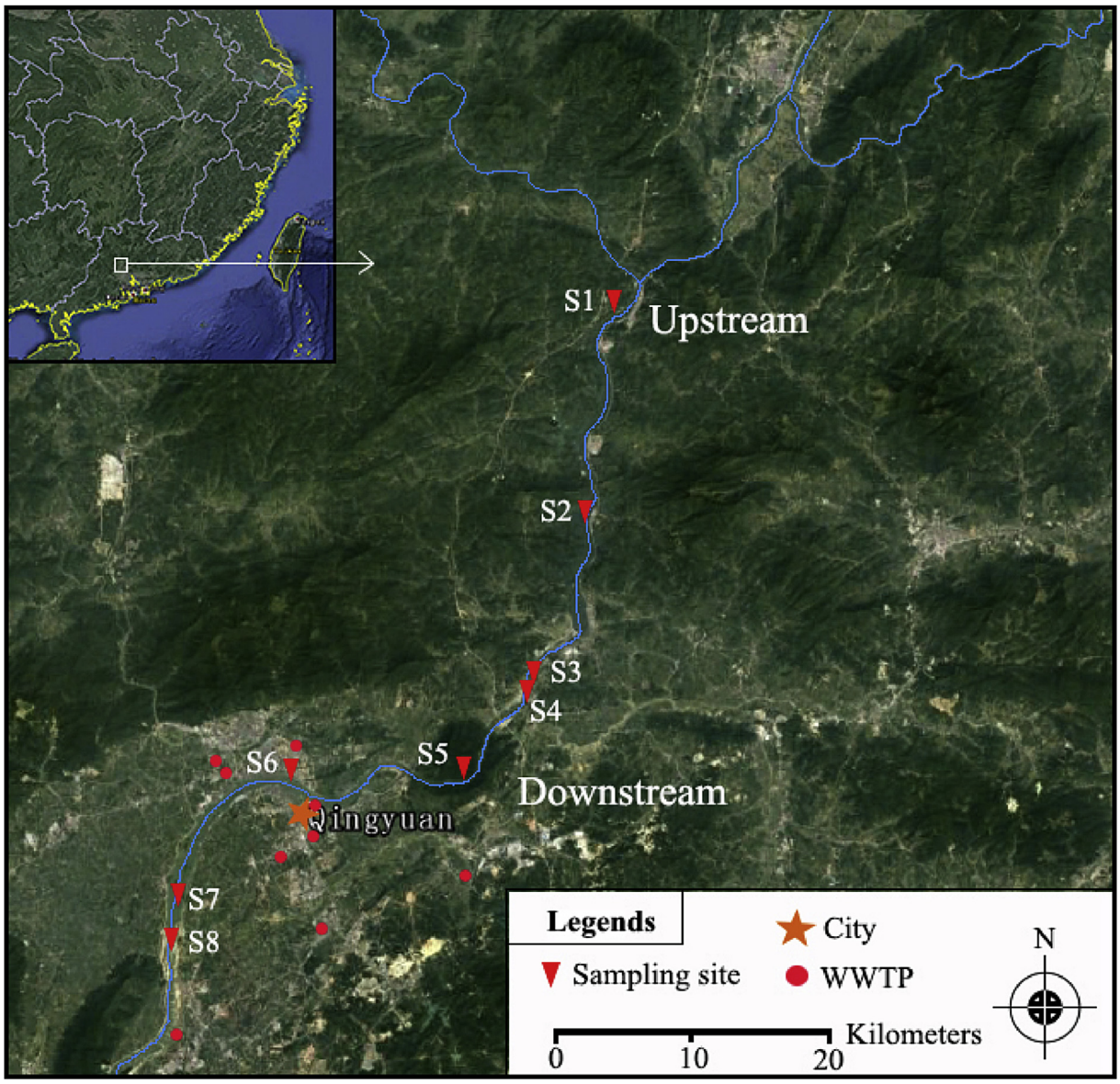

Fig. 1. Location of the studied surface sediments sites from the Beijiang River littoral zone (9 WWTPs were marked while the others were mainly located in the upstream but were not in the geographical region of this figure.).

triplicate samples and expressed in the number of items per unit mass of dry sediment (items/kg). Acquired data were expressed as Mean and standard deviation (SD) concentration.

2.4. SEM/EDS analysis

To understand the surface characteristics and the type of metals accumulation by microplastics after ultrasonic cleaning, samples were studied by scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM/EDS). After being identified as microplastics by μ-FTIR analysis, samples were coated with a thin film of platinum, and then imaged using a field emission SEM (JSM-6510, JEOL) operating at 20 keV. Qualitative elemental composition of microplastics was confirmed by EDS (X-Act, Oxford). Due to the eroded samples were heterogeneous, the visualization was repeated at different surface sites, i.e., at least three relatively smooth or rough sites.

