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Adsorption of heavy metals on biodegradable and conventional microplastics in the Pearl River Estuary, China☆

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ABSTRACT

In recent years, microplastics (MPs) as emerging carriers for environmental pollutants have attracted increasing worldwide attention. However, the adsorption of heavy metals on MPs, especially for biodegradable MPs, has been still poorly understood in estuarine environments. In this study, we investigated the aging of biodegradable and conventional MPs in the Pearl River Estuary after long-term exposure and their impacts on the adsorption of heavy metals from seawater. The results showed that the changes in surface characteristics were more prominent on biodegradable MPs than on conventional MPs after aging. Both biodegradable and conventional MPs could adsorb heavy metals, and their adsorption capacities fluctuated greatly on different MPs and different exposure times. The adsorption capacities of Cu, Pb, and As on biodegradable MPs were higher than those on conventional MPs, whereas Mn, Cr, and Co had lower adsorption on biodegradable MPs after 9–12 months by inductively coupled plasma-mass spectrometry (ICP-MS). The aging characteristics (CI, O/C, and X_c) of MPs accounted for a contribution of 51.0% on heavy metal adsorption, while the environmental factors (temperature, salinity, pH, and heavy metal concentration) only contributed to 13.2%. Therefore, the present study can provide important evidence on the environmental behaviors and ecological risks of biodegradable and conventional MPs in estuarine systems.

1. Introduction

Microplastics have gained worldwide attention due to their widespread distribution in the land, freshwater, and marine environments (Rochman, 2018). There are 80% of marine plastic debris derived from land sources and rivers have become an important pathway for plastic inputs from land into the oceans (Jambeck et al., 2015; Lebreton et al., 2017). Due to the hydrophobicity and high specific surface area, MPs can serve as new vectors for the adsorption and transportation of other environmental pollutants (e.g., POPs and heavy metals), thus posing potential risks to the marine ecosystem and human health (Dobaradaran et al., 2018; Feng et al., 2022; Khalid et al., 2021; Li et al., 2022; Wang et al., 2022b). The urgency of MPs pollution is an emerging threat to the global challenge. Researchers and scientists endeavor to find promising alternatives for conventional plastics to solve the serious plastics and MPs pollution (Rujnić-Sokele and Pilipović, 2017).

Biodegradable plastics are regarded as a substitute for conventional plastics and can degrade to CO_2 and H_2O in a composting environment (Lambert and Wagner, 2017; Tokiwa et al., 2009). Environmental conditions such as ultraviolet light, microorganism colonization, high temperature and humidity can speed up plastics degradation by breaking the polymer chain (Luo et al., 2022; Tabasi and Ajji, 2015; Tokiwa et al., 2009; Wu et al., 2021). However, those specific conditions for the rapid degradation of biodegradable plastics may not exist extensively in the natural environments, especially in the oligotrophic marine environment (Nazareth et al., 2019). Therefore, the degradability, fates, and ecological impacts of biodegradable plastics in the natural environments are still limited known (Shen et al., 2020; Viera et al., 2021). A study documented that polyhydroxyalkanoates (PHAs) failed to completely degrade after 160 days in seawater (Volova et al.,

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2010). Moreover, biodegradable plastics can generate much more secondary MPs in a short term (Kubowicz and Booth, 2017; Liao and Chen, 2021). For example, MPs formation was found with an abundance of 441 ± 326 and 2103 ± 131 item/g plastic after poly (*p*-dioxanone) degradation in the air and soil environments (Liao and Chen, 2021). In a laboratory experiment, thousands of MPs per gram of biodegradable blended plastic were generated after 90 days in the air, deionized water, and seawater (Bao et al., 2022). It should be noted that biodegradable MPs as a new part of MPs may interact with the coexisting pollutants (such as heavy metals) in the natural environments (Li et al., 2020; Qin et al., 2021). Hence, it is essential to assess the environmental behaviors and ecological risks of biodegradable MPs before promoting their wide application in commercial uses.

Generally, the adsorption mechanisms of heavy metals on MPs involve electrostatic interaction, complexation, π-π interaction, and hydrophobic interaction (Aghilinasrollahabadi et al., 2021; Luo et al., 2020; Sun et al., 2022; Zhou et al., 2020). The adsorption of heavy metals can be affected by the physicochemical characteristics of MPs and the ambient concentration of heavy metals, as well as the environmental factors including temperature, salinity, pH, etc. (Fu et al., 2021; Guo and Wang, 2019; Holmes et al., 2014). Additionally, the aging of MPs also plays an important role in the adsorption behavior of metals on their surfaces. In the actual environments, MPs would undergo aging caused by photothermal oxidation, mechanical wear, biodegradation, and other processes (Alimi et al., 2018). Compared with conventional MPs, biodegradable MPs may be more susceptible to aging, resulting in increased surface area, hydrophilicity, and oxygen-containing groups. Those obvious changes may result in higher affinities to heavy metals in the ambient environments. For example, weathered biodegradable poly (butylene adipate-*co*-terephthalate) MPs in the soil incubation exhibited higher heavy metals adsorption capacity when compared to polyethylene MPs (Li et al., 2020). The adsorption capacity of Pb(II) on aged polylactic acid (PLA) MPs was stronger than those virgin MPs, possibly due to the aged MPs surface with lower zeta potential and more oxygen-containing groups that increased Pb(II) adsorption through electrostatic interaction and surface complexation (Liu et al., 2022b). So far, the current studies have focused on the conventional MPs interacted with toxic metals in field and lab experiments, whereas overlooked the potential threats of so-called biodegradable MPs due to their negligible output. Although a few studies reported the adsorption/desorption of heavy metals on biodegradable MPs through simulation experiments in the laboratory (Guan et al., 2022; Liao and Yang, 2020), there is still a knowledge gap on whether biodegradable MPs can act as a novel carrier of heavy metals in the actual environments.

The Pearl River Estuary (PRE) is the largest estuary in southern China and the Pearl River Delta has become the most important regions of urbanization, industrialization, and population intensification. The intensively anthropogenic activities along the PRE resulted in large amounts of contaminants such as MPs and heavy metals inputs. It was estimated that approximately 66 tons of MPs entering to the South China Sea through eight major outlets of the PRE in 2018 (Mai et al., 2019). Additionally, the PRE region is a hotspot of heavy metal pollution (Chen et al., 2012; Zhao et al., 2018). The annual inputs of Cd, Pb, As, Cu, and Zn into the PRE and South China Sea were 43.9, 471.7, 621.9, 1524.6, and 3819.6 tons per year, respectively (Zhen et al., 2016). Although the widespread MPs and heavy metals in the PRE, their interactions and potential ecological risks are less known (Xie et al., 2021b). In recent years, the production capacities of biodegradable plastics have increased rapidly (European-Bioplastics, 2021). However, it is worrying that the potential of biodegradable plastics to generate more secondary MPs could pose a threat to future environment (Fojt et al., 2020; Shruti and Kutralam-Muniasamy, 2019). Thus, it is important to evaluate whether biodegradable MPs will have negative influences on the ecological environment for the promotion and application of biodegradable plastics.

In this study, we conducted a comprehensive investigation on the adsorption of heavy metals on biodegradable and conventional MPs after exposing them to surface seawaters for 3–12 months in the PRE. Our central goals are: (1) to explore the physicochemical changes in biodegradable and conventional MPs being exposed in the estuarine environment; (2) to assess the adsorption of heavy metals from surrounding seawater on different types of MPs; and (3) to discuss the affecting factors (e.g., environmental parameters, MPs aging characteristics) on the adsorption capacity of heavy metals. We believe these results will be valuable for a better understanding the environmental behaviors and ecological risks of MPs in the natural environments.

2. Materials and methods

2.1. Microplastics selection

Three representative biodegradable MPs, including polylactic acid (PLA), poly (butylene adipate-*co*-terephthalate) (PBAT), and polycaprolactone (PCL), were selected due to their considerable proportions in global plastic production (European-Bioplastics, 2021). The conventional MPs, polyethylene (PE), was also chosen as a control given that they were abundant in the environmental pollution. The above raw MPs pellets were purchased from Shunjie Plastic Technology Co., Ltd. (Dongguan, China). All chemical solvents were purchased from ANPEL Laboratory Technologies Co., Ltd. (Shanghai, China).

2.2. Experimental design

To investigate the aging of MPs and the adsorption of heavy metals, an in situ field experiment was conducted from July 2020 to July 2021 in Guishan Island (22°08′38″N, 113°48′53″E) of the PRE (Fig. 1). Biodegradable (PLA, PBAT, PCL) and conventional (PE) MPs were cleaned with 70% alcohol and then rinsed with ultrapure water before use. 100 g MP pellets were weighed as a sample and four repeats were prepared for a given polymer type (Fig. S1). The sample was placed in a nylon mesh bag (pore size 1 mm) and subsequently put inside a stainless-steel case (pore size 1.2 mm) to reduce the organism interference during experiment. The stainless-steel cases with different types of MPs were finally placed into a large stainless-steel cage (49 × 36 × 21 cm^3). Four stainless-steel cages were set for the sample collection after 3, 6, 9, and 12 months of exposure to the seawater. In the field, the stainless-steel cages were hung on an artificial raft and submerged into a water depth of 0.5 m. During MPs collection, seawater samples were also collected at 3, 6, 9, and 12 months respectively and the water quality was detected by using a YSI multi-parameter water quality analyzer (professional plus, USA). All the samples were stored at −20 °C until laboratory analysis.

