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Research Paper

Interactions and co-pollution effects of fluorinated liquid crystal monomer and microplastics on aquatic sediment microbiota

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ABSTRACT

Fluorinated liquid crystal monomers (FLCMs) are emerging aquatic pollutants that co-occur with microplastics (MPs); however, their combined ecological impacts remain poorly understood. This study investigated the interactions between a representative FLCM, 4-Ethoxy-2,3-difluoro-4′-(trans-4-propylcyclohexyl) biphenyl (EDPB), and four major types of MPs: polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC). The results revealed plastic-type-dependent adsorption capacities (PE > PS > PP > PVC; 380–850 μg/g) through distinct mechanisms: hydrophobic interactions predominantly influenced PE and PP adsorption, while π-π coordination enhanced PS binding. Microcosm experiments demonstrated that MP-EDPB composites significantly altered sediment microbiomes, showing consistent declines in *Proteobacteria* abundance (27–29 % vs 36.8 % in controls), pathogen enrichment in marine sediments (*Acinetobacter* 1.2 → 3.5 %; *Vibrio* 0.8 → 2.1 %), and ecosystem-specific functional disruptions. Notably, marine systems exhibited greater biodiversity shifts, while freshwater environments showed stronger nitrogen cycle inhibition. These findings provide mechanistic insights into FLCM-MP co-pollution effects on aquatic ecosystems.

Environmental implication: Liquid crystal monomers (LCMs) and microplastics (MPs) are emerging contaminants that increasingly co-occur in aquatic ecosystems, yet their interactions and co-exposure risks remain poorly understood. This study demonstrated that the adsorption of LCMs onto microplastics was significantly influenced by plastic type, with equilibrium capacities (Q_{max}) following the order: PE (849.5 ± 1.2 μg/g) > PS (825.3 ± 0.8 μg/g) > PP (629.1 ± 0.3 μg/g) > PVC (380.2 ± 0.2 μg/g). The MPs-LCMs composites affected microbial composition and functions in sediments across both freshwater and seawater environments. These findings provide a quantitative basis for assessing the environmental partitioning and potential ecological risks associated with MPs-LCMs composite pollutants.

1. Introduction

The liquid crystal display (LCD) industry has experienced rapid growth since the Radio Corporation of America invented LCD using synthetic liquid crystal monomers (LCMs) in 1968 [1]. The global production of display panels (including both organic light-emitting diode and LCD technologies) is forecasted to reach 450 million m² in 2025 [2], driven by sustained demand for smart electronics in the digital era. This exponential growth has been accompanied by a 2.6-fold increase in LCMs production, rising from 500 tons in 2011 to 1300 tons in 2021, with current annual output exceeding 1020 tons [3,4]. As one of the leading producers and consumers of LCDs, China accounts for approximately two-thirds of global production and 40 % of worldwide demand [5]. This substantial output, along with the inherent nature of LCMs, which are only filled by physical filling (not chemical bonding), significantly increases the risk of release to the environment during production, use and disposal [6].

Typical LCMs structures feature biphenyl rings linked to various side chains and functional groups, mainly alkoxy, cyano, and halogen substitutes. Such compounds have air–water partition coefficients ($\log K_{aw}$) ranging from −5 to −1, indicating their widespread distribution in the environment [7]. In a study of 1173 LCMs, approximately 40 % exhibited persistence and bioaccumulation characteristics, and over one-quarter were identified as contaminants of Arctic concern that could

bioaccumulate [8]. In particular, fluorinated-LCMs (FLCMs) are more stable in the environment and less susceptible to metabolic degradation due to strong covalent carbon-fluorine bonds [9]. There are 27 FLCMs that have octanol–water partition coefficients (log K_{ow}) higher than 5 [7], indicating a slow tissue-blood exchange, which increases their bioaccumulation potential. This is supported by findings showing FLCMs' concentrations of approximately 130 ng/g of lipid weight in serum and breast milk within a non-occupational population [10]. Recent studies have detected LCMs in aquatic environments, where pervasive microplastics accumulate, thus raising questions about their combined environmental fate, potential synergistic toxicity, and ecological risks, which have yet to be systematically explored.

Microplastics (MPs) are increasingly recognized as vectors for emerging contaminants. Previous studies have demonstrated that hydrophobic organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), readily adsorb onto MPs, resulting in concentrations on MPs that are orders of magnitude higher (up to ppm levels) than their freely dissolved forms in water (ppt levels) [11,12]. Substantial quantities of MPs and LCMs have been detected in various aqueous environments. For instance, Zhan et al. reported the presence of LCMs and MPs in the final effluent of a wastewater treatment plant in Hong Kong at concentrations of 1.69 ng/L and 143 ± 42 items·L^{-1} [13], respectively, suggesting a possible environmental accumulation and unknown combined risks. While extensive research has elucidated the role of MPs as vectors for co-occurring PCBs and PAHs, including their environmental fate and associated risks, comparable investigations on FLCMs remain scarce. Although FLCMs share certain physicochemical characteristics with PCBs and PAHs — such as hydrophobicity and halogenated aromatic structures (Table S12) — they possess distinct features including fluorescence properties, enhanced photolytic activity, and variable water solubility, which may influence their interactions with MPs. For example, Feng et al. demonstrated that polystyrene (PS) nanoplastics significantly enhance the photolysis of a representative FLCM [3], 4-cyano-3-fluorophenyl 4-ethylbenzoate, and the toxicity to *Daphnia magna* exhibited complexity dependent on the concentration of PS nanoplastics. These differences suggest that the sorption mechanisms, persistence, and transformation pathways of FLCMs on MPs may diverge from those of classical hydrophobic pollutants.

The co-occurrence of LCMs and MPs in aquatic systems may also have implications for microbial communities and ecosystem functions, mediated by complex and poorly understood interactions. For example, exposure to a combination of MPs and PAHs such as phenanthrene has been shown to significantly inhibit the growth and activity of microbial communities in sediments, particularly reducing the relative abundance of *Proteobacteria* [14]. Similarly, a significant reduction in α-diversity among freshwater sediment microbial communities, along with reduced CO_2 and CH_4 emissions, has been observed with PCBs adsorbed onto MPs [15,16]. These findings underscore the ecological impact of composite contaminants formed via the adsorption of organic pollutants onto MPs, affecting microbial community structure and ecosystem processes.

In view of that FLCMs share some physicochemical similarities with well-studied contaminants like PCBs and PAHs, we hypothesize that interactions between MPs and FLCMs may alter the environmental fate, bioavailability, and toxicity of FLCMs, thereby modulating their ecological risks. In particular, Feng et al. reported that MPs can enhance the transformation of FLCMs and modulate their aquatic toxicity in a concentration-dependent manner, indicating complex toxicity profiles [3]. Based on these insights, we further hypothesize that the adsorption of FLCMs onto MPs alters their persistence and bioaccumulation potential, leading to modified microbial community responses and ecosystem functions compared to exposure to FLCMs or MPs alone. Assessing FLCM-MP interactions is therefore essential to evaluate their combined ecological risks related to bioavailability, transport, and toxicity, and to advance our understanding of emerging pollutant

dynamics and their integrated environmental impacts.

To evaluate the potential ecological impacts of FLCMs, particularly focusing on co-occurring MPs in diverse aquatic environments, we investigated the adsorption kinetics and isothermal behavior of one of the most prevalent FLCMs, 4-Ethoxy-2,3-difluoro-4′-(trans-4-propylcyclohexyl) biphenyl (EDPB), onto various types of MPs. Polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), and polystyrene (PS) — representing over 80 % of global plastic production [17] and spanning non-polar, aromatic, and polar polymer classes — were selected to enable mechanistic insights into FLCMs adsorption behavior across environmentally dominant plastic types. In this study, we chose a typical estuarine site (e.g., Shenzhen Bay) in the Shenzhen city, which represents a highly urbanized city facing contemporary environmental challenges. Subsequently, we examined the intertwined risks posed by MP-EDPB interactions on sediment-dwelling microorganisms across these different aqueous environments.

