Journal of Hazardous Materials 447 (2023) 130763

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Impact of microplastics on lead-contaminated riverine sediments: Based on the enzyme activities, DOM fractions, and bacterial community structure

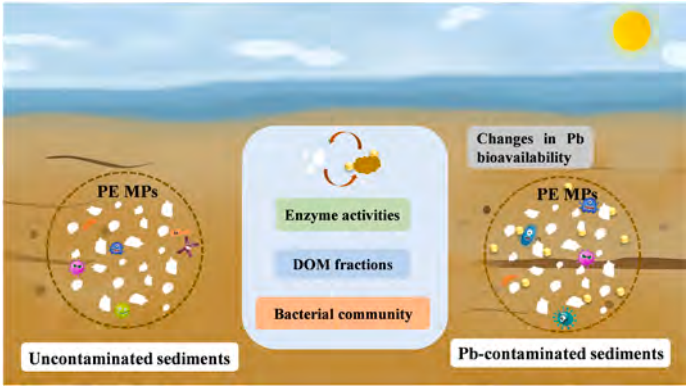
Si Liu [a,b], JinHui Huang [a,b,*], WenJuan He [a,b], Wei Zhang [a,b], KaiXin Yi [a,b], ChenYu Zhang [a,b], HaoLiang Pang [a,b], DanLian Huang [a,b], Jun Zha [c], Cong Ye [c]

[a] College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China
[b] Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, PR China
[c] Hunan Yixin Environmental Engineering Co., Ltd., Changsha 410004, Hunan, PR China

HIGHLIGHTS

- The adsorption capacity of sediment for Pb(II) decreased with the content of MPs.
- The changes in sediment enzyme activities and DOC structures varied with MPs concentration.
- High doses of MPs increased the bioavailability of Pb in sediments.
- MPs had a greater impact on bacterial community in Pb-contaminated sediments.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Dr. R Teresa

Keywords:
Microplastics
Sediments properties
Lead
Microbial community
Combined exposure

ABSTRACT

Microplastics (MPs) are able to interact with diverse contaminants in sediments. However, the impacts of MPs on sediment properties and bacterial community structure in heavy metal-contaminated sediments remain unclear. In this study, we investigated the adsorption of Pb(II) by sediment-MPs mixtures and the effects of different concentration MPs on sediment enzyme activities, DOM fractions, and Pb bioavailability in riverine sediments, and further explored the response of sediment microbial community to Pb in the presence of MPs. The results indicated that the addition of MPs significantly decreased the adsorption amount of Pb(II) by sediments, especially decreased by 12.6% at 10% MPs treatment. Besides, the changes in enzyme activities, DOM fractions exhibited dose-dependent effects of MPs. The higher level of MPs (5% and 10%) tends to transform Pb into more bioavailable fractions in sediments. Also, MPs amendment was observed to alter sediment bacterial community structures, and community differences were evident in the uncontaminated and lead-contaminated sediments. Therein, significant increase of *Bacteroidota*, *Proteobacteria* and decrease of *Firmicutes* abundance in Pb-

* Corresponding author at: College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China.
E-mail address: huangjinhui_59@163.com (J. Huang).

https://doi.org/10.1016/j.jhazmat.2023.130763
Received 1 November 2022; Received in revised form 29 December 2022; Accepted 8 January 2023
Available online 11 January 2023

contaminated sediment at the phylum level were observed. These findings are expected to provide comprehensive information for assessing the combined ecological risks of heavy metals and MPs in riverine sediments.

1. Introduction

In recent years, the use of plastic products has been integrated into all aspects of our lives due to its convenience, durability, and lightweight properties. Global plastic demand has increased to 359 million tons by 2018, of which more than 50% of plastics are disposable [42]. However, with improper disposal and loose environmental management, it is estimated that 4.8–12.7 million tons of plastic litter enter the aquatic environment annually [46]. Plastic pollution and pervasive plastic debris have been found in the coastal areas, open ocean, and polar regions transported by the ocean current, even sinking to the abyssal depths of the ocean [89]. Rivers serve as key vectors for plastic transport into the seas. A growing number of studies have focused on investigating the distribution and ecological impact of plastic debris in freshwater environments. Noteworthy, due to the influence of diverse environmental stresses and their resistance to degradation, large plastic debris existing in the environment become brittle and breakdown into smaller particles [33,36], with the microplastic pollution being the focus of special concern and research.

Microplastics (MPs), also known as marine "PM2.5″, are typically defined as plastic particles with a size of less than 5 mm [51]. A number of studies have reported that microplastics are ubiquitous in aquatic environments, especially in estuaries and urban rivers in densely populated areas [18]. Generally, the surface properties of MPs will be changed upon entering the aquatic environment, which is attributed to fragmentation and degradation by physicochemical and biological processes, such as mechanical abrasion, light radiation, and microbial degradation. Simultaneously, it is believed that MPs provide attachment substrates for the colonization of microorganisms and form heterogeneous aggregation with other impurities, thus promoting the sinking of MPs [32,38]. Niu et al. [51] revealed that the average concentration of MPs increased with the increasing sediment depth and confirmed that the degradation rate was greater in the deep layers. Therefore, most of the MPs will eventually accumulate in sediments which will serve as the long-term sinks for MPs. Several studies have reported the widespread distribution of MPs in sediments around the world. For instance, Klein et al. [34] found that the abundance of MPs extracted from sediments along the Rhine River in Germany ranged from 228 to 3763 particles kg^{-1}, where polyethylene (PE), polypropylene (PP), and polystyrene (PS) were mainly observed in sediments at relatively high concentrations. It was reported that MPs have been detected in the sediment of Kavery river, South India, with the abundance of 187.00 ± 103.00–699 ± 66.00 items kg^{-1} [49]. Besides, MPs pollution was also found in the sediments of China's mainstream and branches of River (e.g., Yangtze River, Yellow River, and Pearl River), and inland lakes along the river (e.g., Dongting Lake, Taihu Lake, and Poyang Lake). These evidences indicated that sediments play a key role in the enrichment and migration of MPs in the aquatic environment [64]. However, few studies evaluating the influence and ecological risk of MPs in freshwater sediment have been conducted.

Owing to its wide distribution and small size, microplastics could be easily ingested by aquatic biota, resulting in toxic effects and spreading throughout the food chain [61,77]. Additionally, MPs might persist in poorly oxygenated sediments for decades, and the long-term accumulation of MPs inevitably interferes with the physicochemical properties and biological process of sediments [81]. Li et al. [41] found that the addition of MPs inhibited the sediment enzyme activities (e.g., catalase, polyphenol oxidase, and urease activities) and reduced the diversity of bacterial communities through 60-day sediment-incubation. Chen et al. [5] compared the effects of pristine and aged PS MPs at 0.5% (w/w) on sediment dissolved organic matter (DOM) characteristics and components, the results suggested that MPs change the electron-donating capacity and structure of DOM to form larger weight DOM fractions, thereby maintaining sediment carbon stability. Additionally, both MPs and heavy metals are persistent pollutants in soil or sediment. MPs may interact with metallic contaminants and affect their bioavailability, toxicity, and mobility. Our previous study reported that natural-aged MPs exhibited higher adsorption capacity for lead(Pb) in the electrolyte solution involving electrostatic interaction, surface complexation, and ionic exchange [47]. In the soil environment, the adsorption ability of soils to heavy metals decreased while the desorption ability increased, thus enhancing their migration and transformation [83]. Xing et al. [70] demonstrated that the increasing concentration of MPs can increase the bioavailability of metals, thus aggravating the toxicity of Cu^{2+} and Ni^{2+} to earthworms. Besides, in a 120-day soil incubation experiment with 0.2% and 2% (w/w) MPs changed the soil properties and heavy metal bioavailability. And the dose of 2% significantly decreased the soil microbial richness and diversity and affected microbial community composition [15]. Sediments may be the final destination of heavy metals once discharged into the river [24,26]. Considering that considerable abundance of MPs is detected in riverine sediments, including heavy metal-polluted sites [9,58], it may affect the physicochemical properties of sediments and thus change the environmental behavior of heavy metals. Xu et al. [72] revealed that the presence of MPs in sediments promoted the transition of Cd^{2+} from acid-soluble fraction to organically bound fraction. Therefore, under the background of heavy metal contamination, the impact of MPs on the microbial community and sediment properties still should be further studied, which is thus of significance for assessing and understanding the environmental risks of MPs co-existing with heavy metals.