2.5. ICP-MS analysis

Thirty to fifty items of microplastics (~40–55 mg) from each site were weighted into individual PTFE vessel and then were digested with 2 mL of hydrogen peroxide (30%, GR), 5 mL nitric acid (65–68%, GR) and 5 mL sulfuric acid (95–98%, GR) by microwave (MARSXpress, CEM, USA) decomposition (Imhof et al., 2016). After digesting, the solution in the PTFE vessel was transferred to heating block (BHW-09C) and heated at 170 °C for about 1 h, and the residue was transferred into individual 50 mL glass volumetric flask with ultrapure water (UPH-II 5/10/20 T). The wall of the PTFE decomposition vessel was washed with ultrapure water three or more times and the washing solutions were also transferred. Resulting solutions were diluted with ultrapure water for analysis and the obtained values were corrected with acid blank values, because the small size microplastics extracted from the sediment were only measured once. Based on the elemental analysis of microplastics by EDS, digests were analyzed for six metals, i.e.,

nickel (Ni), cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), and titanium (Ti) by collision-inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7700 Series, USA). ICP-MS was calibrated using mixed, acidified standards, and internal standardization was achieved by the addition of ^{45}Sc, ^{72}Ge, ^{115}In, ^{209}Bi. ICP-MS was performed with the carrier gas flow rate of 1.08 L/min, nebulizer gas flow rate of 0.15 L/min, plasma gas flow of 15.0 L/min, auxiliary gas flow rate of 1.0 L/min, cooling gas flow rate of 15 L/min, and RF power of 1550 W. Certified reference materials (i.e., GBW10044 and GBW10047) were purchased to evaluate the accuracy of the analytical determinations and the analytical precision was within 10% variability (shown in the S1 in the Supplementary data).

In order to assess the level of metal carried by microplastics, sediments in each site were also digested. Dried sediments were ground and then triplicate 200 mg were digested with 8 mL nitric acid (65–68%, GR) and 2 mL hydrofluoric acid (≥40%, GR). After digesting, the solution in the PTFE decomposition vessel transferred to heating block and then 0.5 mL perchloric acid (70–72%, GR) was added and heated at 170 °C for about 1 h. Resulting solutions were also diluted into 50 mL glass volumetric flask with ultrapure water pending analysis. Besides, the analyses of grain size and total organic carbon (TOC) of sediments were carried out. The grain size was performed by wet sieving (Koukina et al., 2016), while the TOC contents were determined according to the method HJ 615–2011 in standard methods for the examination of sediments, i.e., the potassium dichromate oxidation spectrophotometric method.

3. Results and discussion

3.1. Abundance

Microplastics were found in triplicate sediment samples from all sites, indicating that the sediments are vulnerable to microplastics pollution and could be good representations for the long-term accumulation of microplastics. Microplastics might be washed ashore from the water surface (Lumpkin et al., 2012) and derived from fragmentation of larger plastics littered on shore sediments as a result of physical, chemical and microbial effects (Cooper and Corcoran, 2010; Zbyszewski and Corcoran, 2011; Zbyszewski et al., 2014; Zettler et al., 2013). The highest and lowest concentrations of microplastics were 544 ± 107 and 178 ± 69 items/kg for site S7 (Dayankeng) and site S6 (Qingyuandaqiao), respectively (shown in Table 1). However, the concentrations of microplastics were underestimated, because microplastics with a density <1.2 g/cm^3 (Claessens et al., 2013; Yu et al., 2016) could be extracted by using the density separation method, while some types of plastics, e.g. PVC, could not be floated up. Data on the presence of microplastics in river sediments were lacking. But it seemed that the abundance of microplastics in this study is significantly smaller than those in some estuarine sites (i.e., 228–3763 and 786–1368 items kg^{-1} for the rivers Rhine and Main in Germany, respectively, Klein et al., 2015). These eight studying sites were along a 40-km stretch of river shoreline, and thus no specific pattern was observed in the abundance of microplastics in the surface sediments from the littoral zone, though the highest concentration was found in the downstream. The variability in abundance may be closely related to river shore accessibility that facilitates such activities as illegal waste dumping (Dris et al., 2015). Moreover, artificial riverbanks were non-consecutively raised between the sampling sites S2 and S7 along the river and mainly raised along certain segment, especially in urban areas, of the river. Most notably, the same types of microplastics were found in the triplicate sediment samples from all sites and a decreasing trend of PE were shown in Table 1, suggesting that microplastics in the river environment might also be transported across large distances and further washed ashore.

