



Field to laboratory comparison of metal accumulation on aged microplastics in coastal waters



Minwei Xie^{a,b,c}, Jun-Lin Huang^a, Zhi Lin^a, Rong Chen^{a,b,c}, Qiao-Guo Tan^{a,b,c,*}

^a State Key Laboratory of Marine Environmental Science and College of the Environment and Ecology, Xiamen University, Xiamen, Fujian 361102, China

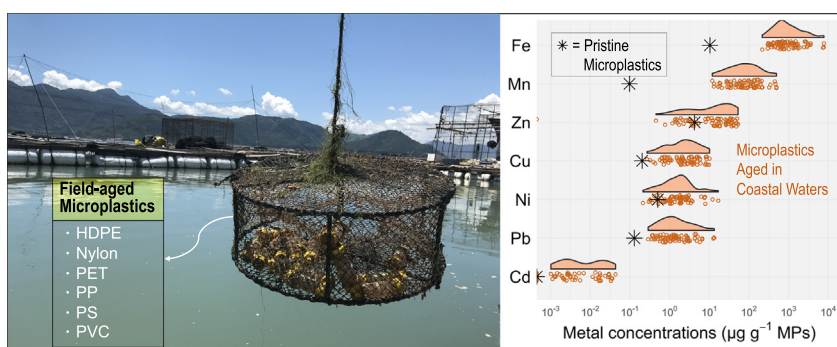
^b Key Laboratory of the Coastal and Wetland Ecosystems of Ministry of Education, Xiamen, Fujian 361102, China

^c Center for Marine Environmental Chemistry and Toxicology, Xiamen University, Xiamen, Fujian 361102, China

HIGHLIGHTS

- Ageing in coastal waters elevates metal adsorption capacity of microplastics.
- Metals accumulated in the field reflect metal contamination of the ageing sites.
- Metals accumulated in the field are affected by polymeric types.
- Lab adsorption of metals on aged microplastics is mediated by Fe/Mn oxide coatings.

GRAPHICAL ABSTRACT



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ABSTRACT

The ubiquity of microplastics in the environment has attracted much attention on their risks. Though newly produced plastics were considered inert to aqueous metals, a few studies suggest aged microplastics can accumulate metals. Still, knowledge gap exists on the comparability of metal accumulation in field condition and that acquired in controlled laboratory settings. Accordingly, we comparatively assessed the field accumulation and laboratory adsorption of metals on aged microplastics in coastal waters. Microplastics of different polymeric types were aged for 8 weeks at three coastal sites with different contamination levels. Microplastics accumulated metals to substantial concentrations during ageing (median concentrations, $\mu\text{g g}^{-1}$: Fe = 950, Mn = 94, Zn = 19, Cu = 2.8, Ni = 1.7, Pb = 1.6, and Cd = 0.005). Adsorption capacity of (aged) microplastics was evaluated in laboratory using a stable isotope tracer method. At environmentally realistic concentrations ($\mu\text{g L}^{-1}$, $^{114}\text{Cd} = 1.7$, $^{65}\text{Cu} = 4.4$, $^{62}\text{Ni} = 5.4$, $^{206}\text{Pb} = 0.5$, and $^{68}\text{Zn} = 13$), the median concentrations of newly adsorbed isotopes on the aged microplastics were 0.01, 1.4, 0.07, 0.56, and $1.1 \mu\text{g g}^{-1}$, respectively, one to two orders of magnitude higher than those adsorbed on pristine microplastics. However, the composition pattern of metals accumulated on aged microplastics differed from the composition of metals newly adsorbed in laboratory: the prior one reflected the contamination status of ageing sites and varied by polymeric types; whereas the laboratory newly adsorbed metals on aged microplastics were uniformly correlated to particulate Fe and Mn concentrations, suggesting Fe and Mn mineral coatings mediated the ensuing metal adsorption. Such discrepancy unveiled the complexity of metal accumulation behavior in the real environment and highlighted that cares should be taken when translating laboratory findings to risk assessment of metal contaminated microplastics in the real environment.

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* Corresponding author at: State Key Laboratory of Marine Environmental Science and College of the Environment and Ecology, Xiamen University, Xiamen, Fujian 361102, China.
E-mail address: tanqg@xmu.edu.cn (Q.-G. Tan).

1. Introduction

Microplastics are ubiquitous and have extended their footprints into almost all types of aquatic ecosystem, including regions that are far away from anthropogenic activities, such as in the Arctic or deep-sea sediments (Koelmans et al., 2016; Obbard et al., 2014; Song et al., 2021; Van Cauwenberghe et al., 2013). The potential threats of microplastic contamination to the health of ecosystems have been increasingly recognized (Mai et al., 2020; Reed, 2015; Wright and Kelly, 2017) and consequently the number of studies on this topic has grown rapidly (Alimi et al., 2018; Yu et al., 2019). Yet, the science of it is still in infancy and knowledge of the risk is fragmentary (Koelmans et al., 2016; Kramm et al., 2018).

Due to the recalcitrant nature of microplastics in aquatic environment, the ecotoxicological consequences caused by their presence have been extensively studied (Burns and Boxall, 2018; Du et al., 2021). After intake, the microplastics may inhibit growth, disorder behavior, reduce feeding, and impair survival and reproduction for different aquatic organisms (Cole et al., 2013; Du et al., 2021; Gardon et al., 2018; Garrido et al., 2019; Lee et al., 2013). The hazards are caused either by physical damages to organisms or by dosing unintentional chemicals they carry (Lambert et al., 2017; Rillig et al., 2021). Although the plastic polymers may contain chemicals at the stage of mass-production, such as hazardous residual monomers or additives, release of these chemicals are often retarded due to the slow diffusion rates in the polymer matrix (Rillig et al., 2021; Rochman et al., 2014). More frequently, the transfer of contaminants by microplastics as a vector from the environment to organism constitutes a more important exposure route (Koelmans et al., 2016).