This study provides critical advances by: (1) revealing how plastic type governs EDPB adsorption through hydrophobic, π-π, and electrostatic interactions, with PE exhibiting a 2–3 times higher capacity than PVC; (2) demonstrating that MP-FLCM composites selectively enrich pathogenic bacteria (e.g., *Acinetobacter*, *Vibrio*) in marine sediments and disrupt nitrogen-cycling functions in freshwater systems; and (3) establishing a framework to assess co-pollutant risks through integrated adsorption-microbiome analysis. These findings address a key knowledge gap in emerging contaminant behavior and offer actionable insights for regulators and the industry managing plastic-associated FLCM pollution in aquatic ecosystems. We envision that understanding fundamental interactions between pristine microplastics and EDPB would serve as an essential baseline to inform future studies on co-pollutant environmental dynamics addressing aged plastics, sediment chemistry, and regional hydraulic variations and so on.

2. Materials and methods

2.1. Materials and chemicals

Various MPs (i.e., PE, PP, PVC, and PS) were purchased from Shanghai Run Vast Trading Co. Ltd., filtered using a 40-mesh sieve, and MP sizes were determined via a laser particle sizer, where the mean diameter is between 131 and 314 μm (Fig. S1 and Table S11). EDPB was purchased from Beijing Enocha Technology Co., China. A 100 mg/L EDPB stock solution was prepared using high-performance liquid chromatography grade acetonitrile as the carrier solvent (< 0.01 %) and stored at 4 °C for subsequent use.

2.2. Batch adsorption experiments

To illustrate the adsorption kinetics between MPs and EDPB, initial adsorption experiments were conducted at elevated concentrations relative to environmentally relevant levels, consistent with methodologies employed in prior studies [18]. The experimental concentration of 5 mg/L for EDPB was selected to simulate long-term ecological risks under cumulative exposure and worst-case scenarios [3]. Similar approaches are well-established in studies of perfluorinated compounds (e. g., 300 mg/L perfluorooctanoic acid in Xu et al., 2020 [19]; 5–60 mg/L perfluorooctanesulfonic acid in Fang et al., 2024 [20]), ensuring measurable impacts within experimental timeframes while addressing plausible long-term risks. In addition, the experimental dose aligns with methodologies for hydrophobic contaminants (log K_{ow} > 4) per ISO 10634:2018 guidelines. While environmental levels of fluorinated LCMs (e.g., 1.69 ng/L in wastewater effluents) appear low [13], industrial hotspots, such as electronics manufacturing discharge points, exhibit LCM concentrations of up to 1120 ng/L in wastewater [21]. Given the extreme persistence (half-life >180 days in water, > 1600 days in sediments) and bioaccumulation potential of EDPB [7], it necessitates evaluating amplified concentrations to account for gradual ecosystem

accumulation. In a typical experiment, 5 mg/L EDPB solutions were incubated at pH 6.5 with 0.5 g/L of various MPs (PE, PP, PVC, and PS) over 120 h. Samples were collected at specific intervals. Isothermal experiments were conducted at pH 6.5 for 96 h. The effect of pH on EDPB adsorption was examined across a range of pH values at 3, 6, 7, 8, and 9.5 in ultrapure water. The adsorption experiments of EDPB on MPs were also conducted in both freshwater and seawater samples (Text S1, Table S1, Table S2). A blank (water spiked with EDPB but no MPs) was included to assess contaminant loss during incubation, while a control group (with MPs but no EDPB) confirmed that no detectable EDPB was released from the MPs. All experiments were performed in triplicate to ensure reproducibility. The formulas for the kinetic simulation calculations are given in Text S2.

2.3. Microcosm assembly

Surficial sediments (1–3 cm) from a local freshwater lake were collected from Swan Lake (22.59°N, 113.96°E) at the Shenzhen Graduate School of Tsinghua University, while nearshore surface sediments (1–3 cm) from seawater were sampled during low tide in February 2024 from Shenzhen Bay Park, Nanshan District, Shenzhen, China (22.50°N, 113.95°E) (Fig. S2). Key water quality parameters, including turbidity, pH, total phosphorus (TP), chemical oxygen demand (COD), total nitrogen (TN), and salinity were measured for both lake and seawater samples. Sediments were also analyzed for TN, total organic carbon (TOC), electrical conductivity and humus content (Table S3).

The microcosm experiments were designed to evaluate the toxicity and the impact of EDPB on microbial communities in environmentally relevant conditions. Based on the adsorption results, four pollution scenarios were performed, i.e., Scenario A: MPs-EDPB composites comprising PVC-EDPB (representing the lowest EDPB adsorption with 380 μg/g EDPB loading on PVC) and PE-EDPB (representing the highest adsorption with 849 μg/g EDPB loading on PE); Scenario B: EDPB only corresponding to Scenario A (i.e., the lowest and highest EDPB concentrations, namely EDPB-L1 and EDPB-L2, respectively); Scenario C: control groups with MPs only (PE only or PVC only); and Scenario D: baseline scenario (Blank) without any contaminants, which were evaluated accordingly. Preliminary experiments were conducted to determine the rate of COD consumption, which indicated a necessity for nutrient mixture replenishment every 72 h to sustain microbial growth.

For each microcosm, 100 g of homogenized sediment on a wet weight basis and 0.5 g of MPs were added to 500 mL conical flasks containing 400 mL of sterile synthetic freshwater or seawater (pH 8.5) [22]. Then, EDPB of designated levels was added and mixed thoroughly for 1 min, and the flasks were sealed with a 0.22 μm filter membrane (BKMAMLAB) before being incubated in the dark at 25 ± 0.1 °C with continuous shaking at 100 rpm. All the experiments were conducted in triplicate. The total incubation period was 20 days, after which the sediment samples were centrifuged at 4000 rpm at 4 °C, and stored at −80 °C for subsequent 16S rRNA microbial community analysis.

2.4. Chemical and microbiological analysis

The pH and conductivity of water samples were measured with portable pH and conductivity meters (Shanghai Leimagnet, DDS-307 A), while the turbidity was measured with a Hash Turbidimeter 2100P. The TOC content was determined via the combustion oxidation-non-dispersive infrared absorption method. The TN and TP were quantified through alkaline potassium persulfate digestion and spectrophotometric analysis using ammonium molybdate, respectively. The humus content of the sediments was extracted with sodium pyrophosphate-sodium hydroxide and measured via potassium dichromate oxidation. EDPB concentration was quantified using an ultraviolet-visible spectrophotometer (Shanghai Avantage UV-1800) at 255 nm, which corresponds to its maximum absorption wavelength. A 7-point calibration curve was established in the range of 0.1–5 mg/L (R^2 = 0.998) using standard

solutions prepared in methanol. The method detection limit was determined to be 0.05 mg/L based on triplicate measurements of the lowest calibration standard (0.1 mg/L, S/N ≥ 3). Sample absorbance was measured in quartz cuvettes (10 mm path length), with all readings corrected against a solvent blank (methanol). The morphological properties of MPs were characterized by scanning electron microscopy (SEM, ZEISS Gemini 300, Carl Zeiss. Co., Ltd., China). Fourier transform infrared (FTIR) spectroscopy was used to determine the changes in surface functional groups before and after microplastic adsorption. X-ray photoelectron spectroscopy (XPS) was used to determine the elemental composition of microplastic surfaces. Total DNA was extracted from microbial communities in sediment samples, followed by PCR amplification and high-throughput sequencing of the 16S rRNA gene (Text S3). Detailed statistical schemes (e.g., PERMANOVA for microbial communities) and kinetic and thermodynamic fitting curves for adsorption were documented in Text S1 and S3 in the supporting information.