2.3. Aging characteristics of microplastics

The MPs used in the tests were selected randomly. The surface structure of five MP pellets from each treatment was observed by stereoscope (OLYMPUS SZX10, Japan) and scanning electron microscope (SEM, Hitachi SU3500, Japan). The functional groups on the aged MPs were identified by using Fourier transform infrared spectroscopy with attenuated total reflectance attachment (ATR-FTIR, Thermo Scientific Nicolet iS50R, USA) at a resolution of 4 cm^{-1}. The carbonyl index (CI) was calculated by the ratio of the absorbance area of carbonyl peak and reference peak to characterize the weathering degrees (Ter Halle et al., 2017). Four individual pellets from each treatment were analyzed, resulting in an average CI value. The selection of carbonyl peaks and reference peaks from different MPs can be referred to in the Supplementary data (Table S1). The carbon and oxygen compositions of one MP pellet from each treatment were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB Xi+, USA). The thermal properties were measured using differential scanning calorimetry (DSC,

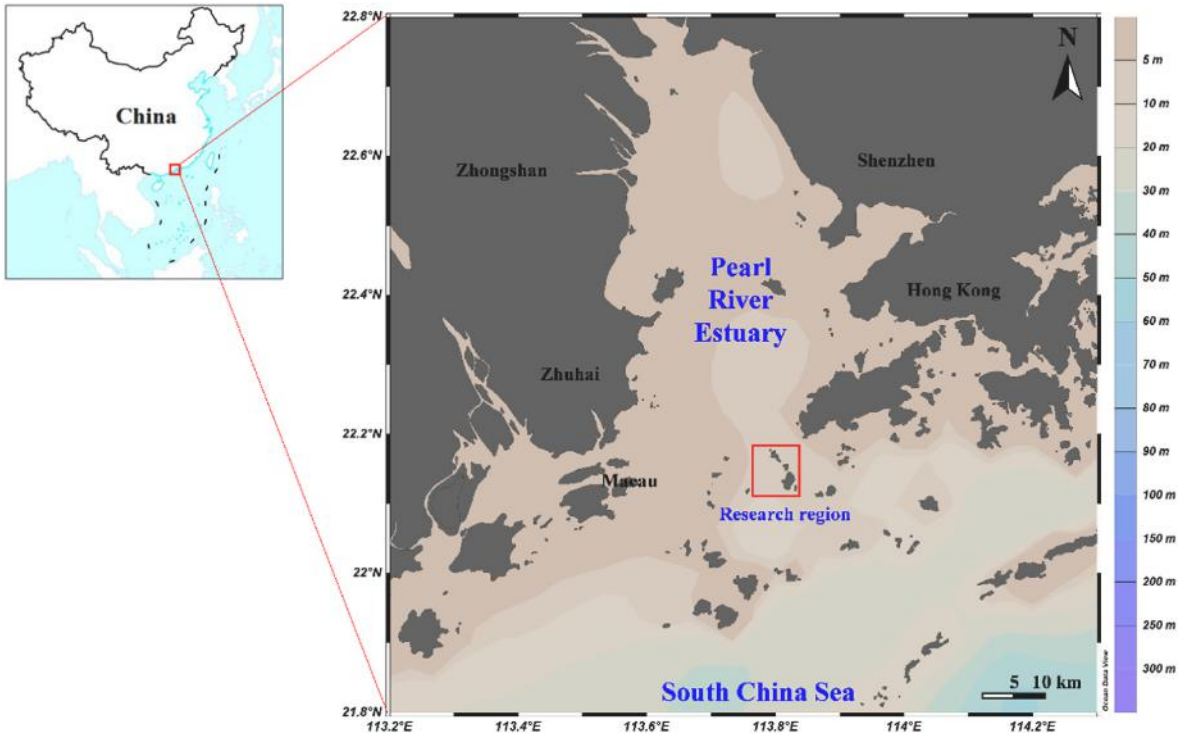

Fig. 1. The field experiment location in the Pearl River Estuary.

Mettler Toledo DSC1, Switzerland). More details on the methods of DSC analysis were provided in the Supplementary data. Crystallinity (X_c) was calculated on the second heating step using the following equation:

$$X_c\ (\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \quad (1)$$

$$X_c\ (\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \times 100 \quad (2)$$

where ΔH_m and ΔH_c were the melting enthalpy and cold crystallization enthalpy, respectively. ΔH_m^0 was enthalpy of melting for a 100% crystalline plastic sample, where PE, PLA, PBAT, and PCL were 293, 93, 114, and 139 J/g, respectively (Chivrac et al., 2006; Fischer et al., 1973; Koenig and Huangt, 1995; Sahebian et al., 2009). Given that the virgin PLA sample had the enthalpy of cold crystallization, which was applied to equation (2). The crystallinity of other samples was calculated using equation (1).

2.4. Heavy metal analysis

MP samples from the field experiment were gently rinsed with ultrapure water to remove the biofilm and sediment on their surfaces. The amount of biofilm and sediment residue on MPs surface can be ignored at the end of pretreatment, and they have negligible effect on the adsorption of heavy metals on MPs (Xie et al., 2021a). Then, 0.2 g MPs (i.e. 7 PE pellets, or 9 PLA pellets, or 5 PBAT/PCL pellets) in each sample were weighted and digested in a microwave oven (Anton Paar Multiwave PRO 41HVT56, Austria) with 1 mL HNO_3 (65–68%, GR), 3 mL HCl (35%, GR), 1 mL H_2O_2 (30%, GR), and 1 mL HF (30%, GR) as digestion solution. After digestion, the acids were removed at 180 °C until 1 mL of digested solution was left. The solution was then transferred to a colorimetric tube and added with ultrapure water to 50 mL. Finally, the supernatant was diluted with 2% nitric acid and analyzed the target metals (Cu, Pb, As, Mn, Cr, and Co) using an inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500 cx, USA). The concentration of heavy metals in virgin MPs was deducted to calculate the adsorption capacity of heavy metals on aged MPs after being exposed to seawater. Target heavy metals were also detected in seawater samples collected at 3, 6, 9, and 12 months. The concentration units of heavy metals in MPs and seawater were μg/g and μg/L, respectively.

The partition coefficient (K_{pw}, mL/g) that described the ability of MPs to adsorb heavy metals from the ambient environment (Brennecke et al., 2016; Gao et al., 2019; Holmes et al., 2014) was given as follows:

$$K_{pw} = \frac{[M_eP]}{[M_eW]} \times 1000$$

where $[M_eP]$ (μg/g) was the concentration of heavy metals adsorbed by MPs, $[M_eW]$ (μg/mL) described heavy metals concentration in seawater.

2.5. Quality assurance (QA) and quality control (QC)

The offshore marine sediment (GBW 07314) was used to evaluate and verify the accuracy of the analytical method. The recoveries of heavy metals were varied from 75% to 115%. The method quantitation limit (MQL) of Cu, Pb, As, Cr, Mn, and Co in MP samples were 0.008, 0.07, 0.18, 0.07, 0.011, and 0.016 μg/g, respectively. The MQL of Cu, Pb, As, Cr, Mn, and Co in seawater samples were 0.12, 0.07, 0.05, 0.05, 0.01, and 0.05 μg/L, respectively. The glassware was soaked in 20% HNO_3 for 24 h and washed several times with ultrapure water before use.

2.6. Statistical analysis

Since the data were not well fit to the homogeneity of variance, non-parametric Kruskal-Wallis tests were adopted. The relationships of heavy metals adsorption and the environmental factors (temperature, salinity, pH, and heavy metals concentration), or the polymer aging properties (carbonyl index, O/C ratio, and crystallinity) were analyzed by Spearman correlation test and redundancy analysis (RDA). Variance partitioning analysis (VPA) was used to test the contribution of environmental factors or the aging properties of MPs on heavy metals adsorption. The FTIR and XPS spectra data were analyzed using OMNIC

9 and Avantage 5.9922, respectively. IBM SPSS Statistics 25, Origin 2021, Canoco 5.0, and Ocean Data View 5.5.1 were used for data analysis and visualization.

3. Results

3.1. Aging characteristics of MPs

The outer surfaces of aged MPs especially PCL underwent a yellowing effect after being exposed to seawater (Fig. S2). From the SEM images, the features of MPs morphology were found at different aging degrees (Fig. 2). After 3 months, both PBAT and PCL surfaces appeared with plentiful cavities and rugged texture, while the PLA surface produced the exfoliation of small pieces. Few changes can be observed in the surface morphology of PE. After 6, 9, and 12 months, the exfoliation of fragments was observed more obviously on the surfaces of PBAT and PCL. The surface cavities were further eroded on the aged PBAT and PCL, resulting in the formation of a rough outer surface and exposures of the inner surface. Overall, the morphological changes in biodegradable MPs (PBAT, PCL, PLA) were more distinct than in conventional MPs (PE).

The FTIR spectra results of MPs surface oxidation were shown in Fig. 3. MPs produced oxygen-containing functional groups after the field exposure. For both conventional and biodegradable MP, two new absorption peaks were observed as C═O (at about 530 cm^{-1}) and O–H (at about 3300 cm^{-1}) after being exposed to seawater. In addition, the peak intensity of C═O increased at 1724 cm^{-1} and C–O formed at 1030 cm^{-1} on the aged PE. For three biodegradable MPs, both C═O stretching (at 1747 cm^{-1}) and C–O stretching (at 1082 and 1180 cm^{-1}) increased significantly on the aged PLA; the intensity of absorption peak of the phenylene ring (at 727 cm^{-1}), O–C (at 1103 and 1270 cm^{-1}), C═O (at 1713 cm^{-1}), and CH_2 (at 2951 cm^{-1}) decreased obviously on aged PBAT; the peak intensity of C–O at 1170 and 1240 cm^{-1} increased evidently for the aged PCL.

According to Fig. S3, the carbonyl index (CI) values of virgin PE MPs was only 0.03, which was obviously lower than those (4.05–10.38) of virgin biodegradable MPs (PLA, PBAT, and PCL). In comparison, the CI values of aged PE increased significantly more than the virgin PE (Kruskal-Wallis tests, $p < 0.05$). For the biodegradable MPs, the CI values of PBAT and PCL continuously decreased to the lowest at 9 months and then increased at 12 months, while the CI values of PLA first increased at 3 months and then decreased to the lowest and finally increased at 12 months.