While microplastics as a vector for organic contaminants is well established (Koelmans et al., 2016), the role as a vector for metals has been studied recently (Dobaradaran et al., 2018; Hodson et al., 2017; Holmes et al., 2012; Holmes et al., 2014; Lee et al., 2021; Rochman et al., 2014). Plastic is generally considered inert to aqueous metals and is thus frequently used to store metal solutions (Giusti et al., 1994; Vedolin et al., 2018). However, increasing evidences showed that microplastics indeed have the potential to adsorb metals (Ashton et al., 2010; Holmes et al., 2012; Holmes et al., 2014; Lee et al., 2021; Rochman et al., 2014), probably due to their larger specific surface area relative to a regular-size plastic container. Adsorption of metals on microplastics was influenced by various factors, including typical water quality parameters (e.g. salinity, pH, and dissolved organic matter) and the properties of microplastics (e.g. particle size, porosity, and morphology) (Godoy et al., 2019; Naqash et al., 2020; Yu et al., 2019). Polymeric type constitutes another important factor and influences the sorption of organic contaminants (Fred-Ahmadu et al., 2020; Rochman et al., 2013), but its effect on the sorption of metals were inconsistently reported (Godoy et al., 2019; Rochman et al., 2014).

Besides, ageing also influenced metal adsorption capacity of microplastics. In multiple controlled laboratory studies (Holmes et al., 2012; Holmes et al., 2014; Turner and Holmes, 2015), the researchers consistently observed enhanced metal adsorption capacity on aged (or beached) microplastics compared with pristine pellets. In these studies, to discriminate metals newly adsorbed from those accumulated in the field, aged microplastics with low pre-accumulated metals were selected on purpose for laboratory adsorption experiments. However, it is unwarranted that microplastics aged in a more contaminated environment exhibit similar adsorption behavior as the “clean” ones. Besides, there is increasing concerns about the questionable comparability resulted from the low similarity between microplastics used in laboratory studies and those from the field (da Costa et al., 2016; Phuong et al., 2016). Thus comparative studies are needed to investigate the accumulation of metals on microplastics in the field and in the laboratory experiments. These knowledge gaps hamper the translation of laboratory findings to assessment of ecotoxicological impacts and exposure risks of microplastics in the real environment.

Accordingly, the primary objective in the present study is to advance our understanding of metal accumulation on aged microplastics, with particular focus to compare the metal accumulation patterns on microplastics aged in the field and in controlled laboratory conditions. To do so, we aged microplastics (of different polymeric types with similar initial conditions) in different coastal waters for 8 weeks, immediately characterized the metal compositions on these freshly aged microplastics, and assessed their adsorption capacity using the metal stable isotope tracer technique. The findings from this comparative assessment should improve our understanding of the difference in metal accumulation behavior of aged microplastics in field condition and in controlled laboratory setting.

2. Materials and methods

2.1. Microplastics and seawater

Six types of microplastics were made in laboratory from daily commercial plastic products made of different polymers, including low-density polyethylene (LDPE), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polystyrene (PS), polypropylene (PP), and polyamide (Nylon) plastics. Shredded pieces of these plastic products (~2 cm × 2 cm) were mechanically pulverized to micron to millimeter-scale fragments. These microplastics were then sieved into two size fractions (180 μm–3 mm and 75–180 μm), each ultrasonicated at 40 kHz for 10 min to remove attached plastic debris, thoroughly rinsed with deionized water, freeze dried, and stored in a desiccator for further characterization and use.

The seawater (salinity = 30, pH = 8.0) used for laboratory adsorption experiments were collected from the Tong'an Bay, Xiamen. The seawater was filtered using a cellulose acetate membrane with a pore size of 0.22 μm before use; pH of the seawater spiked with metal isotopes (stored in 5% HNO₃) was adjusted back to 8.0 if necessary by adding microliters 4.0 mol L⁻¹ NaOH. All plastic and glass containers used in the present study were cleaned by soaking into 10% HNO₃ for 24 h, followed by thoroughly rinsing with deionized water (18.2 MΩ cm, Millipore).

2.2. Ageing sites

Microplastics were aged in different estuarine-marine environments at three sites respectively located in an estuary (Jiulong River Estuary), an inner bay (Tong'an Bay), and an open bay (Shenhu Bay) (Fig. S1). These three areas are all heavily impacted by different anthropogenic activities, and show different extents of metal contamination. Jiulong River Estuary was previously reported to have substantially elevated metal concentrations due to domestic and industrial wastewater discharge from upstream (Tan et al., 2015), and thus is the most contaminated among the three areas. The Tong'an Bay is an inner bay and has low hydrodynamics. This site locates near an aquaculture region and receives water with excess organics and nutrients but less metals. The Shenhu Bay is an open bay that experiences intense hydrodynamic exchange with the open sea and is affected by many anthropogenic activities (such as cargo-shipping) that cause intermediate level of metal contamination.

2.3. Field ageing of microplastics

To mimic microplastic recovered in natural waters, the laboratory made microplastics were aged in the three estuarine-marine sites. Ageing of microplastics in the environment is an ongoing process that continuously occurs for many years (Rochman et al., 2014). For logistic considerations (e.g. feasibility, costs), the microplastics were aged for 8 weeks, which is reasonably long enough to see substantial ageing and metal adsorption of microplastics (Ashton et al., 2010). Self-made exposure chambers were made by gluing two half pieces (the cap-end half) of 50 mL centrifuge tubes together (Fig. S2). The two caps were cut open and covered by nylon meshes (75 μm pore size), allowing

seawater to flow freely through the chamber while retaining microplastics within the chamber during exposure. These chambers were placed within a large crab trap (cylindrical shape, 0.5 m in diameter and 0.2 m in height, 1 cm pore size of the mesh), and immersed into water at around 3 m depth.