Pb-contaminated sediments are commonly occurred due to the wide application in electroplating industries, electrical industries, and agriculture, resulting in a potential threat to ecological safety and human health [23]. Especially, high concentrations of Pb were observed in riverine sediments affected by mining. Wan et al. [65] detected Pb concentration of 589.7 mg kg^{-1} in Xiawangang River sediments, Hunan. The high concentration of Pb ranged from 340 to 4379 mg kg^{-1} also reported in the sediments of Xiangjiang river [55]. In this study, we conducted 30 d incubation experiments to study the effects of MPs at the concentration of 0.05%, 0.5%, 5%, and 10% (w/w) on Pb-contaminated and uncontaminated sediment. The main objectives of our study were (1) investigate the adsorption behaviors of Pb in the sediment with different concentrations of MPs; (2) explore their effect on sediments DOM, enzyme activity, and Pb availability; (3) analyze the changes of bacterial community structure. It is expected that the results would contribute to evaluating the ecotoxicological effects and associated risks.

2. Materials and methods

2.1. Sediment and microplastics

Riverine sediment (0–5 cm) using a columnar sampler was collected from Changsha section of the Xiangjiang River (28°8′22.74″N, 112°57′8.54″E) in June 2021. Detailed sampling methods were provided in the Supplementary Material. According to Yin et al. [79], the MPs abundance in the sediment of Xiangjiang river ranged from 144 to 510 items kg^{-1} (dry weight). The detected concentration of MPs in the sediment used in this study was 184 particles kg^{-1} (dry weight), which indicated that MPs pollution was relatively low in this area. Prior to the experiments, the sediment sample was air-dried in a clean environment for two weeks. The dried samples were grounded, sieved in 0.5 mm

mesh sieve, and manually homogenized. The physicochemical properties of sediment were shown in Table S1. The contaminated sediment was prepared by spiking Pb with the following procedures. Firstly, Pb spiking solution was prepared by diluting the Pb stock solution (2 g L^{-1}, as pure Pb from $Pb(NO_3)_2$). Then, the solution was spiked into the sediment and stirred continuously to achieve homogenization. Finally, the sediment was stabilized in the dark for two weeks and maintained at 50% humidity (v/w). The final concentration of Pb in the artificially contaminated sediment was 445.56 mg kg^{-1}. The concentration of Pb in the sediment was determined by considering the environmental concentration of lead and the quality standard of river sediment.

The virgin PE MPs (density: 0.94–0.96 g cm^{-3}, size: 150 μm) were purchased from Zhongcheng Plastic Co. Ltd, China. The surface morphology of MPs was characterized by Scanning Electron Microscope (SEM, Sigma 300, Germany). The elements distribution on the MPs surface was measured by Energy Dispersive Spectroscopy (EDS, Smartedx, Germany). The functional groups of MPs between 400 and 4000 cm^{-1} were determined by Fourier Transform Spectroscopy (FTIR, Thermo Scientific Nicolet iN10, USA).

2.2. Sediment incubation test

Beaker experiments in the climatic incubator with an exposure period of 30 days were conducted. The incubation conditions were kept at dark and room temperature (25 ℃). Approximately 100 g of Pb-contaminated and uncontaminated sediments were placed into a 500 mL beaker. Four concentrations (0.05%, 0.5%, 5%, 10%) of PE MPs were added to the sediment as well as a control treatment group without MPs. A total of ten treatment groups in triplicate were displayed in Table S2. The sediment was weighed daily to ensure that the humidity was kept at 50% (v/w). After the 30 d incubation, MPs were re-extracted from sediments based on the density separation method [63]. Detailed MPs extraction procedures were shown in Text S1.

2.3. Adsorption experiments

The adsorption experiments were conducted in centrifuge tubes containing Pb(II) solutions of various concentrations (from 60 to 100 mg/L), using 0.2 g sediment with the 0.05%, 0.5%, 5%, and 10% PE MPs (w/w) concentrations. The background solution contained $CaCl_2$ (0.01 M) to maintain ionic strength and adjusted to pH of 6 using 0.1 M HNO_3 or 0.1 M NaOH solution. The tubes were placed on a thermostat shaker at 150 rpm at room temperature (25 ℃) for 6 h. Our preliminary test indicated that 6 h was sufficient to achieve adsorption equilibrium (Fig. S1). The concentration of Pb(II) was determined by Flame Atomic Absorption Spectrophotometer (FAAS, PinAAcle900F, China). The related adsorption models were shown in Text S2. The control group was performed using the same conditions and procedures but without MPs. Each test was run in triplicate.

2.4. Analytical methods

2.4.1. Measurement of enzyme activity

Enzyme activities in the sediment were considered to be an important indicator for comparing the related microbial activities and nutrient cycling. Different treatment groups were sampled to measure the activities of dehydrogenase and urease. Dehydrogenase activity was assayed with 2,3,5-triphenyltetrazolium chloride spectrophotometry based on the method described previously [48]. Urease activity was determined by indophenol blue spectrophotometry described by Song et al. [62]. More details are shown in Text S3.

2.4.2. DOM extraction and analyses

Sediment DOM was extracted with ultrapure water (w/v = 1:5) in a reciprocal shaker at 200 rpm for 24 h at room temperature. Next, the mixture was centrifuged at 8000 rpm for 10 min and filtered through 0.45 μm membrane. The DOM concentrations were generally expressed as the dissolved organic carbon (DOC) concentration [30], which was determined by the total organic carbon (TOC) analyzer (TOC-V CPH, Shimadzu, Japan). The fluorescence excitation–emission matrix (EEM) spectra for the DOM were measured by fluorescence spectrometer (F7000, Hitachi, Japan). The setting of instrument parameters and EEM spectra analysis method using parallel factor analysis (PARAFAC) are displayed in Text S4.

2.4.3. BCR sequential extraction and toxicity characteristic leaching procedure (TCLP)

The chemical speciation of Pb in sediment was determined by the European Community Bureau of Reference (BCR) sequential extraction procedure with some modification [56]. And toxicity characteristic leaching procedure (TCLP) was measured as described by previous research [69]. All the extract fluids were through 0.45 μm filter membrane, and then the filtrate was analyzed by FAAS. The detailed procedures of BCR and TCLP tests could be found in Text S5.

2.4.4. DNA extraction and 16 S rRNA gene analysis

Sediment samples were taken at the end of incubation for bacterial community analysis. DNA of sediment was extracted using the FastDNA®Spin Kit for soil (MP Biomedicals, USA) in accordance with the manufacturer's instructions. Subsequently, the extracted genomic DNA was checked by 1% agarose gel electrophoresis. The V3–V4 regions of bacterial 16 S rRNA were amplified by polymerase chain reaction (PCR) with the forward primers 338 F (5′-ACTCCTACGGGAGGCAGCAG-3′) and reverse primers 806 R (5′-GGACTACHVGGGTWTCTAAT-3′). The obtained PCR product was purified and sequenced on the Illumina MiSeq platform (Majorbio Bio-pharm Technology Co., Ltd, Shanghai, China). Details are described in Text S6.