3. Results and discussion

3.1. Adsorption kinetics and isotherms

The pseudo-first-order model and pseudo-second-order model were selected to describe physisorption/diffusion-limited processes, and chemisorption processes, respectively. The adsorption of EDPB onto MPs involves multiple interacting forces, with the process initially being rapid and subsequently becoming slow (Fig. 1a). EDPB adsorption gradually increased as reaction time progresses, with the adsorption affinities for EDPB following the order of PE > PS > PP > PVC. The kinetic parameters (Table S5) showed that the quasi-second-order model (R^2 = 0.980–0.996) outperformed the quasi-first-order model (R^2 = 0.973–0.995). Specifically, rubberized plastics, such as PE, have a higher adsorption capacity for many organic pollutants, such as bisphenol analogues, musk, and antibiotics, than more rigid plastics (e. g., PP, PVC and PS) [23]. This can be attributed to the larger distances between the polymer chains in the PE structure compared to those in PP, PVC or PS, with the larger internal cavities making it easier for EDPB to diffuse into the polymer [24,25].

The Langmuir and Freundlich isotherm models were employed to assess homogeneous monolayer adsorption and heterogeneous multi-layer adsorption. The Langmuir and Freundlich isotherm models showed that the equilibrium adsorption of EDPB increased with its concentration (Fig. 1b). Consistent with the adsorption kinetics tests, the equilibrium Qe values followed the same order: PE > PS > PP > PVC (Table S5). In this study, the R^2 values of the Langmuir model for PS, PE, and PP adsorption (0.990–0.998) were higher than the R^2 values of the Freundlich model (0.987–0.998), indicating that EDPB adsorption onto PS, PE, and PP is more consistent with homogeneous site adsorption. Nonetheless, the R^2 value of the Langmuir model (0.985) for PVC was slightly lower than that of the Freundlich model (0.993), consistent with the organophosphates and bisphenol adsorption onto PVC [26]. The predicted maximum adsorption capacities for PS, PE, and PP (5.520 mg/g, 7.247 mg/g, 4.673 mg/g) using the Langmuir model diverged from the actual experimental data (1.510 mg/g, 1.785 mg/g, 1.276 mg/g). The discrepancies between the Langmuir model predictions and experimental adsorption capacities highlight the limitations of the model in describing EDPB-MP interactions. The Langmuir isotherm assumes monolayer adsorption on a homogeneous surface, which does not fully reflect the heterogeneous nature of microplastics. As also reported by Li et al. for tetrabromobisphenol A onto MPs [27], surface cracks (Fig. 2c) and diverse oxygen-containing groups (Fig. S3) on MPs create varied adsorption sites, contradicting the Langmuir assumption of surface homogeneity. Additionally, the bulky structure of EDPB may introduce steric hindrance and dipole-dipole repulsion, further reducing effective site occupancy and unaccounted for in the Langmuir framework. These factors likely contribute to the observed differences, suggesting that
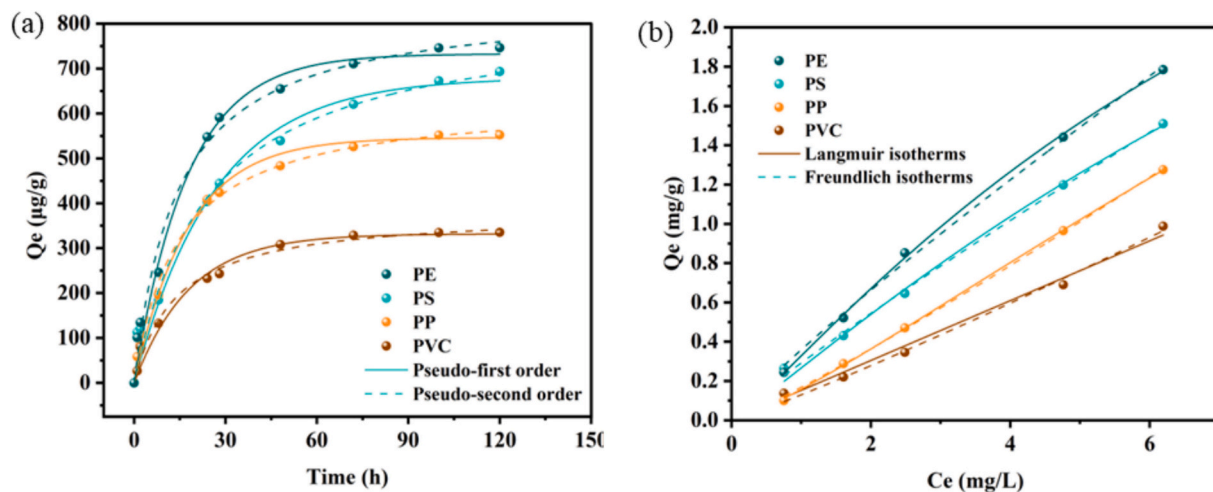
Fig. 1. Kinetic and thermodynamic mechanisms of EDPB adsorption on microplastics. Fitting of (a) quasi-first-order and quasi-second-order models for PE, PS, PP, and PVC, adsorbed EDPBs, and (b) adsorption isotherms of EDPB on PE, PS, PP, and PVC.
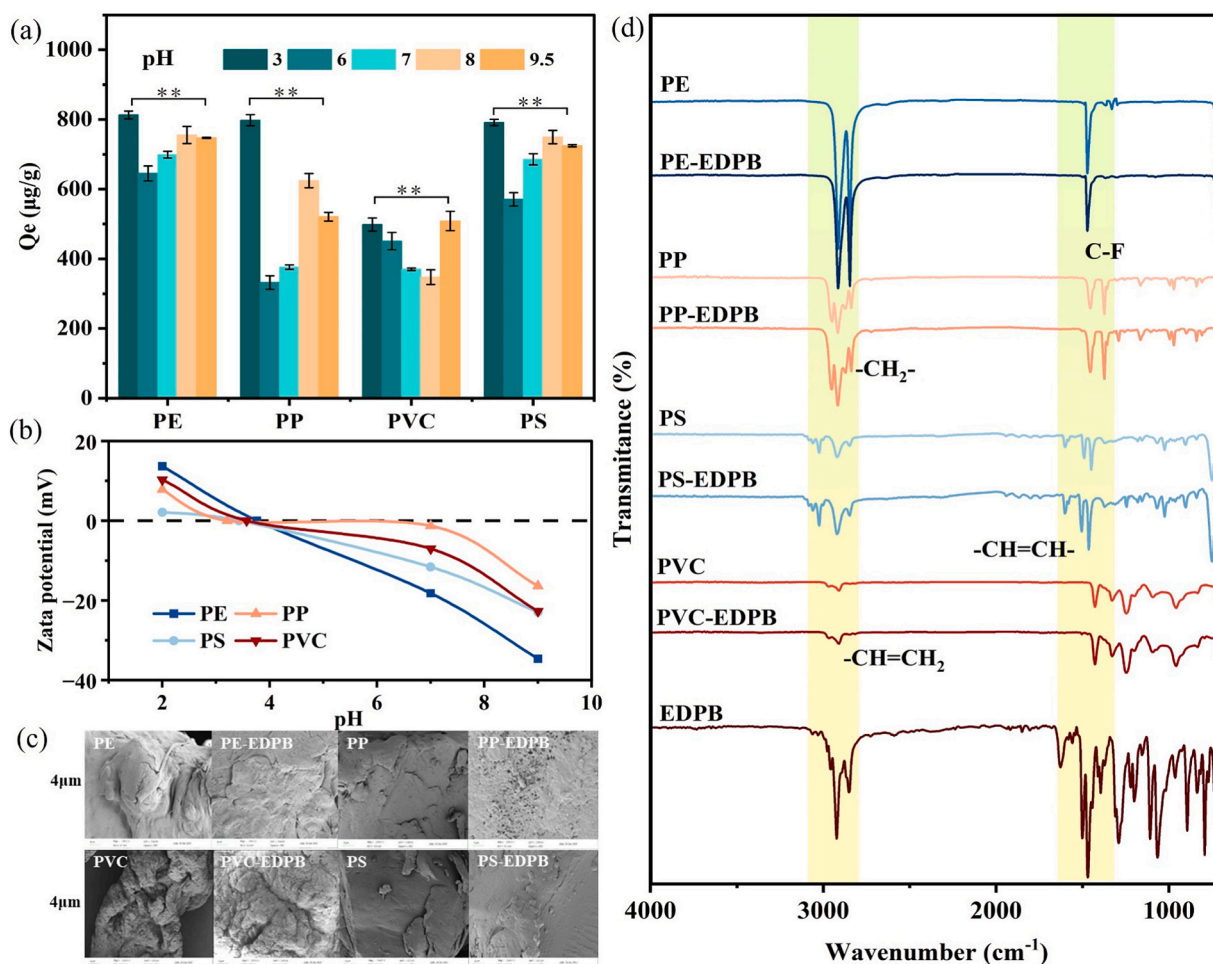
Fig. 2. Characterization of the adsorption behavior of EDPB on MPs. (a) Influence of pH on adsorption efficiency; (b) Zeta potential measurements of MPs; (c) SEM images of MPs and the corresponding EDPB adsorbed images; (d) FTIR spectra illustrating EDPB sorption on MPs (PX-EDPB indicating the adsorbed contaminant). Error bars represent mean ± standard deviation. **$p < 0.01$ denotes statistically significant differences between groups.