3.2. Composition

As shown in Fig. 2, polyethylene (PE), Polypropylene (PP), copolymer, and paint particle were identified, and the brown microplastics and the blue paint particle (Song et al., 2014) would lead to misidentification, giving an indication of the difficulties in purely visual determination. Copolymers were found in all sampling sites (shown in the S2 of the Supplementary data), and also found in the southern shore of Lake Victoria (Biginagwa et al., 2015). Though there are few reports on copolymers, their production could be increased because copolymerization processes could create new materials with novel and enhanced properties (Stephens et al., 2006). Besides, some particles in the environment were not completely identified by μ-FTIR, which was an ideal means of polymer identification for micro-particles (Song et al., 2015), and was widely used (Frias et al., 2014; Li et al., 2016; Ng and Obbard, 2006; Vianello et al., 2013; Yu et al., 2016). On the one hand, weathering of the microplastics would change the resulting spectra. On the other, the libraries include thousands of spectra as references. For example, the match result of one particle was “PE white layer (TiO_2)” with a match degree of 75.8% (shown in Fig. 3). Such particles may be TiO_2-polymer composites. Though the match degree was not high, EDS spectra demonstrated the presence of titanium (Ti) and oxygen (O). In addition, content of metals available to dilute mineral acid digestion by microwave decomposition included large amounts of Ti and its concentration was up to 38,823.7 μg/g (shown in Table 2). And TiO_2 nanoparticles are commonly applied to plastics in local productions (Wang et al., 2010; Zhang et al., 2003, 2014). TiO_2 was also detected in the marine and limnetic microplastics (Fries et al., 2013; Imhof et al., 2016; Lenz et al., 2015). When counting the abundance of microplastics, such particles, however, were classified as the plastic type “others” (shown in Table 1), because this type is open to bias.

Table 1
Type distribution and abundance of microplastics in each sampling site.

Sites	Site names	PE (%[a])	PP (%)	Copolymer (%)	Other (%)	Abundances[b] (Items/Kg)
S1	Lianjiangkou	65.5 ± 11.0	17.2 ± 2.6	6.9 ± 2.7	10.3 ± 8.1	256 ± 158
S2	Shenping	58.8 ± 8.0	29.4 ± 9.4	5.9 ± 0.7	5.9 ± 2.8	333 ± 176
S3	Jiangkou	55.6 ± 13.9	33.3 ± 6.5	5.6 ± 0.8	5.6 ± 2.1	278 ± 184
S4	Feilaixia	53.8 ± 7.1	30.8 ± 11.7	7.7 ± 0.6	7.7 ± 2.0	356 ± 96
S5	Baimiao	56.3 ± 6.0	18.8 ± 8.9	18.8 ± 4.3	6.3 ± 2.5	222 ± 135
S6	Qingyuandaqiao	41.7 ± 18.9	33.3 ± 6.6	16.7 ± 3.5	8.3 ± 3.2	178 ± 69
S7	Dayankeng	60.7 ± 5.1	17.9 ± 2.2	14.3 ± 1.6	7.1 ± 0.9	544 ± 107
S8	Shijiao	42.1 ± 2.5	21.1 ± 3.5	31.6 ± 7.9	5.3 ± 0.8	333 ± 88

[a] The percentages of each type of microplastics were calculated with the sum of all the number in the triplicate sediment samples.
[b] The abundances of microplastics were calculated with the number of microplastics in the triplicate sediment samples and expressed as Mean and standard deviation (SD) concentration.

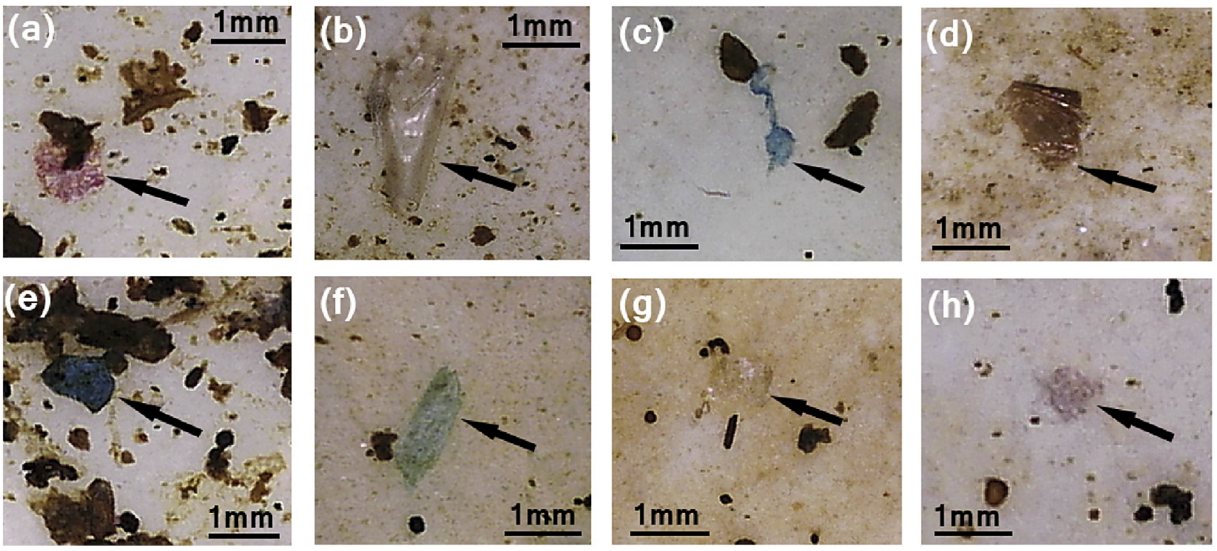

Fig. 2. Optical microscope images of selected particles on the filters. (a–b) PE; (c–d) PP; (e) paint particle; (f–h) Copolymer. (The arrows were used to point to the microplastics.)