2.5. Statistical analysis

Statistical procedures were performed in IBM SPSS 27.0 and Origin 2018. One-way ANOVA was used to evaluate significant differences ($p < 0.05$) among different treatments. Sequence reads were clustered under different operational taxonomic units (OTUs) at 97% similarity. The β-diversity differences were evaluated by the non-metric multidimensional scaling (NMDS) plots based on weighted UniFrac distances. The Linear discriminant analysis (LDA) effect size (LEfSe) method was carried out to identify the feature bacterial taxa.

3. Results and discussion

3.1. Changes of MPs properties before and after exposure

The SEM images of PE MPs before and after the incubation were shown in Fig. 1. It could be clearly seen that the surface of the virgin PE MPs (Fig. 1a) was relatively flat, almost free of pores and other substances. In contrast, the retrieved PE MPs (Fig. 1b, c) presented rough and cracked surfaces. The EDS analysis verified that a higher proportion of Si and Al was attached to the surface of aged PE MPs (Fig. S2), indicating that MPs are able to adhere to clay materials. Additionally, the surface functional groups of MPs were characterized by FTIR and displayed in Fig. 1c. The similar variation of aged PE MPs was observed in uncontaminated and Pb-contaminated sediments. Compared with the virgin PE MPs, the aged PE MPs exhibited new and stronger peaks at 1033, 534, and 469 cm^{-1}. The new peak located in 1033 cm^{-1} was assigned to the C-O-C stretching of ester [76]. Moreover, the new peak appearing at 534 cm^{-1} could be attributed to the C═O bending vibration in aliphatic ketone [47]. Whereas the peak at 469 cm^{-1} was responsible for the wobble of CO_2^-, which may be related to the attachment of organic matter [17]. The above variations in aged PE MPs indicated the formation of oxygen-containing functional groups caused by the synergistic effect of chemical oxidation and biodegradation when

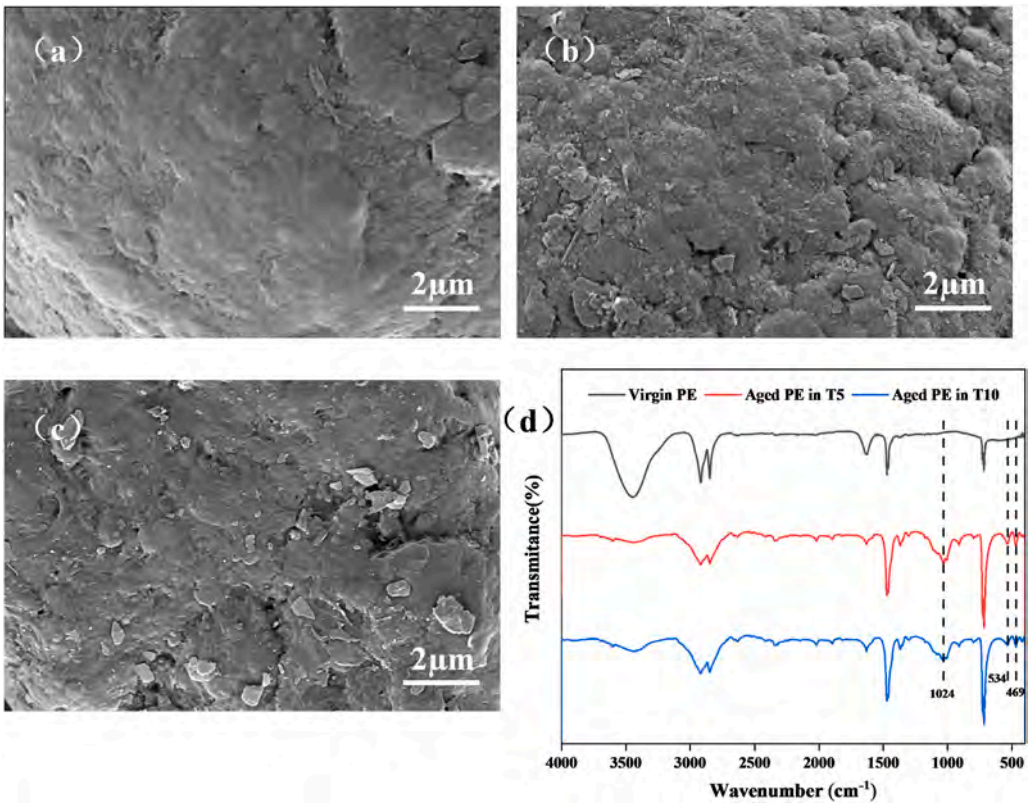


Fig. 1. SEM images of virgin PE MPs (a) and aged PE MPs extracted from uncontaminated sediment (b) and Pb-contaminated sediment (c) after 30 d incubation; FTIR spectrum of virgin PE MPs and aged PE MPs (extracted from T5 and T10) (d).

MPs are exposed to sediments, which may further increase the ecological effects in aquatic environments.

3.2. Effect of MPs on the adsorption of Pb(II) by sediment

The adsorption isotherms curves of Pb(II) onto sediment and sediment-MPs mixture were shown in Fig. 2. And the parameters fitted by Langmuir and Freundlich models were listed in Table S3. The high R^2 value for each model revealed that they both clearly describe adsorption isotherms, indicating that the adsorption process of Pb(II) by sediment was a state of physical and chemical adsorption simultaneously. The presence of MPs in sediment significantly decreased the adsorption of Pb (II). With the increase of MPs concentration, the maximum sorption capacity (Q_m) was 10.5008 mg kg^{-1}, 10.6767 mg kg^{-1}, 10.3608 mg kg^{-1}, 10.006 mg kg^{-1}, respectively, which was much lower than the pure sediment (Q_m = 11.4489 mg kg^{-1}). Particularly, the higher level of MPs exhibited a stronger inhibitory effect of Pb(II) onto sediments. Li et al. [43] also reported similar results of Cd (II) adsorption at the same MPs addition ratio. Compared to single MPs in the water system, the interaction between heavy metals and sediment-MPs systems could be altered. On the one hand, due to its unique properties, the presence of MPs may change the adsorption behavior of Pb^{2+} as an important factor [4]. MPs could occupy the adsorption sites of the sediment through electrostatic and hydrophobic interactions, resulting in the decrease of Pb^{2+} adsorption by the sediments [21]. On the other hand, changes in sediment structure by MPs would indirectly affect the adsorption behavior. Particularly, the presence of MPs would be incorporated with sediment aggregates, interfering with the formation of macro-aggregates [3,90]. Besides, the abundant mineral components contained in sediments play a vital role in the adsorption of heavy metals. The organic components (e,g., mineral components) were more likely to accumulate in soil macro-aggregates [8]. Chen et al. [4] found that the addition of MPs resulted in much higher q_e value for Pb(II) in soil macro-aggregate than in micro-aggregate.