monolayer sorption driven by electrostatic force may not be the main process.

3.2. Adsorption behavior and mechanisms

3.2.1. pH-dependent adsorption trends

In natural aqueous environments, pH significantly affects MP

adsorption behavior. Therefore, adsorption experiments were conducted under various pH conditions to evaluate the adsorption capacity of four MP types for EDPB in water at different pH levels (Fig. 2a). The data showed a similar trend in the effect of pH on EDPB adsorption by PE, PP, and PS. Specifically, the adsorption of EDPB by PE, PP, and PS increased as the pH rose from 6 to 8 but decreased when the pH exceeded 9. In contrast, PVC displayed an opposite trend: the adsorption of EDPB by PVC decreased as the pH increased from 6 to 8, then increased at pH above 9. At a pH of 3, the adsorption capacities of PE, PP, PVC, and PS for EDPB were found to be 813.18 µg/g, 798.15 µg/g, 498.77 µg/g, and 791.77 µg/g, respectively.

3.2.2. Molecular interaction mechanisms

As detailed in Section 3.2.1, pH significantly influenced adsorption capacity. At low pH, stronger positive charges on microplastics may reduce their homologous aggregation through enhanced electrostatic repulsion (Fig. 2b) [3]. This decreased aggregation could improve EDPB adsorption by exposing more available surface sites. This mechanism may explain the observed maximum EDPB adsorption on microplastics at pH 3. The Log K_{ow} of organic pollutants is pivotal for their adsorption onto MPs, where hydrophobic interactions were the dominant mechanism [28]. Given the high adsorption capacity of EDPB on MPs, it can be inferred that hydrophobic interactions will play a significant role here. Among the four types of MPs, PE has the strongest hydrophobicity [29], which corresponds to its greater adsorption capacity. This explains the observed results, where PE exhibited the highest adsorption for EDPB. The adsorption of EDPB on PE, PP, and PS showed an increasing trend as the pH increased from 6 to 8. This phenomenon can be attributed to the salting-out effect induced by elevated OH^- concentrations in the solution, which enhances the partitioning of EDPB from the aqueous phase to the hydrophobic surfaces of MPs. These surfaces provide low-energy binding sites through dominant hydrophobic interactions. This mechanism aligns with reported studies on MPs' adsorption of PAHs [30]. In contrast, the decreased adsorption capacity of PVC likely results from the deprotonation of surface carboxyl groups, which increases surface hydrophilicity and reduces hydrophobic binding sites for EDPB. As the pH exceeded 9, previous studies have reported that high alkalinity can erode the surface area of MPs, expanding their surface area and consequently increasing the adsorption by PVC [31].

The SEM imaging and FTIR analysis offered further indications regarding the possible mechanisms underlying EDPB adsorption onto MPs. High-resolution SEM imaging (Fig. 2c) revealed localized accumulation of EDPB nanoparticles (20–50 nm in diameter) within surface pores of MPs, suggesting that pore filling may contribute to the adsorption process. FTIR analysis (Fig. 2d) provided additional insight into the interaction dynamics. Specifically, a 12 cm^{-1} bathochromic shift in the C—F stretching band (from 1320 to 1308 cm^{-1}) was observed, which may reflect weakened bond vibrations due to electron density redistribution associated with EDPB-MP interactions. For the case of PS, the benzene ring –CH=CH– stretching modes were shifted to higher wavenumbers ($\Delta\nu_1 = +13\ cm^{-1}$, $1492 \rightarrow 1505\ cm^{-1}$; $\Delta\nu_2 = +15\ cm^{-1}$, $1449 \rightarrow 1464\ cm^{-1}$). These shifts were indicative of reduced electron density in aromatic systems and consistent with trends reported for π-π interactions [32]. The absence of new peaks in the 1700–1800 cm^{-1} region (associated with carbonyl formation) further supported the predominance of non-covalent adsorption mechanisms, such as hydrophobic and π-π interactions. Taken together, these observations indicate that physical adsorption potentially involving pore filling, π-π interactions, and hydrophobic effects may play a major role in EDPB-MPs interactions under the studied conditions.

3.3. Adsorption of EDPB in simulated aqueous environment

Freshwater and seawater were used as background solutions to investigate the adsorption behavior of EDPB and MPs in real-world scenarios. Adsorption occurred in seawater for all four MP types (PE,

PS, PP, PVC), with adsorption capacity (EDPB per gram of MPs) 5.56, 7.56, 7.95, and 7.81 fold greater than the adsorption by the corresponding MP type under freshwater scenarios (Fig. 3). This can be explained by the humic acid concentrations of the water samples. The presence of humic acid in freshwater might play a critical role during adsorption due to its complex composition [33]. Bulkier components of humic acid may clog the pores of the adsorbent, impeding the access of organic pollutants to the adsorption sites [34]. Ter Laak et al. also shared a similar opinion, stating that incorporating humic acid can induce alterations in the adsorption equilibrium of contaminants [35]. In our study, the XPS results showed significant alterations in the surface carbon and oxygen content of the MPs in freshwater (Table S6, Fig. S3), likely due to the occupation of adsorption sites by phenolic hydroxyl and carboxyl groups from humic acid, which compromised the adsorption of EDPB in freshwater samples. In contrast, significantly higher adsorption of EDPB by MPs in seawater is likely due to the salting-out effect, which reduces EDPB solubility and enhances hydrophobic interactions between EDPB and the MPs. Thus, the increased adsorption observed in seawater is primarily due to the salinity-driven enhancement of hydrophobic interactions.