Following 8 weeks of ageing, the microplastics were retrieved, transported back to the laboratory, and gently rinsed with deionized water to remove apparent sediment particles attached. Each type of microplastics was then separated into two aliquots, one was freeze-dried for metal concentration analysis, and the other aliquot (fresh microplastics) was used for laboratory adsorption experiments.

2.4. Laboratory adsorption experiments

To assess the adsorption capacity of aged and pristine microplastics, two types of adsorption experiments were executed in laboratory. In the first type of experiment, both pristine and aged microplastics were immersed in the same batch of solution that was added with a cocktail of different metal isotopes (^{114}Cd : $1.7 \mu\text{g L}^{-1}$, ^{65}Cu : $4.4 \mu\text{g L}^{-1}$, ^{62}Ni : $5.4 \mu\text{g L}^{-1}$, ^{206}Pb : $0.5 \mu\text{g L}^{-1}$, and ^{68}Zn : $13 \mu\text{g L}^{-1}$; isotopic purity: 99.07% for ^{114}Cd , 99.5% for ^{65}Cu , 98.02% for ^{62}Ni , 99.51% for ^{206}Pb , and 99.26% for ^{68}Zn , ISOFLEX, San Francisco, California, USA). The second type of adsorption experiment aims to measure the adsorption capacity of microplastics under varying metal concentrations. Here, for logistic considerations (work load, cost, and the amount of microplastics required) and Cu being usually the most abundant and toxic among the five metals investigated (Ni, Cu, Zn, Pb and Cd) in aquatic systems (saltwater criterion continuous concentration of Cu is $3.1 \mu\text{g L}^{-1}$, lower than Cd $7.9 \mu\text{g L}^{-1}$, Ni $8.2 \mu\text{g L}^{-1}$, Pb $8.1 \mu\text{g L}^{-1}$, and Zn $81 \mu\text{g L}^{-1}$) (USEPA, 2007; Xie et al., 2021), only the adsorption isotherms of Cu were determined for the PP microplastic. In order to differentiate the metals newly adsorbed from those pre-accumulated during ageing in the field, stable metal isotopes (^{62}Ni , ^{65}Cu , ^{68}Zn , ^{206}Pb and ^{114}Cd) were used in both types of adsorption experiments to track the metals newly adsorbed.

2.4.1. Adsorption in metal (isotope) mixture solution

About 0.05 g (fresh weight) of aged and pristine microplastics were wrapped in nylon meshes (75 μm pore size), which were then attached on plastic rods, and immersed in a tank containing 10 L of seawater spiked with different metal isotopes. The target concentrations were set at environmentally realistic levels (Table S1, Supplementary Material). The seawater was continuously stirred and microplastics were equilibrated for a period of 24 h. Although it is desirable to do time-series measurements and thus obtain information on adsorption kinetics, we chose a single time point of 24 h as this is usually long enough to reach adsorption equilibrium (Holmes et al., 2012; Lin et al., 2021; Turner and Holmes, 2015), and to control the scale of the experiment so that we could adequately handle. The microplastics were then retrieved, rinsed with deionized water, freeze dried and stored for metal extraction and analysis. Seawater samples at the beginning and the end of the equilibration were also collected, acidified with nitric acid to a pH < 2, and stored for metal analysis.

2.4.2. Cu adsorption isotherm determination

Batched experiments were performed to determine the adsorption isotherm for Cu. Approximately 0.05 g PP microplastics were equilibrated in 15-mL centrifuge tubes containing 10 mL of seawater with different ^{65}Cu concentrations (nominal concentrations ranging from 10 to 1000 $\mu\text{g L}^{-1}$ in triplicates). The centrifuge tubes were rotated end-over-end at a rate of 30 round min^{-1} at $21 \pm 1 \text{ }^\circ\text{C}$ for 24 h. Following 24-h equilibration, the microplastics were separated from seawater by vacuum filtration (0.2 μm pore size, Isopore). The retained microplastics were gently rinsed with deionized water to remove solution remaining on particle surface, and then freeze dried and stored for metal extraction and analysis. The filtered seawater was also acidified to a pH < 2, and stored for metal concentration determination.

2.5. Characterization of microplastics

Physicochemical properties of pristine and aged microplastics were characterized for appearance, morphology and extractable metal concentrations. Both color and shape of pristine and aged microplastics were visually observed under a stereomicroscope (SMZ-1500, Nikon, Japan). A scanning electron microscope (SEM, Hitachi S4800) was used to observe the surface texture of microplastics before and after the ageing experiments. Since the open bay site has the most intensive hydrodynamics that may impact the surface texture of microplastics during ageing, the pristine microplastics and those aged in the open bay site were scanned and compared. Concentrations of metals bound to microplastics were determined by digesting ~0.05 g microplastics in 0.5 mL of concentrated HNO_3 at 80 $^\circ\text{C}$ for 12 h, and measuring dissolved metals in the digest.