The variation in surface carbon and oxygen composition of MPs was further confirmed by XPS (Fig. S4 and Table S2). The peaks at 284.80 and 288.09 eV on the surface of virgin PE represented C–C/H and C═O, respectively, while new peaks (C–O) at about 286.50 eV were shown on the aged PE. For three biodegradable MPs, the percentage of O–C═O decreased clearly on the aged PLA, while the percentage of C–O increased on the aged PBAT and PCL (Table S2). Compared with the virgin biodegradable MPs, the O/C ratio of virgin PE was relatively lower. In general, the O/C ratio of MPs increased and then decreased

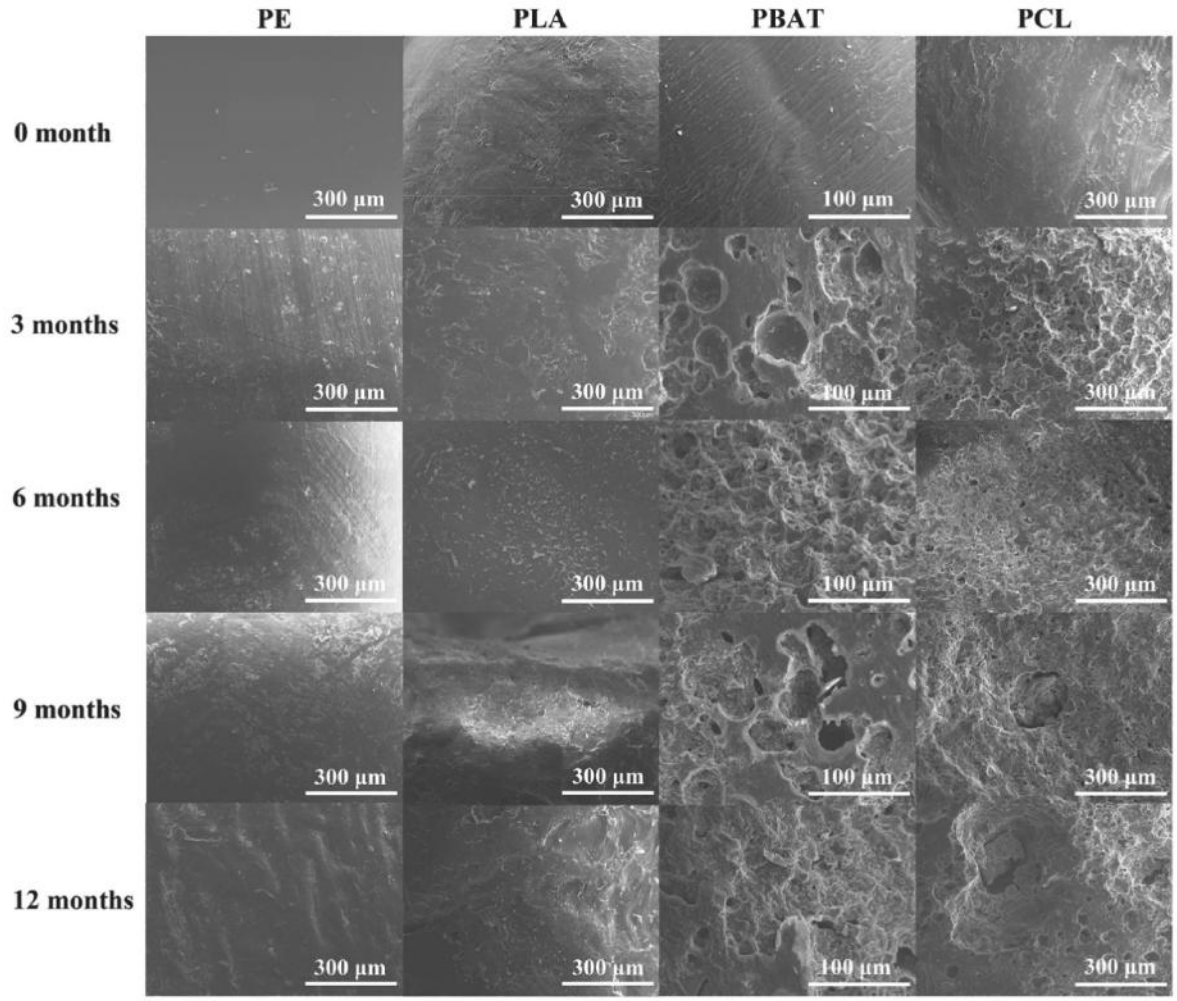

Fig. 2. SEM images of biodegradable and conventional MPs before and after exposure in seawater.

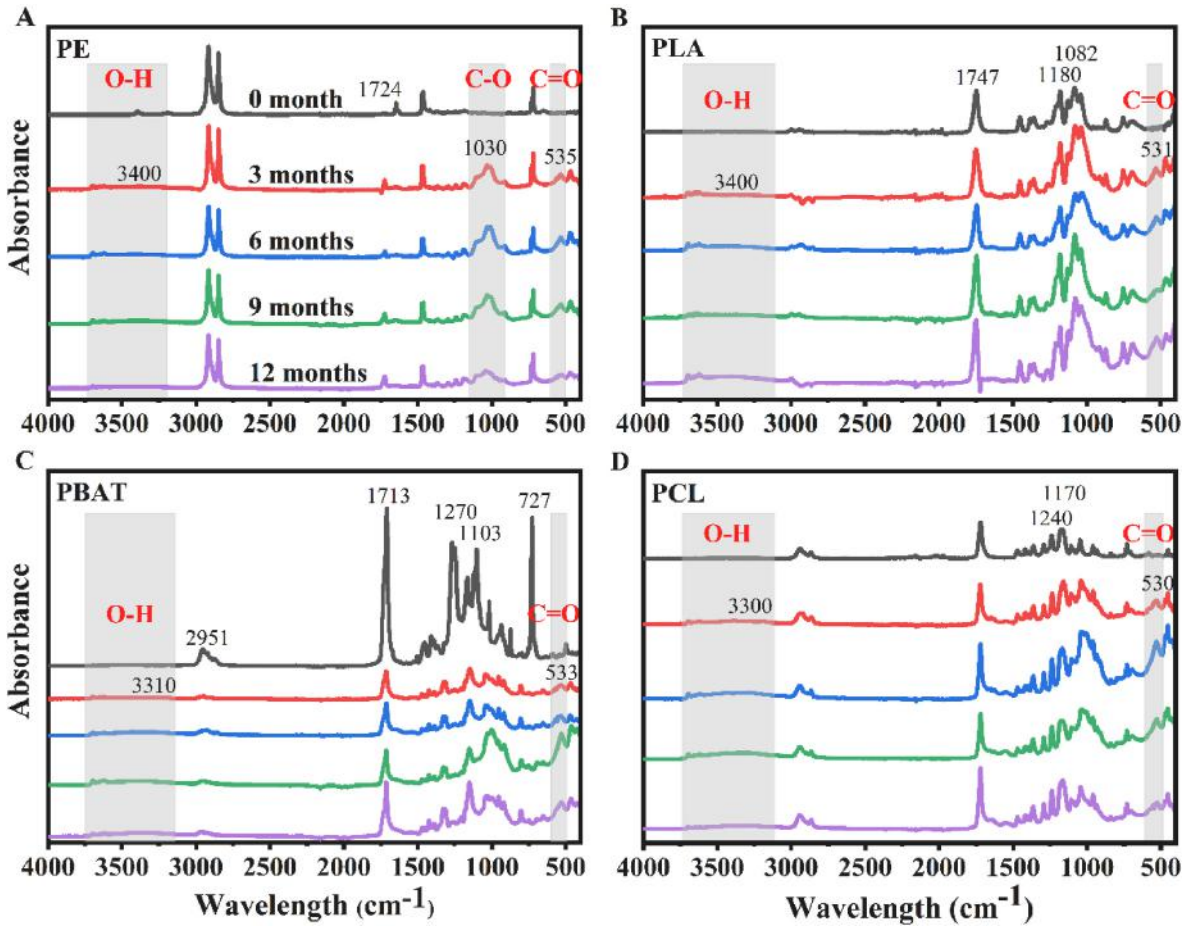

Fig. 3. FTIR spectra of PE (A), PLA (B), PBAT (C), and PCL (D) being exposure to seawater for 0–12 months in wavenumber of 4000–400 cm^{-1}. The shaded areas represented new functional groups on the aged MPs surfaces.

after being exposed to seawater.

The variation in thermal parameters of plastics can be seen from the DSC results (Fig. S5 and Table S3). The melting temperature (T_m) of virgin PE was 111 °C, while that of aged PE was about 132 °C. By contrast, the T_m of both PLA and PBAT decreased evidently after the field experiment. The crystallinity (X_c) of PE and PBAT increased after aging, whereas the X_c of aged PLA decreased. In addition, PLA had an enthalpy relaxation peak at around 60 °C, and the cold crystallization peak at approximately 110 °C disappeared for the aged PLA. The T_m and X_c of PCL samples varied slightly throughout the aging process.

3.2. Adsorption of heavy metals

In Fig. 4, the adsorption of heavy metals on MPs was variable during the field experiment. Generally, heavy metals adsorption on biodegradable and conventional MPs was in the following order: Mn > Cr > Pb > As and Cu > Co. After 3 months of exposure, the adsorption capacity of Cu, Pb, As, and Co on aged PE was lower than the method quantitation limit (MQL). The adsorption capacity of metals (except Pb) was relatively higher at 9 or 12 months of aged PE. On the contrary, the biodegradable MPs (PLA, PBAT, and PCL) had a low adsorption capacity for most of the targeted metals at 9 or 12 months. In addition, the adsorption of heavy metals on different types of MPs was variable greatly. Generally, the accumulation of Cu, Pb, and As on biodegradable MPs was higher than on PE, while the adsorption capacity of Mn, Cr, and Co was relatively higher on PE after 9–12 months of exposure.