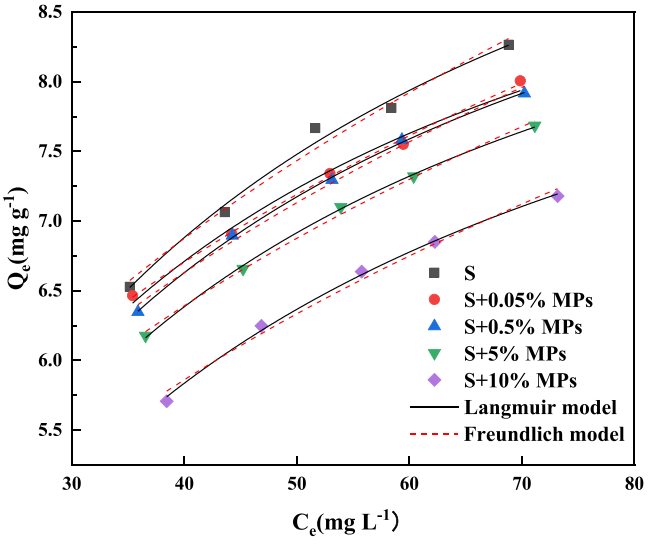


Fig. 2. Adsorption isotherms of Pb(II) on sediments with different concentration of MPs. Note that "S" denote sediment, "0.05%, 0.5%, 5%, 10% MPs" denote the concentration of PE MPs in sediments.

3.3. Effects of MPs on enzyme activity in sediments

Fig. 3a shows the change in dehydrogenase activity with different MPs concentrations in sediment. After 30 d of incubation, the uncontaminated sediment exhibited a slightly lower dehydrogenase activity than that of Pb-contaminated sediment. Compared with the sediments without MPs (T1 and T2), the addition of 0.05%, 5%, and 10% MPs had

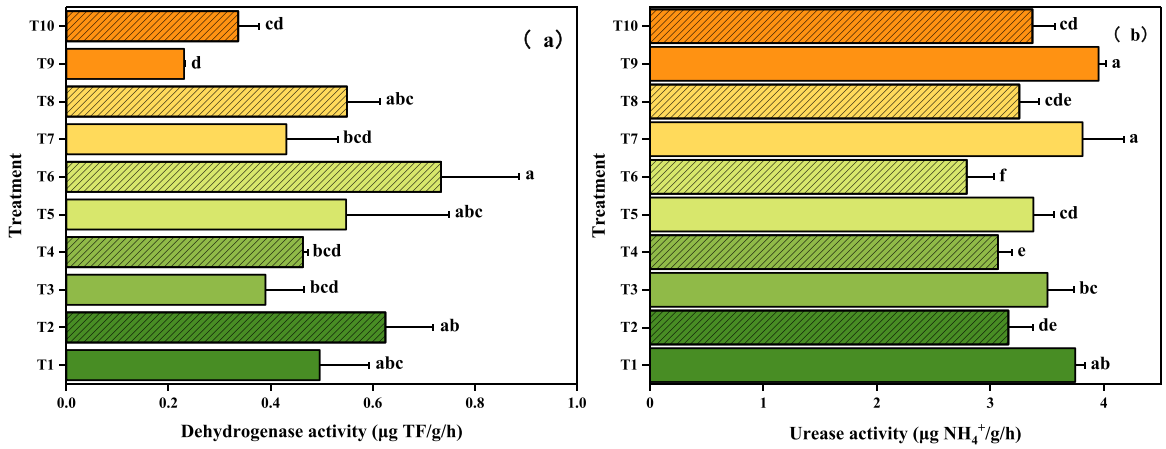


Fig. 3. Dehydrogenase activity (a) and urease activity (b) in the sediments with different concentration of MPs. Different letters mean significant differences ($p < 0.05$) between treatments. (T1: Blank control; T2: Pb; T3: 0.05% MPs; T4: Pb + 0.05% MPs; T5: 0.5% MPs; T6: Pb + 0.5% MPs; T7: 5% MPs; T8: Pb + 5% MPs; T9: 10% MPs; T10: Pb + 10% MPs).

an inhibitory effect on the dehydrogenase activity. The availability of the substrates was reduced by MPs, leading to the inhibition of sediment dehydrogenase activity. Especially, high level (10%) of PE MPs addition significantly decreased enzyme activity in sediment (T9 and T10). It was suggested that the presence of MPs had an antibacterial effect. The result is consistent with the finding of Wang et al. [66], in which they found that soil dehydrogenase activity decreased significantly with the increase of plastic film residue exposure. Noteworthy, MPs with the concentration of 0.5% treatment (T5 and T6) displayed slightly increased in dehydrogenase activity. The reason could be attributed to the promotion of metabolic activity on carbon substrates due to the higher energy consumption of microbes caused by MPs stress at this concentration [62].

The change of urease activity among different treatments was illustrated in Fig. 3b. In comparison, the significant inhibitory effects of urease activity occurred in Pb-contaminated sediment ($p < 0.05$), indicating that Pb induces toxic effects on the related microbial metabolism. In addition, the low concentration of MPs (0.05%, 0.5%) resulted in inhibition in urease activity, which may be attributed to inverse dose-dependent effects. Enzyme activities related to the nitrogen cycle generally decrease with decreasing carbon availability [78]. Low-dose microplastics affected sediment carbon consumption, leading to the decrease in urease activity. Similarly, Dong et al. [13] reported that low levels of MPs (0.25%, 0.5%, w/w) reduce the activity of soil urease by altering the tertiary structure of the enzyme. However, the urease activity was slightly increased in sediment amended with 5% and 10% MPs (T7-T10). On the one hand, the higher level of MPs may exert a stabilizing effect on microbial activities associated with urease. Fei et al. [14] reported that the higher urease activity spiked with 1%, 5% (w/w) MPs might result from the increase of diazotrophs abundance. On the other hand, the stimulation of urease was related to the sediment water holding capacity [14,57]. de Souza Machado et al. [8] found that the water holding capacity of sediment will be enhanced with the increasing concentration of MPs, therefore sediment spiked with high-dose of MPs could maintain moisture for a longer time.

3.4. Effects of MPs on the contents and compositions of DOC

As shown in Fig. 4a, for the sediments uncontaminated with Pb, the DOC content significantly decreased by 16.37%, 24.83%, and 14.14% in the presence of 0.05%, 0.5%, and 5% MPs (T3, T5, and T7), respectively. The possible explanation is that the interaction between MPs and the aromatic structure of DOM occurred via π-π conjugation [7], leading to the increase of the adsorption capacity of MPs on sediment DOC. This result was consistent with the findings of Chen et al. [4], in which they observed that adding 0.5% (w/w) of three MPs all decreased the soil DOC content. An evident decrease in DOC concentration was found in the Pb-contaminated sediment without adding MPs (T1 and T2), which may be related to the complexation between the DOM components and Pb(II) [88]. Additionally, the sediments contaminated with Pb showed no significant difference in DOC content (except for T10), suggesting the relative stability of sediment organic matters under short-term co-exposed conditions. Compared with the uncontaminated sediments, the DOC content of Pb-contaminated sediments amended with 0.05%, 0.5%, and 5% (T4, T6, and T8) significantly increased by 7.94%, 14.26%, and 10.41%, respectively. The reason for the increase may be that the Pb(II) was liable to be adsorbed on the surface of negatively charged MPs due to electrostatic attraction, resulting in weaker interaction affinity of DOM-MP [47]. Particularly, the addition of 10% PE MPs instead increased the DOC content of sediments (T9 and T10), indicating higher level of MPs in sediment facilitated the accumulation of labile carbon. A similar phenomenon was also reported by Liu et al. [45].