2.6. Metal analysis and isotope data analysis

Concentrations of metals and metal isotopes were measured using an inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700x). Seawater samples were diluted 10-fold before metal analysis to minimize the interference of dissolved salts. Quality control processes include using internal standards, including ^{72}Ge , ^{103}Rh , ^{115}In , and ^{209}Bi , to correct sample matrix effect and instrument drift, measuring quality control standards ($10 \mu\text{g L}^{-1}$) after every 20 samples, and analyzing a standard reference material (SRM) sample. Because there is no SRM for analyzing microplastic-associated metals, the widely used mussel-tissue SRM (SRM 2976) was analyzed together with the samples to validate the performance of the ICP-MS instrument. Analyses were considered acceptable when the recoveries of metals were within 10% deviation from the certified values.

Concentration of newly adsorbed metal isotopes (new $[\text{xxxM}]$) was calculated by subtracting the background concentration from the current concentration (i.e., concentration after adsorption) using the following equation:

$$\text{new } [\text{xxxM}] = \left([\text{total M inferred from } \text{xxxM}] - [\text{total M inferred from unspiked M}] \right) \cdot \text{xxx}f \quad (1)$$

where xxxM is the spiked isotope of metal M, including ^{114}Cd , ^{65}Cu , ^{62}Ni , ^{206}Pb , and ^{68}Zn ; unspikedM is the unspiked isotope of M for background subtraction, including ^{111}Cd , ^{63}Cu , ^{60}Ni , ^{208}Pb , and ^{66}Zn , respectively; $[\text{total M inferred from } \text{xxxM}]$ and $[\text{total M inferred from unspiked M}]$ are the total concentrations of M reported by the ICP-MS instrument, when selecting the isotopes xxxM and unspikedM as the analyte, respectively; $\text{xxx}f$ is the natural relative abundance of xxxM (^{114}Cd : 28.73%; ^{65}Cu : 30.83%; ^{62}Ni : 3.634%; ^{206}Pb : 24.1%; ^{68}Zn : 18.75%). As the calibration standards were not prepared with pure isotopes but were a mixture of metal isotopes of natural relative abundance (Agilent, part number 5183–4688), the concentrations reported by the ICP-MS was the inferred total concentration of the metal rather than the concentration of the analyte isotope. Therefore, $[\text{total M inferred from } \text{xxxM}] \cdot \text{xxx}f$ is the concentration of xxxM after adsorption and $[\text{total M inferred from unspiked M}] \cdot \text{xxx}f$ is the background concentration of xxxM . More detailed information on stable isotope analysis is available in our previous papers (Lin et al., 2020; Tan et al., 2019).

2.7. Statistical analysis

The statistical analyses, including Pearson's correlation analysis (function *cor.test* and function *ggpairs* in package *GGally*), principal component analysis (PCA, function *prcomp* for analysis and package *factoextra* for visualization), two-way analysis of variance (ANOVA, function *aov*), and analysis of covariance (ANCOVA, function *aov*), were conducted in R (v4.0.3). Two-way ANOVA was used to compare concentrations of adsorbed metals across ageing sites and polymeric types. Concentrations

were logarithmic transformed when necessary to meet the assumptions of normal distribution (Shapiro-Wilk normality test) and homogeneity of variance (Levene's Test). Interaction effects were significant ($p < 0.05$) in all cases; therefore, the simple effects of sites and microplastic types were analyzed using post hoc multiple comparisons (Tukey's method for p value adjustment, function *emmeans* of package *emmeans*). Differences were considered significant when $p < 0.05$.

3. Results

3.1. Physical properties of pristine and aged microplastics

The pristine microplastics were in different shapes (Fig. S3). The PET microplastics were characterized by small heterogeneous flakes and chips, with angular edges; in contrast, the PVC, LDPE, PP and PS plastics were characterized by small pellets with more rounded edges. As the nylon microplastics were fragmented from nylon strings, they were mainly in the shape of short rods.

The SEM images showed that the surface texture of the pristine microplastics were mainly flaking (Fig. S4), without pits, notches, fractures, and other textures indicating oxidation or degradation (Cooper and Corcoran, 2010). The microplastics were aged in small chambers at a depth of 3 m and were not exposed to substantial hydrodynamic abrasion and solar radiation (Koelmans et al., 2016). Therefore, the 8-week ageing did not induce any drastic change on the surface texture (Fig. S4). However, the surface of these aged microplastics underwent a yellowing or browning effect, likely caused by the lodging of Fe rich minerals (Fig. S3) and this was evidenced by the elevated Fe concentrations on aged microplastics (Fig. 1 and Fig. S5).

3.2. Complex composition of metals on aged microplastics

Microplastics accumulated metals when aged in the field (Fig. 1). The median concentrations of Fe, Mn, Zn, Cu, Ni, Pb, and Cd on the aged microplastic were 950, 94, 19, 2.8, 1.7, 1.6, and $0.005 \mu\text{g g}^{-1}$, respectively. Compared with the pristine microplastics, concentrations of Fe, Mn, Cu, Pb and Cd were substantially elevated on the aged microplastics, while Ni and Zn concentrations in the majority of microplastics were slightly elevated or not influenced (Fig. S5).

Both ageing environment and polymeric types influenced metal compositions on microplastics. The PCA retained 84.8% of the data variance with three principal components (PC) (Fig. 2). The clustering of

metal variables and the distribution of data points (microplastics) on the biplot revealed compositional characters of metals on different microplastics. The projection of a data point on a metal vector indicated the concentration of this metal on the microplastic.

Metal compositions on microplastics differed between ageing environment (Fig. 2a). The inner bay site data points had low scores on both PCs, suggesting microplastics aged at the inner bay site accumulated relatively less metals. The data points from the open bay site scattered alongside the Ni and Cu vectors, but consistently registered low scores on PC1 represented by Fe, Pb, Mn, and Cd, suggesting the microplastics aged at this site varied considerably in Ni and Cu accumulation, but were consistently depleted of Fe, Pb, Mn, and Cd. The data points of the estuary site showed a bimodal distribution, with some of them showed high projections on all seven metal vectors, while the remaining exhibited low projections, indicating the bimodal distribution of metal concentrations on microplastics of different types.