In seawater, the concentration of Cr and Pb was relatively lower when compared to other metals (Fig. S6). The partition coefficients (K_{pw}) can reflect the accumulation rate and adsorption ability of metals. Accumulation of heavy metals on MPs at 12 months and the annual average concentration of heavy metals in seawater were used to calculate the partition coefficients (Table 1). MPs exhibited the adsorption ability of heavy metals in the following orders: (1) PE MPs: Cr > Mn > Pb > As > Co > Cu; (2) PLA MPs: Pb > Cr > Mn > As > Cu > Co; (3) PBAT MPs: Pb > Cr > Mn > Cu > As > Co; (4) PCL MPs: Pb > Cr > Mn > Cu > As > Co. Generally, for different types of MPs, the K_{pw} of Pb and Cr was much higher than that of other metals. The K_{pw} of Pb, Cu, and As was higher for biodegradable MPs, whereas the K_{pw} of Mn, Cr, and Co was higher for PE.

3.3. The affecting factors on heavy metals adsorption

Spearman correlation analysis was used to explore the relationship between heavy metals adsorption and the specific factors, such as water parameters, CI, O/C, and X_c (Fig. 5). The adsorption capacity of Cu, Pb, and As on MPs was positively correlated with CI values, whereas the adsorption capacity of Mn, Cr, and Co was negatively correlated with CI values. The O/C ratio and X_c had opposite effects on As and Cr adsorption capacity. The adsorption capacity of Pb, Mn, Cr, and Co was negatively correlated with seawater salinity. In addition, pH and the coexisting metals in seawater were related to the adsorption capacity of heavy metals. However, water temperature showed no correlation with the adsorption capacity of heavy metals.

The adsorption capacity of heavy metals on PE and PLA were positively correlated with X_c and O/C, respectively (Fig. 6A). Heavy metals adsorption on PBAT or PCL was positively correlated with CI values. It was noteworthy that environmental factors accounted for 13.2% of the total contribution to the heavy metal adsorption on MPs, which was

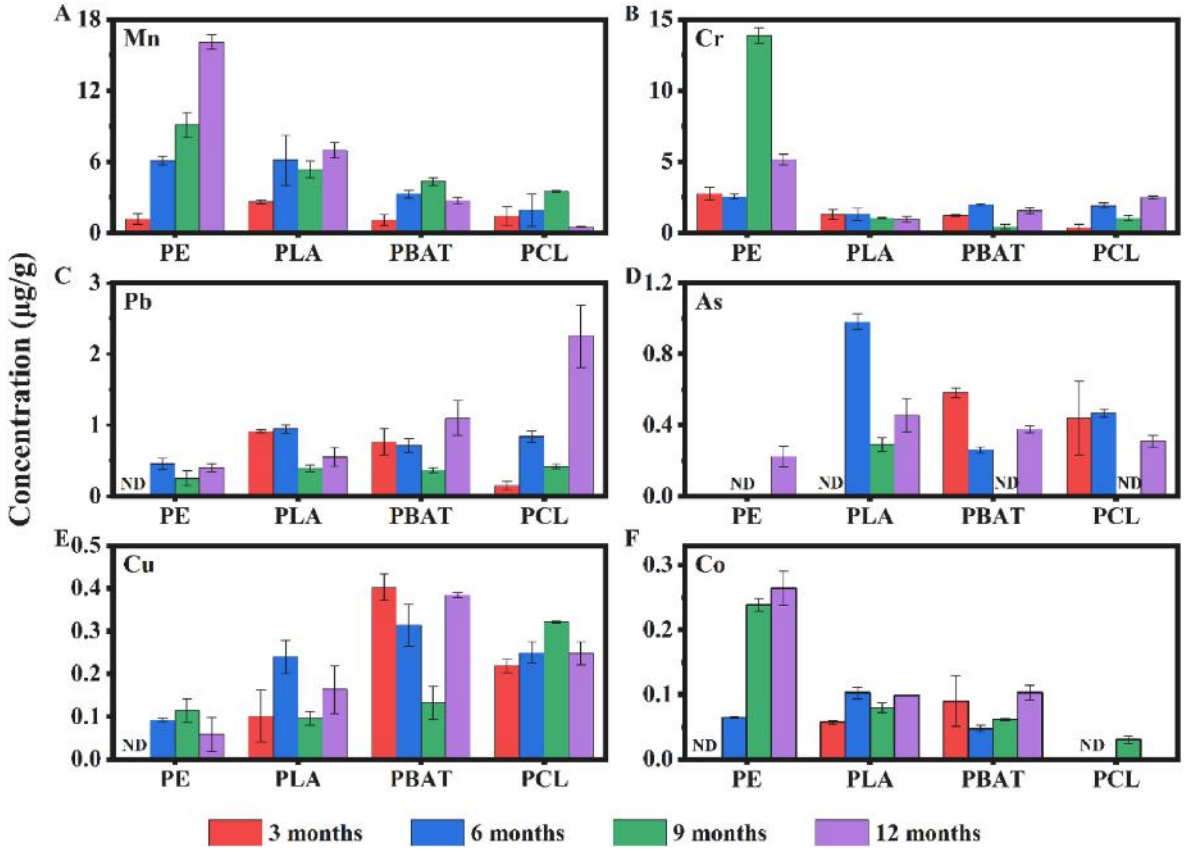

Fig. 4. The concentration of heavy metals on biodegradable and conventional MPs. ND meant the value was lower than method quantitation limit (MQL).

Table 1
The partition coefficients (K_{pw}) of heavy metals between seawater and MPs at 12 months.

MPs	Cu	Pb	As	Mn	Cr	Co
PE	32.87	2747.33	95.29	5150.75	17,776.13	61.84
PLA	91.26	3752.62	194.02	2221.73	3282.02	23.01
PBAT	214.10	7444.25	160.87	871.55	5396.51	24.13
PCL	138.29	15,306.41	131.16	163.25	8594.37	0.00

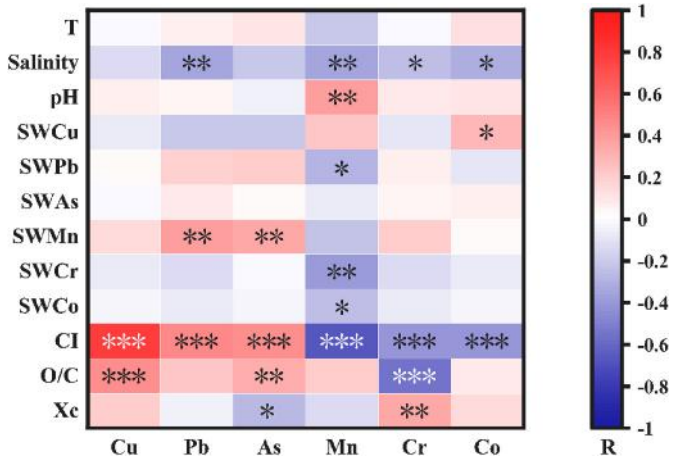

Fig. 5. Spearman correlation between heavy metal adsorption capacity and the MPs or environmental parameters. Water temperature (T), the concentration of Cu (SWCu), Pb (SWPb), As (SWAs), Mn (SWMn), Cr (SWCr), and Co (SWCo) in seawater, the carbonyl index (CI), O/C ratio (O/C), and crystallinity (X_c) of MPs. "*" $p < 0.05$, "**" $p < 0.01$, "***" $p < 0.001$.

significantly lower than the contribution (51.0%) of MPs aging properties including CI, O/C, and X_c (Fig. 6B).

4. Discussion

4.1. Changes in physicochemical characteristics of MPs during aging

MPs were subject to aging or weathering in the marine environment (Jahnke et al., 2017; Luo et al., 2022). During the aging process, the physicochemical properties of MPs (e.g., surface morphology, functional groups, and crystallinity) would change to different degrees, which subsequently affect the adsorption of environmental pollutants. In this study, biodegradable and conventional MPs suffered various degrees of yellowing effects, which may be related to the formation of chromophore products in the degradation process (Guo and Wang, 2019). Moreover, there were evident fragments, pits, and cavities on the aged MPs, indicating the occurrence of surface erosion (Fig. 2). The surface of MPs especially biodegradable MPs was further eroded with increasing exposure time, resulting in the loss of the highly aged outer layer and the appearance of a new inner layer. However, the aging mechanism of biodegradable and conventional MPs may be very complex in this study because they were exposed to the variable seawater environment in the PRE for a long time.

Generally, the polymer chain of MPs can break down and produce free radicals during aging, and eventually, their surfaces are oxidized and formed oxygen-containing groups including carboxylic acid, aldehydes, and ketones (Mao et al., 2020). The oxygen element on the surface of virgin PE MPs may be attributed to the oxidation that occurred during production and transportation (Mao et al., 2020). In this study, we found that all the aged MPs could generate new oxygen-containing groups, such as C═O at about 530 cm^{-1} and O–H at about 3300 cm^{-1}. Similarly, a previous study found a new band (535 cm^{-1}) on aged