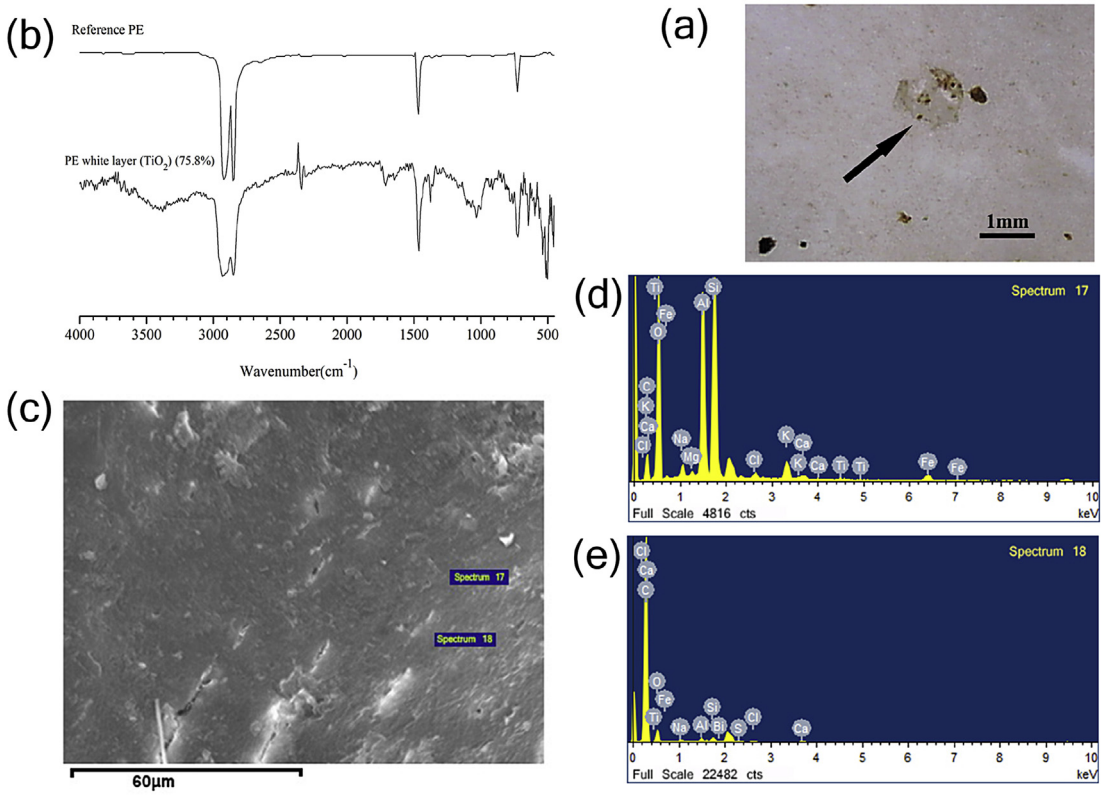

Fig. 3. (a) Optical microscope images of TiO_2-polymer composite; (b) The resulting FTIR spectra and the match degrees with the standard spectra; (c–e) EDS spectra showing the presence of titanium (Ti).

3.3. Surface textures

SEM images illustrated that all the examined microplastics in the surface sediments from Beijiang River littoral zone experienced different levels of mechanical erosion and chemical weathering. Pits, fractures, flakes and adhering particles were the common patterns of degradation (shown in Fig. 4) and were mainly attributed to mechanical abrasion such as wave action and sand grinding. And these patterns were similar to those observed in both marine beaches (Cooper and Corcoran, 2010; Corcoran et al., 2009) and lakes (Zbyszewski and Corcoran, 2011; Zbyszewski et al., 2014).

Chemical weathering of microplastics in the environment would occur and could be confirmed by FTIR spectra. As shown in Fig. 5, two FTIR spectra resulting from two different surface sites of individual microplastic were collected in order to obtain higher match degrees and the absorption peaks of developed functional groups. Firstly, microplastics were identified by the higher match degrees (88.6% for PE and 94.0% for PP) with the standard spectra.

Table 2
Mean concentrations[a] of metals in the microplastics and surface sediments from Beijiang River littoral zone.