The effects of polymeric type on metal enrichment becomes more visible in the biplot of PC1 and PC3 (Fig. 2b). Microplastics made of different polymers were separated more clearly on PC3, with PS and PVC microplastics had the highest positive scores while PET microplastics had the highest negative scores. Fe, Mn, Pb and Cu were correlated with PET, Nylon and LDPE while Cd, Ni and Zn were correlated with PS and PVC. Also need to note that the PS and PVC microplastics showed high projections on the Zn vector, indicating these two types of aged microplastics contained high Zn concentrations. However, this Zn enrichment was unlikely caused by ageing, but instead may be introduced during the fabrication process, as evidenced by the high Zn concentrations in the corresponding pristine microplastics (Fig. S5).

Overall, the PCA demonstrated complex composition of metals on aged microplastics. There lacked a simple and uniform correlation between microplastics and metals, suggesting that metal accumulation during ageing was influenced by multiple factors and processes and thus dependent on characteristics of both the sites and microplastics.

3.3. Uniform adsorption behavior of aged microplastics observed in laboratory

The use of metal stable isotopes discriminated metals newly adsorbed in the laboratory experiment from those accumulated in the field. The median concentrations of newly adsorbed ^{68}Zn , ^{65}Cu , ^{62}Ni , ^{206}Pb , and ^{114}Cd on aged microplastics were 1.1, 1.4, 0.07, 0.56, and $0.01 \mu\text{g g}^{-1}$, respectively (Fig. 3). Ageing substantially increased the adsorption capacity of metals on microplastics: compared with low concentrations of metal isotopes adsorbed on the pristine microplastics, the adsorptions on aged microplastics were at least an order of magnitude higher.

The concentration of metals newly adsorbed on aged microplastics were intercorrelated (Fig. S6), suggesting the adsorption of these metal isotopes may occur simultaneously and by the same mechanism. We suspect that the Fe and Mn minerals coated on the aged microplastics mediated the adsorption. This was supported by the unified correlations between concentrations of metal isotopes and the Fe and Mn concentrations across different types of microplastics ($p < 0.01$ for all metals, Fig. S7 and S8).

Besides the adsorption of metal isotope mixture at environmentally realistic levels, we also investigated the adsorption of ^{65}Cu at varying concentrations (ranging over two orders of magnitude) by determining the adsorption isotherms.

On a double logarithm scale, the ^{65}Cu adsorbed on the microplastics increased linearly with the dissolved ^{65}Cu concentrations at equilibrium (Fig. 4). Consistent with metal adsorption in isotope mixture solution, ^{65}Cu adsorbed on aged microplastics was significantly higher than that on pristine microplastics. The ageing history did not influence the adsorption of ^{65}Cu . The adsorption data was best fitted with a Freundlich model (Stumm and Morgan, 2012) and adsorption isotherms were generated for treatments with different ageing locations. When presented on a double logarithm scale, these linear adsorption isotherms showed similar

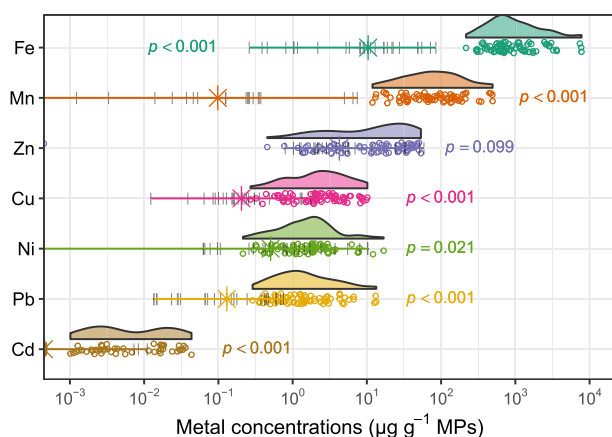


Fig. 1. Metal concentrations on pristine and aged microplastics. Raincloud plots show the distribution of metal concentrations on aged microplastics (the open circles represent individual samples); the stars indicate the median metal concentrations of the pristine microplastics (the rugs represent individual samples); p values indicate significance of the differences in metal concentrations between aged and pristine microplastics (post hoc multiple comparison after two-way ANOVA). Data on microplastics of different polymeric types are pooled in the plot; detailed data on each polymeric types are presented with Fig. S5.

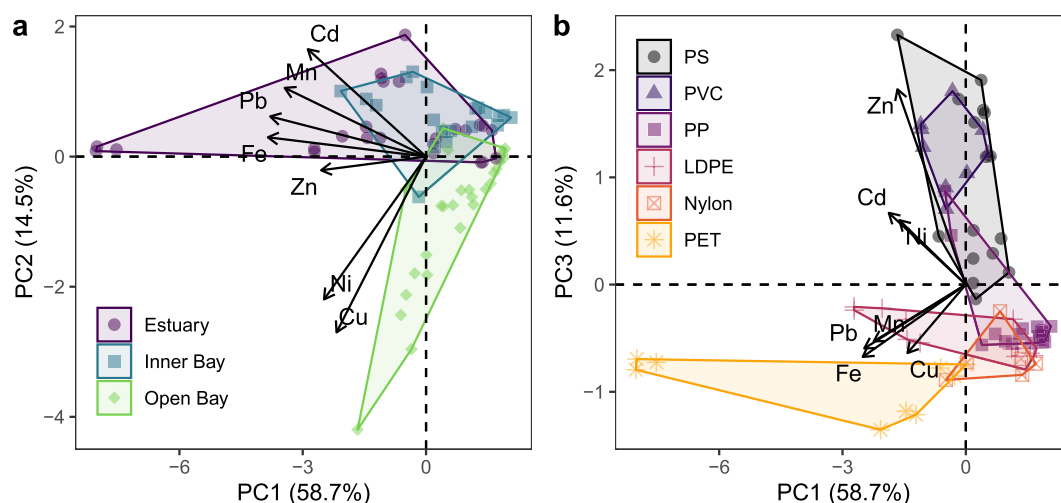


Fig. 2. Principal component analysis revealed complex composition of metals bound with aged microplastics, influenced by ageing environment and polymeric types.