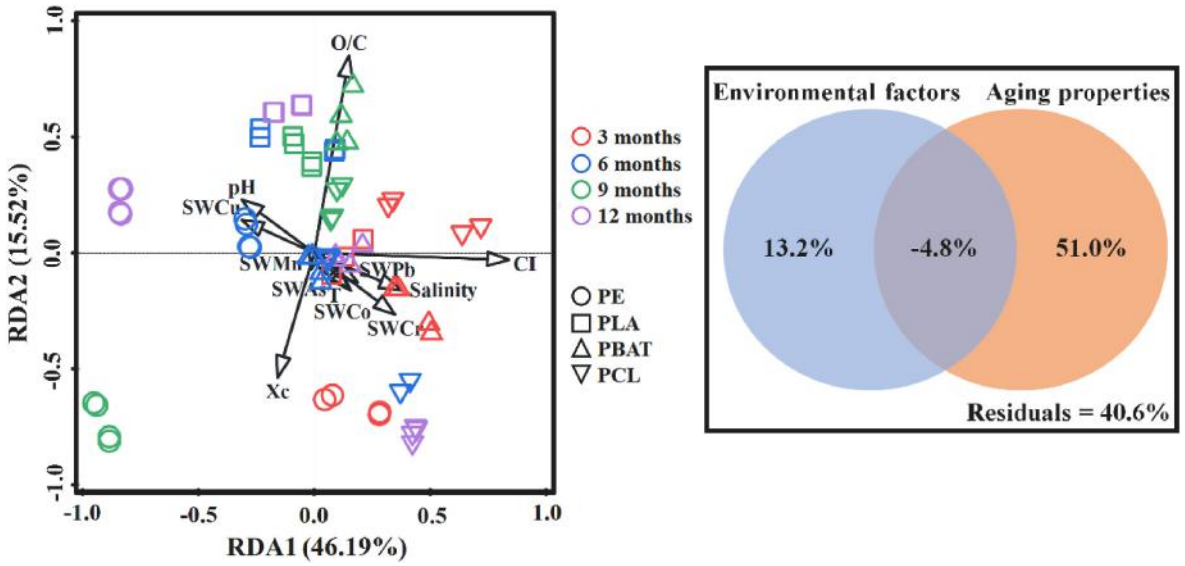

Fig. 6. RDA of heavy metals adsorption on different MPs (A), and VPA differentiating the impacts of environmental factors (temperature, salinity, pH, and heavy metals concentration) and MPs aging properties (carbonyl index, O/C ratio, and crystallinity) (B).

MPs surfaces, and another study identified O–H region (3000 - 3800 cm^{-1}) on aged PP MPs in ultrapure water, estuarine water, and seawater (Wu et al., 2021; Ye et al., 2020). Furthermore, absorption peaks at 2951, 1713, 1270, and 727 cm^{-1} were significantly weakened on the aged PBAT, indicating that the molecular chain might have been broken under the impacts of photo-oxidation, hydrolysis, and microorganism interaction (Jia et al., 2021; Kanwal et al., 2021). Compared to the virgin MPs, the strength of peaks at 1100 cm^{-1} increased significantly on the aged PE, PLA, and PCL in the present study, which might be owed to the changes caused by the degradation process of plastic chemical structure (Beltrán-Sanahuja et al., 2021). In addition, the percentage of O–C═O decreased for aged PLA, which could be attributed to the hydrolysis of ester groups in molecular chains (Lv et al., 2018). In general, the O/C ratio was higher for aged MPs than for virgin MPs, indicating a raising of oxygen-containing groups on the aged MPs surface (Wang et al., 2022a). In the aging process, the decreased CI values and O/C ratio of biodegradable MPs might be attributed to the exposure of less oxidized inner layer due to the fragmentation of the outer surface, or the transfer of carboxylic acid to seawater environment, or the assimilation of carbonyl compounds by microorganisms (Briassoulis et al., 2015; Hakkarainen and Albertsson, 2004; Müller et al., 2018; Song et al., 2017; Wang et al., 2022a).

In this study, the increased crystallinity of PE and PBAT may be stemmed from the preferential degradation of amorphous polymers, and the chemical crystallization of polymers with low molecular weight was produced by chain scission in the aging process (Lv et al., 2015; Rouillon et al., 2016). The melting enthalpy and crystallinity of aged PLA decreased and even disappeared after 12 months of exposure to seawater, which may be dominated by the defects caused by oxygen-containing functional groups generated in the aging process (Chen et al., 2021b; Liu et al., 2021). The T_m of both aged PLA and PBAT exhibited a left shift, indicating the reduction of the chain length of MPs (Lv et al., 2017). However, the T_m of aged PE MPs increased from 111 °C to 132 °C, implying that aging had different effects on the thermal properties of PE MPs (Liu et al., 2019; Liu et al., 2021). During the aging period, PLA MPs showed an enthalpy relaxation peak at about 60 °C, which further suggested that PLA underwent aging effects (Martucci and Ruseckaite, 2015). In addition, the cold crystallization peak (at approximately 110 °C) of the aged PLA disappeared, indicating the aging change of thermal properties of MPs. Compared with PE, PLA, and PBAT, the aged PCL had relatively slight changes in the thermal properties. Similarly, a previous study found that the thermal parameters (T_m and X_c) of PCL varied slightly compared with poly-β-hydroxybutyrate (PHB) during thermal aging, which might be attributed to the stable thermal properties of PCL (dos Santos Rosa et al., 2004).

4.2. Heavy metals adsorption on MPs

In this study, both biodegradable and conventional MPs could adsorb heavy metals from surrounding seawater in the PRE, and their adsorption fluctuated greatly during the field experiment. The adsorption mainly depends on intermolecular interactions between the polymers and heavy metals (Godoy et al., 2019). Heavy metal ions can be adsorbed to the charged or polar regions on MPs surface by electrostatic action, whereas the neutral metal-organic complexes can be adsorbed to MPs surface through non-specific interactions (Cao et al., 2021; Holmes et al., 2012; Holmes et al., 2014). Besides, metals can co-precipitate with or adsorb onto the oxides/hydroxides of Fe and Mn on the MPs surface (Ashton et al., 2010; Xie et al., 2021a). The fouling (e.g., biofilms and natural organic substances) on MPs surface also contributes to heavy metals adsorption. Therefore, MPs acting as emerging carriers may affect the environmental behavior and fate of heavy metals in the marine ecosystem.

Adsorption of heavy metals on MPs was greatly variable among different metals. In our study, the order of accumulation of heavy metals on four types of MPs was roughly shown as Mn > Pb > Cu. The result was consistent with the adsorption of Mn, Pb, and Cu on PE, polyvinyl chloride (PVC), and PP pellets that were exposed to seawater (Ashton et al., 2010). In this study, Pb and Cr concentration was relatively lower than that of other metals in seawater, while the adsorption capacity of Pb and Cr was relatively higher on different MPs. This phenomenon indicated that MPs were preferential to adsorb Pb and Cr from the ambient environment, which may be attributed to the strong reactivity, high ion exchange capacity, and large partition coefficient of Pb and Cr (Purwiyanto et al., 2020).

The present study documented that biodegradable and conventional MPs exhibited different affinities for special metals. Our results showed that biodegradable MPs can adsorb higher concentrations of Cu, Pb, and As than the conventional PE. Similarly, a previous study found that the adsorption capacity of Pb on PLA was higher than that on PE (Guan et al., 2022). In another study, PLA had the weakest Cr adsorption capacity when compared to conventional MPs (PE, PVC, PS, and PP), which was consistent with our results (Liao and Yang, 2020). However, heavy metals adsorption on conventional MPs was not dependent on

polymer types after a long-term immersion in San Diego Bay, which may be because the adsorption of heavy metals on different types of MPs was dominated by the surface biofilms (Rochman et al., 2014).

In a laboratory experiment, heavy metals adsorption capacity on MPs increased with the exposure time and tended to be stable after reaching equilibrium (Chen et al., 2021a; Wang et al., 2022b). A previous study found that Cr and Pb adsorption on both PP and PVC was strongly related to the metals concentration in seawater, indicating that the metals adsorption was in dynamic exchange between MPs and seawater (Gao et al., 2019). However, in our study, the adsorption trends of heavy metals on both biodegradable and conventional MPs were not synchronous with the variation of metal concentration in the seawater. Additionally, heavy metal adsorption was found to vary greatly on biodegradable MPs than on conventional MPs, which might be due to the shedding of the aged outer layer and the loss of oxygen-containing groups on the aged biodegradable MPs.

4.3. Factors influencing heavy metals adsorption

In this study, we demonstrated that MPs could adsorb heavy metals from the surrounding environment. Their adsorption process may be affected by various factors, including environmental parameters and the aging characteristics of MPs (Cao et al., 2021). The adsorption capacity of Pb, Mn, Cr, and Co on MPs was negatively related to salinity in this study. This may be because the saltwater environment can contribute to the formation of electrostatic shielding between positive metals and negative MPs surfaces, and the salt ions may compete for the limited adsorption sites on MPs surfaces (Yu et al., 2021). Besides, we found that the accumulation of Mn on MPs was positively correlated with the water pH, which may be due to the electrostatic interaction, as illustrated in Fig. S7. With the increase of pH, the negatively charged MP surfaces could be able to attract more metal cations (Guo et al., 2020). In our study, there was no statistical correlation between heavy metals adsorption on MPs and the environmental concentration of corresponding metals in seawater (Spearman correlation analysis, $p > 0.05$). This was in line with the previous observations of Cu and Mn concentration on MPs (Gao et al., 2019). However, heavy metals adsorption on MPs may be affected by other coexisting metals. We found that Mn concentration in seawater was positively related to the adsorption of Pb and As on MPs, whereas the concentration of Cu in seawater showed a positive correlation with the accumulation of Co on MPs. This indicated the promoting effects among metals in a complex seawater environment (Liu et al., 2022a). Additionally, limited adsorption sites on MPs surface could lead to a competitive effect, e.g., the inhibition of Pb, Cr, and Co existed in the adsorption of Mn on MPs.

In addition, heavy metal adsorption is related to the physical and chemical properties of MPs. It has been concluded that PVC absorbs more Cu than PS due to its larger surface area and higher polarity (Brennecke et al., 2016). Furthermore, the chemical groups on MPs surface can affect heavy metals adsorption. For example, metal ions can bind to some functional groups such as –COOH, $–NH_2$, and phenyl-OH by complexation (Cao et al., 2021). In this study, three types of biodegradable MPs (PLA, PBAT, and PCL) had abundant oxygen-containing groups, which might increase polymer polarity and facilitate heavy metals adsorption on MPs (Li et al., 2019; Mato et al., 2001).