The observed differences in adsorption behavior between seawater and freshwater environments may exert different ecological implications, potentially disrupting microbial biodiversity and impairing ecological functions, as described in the following section.

3.4. Characterization of microbial communities in polluted sediments

Following prior adsorption results, this study further examined the impacts of composite MP-EDPB on the biodiversity of the exposed sediment microbiome. As depicted in Fig. S4, the sparse profiles of 16S rRNA gene amplicons indicate that the sampled populations encompassed most microbiome members within each group, demonstrating high quality for subsequent diversity analysis (Table S7, Table S8).

3.4.1. Disruptions of diversity of the sediment microbial community

Exposure to MPs, EDPB, and their composite aggregates elicited distinct microbial responses in SS (sea sediment) and LS (lake sediment) communities under different pollution scenarios (Fig. 4a and b). In general, the seawater environment exhibited more pronounced microbial changes, primarily characterized by increased biodiversity. This suggests that marine sediment microbes are potentially more sensitive and responsive to EDPB stressors compared to their freshwater
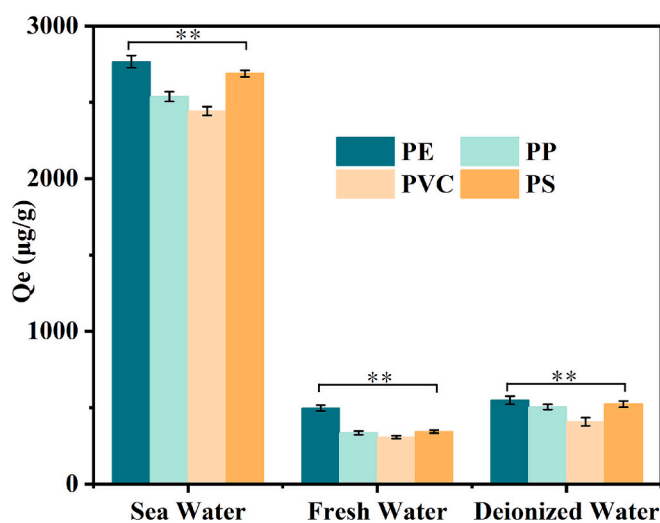

Fig. 3. Simulation of MPs adsorption of EDPB in an environment of freshwater and seawater (Error bars represent mean ± standard deviation. ** denotes significant differences between groups; $p < 0.01$).
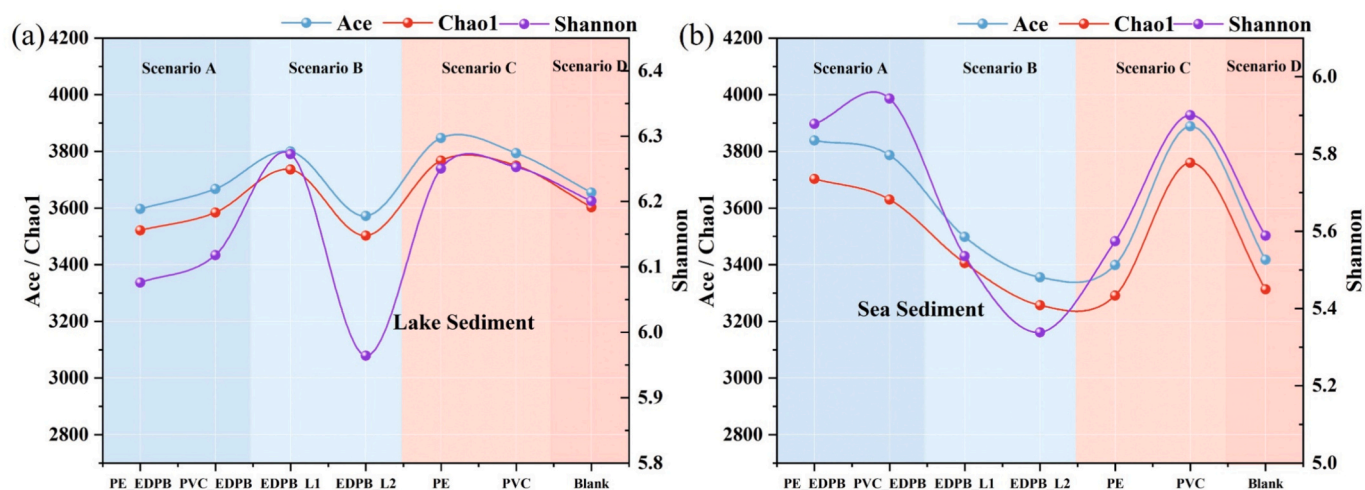
Fig. 4. Ecological impacts of MP-EDPB co-pollution on sediment microbiomes. Species diversity indices of microbial communities in (a) lake sediment, and (b) sea sediment.

counterparts. This observation aligns with previous findings that high microbial diversity often serves as a crucial adaptive strategy for survival under fluctuating and stressful environmental conditions, including exposure to man-made chemicals and complex synthetic molecules [36]. The observed salinity effects likely result from reduced EDPB solubility via the salting-out effect, consistent with preceding adsorption experiments conducted in simulated aqueous environments, which in turn increases sediment partitioning (log K_{oc} = 3.5–4.2). Additionally, competitive displacement by chloride ions in saline conditions may promote EDPB desorption; these mechanisms collectively increase EDPB bioavailability to marine sediment microbiota in marine systems.

In pollution Scenario A, involving composite exposure of PE-EDPB (i. e., highest EDPB adsorption) and PVC-EDPB (i.e., lowest EDPB adsorption), a slight reduction in microbial diversity was observed in LS (Shannon index = 6.07 and 6.12) compared to the unpolluted control group (Shannon index = 6.20) and the corresponding MPs-only pollution group. Conversely, SS exhibited an increasing trend in diversity indices under the same contamination scenario, with PE-EDPB and PVC-EDPB, indicating enhanced community diversity and richness. This unique trend suggests possible hormetic responses by the indigenous sea sediment bacteria as an adaptive strategy during composite xenobiotic threats caused by MPs-EDPB. Specifically, while low and high concentrations of EDPB alone slightly inhibited the growth and diversity of the SS microbiota, these parameters were significantly enhanced under composite exposure, displaying an opposite trend. Although direct transcriptomic evidence of stress-response pathways (e.g., *soxR*, *katG*, | *log2FC*| = 1.3–1.4) was beyond the scope of this study, PICRUSt2 predicted significant upregulation of oxidative stress defense genes (*sodA*, *ahpC*; |*log2FC*| = 1.0–1.2, *p* < 0.05) and efflux pumps (*acrB*, *mexF*; | *log2FC*| = 1.2–1.3) in SS under composite exposure (Table S14). This stimulatory effect resembles bacterial hormesis [37] and highlights the significance of the co-effects of MPs and LCM compounds.

In pollution Scenario B, notable differences in microbial community diversity were observed in both lake sediment (LS) and sea sediment (SS) microcosms between the EDPB-L1 (lowest EDPB concentration) and EDPB-L2 (highest EDPB concentration) groups. Although the EDPB concentrations used in this study were higher than typical environmental levels, the potential risks associated with increasing EDPB levels in future environmental conditions necessitate proactive and preemptive considerations [38]. As anticipated, EDPB-L1 had a minimal impact on community diversity, whereas EDPB-L2 effectively reduced microbial diversity, confirming that high EDPB concentrations negatively affect both the richness and overall diversity of microbial

communities in both freshwater and seawater environments (In LS, the Chao1 values for EDPB-L1 and EDPB-L2 were 3735.7 and 3502.0, respectively; in SS, the Chao1 values for EDPB-L1 and EDPB-L2 were 3406.0 and 3256.8, respectively).