slopes ($p > 0.05$, ANCOVA), suggesting ageing history did not influence the affinity of the aged microplastics for Cu. The slopes of the adsorption isotherms were also similar for the microplastics with different sizes ($>180 \mu\text{m}$ and $75\text{--}180 \mu\text{m}$) (Fig. 4), suggesting at these two size ranges tested, the PP plastic affinity for Cu was not influenced by particle size.

Therefore, the adsorption behavior of metals on aged microplastics in laboratory adsorption experiments followed unified patterns, and is relatively more predictable, regardless of the ageing history of the microplastics.

4. Discussion

4.1. Elevated metal adsorption capacity of aged microplastics

In the present study, we assessed the effects of ageing on metal accumulation in microplastics. We observed that the ageing process, regardless of the polymeric types and ageing locations, elevated metal concentrations on microplastics and enhanced the adsorption capacity (Figs. 1 and 3). This was consistent with the findings from multiple other studies that also observed elevated adsorption capacity of aged microplastics (Ashton et al., 2010; Holmes et al., 2012; Holmes et al., 2014; Huang et al., 2020; Mao et al., 2020; Turner and Holmes, 2015), although these microplastics were aged under different conditions. The term “ageing” is a collective concept and the underlying mechanism for ageing elevated adsorption is diverse: mechanical weathering alters surface texture, produces excessive grooves and fractures, provides favorable sites for ensuing chemical weathering, and eventually leads to breakdown of plastics (Cooper and Corcoran, 2010); when the size of plastic shrinks, its adsorption capacity for contaminants increases because of higher specific surface area (Ma et al., 2019; Wang et al., 2019); chemical and biological fouling coat the plastic and provide additional sites for contaminant adsorption (Holmes et al., 2012; Kooi et al., 2017; Leiser et al., 2020; Richard; Rochman et al., 2014). Here, we did not observe drastic change on the surface texture of microplastics, but noticed the change in colors of plastic surface and correlations between concentrations of Fe and other metals. Therefore, chemical fouling—formation of Fe and Mn mineral coatings—may be responsible for the elevated adsorption capacity of aged microplastics.

4.2. Metal contamination in aquatic environments reflected by microplastics

The difference in metal compositions on aged microplastics reflects the metal contamination levels of the three ageing sites. Water in the Estuary site originates from the Jiulong River that was previously found polluted by multiple metals (Tan et al., 2015). The Open Bay site is also influenced by many anthropogenic activities such as cargo shipping. In

contrast, the Inner Bay site was close to an aquaculture region and is less influenced by metal contamination. Accordingly, waters in the prior two sites are expected to be more contaminated by metals relative to the last site, which was evidenced by an oyster-based biomonitoring we previously conducted near the three sites (Fig. S9). This was also consistent with the composition of metals measured on the aged microplastics: higher metal concentrations on microplastics from the prior two sites and lower metal concentrations at the Inner Bay site (Fig. 2 and S4).

To our knowledge, the finding that aged microplastics reflected the contamination of the site has not been reported by other studies. The following reason may be responsible: the majority of other studies investigating metal enrichments on microplastics recovered plastic pellets directly from the field with indefinite ageing history (durations and condition of ageing, source) or varied properties (color, size, shape and polymeric types) (Ashton et al., 2010; Holmes et al., 2012; Rochman et al., 2014; Vedolin et al., 2018), which lowered the comparability of microplastics from different regions. Here, we aged pristine microplastics with similar initial conditions following the same protocol, which ensures microplastics from different locations were directly comparable. Thus the finding highlights the contamination status of waters influence the metal contaminants enriched on microplastics, and thus the necessity to consider ageing history when assessing the environmental risks of aged microplastics.

4.3. Fe/Mn coatings underlie metal adsorption capacity of aged microplastics

The composition of particulate metals also varied between different polymeric types, indicating the affinity for metals differed between different types of microplastics during the ageing process (Fig. 2b). Polymeric type was recorded as a well-known factor influencing the sorption behavior of organic contaminants, because the differences in the polymer structures, such as presence of pores, arrangement of molecular chains and crystallinity (Fred-Ahmadu et al., 2020; Rochman et al., 2013). However, its effects on metal adsorption were less studied and the available studies showed inconsistent patterns. Godoy et al. (2019) observed increasing adsorption capacity for multiple metals following the order of PE $>$ PVC $>$ PS $>$ PP $>$ PET. But they highlighted that the source, roughness and other potential factors may jointly influence the adsorption capacity (Godoy et al., 2019). Brennecke et al. (2016) reported greater adsorption of Cu to PVC than to PS microplastics, probably due to higher surface area and polarity in PVC polymer. Rochman et al. (2014) observed HDPE microplastic had lower metal affinities relative to PET, PVC, LDPE and PP microplastics.