The aging of MPs also plays a vital role in metals adsorption. The generation of oxygen-containing groups and variation in crystallinity may affect metals adsorption during MPs aging (Zhou et al., 2020). We found that the adsorption capacity of Cu, Pb, and As on MPs was positively correlated with the carbonyl index used to characterize the aging degree of MPs, indicating that those metals may adsorb onto MPs by electrostatic interaction or/and surface complexation with oxygen-containing functional groups. However, in this study, Cr adsorption on MPs was negatively correlated with CI and O/C, which may be due to the oxyanions form being the dominant species of Cr in seawater (Marinho et al., 2018). Oxygen-containing groups, such as carboxyl and hydroxyl groups, can increase the negative surface charges on MPs, and electrostatic repulsion between MPs and oxyanions led to a decrease in adsorption amount (Liu et al., 2020; Zhou et al., 2020). Moreover, those groups can form hydrogen bonds with water molecules, resulting in the reduction of adsorption sites on MPs surface and the obstruction of heavy metals adsorption (Hüffer et al., 2018). Thus, the negative correlation between Mn/Co adsorption and the CI values of MPs could also be well explained in this study. The crystallinity was negatively correlated with the adsorption capacity of As but positively correlated with Cr adsorption. This indicated that interaction between MPs and As was dominated by the internal partition in amorphous regions, while Cr adsorption on MPs was induced by the surface interaction in crystalline regions (Velez et al., 2018).

In the natural environment, the adsorption mechanism of heavy metals on MPs is extremely complex. Compared with the environmental factors, changes in carbonyl index, O/C, and crystallinity of aged MPs were found to have significant effects on heavy metals adsorption in this study. Furthermore, these aging parameters had greatly variable effects on the adsorption of different heavy metals on MPs. In a previous study, the adsorption behavior of Pb onto MPs correlated with electrostatic interactions, while surface complexation was important for MPs to adsorb Cd and Cu (Zou et al., 2020). Additionally, the adsorption mechanism of heavy metals may be variable on different MPs. For example, Cd (II) adsorption onto polyamide and acrylonitrile butadiene styrene was related to the π-π interaction, while oxygen-containing functional groups determined the adsorption process of Cd (II) on PVC, PS and PET to some extent (Zhou et al., 2020). Therefore, the adsorption mechanism of specific heavy metals on MPs should be further explored in future studies.

5. Conclusion

In this study, we revealed the physicochemical changes in aged biodegradable and conventional MPs, and their effects on heavy metals adsorption after 3–12 months of exposure to the seawater environment in the PRE. The appearance of new oxygen-containing groups on the rough surface and the changes in carbonyl index, O/C ratio, and crystallinity of polymers indicated that both biodegradable and conventional MPs had undergone an aging process in the field. Generally, the characteristic changes in the aged biodegradable MPs were more prominent than in the conventional MPs. The adsorption capacity of Cu, Pb, and As on biodegradable MPs was found higher than that on PE. The fluctuant adsorption of heavy metals on MPs was related to the seawater parameters (e.g., salinity, pH, heavy metals concentration) and the aging characteristics of MPs (e.g., carbonyl index, O/C ratio, and crystallinity). And the latter had significant effects on the adsorption capacity of heavy metals on MPs, accounting for 51.0% of the contribution. Thus, it can be documented that biodegradable and conventional MPs will pose physical and chemical risks to the environment. When considering that the widespread adoption of biodegradable plastics as a substitute for conventional plastics, the potential threats of biodegradable plastics and their generated MPs to marine ecosystems and human health should be deserved more attention in future research.

Author statement

Min Shi: Methodology, Investigation, Formal analysis, Visualization, Writing - original draft, Writing - review & editing. Qun Xie: Methodology, Writing - review & editing. Zhen-Liang Li: Investigation, Data curation. Yun-Feng Pan: Investigation. Zhen Yuan: Investigation. Lang Lin: Writing - review & editing. Heng-Xiang Li: Conceptualization, Investigation, Writing - review & editing, Supervision, Funding acquisition. Xiang-Rong Xu: Writing - review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2023.121158.

References

Aghilinasrollahabadi, K., Salehi, M., Fujiwara, T., 2021. Investigate the influence of microplastics weathering on their heavy metals uptake in stormwater. J. Hazard Mater. 408, 124439 https://doi.org/10.1016/j.jhazmat.2020.124439.

Alimi, O.S., Farner Budarz, J., Hernandez, L.M., Tufenkji, N., 2018. Microplastics and nanoplastics in aquatic environments: aggregation, deposition, and enhanced contaminant transport. Environ. Sci. Technol. 52 (4), 1704–1724. https://doi.org/10.1021/acs.est.7b05559.

Ashton, K., Holmes, L., Turner, A., 2010. Association of metals with plastic production pellets in the marine environment. Mar. Pollut. Bull. 60 (11), 2050–2055. https://doi.org/10.1016/j.marpolbul.2010.07.014.

Bao, R., Pu, J., Xie, C., Mehmood, T., Chen, W., Gao, L., Lin, W., Su, Y., Lin, X., Peng, L., 2022. Aging of biodegradable blended plastic generates microplastics and attached bacterial communities in air and aqueous environments. J. Hazard Mater. 434, 128891 https://doi.org/10.1016/j.jhazmat.2022.128891.

Beltrán-Sanahuja, A., Benito-Kaesbach, A., Sánchez-García, N., Sanz-Lázaro, C., 2021. Degradation of conventional and biobased plastics in soil under contrasting environmental conditions. Sci. Total Environ. 787, 147678 https://doi.org/10.1016/j.scitotenv.2021.147678.

Brennecke, D., Duarte, B., Paiva, F., Caçador, I., Canning-Clode, J., 2016. Microplastics as vector for heavy metal contamination from the marine environment. Estuar. Coast Shelf Sci. 178, 189–195. https://doi.org/10.1016/j.ecss.2015.12.003.

Briassoulis, D., Babou, E., Hiskakis, M., Kyrikou, I., 2015. Analysis of long-term degradation behaviour of polyethylene mulching films with pro-oxidants under real cultivation and soil burial conditions. Environ. Sci. Pollut. Res. 22 (4), 2584–2598. https://doi.org/10.1007/s11356-014-3464-9.

Cao, Y., Zhao, M., Ma, X., Song, Y., Zuo, S., Li, H., Deng, W., 2021. A critical review on the interactions of microplastics with heavy metals: mechanism and their combined effect on organisms and humans. Sci. Total Environ. 788, 147620 https://doi.org/10.1016/j.scitotenv.2021.147620.

Chen, B., Liang, X., Xu, W., Huang, X., Li, X., 2012. The changes in trace metal contamination over the last decade in surface sediments of the Pearl River Estuary, South China. Sci. Total Environ. 439, 141–149. https://doi.org/10.1016/j.scitotenv.2012.09.025.

Chen, C.C., Zhu, X., Xu, H., Chen, F., Ma, J., Pan, K., 2021a. Copper adsorption to microplastics and natural particles in seawater: a comparison of kinetics, isotherms, and bioavailability. Environ. Sci. Technol. 55 (20), 13923–13931. https://doi.org/10.1021/acs.est.1c04278.

Chen, Q., Wang, Q., Zhang, C., Zhang, J., Dong, Z., Xu, Q., 2021b. Aging simulation of thin-film plastics in different environments to examine the formation of microplastic. Water Res. 202, 117462 https://doi.org/10.1016/j.watres.2021.117462.

Chivrac, F., Kadlecová, Z., Pollet, E., Avérous, L., 2006. Aromatic copolyester-based nano-biocomposites: elaboration, structural characterization and properties. J. Polym. Environ. 14, 393–401. https://doi.org/10.1007/s10924-006-0033-4.

Dobaradaran, S., Schmidt, T.C., Nabipour, I., Khajeahmadi, N., Tajbakhsh, S., Saeedi, R., Mohammadi, M.J., Keshtkar, M., Khorsand, M., Ghasemi, F.F., 2018. Characterization of plastic debris and association of metals with microplastics in coastline sediment along the Persian Gulf. Waste Manage. (Tucson, Ariz.) 78, 649–658. https://doi.org/10.1016/j.wasman.2018.06.037.

dos Santos Rosa, D., Calil, M.R., das Gracas Fassina Guedes, C., T.C R., 2004. Biodegradability of thermally aged PHB, PHB-V, and PCL in soil compostage. J. Polym. Environ. 12, 239–245, 10.1007/s10924-004-8151-3.

European-Bioplastics, 2021. Bioplastic Market Development Update 2021. https://www.european-bioplastics.org/market/.

Feng, H., Liu, Y., Xu, Y., Li, S., Liu, X., Dai, Y., Zhao, J., Yue, T., 2022. Benzo[a]pyrene and heavy metal ion adsorption on nanoplastics regulated by humic acid: cooperation/competition mechanisms revealed by molecular dynamics simulations. J. Hazard Mater. 424, 127431 https://doi.org/10.1016/j.jhazmat.2021.127431.

Fischer, E.W., Sterzel, H.J., Wegner, G., 1973. Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical reactions. Kolloid-Z. u. Z. Polymere 251, 980–990. https://doi.org/10.1007/BF01498927.

Fojt, J., David, J., Prikryl, R., Řezáčová, V., Kučerík, J., 2020. A critical review of the overlooked challenge of determining micro-bioplastics in soil. Sci. Total Environ. 745, 140975 https://doi.org/10.1016/j.scitotenv.2020.140975.

Fu, Q., Tan, X., Ye, S., Ma, L., Gu, Y., Zhang, P., Chen, Q., Yang, Y., Tang, Y., 2021. Mechanism analysis of heavy metal lead captured by natural-aged microplastics. Chemosphere 270, 128624. https://doi.org/10.1016/j.chemosphere.2020.128624.

Gao, F., Li, J., Sun, C., Zhang, L., Jiang, F., Cao, W., Zheng, L., 2019. Study on the capability and characteristics of heavy metals enriched on microplastics in marine environment. Mar. Pollut. Bull. 144, 61–67. https://doi.org/10.1016/j.marpolbul.2019.04.039.