The composite pollutants (PE-EDPB and PVC-EDPB) exerted higher potency by reducing the microbial richness in LS, consistent with trends observed in the Ace index. Given EDPB's known acute and developmental toxicity, its presence likely suppresses microbial community diversity [39]. Numerous studies have demonstrated that fluorinated alkyl compounds can exert cellular and molecular toxicities on various biological systems, impacting reproductive, immune, endocrine, and neurological functions and also inducing oxidative stress [40], inflammation, neurotoxicity, apoptosis, and other bodily reactions, potentially leading to cell death [41]. Consequently, high concentrations of EDPB negatively impact microbial richness and diversity in sediments, with the effects of the composite pollution largely influenced by the characteristics of the carrier MPs. Such a reduction in microbial diversity may degrade ecosystem functions, compromising the system's capacity for self-regulation and resilience against external disturbances.

The presence of MPs alone (Scenario C) enriched bacterial biodiversity, with a slight increase observed in LS and a more notable enrichment in PVC-contaminated SS. This pattern likely arises because MPs can serve as supplementary carbon sources, providing energy substrates for microbial communities [42]. Moreover, the amorphous and porous features of MPs offer high specific surface areas conducive to biofilm development and microbial aggregation, which contribute to overall microbial diversity [43]. MPs can also absorb organic matter and nutrients, increasing their bioavailability to sediment microbes and further stimulating microbial growth and diversity. In SS, PVC groups exhibited greater microbial diversity than PE, a trend not observed in LS. This discrepancy may be attributed to PVC's increased susceptibility to aging through dehydrochlorination of the chlorine atoms [44], leading to subsequent polymer degradation [45] in seawater environments, thereby creating microsites and bioavailable carbon sources favourable for bacterial colonisation and growth.

3.4.2. Differential response of core microbial community

Owing to the distinct indigenous sediment microbial compositions and water chemistry in lake and sea environments, the presence of unique microbial taxa within each treatment reflects microbial-specific responses to pollution in an aquatic niche (Table S9, Table S10). In the various treatment groups within LS, *Proteobacteria* predominated the microbial composition (Fig. 5a and b), forming the core community alongside *Firmicutes*, *Chloroflexi*, and *Bacteroidetes*. These phyla are well-
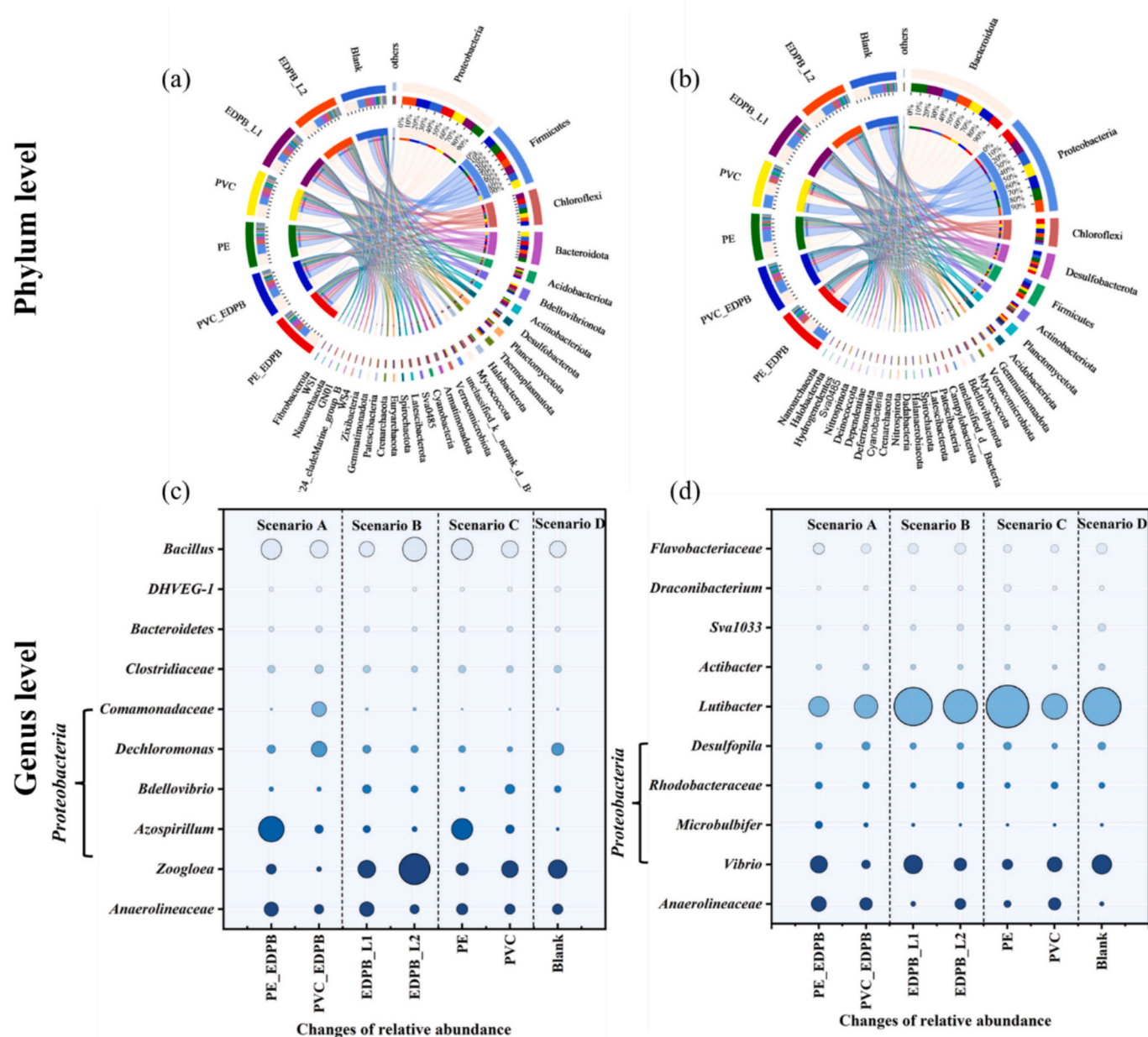
Fig. 5. Microbial taxonomic shifts in sediment microbiomes under MP-EDPB co-exposure with a circus diagram displaying changes in relative abundance at the phylum level in (a) lake sediment (LS); and (b) sea sediment (SS). Bubble plots displaying comparisons for selected genus-level abundance between (c) LS; and (d) SS.

documented as the dominant microorganisms in sediments and on the surfaces of MPs where biofilms develop [46,47]. By contrast, SS samples primarily featured *Bacteroidetes*, followed by *Proteobacteria*, *Chloroflexi*, and *Desulfobacterota*.

Permutational ANOVA revealed significant treatment effects on *Chloroflexi* abundance ($p = 0.003$). In LS, high EDPB exposure (EDPB-L2) caused a 23.6 % reduction in *Chloroflexi* abundance compared to controls (9.45 % vs. 12.77 %, $p = 0.012$), while low exposure (EDPB-L1) showed no significant change (12.77 % vs. 11.83 %, $p = 0.214$). Conversely, in marine SS, showed dose-dependent *Chloroflexi* enrichment, peaking at 129 % increase under high EDPB (10.13 % vs. 4.42 % control, $p < 0.001$) – the strongest taxon-level response observed. Genomic predictions (PICRUSt2) explain this divergence as marine *Chloroflexi* significantly upregulated reductive dehalogenase genes (e.g., *dehH*, $|log2FC| = 1.62$, $padj < 0.01$). This suggests that they can utilize EDPB as an electron acceptor through reductive dehalogenation [48], with salinity further stabilizing their membrane-bound dehalogenases,

promoting sustained enzymatic activity under pollutant stress [49]. Freshwater *Chloroflexi*, however, exhibited minimal activation of *dehH* genes ($|log2FC| = 1.02$, $padj = 0.12$) and were dominated by non-dehalogenating lineages (e.g., *Anaerolineae*), rendering them vulnerable to EDPB toxicity because they are less capable of metabolizing EDPB.