Sites	Ni		Cd		Pb		Cu		Zn		Ti	
	Microplastics	Sediments	Microplastics	Sediments	Microplastics	Sediments	Microplastics	Sediments	Microplastics	Sediments	Microplastics	Sediments
S1	0.54	0.04 ± 0.02	2.160	0.684 ± 0.152	63.03	31.49 ± 7.01	80.9	19.6 ± 7.0	2414.8	103.8 ± 36.5	14063.1	16208.7 ± 4123.5
S2	1.43	0.03 ± 0.01	8.413	2.458 ± 0.731	131.11	40.83 ± 8.04	351.8	27.3 ± 6.4	5902.3	151.4 ± 41.4	23118.9	15232.1 ± 1456.5
S3	1.32	0.05 ± 0.03	4.828	1.674 ± 0.237	52.40	41.21 ± 14.50	137.4	36.3 ± 13.0	5331.1	176.0 ± 32.1	13617.0	28163.6 ± 6498.0
S4	1.68	0.02 ± 0.01	17.563	2.052 ± 0.348	89.83	33.63 ± 4.32	329.4	24.9 ± 7.6	11284.9	156.0 ± 44.5	20210.9	16003.8 ± 2520.2
S5	1.04	0.06 ± 0.02	6.258	0.728 ± 0.030	76.85	52.09 ± 4.83	143.5	62.4 ± 4.9	6162.3	349.2 ± 90.0	29686.6	24906.0 ± 2388.4
S6	2.39	0.04 ± 0.04	15.581	0.575 ± 0.101	93.21	54.67 ± 5.69	500.6	34.2 ± 3.7	14815.3	220.7 ± 79.0	38823.7	28575.2 ± 3153.9
S7	1.14	0.07 ± 0.03	6.346	0.838 ± 0.324	87.13	57.93 ± 12.14	393.1	79.5 ± 14.5	8971.6	239.2 ± 54.5	22229.0	21471.9 ± 4617.0
S8	1.07	0.03 ± 0.01	5.021	0.161 ± 0.019	38.24	19.91 ± 7.44	134.5	9.7 ± 2.5	11057.9	74.6 ± 16.0	20979.2	15190.0 ± 4003.3

[a] The unit of all concentrations was given in μg/g (μg element per g sample).

Then the chemical weathering of these microplastics could be confirmed by the absorption peaks at about 1715 cm^{-1} (shown in the spectra with lower match degrees, 72.8% for PE and 74.4% for PP) indicating the ketone (C═O) groups in the absence of virgin PE and PP were developed. Possible mechanism was chemical weathering because microplastics in the environment, especially in surface sediments, have high oxygen availability and direct exposure to sunlight so will be chemically weathered. And SEM images (shown in Fig. 5 (b) and (d)) illustrated that the chemical weathering were characterized by obviously rough textures on parts of the surface. In contrast, the surface of virgin plastics exhibited relatively homogeneous smooth features in Fotopoulou and Karapanagioti, (2012) and observation of five types of virgin plastics in this study (shown in the S3 and S4 in the Supplementary data, respectively).

3.4. Interaction with heavy metals

3.4.1. Accumulation of heavy metals

Except for observation on the surface textures, the surface elemental composition of microplastic could be analyzed by SEM equipped with EDS. Prior to the analysis, most of the loosely adhered materials were removed from the surface of microplastics after ultrasonic cleaning with the exception of those that are resistant to ultrasonication. However, the residues on the surface of microplastics would be extremely important for their potential exposure to the ingested organisms. EDS spectra demonstrated the presence of multiple types of metal elements (both the major and trace elements) on the surface of microplastics firstly identified by μ-FTIR analysis. Though metals are commonly added as inherent load (e.g., catalysts, pigments, and stabilizers) during plastic manufacturing (Becker et al., 2010; Fries et al., 2013; Nakashima et al., 2012; Noik et al., 2015; Takahashi et al., 2008; Wäger et al., 2011), EDS spectra displayed great difference in the elemental types of metals on the different surface sites of individual microplastic (shown in Fig. 3 (d) and (e)), indicating that some metals carried by microplastics were not inherent but were derived from the environment. And metals accumulation by microplastics was not just attributed to the adherence or entrapment of the extraneous materials that were resistant to ultrasonication. A common understanding is that plastics are relatively inert towards aqueous metals. However, loss of metal to plastic containers from solution samples has been previously reported during incubation (Cobelo-Garcia et al., 2007; Fischer et al., 2007; Giusti et al., 1994; Li et al., 2001). Moreover, laboratory experiments (Ashton et al., 2010; Holmes et al., 2012, 2014; Turner and Holmes, 2015) and environmental monitoring (Rochman et al., 2014) have showed that plastic debris could accumulate metals from the surrounding environment. Possible mechanisms are associated with the modification of the surface by the adhered organic matters (Turner and Holmes, 2015), which are characterized by forming water-soluble and water insoluble complexes with metal ions and hydrous oxides and by interacting with silt and clay that could accumulate metals (Burton, 2002). Cations or complexes would directly interact with the charged sites or neutral regions of the surface of the microplastic, and co-precipitate with or sorption onto hydrous oxides (Ashton et al., 2010). Accumulation of metals may proceed through interactions between bivalent cations and oxyanions with charged or polar sites of the plastic surface, and through non-specific interactions between neutral metal-organic complexes and the hydrophobic surface (Holmes et al., 2012). Besides, the developed biofilms in the environment would enhance the accumulation of metals (Artham et al., 2009; Rochman et al., 2014; Tien and Chen, 2013). Notably, polar functional groups such as ketone developed in the weathered plastics are favorable for the interaction with