Here, we observed that the composition of metals accumulated on microplastics varied by polymers, but it should not be attributed to

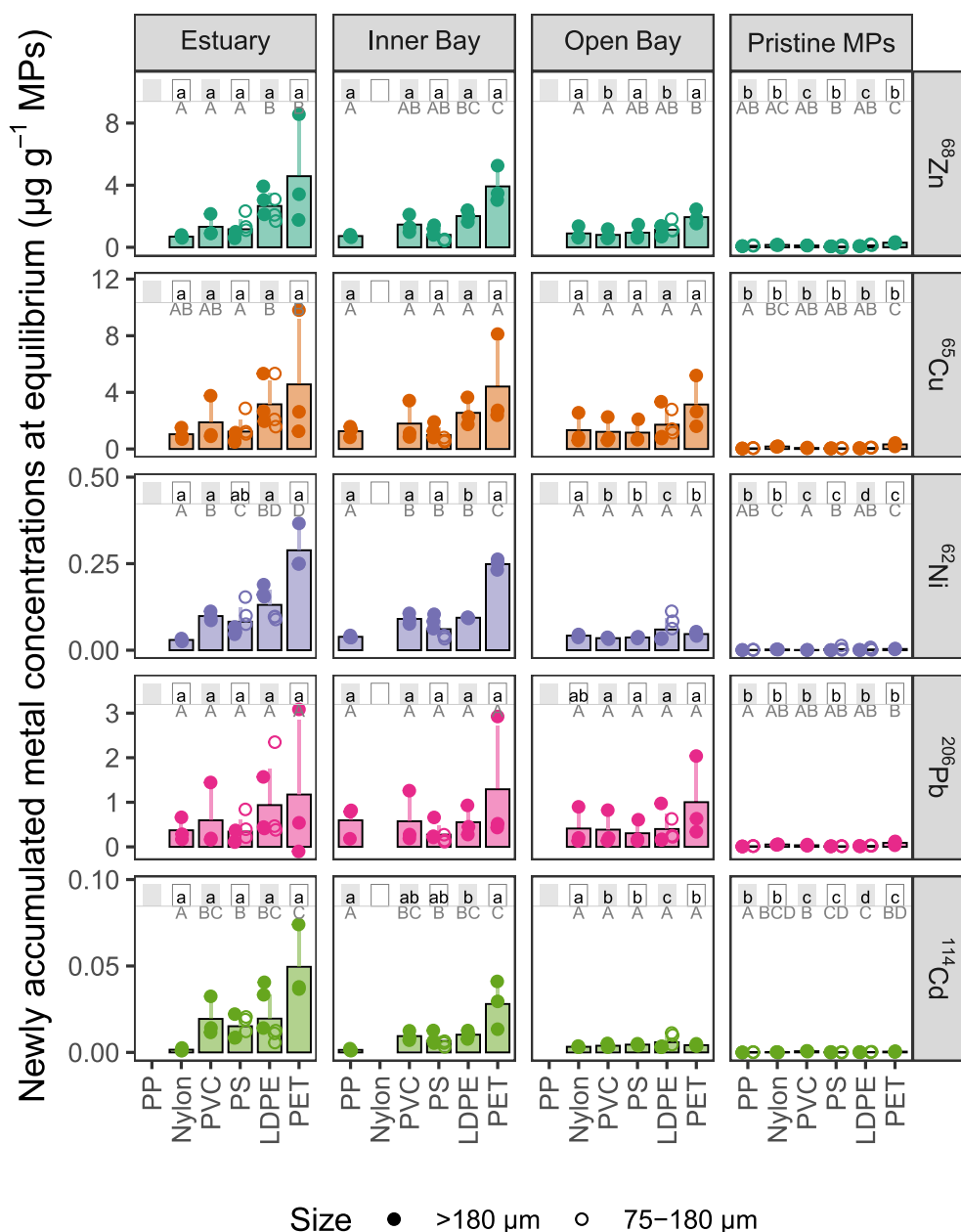


Fig. 3. Metal isotopes newly adsorbed on aged and pristine microplastics in controlled laboratory adsorption experiments. Values represented by the bars and error bars are mean and standard deviation. Each filled and open circle represents one microplastic sample. Mean values (at each site) across different microplastic types sharing no common upper case letters are significantly different ($p < 0.05$); mean values (of each type of microplastics) across different sites sharing no common lower case letters are significantly different ($p < 0.05$).

the differences in intrinsic properties of the polymers, as the adsorption capacity of pristine microplastics for different metals were uniformly low (Fig. 3). Therefore, certain processes may work synergistically during ageing and result in different metal affinities among plastic polymers. For example, the PET microplastics enriched very high concentrations of Fe, Mn, Cu and Pb (Fig. S5). We suspect the plastic morphology played the major role. Unlike other microplastics that were in pellet or rod shapes with relatively smoother surface, the pristine PET microplastics were in chips and flakes with more cracks and pores (Fig. S3). This may provide additional sites for Fe and Mn minerals to be lodged during the ageing process (Cooper and Corcoran, 2010), which in turn promoted the accumulation of Cu and Pb.

Though the composition of metals on microplastics varied by ageing locations and polymeric types, the short-term accumulation of aged

microplastics in controlled laboratory setting exhibited uniform patterns. When exposing the aged microplastics to a cocktail of metals at environmentally realistic concentrations, the metals adsorbed were correlated to the particulate Fe and Mn concentrations (Fig. S7 and S8). This was consistent with previous studies that attributed Fe and Mn oxide surface coatings as a controlling factor for metal adsorption onto aquatic particles (Davis and Kent, 1990; Dzombak and Morel, 1990; Gadde and Laitinen, 1974; Lion et al., 1982; Manceau et al., 1992; Xie et al., 2019; Xie et al., 2016). At least two mechanisms might have been involved in the association between Fe/Mn and other metals: (1) coprecipitation of metals with Fe and Mn oxides/hydroxides on microplastic surface during the coating processes; (2) surface adsorption of metals on the Fe/Mn coatings. In the field, both mechanisms worked; in the laboratory adsorption experiments, the later mechanism played a major role.