The overall abundance of *Proteobacteria* in SS exposed to composite pollutants PE-EDPB and PVC-EDPB decreased to 27.69 % and 29.34 %, respectively, compared to 36.8 % in the blank control group (Table S15). However, niche-specific selection occurred within this phylum, which showed slight increase under exposure to composite PE-EDPB, as observed in *Azospirillum* spp. in lake sediment and *Vibrio* spp. in sea sediment (Fig. 5c and d). Comparison of *Proteobacteria* in Scenario A, B, C, and D indicated that MPs alone (Scenario C) did not significantly inhibit *Proteobacteria* ($p = 0.12$), whereas composite contamination (Scenario A) inhibited them by 20–25 % ($p < 0.01$), correlating with higher EDPB adsorption capacity (Table S13). This is particularly

noteworthy as *Proteobacteria*, especially the *γ- Proteobacteria* and *α-Proteobacteria*, are key colonizers of plastic particles in marine environments [50]. Notably, the abundance in the PE and PVC groups was higher, at 37.24 % and 32.45 %, respectively, suggesting that EDPB adsorbed onto the surface of MPs influenced specific microbial guilds in sediments. The role of *Proteobacteria* extends beyond community dynamics; they are essential for nitrogen fixation [51]. A decrease in their relative abundance could therefore disrupt the nitrogen cycle in sediments, highlighting the broader ecological implications of composite pollutants and EDPB exposure. Our results underscore the importance of understanding microbial community responses to emerging contaminants, as these dynamics can significantly impact microbial ecosystem functions.

We further investigated the microbial communities at the genus level within microcosms exposed to EDPB conditions (Fig. S5). Taxonomic niche partitioning analysis revealed dose-dependent responses to EDPB exposure, with elevated EDPB levels significantly reducing microbial diversity (Shannon index decreased by 5.2 % and 3.7 % in LS and SS, respectively, $p < 0.01$), driving a selective enrichment of potential pollutant-tolerant genera (e.g., *Desulfobacter* and *Paraeggerthella*) within specific ecological niches, while stress-sensitive taxa were progressively excluded. Whereas low EDPB concentrations showed no significant impact on niche partitioning, maintaining baseline community structure

(Fig. S5). This suggests that elevated EDPB levels may compromise the stability and resilience of micro-ecosystems in sediments by reducing overall biodiversity. Low EDPB concentrations, nevertheless, may still impact ecologically relevant functions and processes by altering the structure of microbial communities.

3.4.3. Adaptive mechanism underlying increased abundance of marine Chloroflexi

Chloroflexi, especially marine *Chloroflexi*, are known for their metabolic versatility, including the ability to degrade complex organic compounds and participate in anaerobic respiration processes such as reductive dehalogenation [52]. Given that fluorinated liquid crystal monomers like EDPB contain halogenated aromatic structures, *Chloroflexi* may exploit their enzymatic machinery to transform or detoxify these xenobiotic compounds, thereby gaining a competitive advantage over less tolerant taxa. Moreover, *Chloroflexi* have been reported to form resilient biofilms [53,54] and exhibit slow but stable growth rates, traits that facilitate survival in chemically stressed and nutrient-limited sediment environments. The increased abundance of marine *Chloroflexi* likely reflects a reciprocal tolerance mechanism, where these microbes adaptively shift community structure towards taxa capable of mitigating pollutant toxicity and maintaining ecosystem functions. The observed microbial diversity shifts and *Chloroflexi* enrichment underscore the
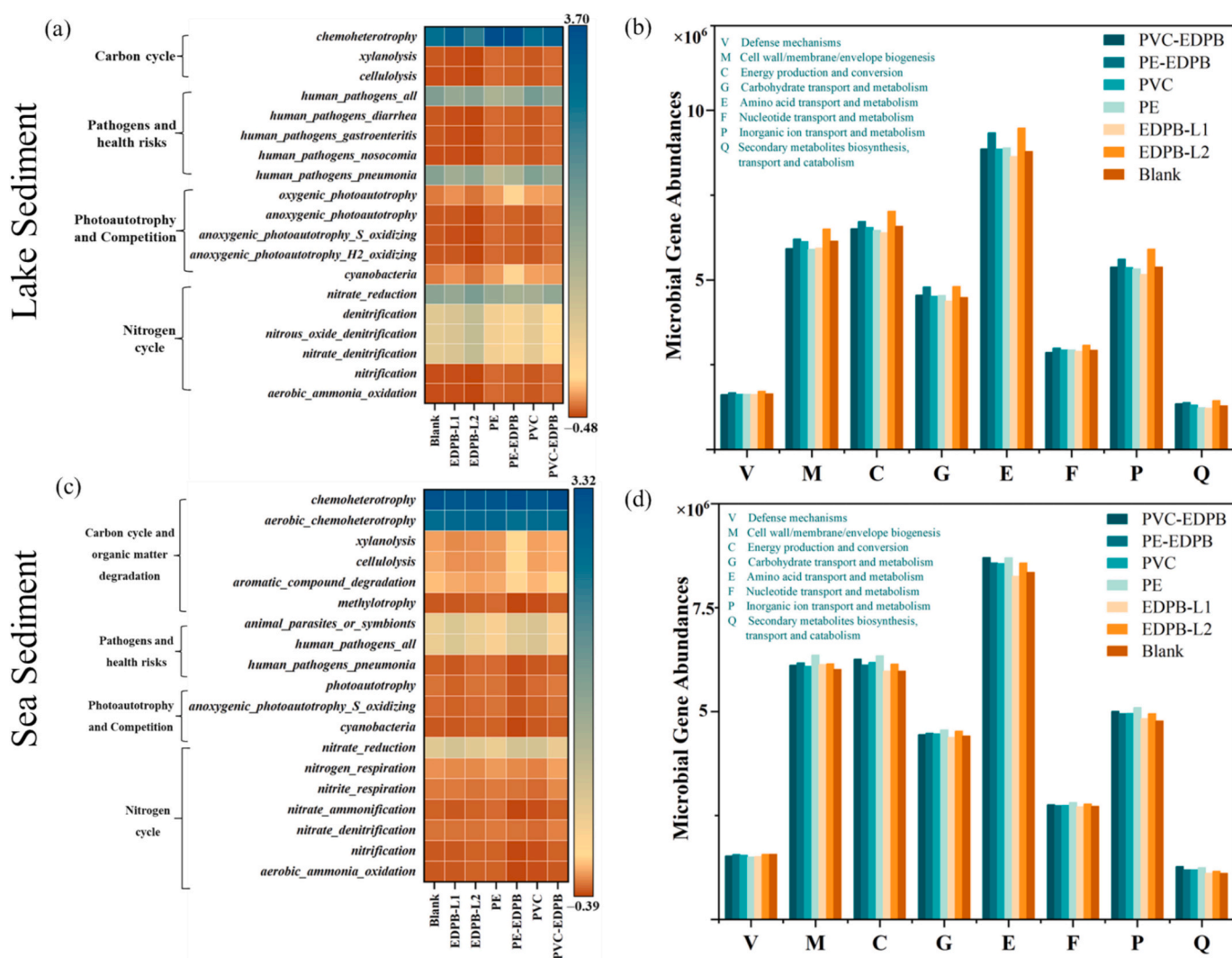

Fig. 6. Functional perturbation and metabolic adaptation of sediment microbiomes. Changes in ecological functions of microbial communities predicted based on the FAPROTAX database in (a) LS and (c) SS; metabolic pathways of microbial communities in each group predicted based on the PICRUSt2 database in (b) lake sediment and (d) sea sediment.

dynamic ecological responses of sediment microbiomes to emerging co-pollutants. These findings highlight the importance of considering microbial functional resilience and adaptive mechanisms when assessing ecological risks posed by complex pollutant mixtures in aquatic sediments.