The EEMs combined with PARAFAC analysis (EEMs-PARAFAC) were often used to determine the fluorescence components of DOM [5]. The studied sediment DOM was divided into three fluorescent components by the PARAFAC model (Fig. 4c). According to the previous studies, Component 1 (C1, Ex/Em = 250/414) and Component 2 (C2, Ex/Em = 270/318) was considered as the humic-like compounds [2,20]. Component 3 (C3, Ex/Em = 265/454) corresponds to the protein-like substance [35,52]. The fluorescence intensities of C1 were significantly higher than that of C2 and C3 among all treatments (Fig. 4b). The C1 is usually produced by microbial degradation of organic matter in terrestrial aquatic environments, which was expected to be composed of compounds with rich aromatic structures and high molecular weight [44,73]. After 30 d incubation, the fluorescence of three components with different level MPs in uncontaminated sediment was quenched, especially for 0.5% PE MPs treatment (T5) significantly decreased C1-C3 component by 11.76%, 12.61%, and 21.49%, respectively, which may be ascribed to a ligand exchange caused by the interaction between DOM and MPs [54]. Another possible reason for the decrease was that MPs stimulated the microbial activity in sediments and facilitated DOM decomposition [75]. In contrast, the fluorescence intensities of C1 and C2 were higher in sediments polluted with Pb, but the differences were not significant. The increase of C1 and C2 components were correlated with the changes of DOC in Pb-contaminated sediment. Due to the adsorption of Pb(II) by MPs, the interaction affinity of DOM to MPs could be reduced. Chen et al. [6] also found that the increase of DOC in PBAT-introduced soil was correlated with the accumulation of humic substances. Additionally, the abundant humic-like substances (C1 and C2) in sediments may have the potential to reduce the toxicity of

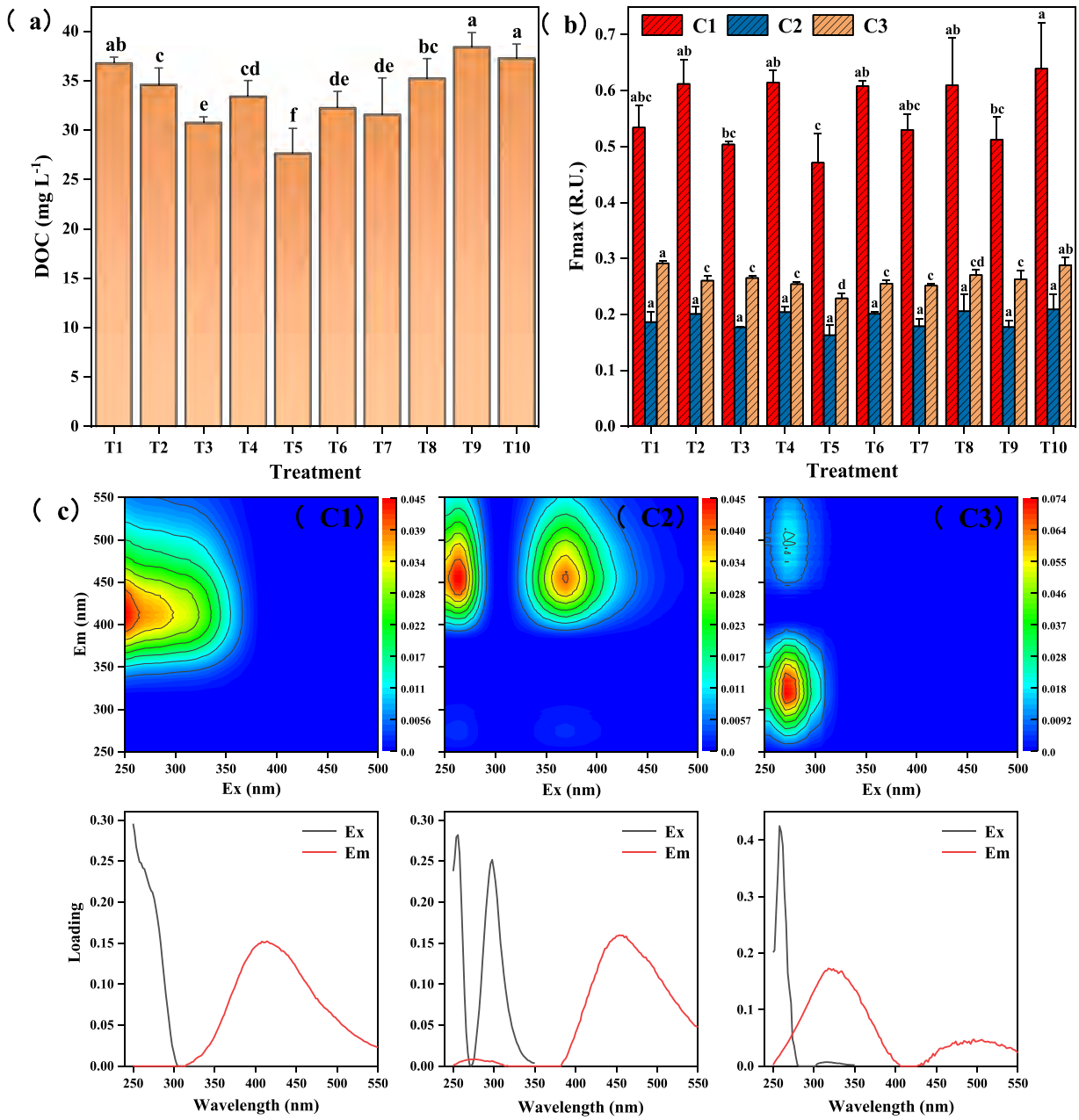


Fig. 4. (a) Content of DOC of sediment DOM from different treatments; (b) The fluorescence intensity (F_{max}) for each EEM-PARAFAC component in sediments; (c) EEM contours of three components and excitation/emission loadings of C1-C3 identified by PARAFAC analysis. The different lowercase letters in (a) and (b) represent significant differences ($p < 0.05$). (T1: Blank control; T2: Pb; T3: 0.05% MPs; T4: Pb + 0.05% MPs; T5: 0.5% MPs; T6: Pb + 0.5% MPs; T7: 5% MPs; T8: Pb + 5% MPs; T9: 10% MPs; T10: Pb + 10% MPs).

contaminants, which was related to the strong complexation between humic-like substances and contaminants through van der Waals forces or electron donor–acceptor [31]. However, a quenching effect was observed for C3 with Pb compared to T1, which showed that Pb (II) was more sensitive to the ligand interaction of fluorescent protein-like substances [87]. The fluorescence intensities of C3 slightly increased in the presence of 5% and 10% MPs. This phenomenon may result from the enhancement of Pb bioavailability promoted by high-dose MPs, leading to changes in the molecular environment of protein-like substances [28].