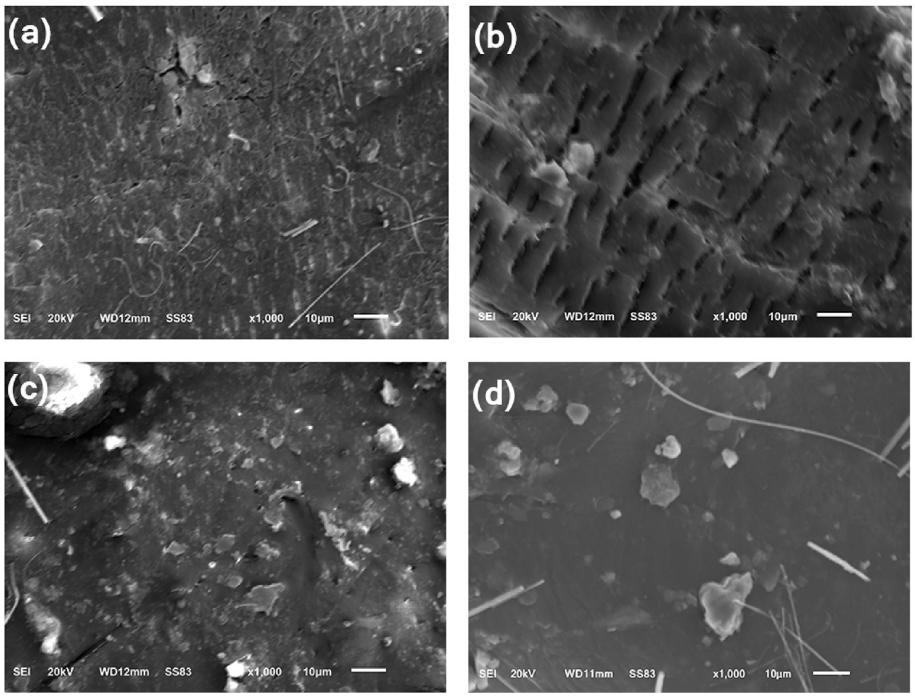

Fig. 4. Mechanical weathering textures of the selected microplastics. (a) Pits on the PP fragment from site S3; (b) Fractures on PE fragment from site S3; (c) Flakes on PE film from site S5; (d) Adhering particles on a PP film from site S1.

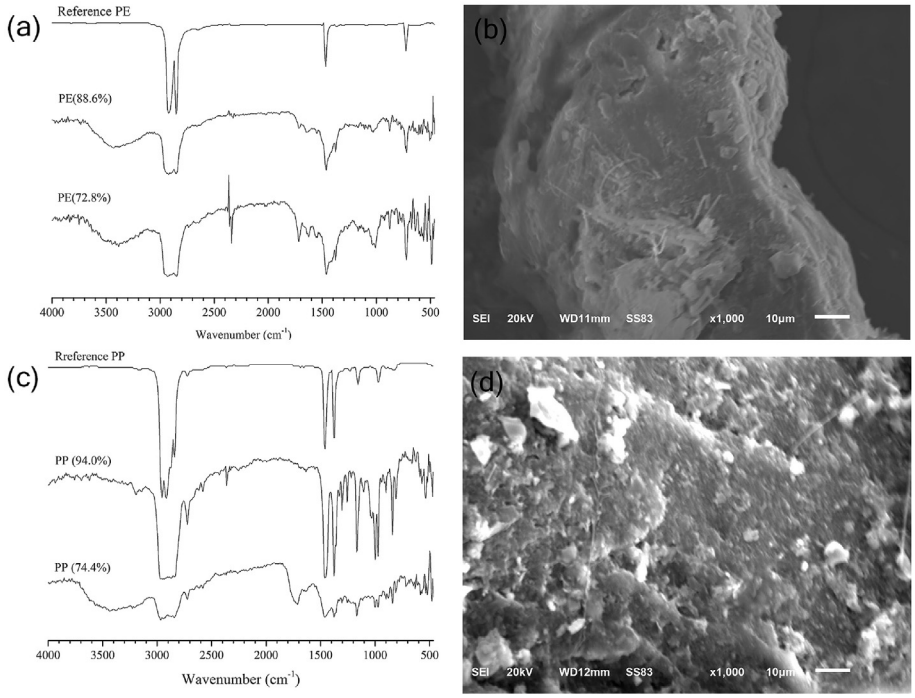

Fig. 5. FTIR spectra and SEM images of chemical weathering microplastics (Two spectra for each sample by detecting two different surface sites). (a–b) are for a PE fragment from site S4. (c–d) are for a PP fragment from site S7.

metals (Fotopoulou and Karapanagioti, 2012), and also found in the microplastics from the surface sediments in the Beijiang River littoral zone.