3.4.4. Metabolic functions of indigenous microbial communities at the OTU level

Alterations in the composition and structure of sedimentary microbial communities can affect the functional roles; hence, the ecosystem functionality of resident microorganisms [55]. This study further utilized the FAPROTAX database to predict changes in the ecological functions of microbial communities (as depicted in Fig. 6a and c) by employing the PICRUSt2 database to forecast changes in microbial gene abundances, which led to inferences about changes in metabolic pathways among different groups (Fig. 6b and d).

3.4.4.1. Potential nitrogen cycling disruptions.
The presence of EDPB, MPs, and their composites disrupted nitrogen cycling in sediments, as indicated by significant taxonomic shifts alongside PICRUSt2-based functional predictions. In LS, the relative abundance of key nitrifying genera (e.g., *Nitrosomonas*) decreased by 4.2 % ($p < 0.01$ vs. control), consistent with predicted reductions in *amoA* gene abundance ($log2FC = -0.04$ to -0.5), $p < 0.05$). Similarly, denitrifying taxa (*Pseudomonas*) in SS declined by 3.1 % ($p = 0.003$), correlating with a significant depletion in nitrate reductase gene (*narG*) predictions ($p = 0.002$). Concurrently, cyanobacteria-related functional genes linked to oxygenic photoautotrophy increased 1.3-fold in PE-EDPB-treated LS ($p < 0.01$), suggesting potential niche competition between photoautotrophs and heterotrophic nitrifiers [56]. While these findings are based on predictive genomic inference rather than direct rate measurements, the strong concordance between taxonomic changes and functional gene predictions, supported by relevant literature [57], indicates that MPs-EDPB exposure preferentially inhibits chemoautotrophic nitrogen transformations, which may exacerbate TN limitation in sediment microbial communities. These functional genes are crucial for the growth of *cyanobacteria*, which play a vital role in regulating the nitrogen pool within the ecosystem [56]. The observed changes suggest that the nitrogen cycle in LS is notably affected. Similarly, predictions from FAPROTAX and PICRUSt2 data indicate perturbations in nitrate reductase genes in the SS treatment groups, further confirming disruptions in the nitrogen cycle. Although 16S rRNA gene-based analysis coupled with PICRUSt2 functional prediction revealed abundance changes in nitrogen-cycling related genes (e.g., *amoA*), these findings still require validation of actual expression levels through omics technologies.

3.4.4.2. Stress-induced metabolic responses.
The metabolic pathways of the 16S rRNA data obtained from each sample were annotated using the COG database, revealing significant changes across all samples. In both LS and SS, EDPB-L2 exhibited increased metabolic pathway genes compared to the blank control group. Specifically, there was a rise in genes related to amino acid transport and metabolism, inorganic ion transport and metabolism, signal transduction mechanisms, and cell wall, membrane, and envelope biogenesis. These genes are crucial to determining the physiological state of microbial cells [58], indicating that high concentrations of EDPB can suppress microbial metabolic activities and affect genes related to protein synthesis. In the composite pollutants' treatment group in LS, metabolic pathways related to defense mechanisms, cell motility, secondary metabolite biosynthesis, transport, and catabolism exhibited notable differences, where increased expression observed in the PVC-EDPB group compared to the PE-EDPB group. These changes enhance microorganisms' ability to adapt to environmental fluctuations and optimize their survival [59]. However, for composite pollutant in SS, the relative abundance of functional genes related to xylanolysis, chitinolysis, and cellulolysis was

significantly reduced in the PE-EDPB group. These catabolic processes, which involve the synergistic action of multiple enzymes, including endonucleases, exonucleases, and β-glucosidases, are essential for breaking down complex polysaccharides [60], allowing microorganisms to acquire vital carbon and energy and release nutrients for other organisms. Therefore, the presence of PE-EDPB substantially impacts nutrient cycling in SS ecosystems. Additionally, the composite pollutants significantly enhanced pathogenic potential in marine sediments, with dose-dependent increases in human pathogens correlated with EDPB adsorption levels ($p = 0.004$). We observed marked enrichment of *Acinetobacter* (1.2 % to 3.5 %, $p = 0.007$) and *Vibrio* (0.8 % to 2.1 %, $p = 0.013$). High-risk OTUs — ANCOM-BC identified *Vibrio cholerae*-associated OTU_7412 showing 2.8-fold enrichment in PE-EDPB groups ($p < 0.05$). These shifts corroborate with the dual role of MPs as both pathogen vectors [61] and interface for selective agents, where EDPB adsorption may exert selection pressure for opportunistic pathogens such as antimicrobial resistance traits [62,63]. Sediment can act as transport vector for these pathogenic microorganisms, posing threats to ecosystem biosecurity, water security, and human health [61].

4. Conclusions and future perspectives

The study investigated the adsorption behavior and mechanisms of EDPB on various MPs, encompassing PE, PP, PVC, and PS. The results revealed that variations in equilibrium adsorption were primarily dictated by the polarity of plastic types, with PE exhibiting the highest adsorption capacity. Comparative adsorption experiments and FTIR analysis revealed that EDPB's adsorption on MPs was driven by hydrophobic interactions, π-π interactions, and electrostatic forces. Furthermore, microcosm experiments found that pollution by EDPB, MPs, and their composites in aquatic systems modified the abundance and structure of microbial assemblages in sediment, causing shifts in dominant guilds. Notably, the presence of these contaminants led to the emergence of unique microbial communities in sediments, and may disrupt specific nitrogen-transforming functions within microbial populations. In addition, the enrichment of pathogenicity-related gene functions in seawater compared to freshwater sediments in the presence of MPs, adds complexity to the environmental behavior of EDPB, with significant implications for transport in natural waters. This study provides foundational insights into the interaction mechanisms between pristine microplastics and EDPB, highlighting acute ecological impacts under worst-case exposure scenarios.

To advance our understanding of MP-EDPB interactions in realistic environmental contexts requires addressing key knowledge gaps. Future research should prioritize the incorporation of environmentally relevant microplastic aging processes to better reflect field conditions and their influence on pollutant adsorption and microbial community dynamics. Long-term exposure experiments, extending beyond 90 days, will be informative to capture microbial adaptive responses, functional shifts in biogeochemical cycles, and the propagation of ecological risks within sediment food webs. Employing integrative multi-omics approaches, such as meta-transcriptomics and targeted proteomics, will be critical for unravelling microbial metabolic pathways and resistance mechanisms in response to combined microplastic and organic contaminant stressors. Overall, collaborative efforts across multidisciplinary partnerships and diverse ecosystems are needed to better elucidate the complex interactions governing pollutant fate, bioavailability, and ecological impacts, thereby enhancing risk assessment and informing effective management of LCMs contaminants.

Notes

The authors declare no competing financial interest.

CRediT authorship contribution statement

Rui Yang: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Sanjeeb Mohapatra:** Writing – review & editing. **Apple Pui-Yi Chui:** Writing – review & editing. **Season Si Chen:** Writing – review & editing, Writing – original draft, Project administration, Conceptualization. **Mui-Choo Jong:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Conceptualization.

Declaration of competing interest

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

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Appendix A. Supplementary data

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