3.5. *Effects of MPs on the bioavailability of Pb in sediment*

Speciation of metal ions accumulated in the sediment exists in diverse forms, which plays a significant role on their bioavailability and ecotoxicity [16]. The bioavailability of heavy metals is related to the physiochemical properties of sediments, such as pH value, organic matter, and enzyme activities [67]. Generally, the availability of Pb was increased in the order of acid-soluble form (F1) > reducible form (F2) > oxidizable form (F3) > residual form (F4) [10,25]. Therefore, to better understand the effect of MPs on the changes in Pb speciation stability, fractionation of Pb in the sediment was performed by the modified BCR extraction method. The speciation distribution of Pb in different treatments was displayed in Fig. 5a. The results showed that there was no significant linear relationship between the change in Pb fraction and PE MP concentrations. It can be observed that the Pb chemical speciation in the control group (T2) consisted of: 16.72% of F1, 61.45% of F2, 10.58% of F3, 11.24% of F4, suggesting that a high level of bioavailability in Pb-contaminated sediment. Peng et al. [55] also

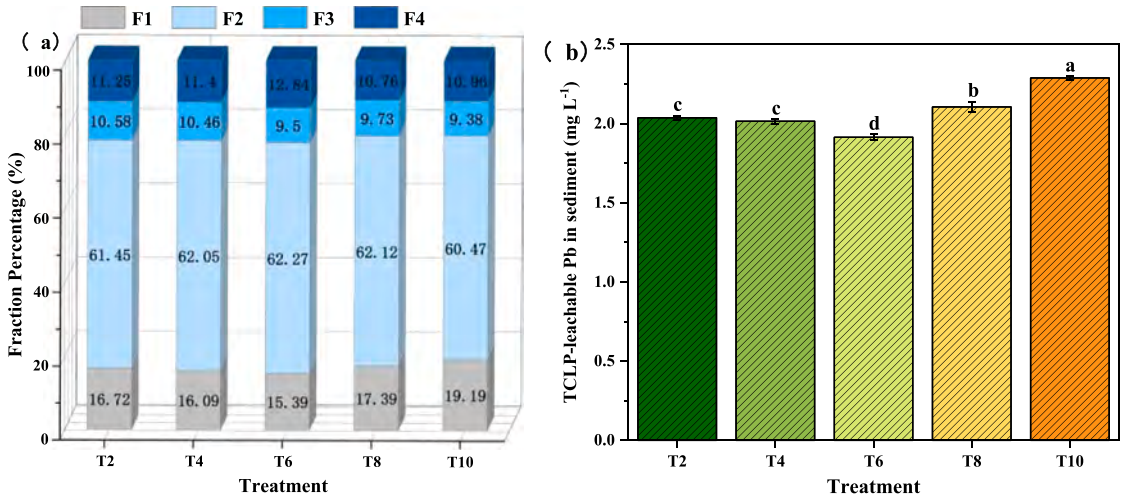


Fig. 5. Changes in the chemical speciation of Pb (a) and TCLP-leachable Pb fraction (b) in Pb-contaminated sediment with different MPs concentration. Different lowercase letters in (b) represent significant differences ($p < 0.05$). (T2: Pb; T4: Pb+0.05%; T6: Pb + 0.5%; T8: Pb + 5%; T10: Pb + 10%).

reported that Pb was dominated by the reducible form in sediments of Xiangjiang river. In contrast, the acid-soluble fraction (F1) percentage was improved by adding 5% and 10% MPs (T8 and T10), while slightly decreased in low-level treatments (T4 and T6), which indicated that high concentration of PE MPs would increase the bioavailability of metals. Whereas the slight increase of F2 fraction of Pb was observed in the presence of 0.05%, 0.5%, and 5% MPs, which may be attributed to the attachment of Fe or Al or Mn hydroxides onto MPs, presenting relatively high affinities for Pb(II) [1]. Noteworthy, the lower F2% of 10% PE MPs further demonstrated that high level of MPs promoted the transformation of Pb to more bioavailable fraction. In addition, F3 fractions in MPs-treated groups (T4-T10) were slightly lower than that in the control group and did not show significant changes. Correspondingly, the residual fraction (F4) percentages of Pb increased in low-level treatment (T2 and T4), with a decline at 5% and 10% MPs in sediments. The above results were in accordance with the adsorption experiments in our study. In comparison, the higher concentration of MPs significantly decreased the adsorption ability of Pb(II) to sediment, thus enhancing the mobility and bioavailability of metals [26,40]. Moreover, the competitive adsorption of metal ions on the sediment or MPs may also be responsible for changes in the chemical speciation of heavy metals [22,60].

TCLP was considered as one of the valuable indicators for evaluating the environmental risk of heavy metals in sediments [27]. To further determine the changes in Pb toxicity in sediment, we performed the TCLP leaching toxicity test in this study. As shown in the Fig. 5b, the TCLP-leachable Pb in T2 was 2.037 mg L^{-1}, which was lower than the critical value (5 mg L^{-1}) specified by the United States Environmental Protection Agency (USEPA) [69], but it still could pose a potential threat to the organisms. Similarly, the TCLP-leachable Pb concentration exhibited the same trend as the F1 fractions: it was decreased in low-dose MPs treatments (T4 and T6), and the opposite results were observed in high-dose MPs treatments (T8 and T10). The concentration of 0.05% and 0.5% MPs was the level of pollution that has been reported to be relevant to the actual environment [19]. 5% concentration was the level associated with areas heavily polluted by MPs [8]. 10% concentration was selected to simulate the extreme conditions above the reported value in the riverine sediment environment [45,71]. In our study, low level of MPs instead led to a decrease in Pb availability after short-term incubation, while no significant differences were observed between the treatments. When high level of MPs was enriched in the sediment or large amounts of MPs were released into the sediment, the bioavailability and toxicity of metals would increase, thus enhancing the ecological impacts and risks of metals to the aquatic biota. Actually, the influence of MPs on the chemical speciation and leaching toxicity of heavy metals was not obvious after 30 d incubation. Yu et al. [80] have found that significant changes in heavy metal speciation were observed between 45 and 120 days, while the rate of change gradually decreased between 120 and 150 days. However, these results can provide a reference for predicting the long-term effects of the speciation transformation of heavy metals in sediments induced by MPs. Feng et al. [15] reported that after 120 d incubation, the availability of Pb in soil was decreased with the addition of low-dose MPs (0.2%), while increased at the high-dose MPs (2%). Similarly, Li et al. [40] also found that high level of PE MPs (10%, w/w) in soil increased the bioavailability of heavy metals. Therefore, more attention should be paid to the long-term transformation process when exploring the influence of microplastics on the chemical speciation of heavy metals.

3.6. *Effects of MPs on the microbial community structure*

The sediment bacterial communities at phylum and genus level were illustrated in Fig. 6. For the uncontaminated sediment, *Firmicutes*, *Proteobacteria*, and *Actinobacteriota* were the dominant species in sediments (Fig. 6a), which accounted for more than 60% of the total bacterial relative abundance. Many studies have reported that the above three bacteria phyla tend to dominate sediment communities [12,41]. Compare with the control (T1), the relative abundance of *Firmicutes* and *Proteobacteria* decreased from 31.62% to 23.02%, and from 27.28% to 19.18%, respectively with the increasing amount of PE MPs, while the *Actinobacteriota* increased from 16% to 20.72%. This indicated that the sediment environment containing MPs was not suitable for the growth of *Firmicutes* and *Proteobacteria*. And the possible reason for the increase of *Actinobacteriota* was that certain species of *Actinobacteriota* are able to degrade PE MPs by synthesizing enzymes [50,86]. Besides, the relative abundances of *Acidobacteriota* and *Chloroflexi*, related to cellulose decomposition and organic degradation, were significantly increased in PE MPs amended treatment, with the highest percentage at 16.06% in T5 and 8.24% in T7, respectively. Contrastively, in addition to having the same dominant bacterial phyla as uncontaminated sediments, the relative abundance of *Bacteroidota* exhibited a significant increase in Pb-contaminated sediments, accounting for 15.92–40.14% of the bacterial community. Meanwhile, the relative abundance of *Firmicutes* showed declines with increasing concentration of MPs and decreased by 31.05% in T4 and 42.50% in T8, respectively. The relative abundances of *Proteobacteria* were elevated in PE MPs amended groups, in spite of insignificant changes in T6, which may be related to its increased degradative metabolism under co-exposure conditions [37].