3.4.2. Content of heavy metals

Six metals including Ni, Cd, Pb, Cu, and Zn listed as priority pollutants by EPA (Environmental Protection Agency), and Ti acting as an indicator of TiO_2 were investigated by ICP-MS. Data on concentrations of metals available to acid digestion by microwave decomposition both in the microplastics and sediments were listed in Table 2. Plastic debris could accumulate organic contaminants from the surrounding environment, increasing their concentrations

even up to the order of 10^6 (Mato et al., 2001). Plastic debris could also accumulate metals from the surrounding environment, which has been demonstrated by laboratory experiments (Holmes et al., 2012, 2014; Turner and Holmes, 2015) and environmental monitoring (Rochman et al., 2014). However, it seemed that the majority of heavy metals carried by microplastics were not attributed to the accumulation from the surrounding environment. Long-term field measurements revealed that concentrations of metals accumulation by pre-production pellets were only a few μg/g (shown in Table 3), though the residence time in the long-term field measurements may be not enough to reach equilibrium and the accumulation capability could be still elevated due to the increase of polarity or surface area with the degradation of plastics in the environment. Concentration of heavy metals in the sediments varied among locations, indicating that metal pollution represents a local problem. Nevertheless, concentrations of all the heavy metals accumulation by pre-production pellets were much less than those in the microplastics. Moreover, concentrations of heavy metals with the exception of Ti (in site 1 and site 3), in the microplastics were generally greater than those in the sediments (shown in Table 2). Metals tend to accumulate onto fine-grained particles, i.e., silt and clay, for their high surface area and the tendency for higher TOC content in the fine-grained particles that have been shown to be correlated with metal pollutants (Burton, 2002; Murray et al., 1999; Zhang et al., 2009). However, it was not surprising herein because the studied surface sediments were predominantly composed of sand (65.2–75.0%) rather than silt (12.6–25.2%) and clay (9.2–17.2%) and the TOC content was greatly low (0.11–0.29%) (shown in the S5 in the Supplementary data). What's more, it might be largely attributed to the inherent load added as additives during plastic production. For example, concentrations of Ni in the microplastics were about equal to those in the macroplastic litters in lake surface sediment and plastic bags. Concentrations of Pb were detected in the same order of magnitude as those in the macroplastic litters on beach. Notably, concentrations of metals both in different fresh products and different color products varied (shown in Table 4), for example, concentrations of Ni and Cu ranged from 0.2 to 571.1, and 0.2–373.7 μg/g, respectively. In fact, the maximal concentrations only occurred in the fresh plastic products with deep colors, e.g., black and dark green. As to Cu and Ti, there are intersections/overlaps between their concentration range of microplastics (80.9–500.6 μg/g for Cu and 13,617–38823.7 μg/g for Ti) and fresh plastic bag products (0.2–373.7 μg/g for Cu and 30.5–14148.4 μg/g for Ti). Data on concentrations of Zn in the macro-litters were lacking. Herein, concentrations of Zn in the microplastics were greater than those reported in the plastic bags and caps, perhaps because the sources (i.e., fragmentation of macroplastics or micro-size plastic production) of microplastics have different metal burden added as additives. Thus, further investigations are also required to determine the metal burden from the more products and macroplastic litters. The greater concentrations of Ti in the microplastics may be mainly because TiO_2 was added during the local plastic manufacturing, functioning as white pigments or UV blockers (Cho and Choi, 2001; Wang et al., 2010; Zhang et al., 2003, 2014). It was noted that TiO_2 could release when the composites degrade in the environment, and thus microplastics act as vectors for TiO_2. More importantly, TiO_2 would be toxic to bacteria, algae, invertebrates and fishes (Handy et al., 2008). Though concentrations of Ni were the lowest in all the detected metals, but such uncommon metals in sublethal concentrations could cause a significant reduction in the body length and brood size of Daphnia magna and thus have a negative effect on survival and reproduction (Münzinger and Monicelli, 1991). Based on data from the long-term sorption of metals by microplastics and a comparison of metal burden between microplastics, macro-litters and fresh plastic products, we suggested that the majority of heavy metals carried by microplastics were derived from inherent load.

3.5. Non-plastics

Microplastics have been typically reported as pellets, fragments and films, while fibers have been recently highlighted (Browne et al., 2011; Dris et al., 2016; Mathalon and Hill, 2014; Woodall et al., 2014, 2015). The microplastic fibers in the environment may be originated from the sewage as a consequence of washing of clothes, and more than 1900 fibers were found in the wastewater from per wash of one single garment by domestic washing machines (Browne et al., 2011). Though several studies have demonstrated that wastewater treatment plants could efficiently remove the vast majority of microplastics from the municipal effluent with a decrease of up to 99% (Carr et al., 2016; Magnusson and Norén, 2014; Murphy et al., 2016; Talvitie et al., 2015), significant amounts of microplastics would enter the environment because large volumes of effluent would be continuously released.

However, many fibers that might be significantly overestimated as microplastics only by visual identification were non-plastics (Lenz et al., 2015; Song et al., 2015), such as cotton and cellulose fibers, which were also found in the surface sediments from the Beijiang River littoral zone by using μ-FTIR (shown in the S6 of the Supplementary data). Cellulose fibers may not be an environmental risk, but could be potentially harmful when associated dyes or additives. By using Raman spectroscopy, industrial dyes that are carcinogenic for vertebrates were found in the artificial fibers (cellulose-based polymers) (Remy et al., 2015). Thus, such fibers should be monitored if they are prevalent in the environment.