Godoy, V., Blázquez, G., Calero, M., Quesada, L., Martín-Lara, M.A., 2019. The potential of microplastics as carriers of metals. Environ. Pollut. 255, 113363 https://doi.org/10.1016/j.envpol.2019.113363.

Guan, Y., Gong, J., Song, B., Li, J., Fang, S., Tang, S., Cao, W., Li, Y., Chen, Z., Ye, J., Cai, Z., 2022. The effect of UV exposure on conventional and degradable microplastics adsorption for Pb (II) in sediment. Chemosphere 286, 131777. https://doi.org/10.1016/j.chemosphere.2021.131777.

Guo, X., Hu, G., Fan, X., Jia, H., 2020. Sorption properties of cadmium on microplastics: the common practice experiment and A two-dimensional correlation spectroscopic study. Ecotoxicol. Environ. Saf. 190, 110118 https://doi.org/10.1016/j.ecoenv.2019.110118.

Guo, X., Wang, J., 2019. The chemical behaviors of microplastics in marine environment: a review. Mar. Pollut. Bull. 142, 1–14. https://doi.org/10.1016/j.marpolbul.2019.03.019.

Hakkarainen, M., Albertsson, A.C., 2004. Environmental degradation of polyethylene. Adv. Polym. Sci. 169, 177–199. https://doi.org/10.1007/b13523.

Holmes, L.A., Turner, A., Thompson, R.C., 2012. Adsorption of trace metals to plastic resin pellets in the marine environment. Environ. Pollut. 160, 42–48. https://doi.org/10.1016/j.envpol.2011.08.052.

Holmes, L.A., Turner, A., Thompson, R.C., 2014. Interactions between trace metals and plastic production pellets under estuarine conditions. Mar. Chem. 167, 25–32. https://doi.org/10.1016/j.marchem.2014.06.001.

Hüffer, T., Weniger, A.K., Hofmann, T., 2018. Sorption of organic compounds by aged polystyrene microplastic particles. Environ. Pollut. 236, 218–225. https://doi.org/10.1016/j.envpol.2018.01.022.

Jahnke, A., Arp, H.P.H., Escher, B.I., Gewert, B., Gorokhova, E., Kühnel, D., Ogonowski, M., Potthoff, A., Rummel, C., Schmitt-Jansen, M., Toorman, E., MacLeod, M., 2017. Reducing uncertainty and confronting ignorance about the possible impacts of weathering plastic in the marine environment. Environ. Sci. Technol. Lett. 4 (3), 85–90. https://doi.org/10.1021/acs.estlett.7b00008.

Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., Law, K.L., 2015. Plastic waste inputs from land intothe ocean. Science 347 (6223), 768–771. https://doi.org/10.1126/science.1260352.

Jia, H., Zhang, M., Weng, Y., Zhao, Y., Li, C., Kanwal, A., 2021. Degradation of poly (butylene adipate-co-terephthalate) by *Stenotrophomonas* sp. YCJ1 isolated from farmland soil. J. Environ. Sci. 103, 50–58. https://doi.org/10.1016/j.jes.2020.10.001.

Kanwal, A., Zhang, M., Sharaf, F., Li, C., 2021. Enzymatic degradation of poly (butylene adipate co-terephthalate) (PBAT) copolymer using lipase B from *Candida antarctica* (CALB) and effect of PBAT on plant growth. Polym. Bull. https://doi.org/10.1007/s00289-021-03946-w.

Khalid, N., Aqeel, M., Noman, A., Khan, S.M., Akhter, N., 2021. Interactions and effects of microplastics with heavy metals in aquatic and terrestrial environments. Environ. Pollut. 290, 118104 https://doi.org/10.1016/j.envpol.2021.118104.

Koenig, M.F., Huangt, S.J., 1995. Biodegradable blends and composites of polycaprolactone and starch derivatives. Polymer 36 (9), 1877–1882. https://doi.org/10.1016/0032-3861(95)90934-T.

Kubowicz, S., Booth, A.M., 2017. Biodegradability of plastics: challenges and misconceptions. Environ. Sci. Technol. 51 (21), 12058–12060. https://doi.org/10.1021/acs.est.7b04051.

Lambert, S., Wagner, M., 2017. Environmental performance of bio-based and biodegradable plastics: the road ahead. Chem. Soc. Rev. 46, 6855–6871. https://doi.org/10.1039/C7CS00149E.

Lebreton, L.C.M., van der Zwet, J., Damsteeg, J.W., Slat, B., Andrady, A., Reisser, J., 2017. River plastic emissions to the world's oceans. Nat. Commun. 8, 15611 https://doi.org/10.1038/ncomms15611.

Li, R., Liu, Y., Sheng, Y., Xiang, Q., Zhou, Y., Cizdziel, J.V., 2020. Effect of prothioconazole on the degradation of microplastics derived from mulching plastic film: apparent change and interaction with heavy metals in soil. Environ. Pollut. 260, 113988 https://doi.org/10.1016/j.envpol.2020.113988.

Li, X., Mei, Q., Chen, L., Zhang, H., Dong, B., Dai, X., He, C., Zhou, J., 2019. Enhancement in adsorption potential of microplastics in sewage sludge for metal pollutants after the wastewater treatment process. Water Res. 157, 228–237. https://doi.org/10.1016/j.watres.2019.03.069.

Li, Y., Wang, X., Wang, Y., Sun, Y., Xia, S., Zhao, J., 2022. Effect of biofilm colonization on Pb(II) adsorption onto poly(butylene succinate) microplastic during its