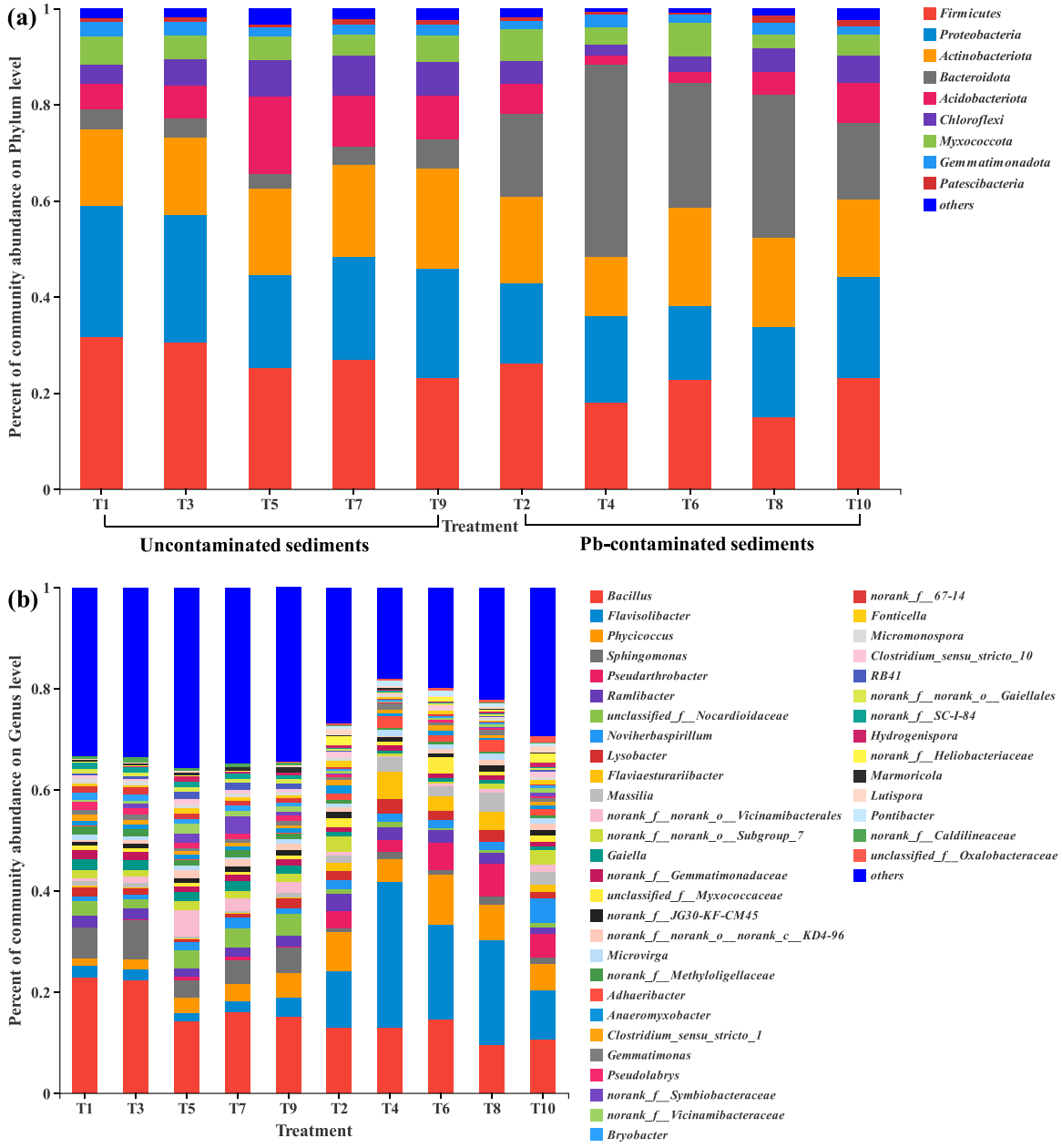


Fig. 6. The relative abundance of bacterial communities in sediments with different concentrations of MPs at phylum (a) and genus (b) level.

At the genus level, *Bacillus*, *Flavisolibacter*, and *Phycicoccus* were identified as the dominant bacterial genus in the sediment (Fig. 6b). The relative abundance of the *Bacillus* was the highest in T1 (22.83%), while decreased under the treatment with the addition of MPs and Pb-contaminated. Additionally, the relative abundance of *Flavisolibacter* showed a slight decrease with the increasing of MPs concentration in uncontaminated sediments (T3, T5, and T7), but the addition of 10% MPs (T9) significantly increased by 59.92%, probably due to the high level of MPs releasing more additives that could act as carbon source for certain bacteria [68]. However, *Flavisolibacter* and *Phycicoccus* displayed higher relative abundance in Pb-polluted sediments, indicating that Pb exposure had the potential to stimulate their growth. Particularly, the relative abundance of genus *Flavisolibacter* and *Phycicoccus* were significant in low-dose MPs treated groups (28.87% in T4 and 10.03% in T6). We noticed the evident enrichment of genus *Pseudarthrobacter* in Pb-contaminated sediments, increasing from 3.37% to 6.52% in the presence of MPs. Contrastively, the inhibitory effects of MPs on *Sphingomonas* and *Ramlibacter* in sediment were also observed.

The dissimilarities of bacterial community at the phylum level under different treatments were visualized on NMDS based on the weighted UniFrac distance (Fig. 7a) and hierarchical clustering analysis (Fig. 7b). All treatments were divided into two groups (A: uncontaminated sediment and B: Pb-contaminated sediments). The results showed a significant separation between the two groups, which suggested that the contamination of Pb change the bacterial community structure. Besides, a closer weighted UniFrac distance of A group in Fig. 7b showed more similarities in bacterial community structure under different concentrations of MPs treated groups, which may be attributed to the selective enrichment of microbes on MPs surface in sediments. Previous studies also verified that the presence of MPs did not lead to significant changes in bacterial community structure in soils [29,74]. Nevertheless, the effect of PE MPs on the dissimilarity of bacterial community structure was greater in the Pb-polluted treatments. It was worth noting that the addition of 0.05% and 0.5% of MPs (T4 and T6) exhibited distinct bacterial communities, especially for T4 which revealed obvious separation from others in clusters. This might be due to the effective