4. Conclusion

In the present study, a preliminary assessment of microplastics pollution in the surface sediments from Beijiang River littoral zone was presented. However, concentrations of microplastics were underestimated, because saturated NaCl solution that was commonly used in previous studies could float up the materials with a density <1.2 g/cm^3 but fail to float up some types of plastics, e.g. PVC. $ZnCl_2$ (Liebezeit and Dubaish, 2012) and NaI (Van Cauwenberghe et al., 2013; Nuelle et al., 2014) solution were also reported but not commonly used for high cost and more

Table 3
Concentrations of metals accumulation by microplastics.

Type	Experimental parameters	Concentrations of metals (μg/g)					Reference
		Ni	Cd	Pb	Cu	Zn	
PE pellets[a]	Harbour, placed for 8 weeks	–	–	1.72 ± 0.92	0.28 ± 0.18	0.25 ± 0.1	Ashton et al., 2010
LDPE pellets	Bay, placed for 12 months	<0.1	<0.1	0.1–1	–	1–10	Rochman et al., 2014
PP pellets	Bay, placed for 12 months	<0.1	<0.1	0.1–1	–	1–10	

[a] Pre-production pellets (<5 mm).

Table 4
Metal concentrations carried by plastic debris in the actual environment.

Types	Environment	Concentrations of metals (μg/g)						Reference
		Ni	Cd	Pb	Cu	Zn	Ti	
PE macro-litter	Beach	–	<LOQ[c]	78 ± 19	–	–	–	Nakashima et al., 2012
PP macro-litter	Beach	–	<LOQ	63 ± 19	–	–	–	
PE (>15 mm)	Lake	1.1	23.6	219.7	19.6	n.i[d]	1046.0	Imhof et al., 2016
PP (>14 mm)	Lake	0.8	<LOQ	<LOQ	36.4	n.i	2654.6	
Plastic bags[a]	Fresh products	0.1–3.4	<LOQ	0.47–41.3	0.2–373.7	1.4–80.7	30.5–14148.4	
PE screw caps	Fresh products	0.3–571.1	<LOQ	<LOQ	0.3–11.1	0.7–315.9	67.6–1637.3	
PP screw caps	Fresh products	0.2–1.1	<LOQ	<LOQ	0.2–41.7	1.0–4.0	295.5–886.5	
Plastics	Materials	–	0.01–1%[e]	<5%	–	–	–	Hansen et al., 2013
Microplastics[b]	River sediment	0.5–2.4	2.1–17.6 (0.21–1.76%)	38.2–131.1 (3.82–13.1%)	80.9–500.6	2414–14815	13617.0–38823.7	present study

[a] Data collected from colorful plastic bags, and polymer of some bags were not identified. More importantly, the plastic bags with deep colors, e.g., black and dark green, have greater metal concentrations, up to several hundred times than those with light colors. The similar phenomenon also occurred in the plastic screw caps.
[b] Mixture of PE and PP films and fragments (<5 mm, mainly 2–3 mm).
[c] Below the limit of quantitation.
[d] Not identified due to the use of zinc chloride solution for separation.
[e] % was used as an inconsistent unit and refer to mass fraction.

interfering substances in the sediments that might be extracted as well. Besides, $ZnCl_2$ was not appropriate to be used when detecting the concentration of Zn carried by microplastics (Imhof et al., 2016).

Here, detection of at least two different surface sites of each sample by μ-FTIR was required to obtain higher match degrees of resulting spectra and more information about developed groups, some of which are favorable for the interaction with metals. In contrast, developed groups may not be obtained by Raman spectroscopy that was also an ideal means of polymer identification, because both PE and PP only showed a slight reduction in intensity of characteristic peaks after exposure to simulated sunlight in air for 1634 h (Lenz et al., 2015). However, it is not only expensive but also time-consuming to identify the plastic-like particles one by one (Song et al., 2015), especially when evaluating the level of priority pollutants carried by microplastics.

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. Besides, both laboratory experiments and environmental monitoring using the plastic pellets have shown that plastics could accumulate metals from the surrounding environment. Thus, it is a worthy concern for the interaction between and microplastics because of their long-term residence in the environment and exposure to organisms. However, it's difficult to only obtain the metals accumulated from the surrounding environment because there was an inherent metal load in microplastics (referred to those derived from fragmentation of larger plastic products) added as additives during plastic manufacturing. Nevertheless, we suggested that the majority of heavy metals carried by microplastics were derived from inherent load based on data from the long-term sorption of metals by microplastics and a comparison of metal burden between microplastics, macro-litters and fresh plastic products. Though impacts on the ingested organisms due to the interaction between microplastics and metals were poorly understood, studies of heavy metals released from microplastics under the simulated physiological conditions could be further investigated, for enhanced leach rates of organic pollutants under gut conditions than in seawater have been shown (Bakir et al., 2014). Ingestion of microplastics provides a potential pathway for the transfer of metals, as well as the unreacted residual monomers, additives and persistent organic pollutants (Wang et al., 2016) to organisms. Thus, microplastics would act as multiple stressors to the ingested organisms in the environment.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2016.12.074.

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