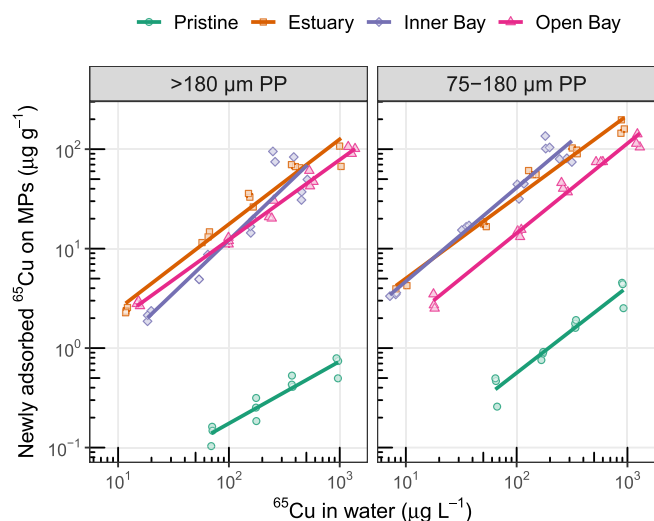


Fig. 4. Adsorption isotherms of ^{65}Cu on aged and pristine polypropylene (PP) microplastics. The microplastics of two different size ranges (i.e., $> 180 \mu\text{m}$ and $75\text{--}180 \mu\text{m}$) were aged at three coastal sites.

The contradiction of metal accumulation patterns on aged microplastics in field and in laboratory conditions thus highlights the caution to directly apply laboratory adsorption findings to interpreting metal accumulations on microplastics in the field. For microplastics ageing for a long time frame and being transported across different aquatic environments, its role as a vector of metals could thus be more complex than predicted in controlled laboratory experiments (Rochman et al., 2014). Modifications of surface properties (texture change, chemical and biological fouling) during ageing and variations of water chemistry in ambient environment would further add to this complexity (Artham et al., 2009; Cooper and Corcoran, 2010; Fotopoulou and Karapanagioti, 2012; Leiser et al., 2020; Rochman et al., 2014).

4.4. Implications on risk assessment of microplastics

Microplastics were considered inert for aqueous metals and the role as a vector of metals has been overlooked for a long time. The majority of studies on their ecotoxicological consequences either focus on the particles or the particle bound organic chemicals (Koelmans et al., 2016). Here we observed that metal adsorption capacity was substantially enhanced on aged microplastics compared with pristine microplastics. When organisms are exposed to these aged microplastics, elevated bioaccumulation of toxic metals may occur when the metal associated microplastics being ingested and assimilated (Abdolahpur Monikh et al., 2020; Zhang and Xu, 2020). Considering the ageing process in environment is gradual (Cooper and Corcoran, 2010), the adsorption capacity of microplastics also varied temporally: “older” microplastics tend to carry more metals than “younger” ones (Rochman et al., 2014). Accordingly, the risk of exposure to “younger” or “older” microplastics may also differ as the hazards exerted by the two are different—shifting from physical damage to the combination of physical damage and metal exposure.

In the present study, “ageing” was accomplished by submerging the microplastics underwater for a long term, and chemical fouling—lodging of Fe and Mn minerals on the surface—appears to be the dominant mechanism controlling the enrichment of metals. The major findings derived from the comparative assessment of metal accumulation in the field and in laboratory condition may not directly apply to other ageing processes, such as mechanical weathering producing more delicate surface texture (Cooper and Corcoran, 2010), altering functional groups and polarizing surface (Fotopoulou and Karapanagioti, 2012), colonizing the surface by microbes (Leiser et al., 2020). Such processes may occur individually or jointly, so the relative importance of each process in affecting metal accumulation needs to be understood. The methods employed

here, particularly the stable isotope tracer technique, are readily applicable when assessing the effects on adsorption induced by different ageing processes. Also with the aid of this tracing technique, we could further advance our understanding of how the ageing processes influence the bioavailability and toxicity of microplastics bound metals (Tan and Wang, 2012).

5. Conclusions

In the present study, we comparatively assessed the effects of ageing on metal accumulation on microplastics both in the field and in controlled laboratory settings. The ageing process substantially enhanced metal accumulations and adsorption capacity of aged microplastics compared with pristine microplastics. Metals accumulated on microplastics over the ageing period were influenced by site-specific contamination level and by the polymeric types and particle morphology. In contrast, regardless of the ageing locations and the polymer types, the adsorption behavior of aged microplastics in controlled laboratory conditions was uniform and appeared to be mediated by the Fe and Mn mineral coatings. Coprecipitation with Fe and Mn oxides/hydroxides and the subsequent adsorption on the Fe/Mn coatings were inferred to be two major mechanisms of metal accumulation on microplastics. In the field, both mechanisms were important; in laboratory assessments, what examined was the mainly the later (adsorption) mechanism. The discrepancy in metal accumulation patterns between in the field and in controlled laboratory conditions unveiled the complexity of ageing process, which should be considered when translating laboratory findings to risk assessment of metal contaminated microplastics in the real environment.

CRedit authorship contribution statement

Minwei Xie: Conceptualization, Writing – review & editing. **Jun-Lin Huang:** Conceptualization, Methodology, Writing – original draft. **Zhi Lin:** Methodology. **Rong Chen:** Conceptualization, Writing – review & editing. **Qiao-Guo Tan:** Conceptualization, Writing – review & editing.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2021.149108>.

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