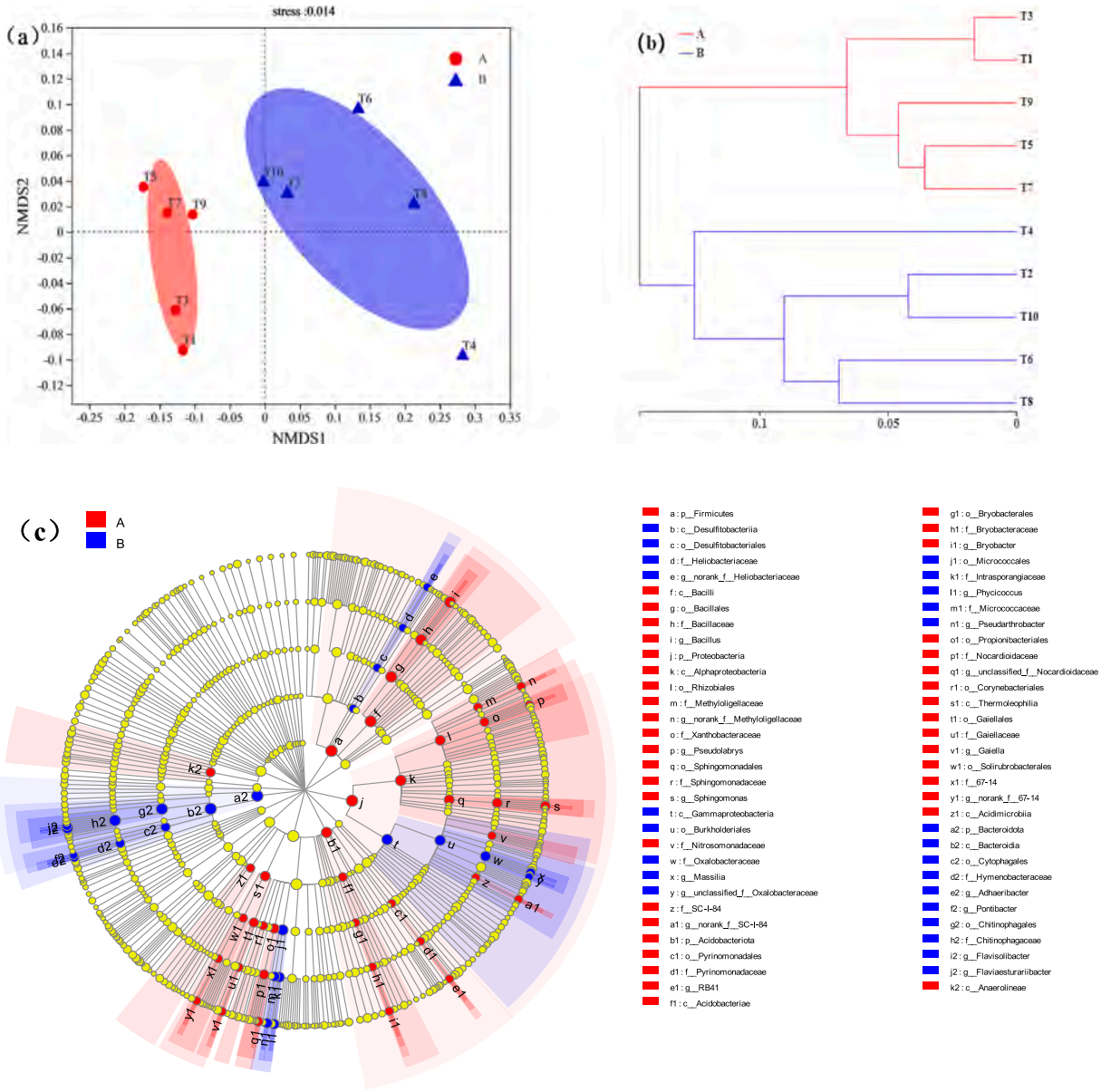


Fig. 7. (a) NMDS plots at the phylum level based on the weighted UniFrac distances; (b) Hierarchical clustering analysis of bacterial communities at the phylum level; (c) LEfSe cladograms for identifying feature bacterial taxa among different groups. All treatments were classified into two groups: A represents uncontaminated sediments (T1, T3, T5, T7, T9); B represents Pb-contaminated sediments (T2, T4, T6, T8, T10).

adsorption of Pb(II) onto MPs at those concentration levels and reduces the bioavailability and toxicity to related bacteria [53,62]. Meanwhile, we found that a similar weighted UniFrac distance occurred when MPs concentrations were extremely high (T9 and T10), indicating that bacterial community structure was more susceptible to MPs than Pb in this case. Therefore, the different PE MPs amounts exhibited stronger effects on the microbial responses in the Pb-contaminated sediments, which may further affect Pb bioavailability and microbial activities.

LEfSe algorithm was used to further identify feature bacterial taxa in the two groups, and the contribution of different taxa was ranked by the logarithmic LDA score [59]. As illustrated in Fig. 7c and Fig. S3, the phylum *Bacteroidota* (log LDA score = 5.01) was the feature bacterial taxa in Pb-polluted sediments. A certain degree of heavy metal pollution alters the competition between species within the original bacterial community, resulting in an increase of microorganisms in sediments that are resistant to heavy metals [85]. It has been reported that *Bacteroidota* is the dominant bacteria phylum in Pb-contaminated soils [11,39]. Contrastively, it was found that much more feature bacterial phyla in uncontaminated treatments including *Proteobacteria* (log LDA score = 4.33), *Acidobacteriota* (log LDA score = 4.40), and *Firmicutes* (log LDA score = 4.47), which was consistent with the results of bacterial community changes at phylum level. As previously reported, the above three phyla were also the main bacterial communities on MPs [82,84]. In conclusion, due to traditional PE MPs are difficult to be biodegraded, the presence of MPs in sediment seems to impose few impacts on bacterial communities in the short-term, and they can instead act as unique habitats or niches [29]. However, Pb exposure exerted significant effect on the bacterial community structures of sediment. Particularly, co-exposure of Pb with low-dose MPs would pose stronger influence on bacterial succession patterns. Such changes may in turn affect the enzyme activities, DOM fractions, and bioavailability of Pb in riverine sediments.

4. Conclusion

In this study, we found that the presence of PE MPs could affect

sediment properties and bacterial community structure. Firstly, the higher level of MPs significantly decreased the Pb(II) adsorption by sediments, which may be related to the changes in sediment structures. Additionally, the addition of 0.5% MPs in sediments increased the dehydrogenase activity but inhibited the urease activity, while 10% MPs exhibited opposite trend. Changes in content and fractions of sediment DOC varied with MPs amounts. However, MPs addition affected the bioavailability of Cd which has indirectly changed sediment chemical properties. Particularly, higher concentrations of PE MPs promoted Pb bioavailability, whereas lower concentrations inhibited bioavailability. These changes could be further explained by shifts of microbial communities in sediments. MPs accumulation made an alteration of the relative abundance of some dominant taxa, resulting in the enrichment of feature bacterial species. Moreover, co-exposure of Pb with MPs exerts synergetic impacts on bacterial community structures. The greater impact on the microbial succession patterns occurred in the presence of low-dose MPs with Pb. Therefore, this study provides valuable information for understanding the potential risks of MPs in sediments and Pb ecotoxicity in the presence of MPs in sediments. However, further research is needed to explore the long-term and field experiments, especially with different types of MPs in sediments polluted by heavy metals, thus determining their single and joint impacts in riverine sediments.

CRediT authorship contribution statement

Si Liu: Methodology, Validation, Investigation, Data curation, Formal analysis Writing – original draft. **Jinhui Huang:** Conceptualization, Methodology, Writing – review & editing, Supervision, Funding acquisition. **Wenjuan He:** Conceptualization, Validation, Formal analysis, Investigation. **Wei Zhang:** Resources, Data curation, Formal analysis. **Kaixin Yi:** Investigation, Visualization, Data curation. **Chenyu Zhang**: Software, Writing – review & editing. **Haoliang Pang**: Investigation, Methodology. **Danlian Huang**: Conceptualization, Supervision. **Jun Zha**: Formal analysis. **Cong Ye**: 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.

Data availability

The authors do not have permission to share data.

Acknowledgments

This study was supported by the Water Conservancy Science and Technology Project of Hunan Province (XSKJ2021000–47; XSKJ 2022068–20) and the Innovative Province Construction Special Fund of Hunan Province (2020SK2016).

Environmental implication

Microplastics (MPs) have been proven to interact with a variety of pollutants in sediments. However, the ecological impacts of MPs co-exposed with heavy metals in riverine sediments are still unclear. This study found that sediment enzyme activities, DOM fractions, and Pb bioavailability changed significantly with increasing microplastic concentration. Meanwhile, mutual effects of MPs and Pb on the sediment microbial community were further analyzed. It provides direct evidence for assessing the environmental risks of the MPs-heavy metals complicated pollution in sediments.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2023.130763.

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