biodegradation. Sci. Total Environ. 833, 155251 https://doi.org/10.1016/j.scitotenv.2022.155251.
Liao, J., Chen, Q., 2021. Biodegradable plastics in the air and soil environment: low degradation rate and high microplastics formation. J. Hazard Mater. 418, 126329 https://doi.org/10.1016/j.jhazmat.2021.126329.
Liao, Y.L., Yang, J.Y., 2020. Microplastic serves as a potential vector for Cr in an in-vitro human digestive model. Sci. Total Environ. 703, 134805 https://doi.org/10.1016/j.scitotenv.2019.134805.
Liu, P., Lu, K., Li, J., Wu, X., Qian, L., Wang, M., Gao, S., 2020. Effect of aging on adsorption behavior of polystyrene microplastics for pharmaceuticals: adsorption mechanism and role of aging intermediates. J. Hazard Mater. 384, 121193 https://doi.org/10.1016/j.jhazmat.2019.121193.
Liu, P., Qian, L., Wang, H., Zhan, X., Lu, K., Gu, C., Gao, S., 2019. New insights into the aging behavior of microplastics accelerated by advanced oxidation processes. Environ. Sci. Technol. 53 (7), 3579–3588. https://doi.org/10.1021/acs.est.9b00493.
Liu, P., Wu, X., Huang, H., Wang, H., Shi, Y., Gao, S., 2021. Simulation of natural aging property of microplastics in Yangtze River water samples via a rooftop exposure protocol. Sci. Total Environ. 785, 147265 https://doi.org/10.1016/j.scitotenv.2021.147265.
Liu, S., Huang, J., Zhang, W., Shi, L., Yi, K., Yu, H., Zhang, C., Li, S., Li, J., 2022a. Microplastics as a vehicle of heavy metals in aquatic environments: a review of adsorption factors, mechanisms, and biological effects. J. Environ. Manag. 302, 113995 https://doi.org/10.1016/j.jenvman.2021.113995.
Liu, Y., Zhang, J., Cao, W., Hu, Y., Shen, W., 2022b. The influence of Pb(II) adsorption on (Non) biodegradable microplastics by UV/O_3 oxidation treatment. J. Environ. Chem. Eng. 10 (6) https://doi.org/10.1016/j.jece.2022.108615.
Luo, H., Liu, C., He, D., Xu, J., Sun, J., Li, J., Pan, X., 2022. Environmental behaviors of microplastics in aquatic systems: a systematic review on degradation, adsorption, toxicity and biofilm under aging conditions. J. Hazard Mater. 423, 126915 https://doi.org/10.1016/j.jhazmat.2021.126915.
Luo, Y., Zhang, Y., Xu, Y., Guo, X., Zhu, L., 2020. Distribution characteristics and mechanism of microplastics mediated by soil physicochemical properties. Sci. Total Environ. 726, 138389 https://doi.org/10.1016/j.scitotenv.2020.138389.
Lv, S., Liu, X., Gu, J., Jiang, Y., Tan, H., Zhang, Y., 2017. Microstructure analysis of polylactic acid-based composites during degradation in soil. Int. Biodeterior. Biodegrad. 122, 53–60. https://doi.org/10.1016/j.ibiod.2017.04.017.
Lv, S., Zhang, Y., Gu, J., Tan, H., 2018. Soil burial-induced chemical and thermal changes in starch/poly (lactic acid) composites. Int. J. Biol. Macromol. 113, 338–344. https://doi.org/10.1016/j.ijbiomac.2018.02.139.
Lv, Y., Huang, Y., Yang, J., Kong, M., Yang, H., Zhao, J., Li, G., 2015. Outdoor and accelerated laboratory weathering of polypropylene: a comparison and correlation study. Polym. Degrad. Stabil. 112, 145–159. https://doi.org/10.1016/j.polymdegradstab.2014.12.023.
Mai, L., You, S.N., He, H., Bao, L.J., Liu, L.Y., Zeng, E.Y., 2019. Riverine microplastic pollution in the Pearl River Delta, China: are modeled estimates accurate? Environ. Sci. Technol. 53 (20), 11810–11817. https://doi.org/10.1021/acs.est.9b04838.
Mao, R., Lang, M., Yu, X., Wu, R., Yang, X., Guo, X., 2020. Aging mechanism of microplastics with UV irradiation and its effects on the adsorption of heavy metals. J. Hazard Mater. 393, 122515 https://doi.org/10.1016/j.jhazmat.2020.122515.
Marinho, B.A., Cristóvão, R.O., Boaventura, R.A.R., Vilar, V.J.P., 2018. As(III) and Cr(VI) oxyanion removal from water by advanced oxidation/reduction processes—a review. Environ. Sci. Pollut. Res. 26 (3), 2203–2227. https://doi.org/10.1007/s11356-018-3595-5.
Martucci, J.F., Ruseckaite, R.A., 2015. Biodegradation behavior of three-layer sheets based on gelatin and poly (lactic acid) buried under indoor soil conditions. Polym. Degrad. Stabil. 116, 36–44. https://doi.org/10.1016/j.polymdegradstab.2015.03.005.
Mato, Y., Isobe, T., Takada, H., Kanehiro, H., Ohtake, C., Kaminuma, T., 2001. Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. Environ. Sci. Technol. 35, 318–324. https://doi.org/10.1021/es0010498.
Müller, A., Becker, R., Dorgerloh, U., Simon, F.G., Braun, U., 2018. The effect of polymer aging on the uptake of fuel aromatics and ethers by microplastics. Environ. Pollut. 240, 639–646. https://doi.org/10.1016/j.envpol.2018.04.127.
Nazareth, M., Marquesa, M.R.C., Leitea, M.C.A., Castro, Í.B., 2019. Commercial plastics claiming biodegradable status: is this also accurate for marine environments. J. Hazard Mater. 366, 714–722. https://doi.org/10.1016/j.jhazmat.2018.12.052.
Purwiyanto, A.I.S., Suteja, Y., Trisno, Ningrum P.S., Putri, W.A.E., Rozirwan, Agustriani F., Fauziyah, Cordova M.R., Koropitan, A.F., 2020. Concentration and adsorption of Pb and Cu in microplastics: case study in aquatic environment. Mar. Pollut. Bull. 158, 111380 https://doi.org/10.1016/j.marpolbul.2020.111380.
Qin, M., Chen, C., Song, B., Shen, M., Cao, W., Yang, H., Zeng, G., Gong, J., 2021. A review of biodegradable plastics to biodegradable microplastics: another ecological threat to soil environments? J. Clean. Prod. 312 https://doi.org/10.1016/j.jclepro.2021.127816.
Rochman, C.M., 2018. Microplastics research-from sink to source. Science 360 (6384), 28–29. https://doi.org/10.1126/science.aar7734.
Rochman, C.M., Hentschel, B.T., Teh, S.J., 2014. Long-term sorption of metals is similar among plastic types: implications for plastic debris in aquatic environments. PLoS One 9 (1), e85433. https://doi.org/10.1371/journal.pone.0085433.
Rouillon, C., Bussiere, P.O., Desnoux, E., Collin, S., Vial, C., Therias, S., Gardette, J.L., 2016. Is carbonyl index a quantitative probe to monitor polypropylene photodegradation? Polym. Degrad. Stabil. 128, 200–208. https://doi.org/10.1016/j.polymdegradstab.2015.12.011.
Rujnić-Sokele, M., Pilipović, A., 2017. Challenges and opportunities of biodegradable plastics: a mini review. Waste Manag. Res. 35 (2), 132–140. https://doi.org/10.1177/0734242X16683272.
Sahebian, S., Zebarjad, S.M., Vahdati Khaki, J., Sajjadi, S.A., 2009. The effect of nano-sized calcium carbonate on thermodynamic parameters of HDPE. J. Mater. Process. Technol. 209 (3), 1310–1317. https://doi.org/10.1016/j.jmatprotec.2008.03.066.
Shen, M., Song, B., Zeng, G., Zhang, Y., Huang, W., Wen, X., Tang, W., 2020. Are biodegradable plastics a promising solution to solve the global plastic pollution? Environ. Pollut. 263, 114469 https://doi.org/10.1016/j.envpol.2020.114469.
Shruti, V.C., Kutralam-Muniasamy, G., 2019. Bioplastics: missing link in the era of microplastics. Sci. Total Environ. 697, 134139 https://doi.org/10.1016/j.scitotenv.2019.134139.
Song, Y.K., Hong, S.H., Jang, M., Han, G.M., Jung, S.W., Shim, W.J., 2017. Combined effects of UV exposure duration and mechanical abrasion on microplastic fragmentation by polymer type. Environ. Sci. Technol. 51 (8), 4368–4376. https://doi.org/10.1021/acs.est.6b06155.
Sun, Y., Wang, X., Xia, S., Zhao, J., 2022. Cu(II) adsorption on poly(lactic acid) microplastics: significance of microbial colonization and degradation. Chem. Eng. J. 429 https://doi.org/10.1016/j.cej.2021.132306.
Tabasi, R.Y., Ajji, A., 2015. Selective degradation of biodegradable blends in simulated laboratory composting. Polym. Degrad. Stabil. 120, 435–442. https://doi.org/10.1016/j.polymdegradstab.2015.07.020.
Ter Halle, A., Ladirat, L., Martignac, M., Mingotaud, A.F., Boyron, O., Perez, E., 2017. To what extent are microplastics from the open ocean weathered? Environ. Pollut. 227, 167–174. https://doi.org/10.1016/j.envpol.2017.04.051.
Tokiwa, Y., Calabia, B.P., Ugwu, C.U., Aiba, S., 2009. Biodegradability of plastics. Int. J. Mol. Sci. 10 (9), 3722–3742. https://doi.org/10.3390/ijms10093722.
Velez, J.F.M., Shashoua, Y., Syberg, K., Khan, F.R., 2018. Considerations on the use of equilibrium models for the characterisation of HOC-microplastic interactions in vector studies. Chemosphere 210, 359–365. https://doi.org/10.1016/j.chemosphere.2018.07.020.
Viera, J.S.C., Marques, M.R.C., Nazareth, M.C., Jimenez, P.C., Sanz-Lázaro, C., Castro, I. B., 2021. Are biodegradable plastics an environmental rip off? J. Hazard Mater. 416, 125957 https://doi.org/10.1016/j.jhazmat.2021.125957.
Volova, T.G., Boyandin, A.N., Vasiliev, A.D., Karpov, V.A., Prudnikova, S.V., Mishukova, O.V., Boyarskikh, U.A., Filipenko, M.L., Rudnev, V.P., Bá Xuân, B., Việt Dũng, V., Gitelson, I.I., 2010. Biodegradation of polyhydroxyalkanoates (PHAs) in tropical coastal waters and identification of PHA-degrading bacteria. Polym. Degrad. Stabil. 95 (12), 2350–2359. https://doi.org/10.1016/j.polymdegradstab.2010.08.023.
Wang, H.J., Lin, H.H.H., Hsieh, M.C., Lin, A.Y., 2022a. Photoaged polystyrene microplastics serve as photosensitizers that enhance cimetidine photolysis in an aqueous environment. Chemosphere 290, 133352. https://doi.org/10.1016/j.chemosphere.2021.133352.
Wang, X., Zhang, R., Li, Z., Yan, B., 2022b. Adsorption properties and influencing factors of Cu(II) on polystyrene and polyethylene terephthalate microplastics in seawater. Sci. Total Environ. 812, 152573 https://doi.org/10.1016/j.scitotenv.2021.152573.
Wu, X., Liu, P., Wang, H., Huang, H., Shi, Y., Yang, C., Gao, S., 2021. Photo aging of polypropylene microplastics in estuary water and coastal seawater: important role of chlorine ion. Water Res. 202, 117396 https://doi.org/10.1016/j.watres.2021.117396.
Xie, M., Huang, J.L., Lin, Z., Chen, R., Tan, Q.G., 2021a. Field to laboratory comparison of metal accumulation on aged microplastics in coastal waters. Sci. Total Environ. 797, 149108 https://doi.org/10.1016/j.scitotenv.2021.149108.
Xie, Q., Li, H.X., Lin, L., Li, Z.L., Huang, J.S., Xu, X.R., 2021b. Characteristics of expanded polystyrene microplastics on island beaches in the Pearl River Estuary: abundance, size, surface texture and their metals-carrying capacity. Ecotoxicology 30 (8), 1632–1643. https://doi.org/10.1007/s10646-020-02329-7.
Ye, S., Cheng, M., Zeng, G., Tan, X., Wu, H., Liang, J., Shen, M., Song, B., Liu, J., Yang, H., Zhang, Y., 2020. Insights into catalytic removal and separation of attached metals from natural-aged microplastics by magnetic biochar activating oxidation process. Water Res 179, 115876. https://doi.org/10.1016/j.watres.2020.115876.
Yu, A., Sun, X., Tang, S., Zhang, Y., Li, M., Wang, X., 2021. Adsorption mechanism of cadmium on polystyrene microplastics containing hexabromocyclododecane. Environ. Technol. Innovat. 24, 102036 https://doi.org/10.1016/j.eti.2021.102036.
Zhao, G., Ye, S., Yuan, H., Ding, X., Wang, J., Laws, E.A., 2018. Surface sediment properties and heavy metal contamination assessment in river sediments of the Pearl River Delta, China. Mar. Pollut. Bull. 136, 300–308. https://doi.org/10.1016/j.marpolbul.2018.09.035.
Zhen, G., Li, Y., Tong, Y., Yang, L., Zhu, Y., Zhang, W., 2016. Temporal variation and regional transfer of heavy metals in the Pearl (Zhujiang) River, China. Environ. Sci. Pollut. Res. 23, 8410–8420. https://doi.org/10.1007/s11356-016-6077-7.
Zhou, Y., Yang, Y., Liu, G., He, G., Liu, W., 2020. Adsorption mechanism of cadmium on microplastics and their desorption behavior in sediment and gut environments: the roles of water pH, lead ions, natural organic matter and phenanthrene. Water Res. 184, 116209 https://doi.org/10.1016/j.watres.2020.116209.
Zou, J., Liu, X., Zhang, D., Yuan, X., 2020. Adsorption of three bivalent metals by four chemical distinct microplastics. Chemosphere 248, 126064. https://doi.org/10.1016/j.chemosphere.2020.126064.