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Research Paper

The release, degradation, and distribution of PVC microplastic-originated phthalate and non-phthalate plasticizers in sediments

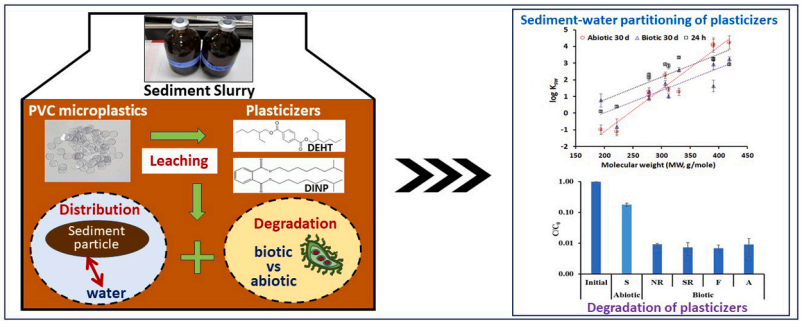
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HIGHLIGHTS

- Leaching and degradation of plasticizers from PVC microplastics is studied.
- The microbial community and functional genes profile were analyzed.
- Higher the initial plasticizer content in microplastics higher is the leaching rate.
- Higher degradation of plasticizers was observed in biotic environment than abiotic.
- Sediment-water partitioning constants were altered differently after degradation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Plasticizer leaching
Abiotic loss
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Partitioning
Bacterial community

ABSTRACT

This study investigated the leaching of phthalate and non-phthalate plasticizers from polyvinyl chloride microplastics (MPs) into sediment and their degradation over a 30-d period via abiotic and biotic processes. The results showed that 35—79% of plasticizers were released into the sediment from the MPs and > 99.9% degradation was achieved. Although a significantly higher degradation was found in plasticizer-added microcosms under biotic processes (overall, 94%), there was a noticeable abiotic loss (72%), suggesting that abiotic processes also play a role in plasticizer degradation. Interestingly, when compared with the initial sediment-water partitioning for plasticizers, the partition constants for low-molecular-weight compounds decreased in both microcosms, whereas those for high-molecular-weight compounds increased after abiotic degradation. Furthermore, changes in the bacterial community, abundance of plasticizer-degrading bacterial populations, and functional gene profiles were assessed. In all the microcosms, a decrease in bacterial community diversity and a notable shift in bacterial composition were observed. The enriched potential plasticizer-degrading bacteria were *Arthrobacter, Bacillus, Desulfovibrio, Desulfuromonas, Devosia, Gordonia, Mycobacterium*, and *Sphingomonas*, among which *Bacillus* was recognized as the key plasticizer degrader. Overall, these findings shed light on the factors affecting plasticizer degradation, the microbial communities potentially involved in biodegradation, and the fate of plasticizers in the environment.

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1. Introduction

Phthalic acid esters (PAEs) are a group of chemical compounds widely employed as plasticizers in polyvinyl chloride (PVC) plastics and other consumer products such as food packaging, medical equipment, industrial piping, upholstery, and agricultural plastic films [1,2]. These compounds can be incorporated into plastics to enhance their flexibility, durability, and other physical properties [3]. Importantly, plasticizers lack chemical bonds with the products to which they are added, potentially enabling them to leach into the environment; [4] once released, phthalates can contaminate soil, water, and air. Thus, PAEs are classified as emerging pollutants because of their detectable presence in various environmental compartments, including air, dust, food, soil, water, sediment, and landfill leachate [5,6]. Notably, PAEs have been designated as priority pollutants by regulatory agencies such as the United States Environmental Protection Agency (USEPA), European Union (EU), and Chinese water regulations owing to their carcinogenic [7] and endocrine-disrupting properties [7,8].

PAEs accumulate in aquatic environments worldwide and pose significant threats to organisms [9]. Staple et al. (1997) [10]reviewed the literature on the acute and chronic aquatic toxicity of 18 phthalate esters, revealing that six esters, dimethyl phthalate (DMP), diethyl phthalate (DEP), diallyl phthalate (DAP), dibutyl phthalate (DBP), diisobutyl phthalate (DIBP), and benzyl butyl phthalate (BBP), have acute or chronic effects on various aquatic animals. The pseudo-persistent nature of PAEs and their potential for prolonged exposure raise significant concerns regarding their impact on both human and environmental health [11].

Different physicochemical methods and advanced oxidation and biological processes are currently used to treat PAEs [12]. Biodegradation is a promising approach to address phthalate pollution in natural environments [12–14]. Numerous studies have emphasized the substantial role of microorganisms in the breakdown of phthalates under diverse environmental conditions [6,15]. Bacterial genera such as *Bacillus, Pseudomonas, Rhodococcus, Mycobacterium, Acinetobacter, Hydrogenophaga, Sphingomonas, Halomonas, Microbacterium,* and *Comamonas* are promising microbial resources that degrade phthalates in various environments [16–18].

Monitoring and studying the fate of plasticizers in sediments and water is crucial for managing and mitigating their environmental impacts. To assess pollution levels and associated risks to the environment, it is imperative to conduct precise studies on the degradation of plasticizers. However, there is currently limited research specifically focusing on plasticizer degradation in sediments by naturally occurring microbes [19]. Despite the widespread distribution of plasticizers, there has been limited research on their leaching behavior from various products.

Therefore, this study aimed to evaluate the degradation of plasticizers in sediment-water slurries under nitrate-reducing (NR), sulfate-reducing (SR), fermentation (F), and aerobic (A) conditions. The main objective was to investigate the abiotic and biotic degradation of plasticizers released from PVC microplastics (MPs) or plasticizer-amended batches. We also evaluated the sorption of plasticizers between sediment and water to interpret their initial distributions in the two media. Furthermore, this study investigated the bacterial community changes in sediments during the pre- and post-biotic degradation of plasticizers. Furthermore, bacterial communities related to plasticizer degradation were assessed. This study presents a comprehensive framework for investigating plasticizer behavior, thus advancing our understanding of the environmental fate of plasticizers and their potential mitigation strategies through a holistic investigation of plasticizer leaching, degradation, sorption dynamics, and microbial communities in sediments.

2. Materials and Methods

2.1. Reagents and materials

All reagents used were of analytical grade. Phthalates and other chemicals were purchased from Alfa Aesar, including dimethyl phthalate (DMP; Germany, 99%), diethyl phthalate (DEP; India, 99%), dibutyl phthalate (DBP; USA, 99 + %), diisobutyl phthalate (DIBP; Japan, 99%), di-n-pentyl phthalate (DNPP; Great Britain, 98%), benzyl butyl phthalate (BBP; Great Britain, 98%), di(2-ethylhexyl) phthalate (DNOP; Japan, 98%), and benzyl benzoate (BB; India, 99 +%). Diisononyl phthalate (DINP; 99 +%) was purchased from Sigma Aldrich (Netherlands) and bis(2-ethylhexyl) terephthalate (DOTP; 97%) from Acros Organics (USA). The physicochemical properties of the phthalates used in this study are summarized in Table S1. Certified reference material (CRM 113–03-006); for PVC containing DMP, DEP, DBP, BBP, DEHP, and DNOP; was purchased from the Korea Research Institute of Standards and Science (KRISS). Dichloromethane (DCM, 99.8%) and n-hexane (>96%) were obtained from Daejung (Korea) and methanol (99.5%) from Sigma-Aldrich (USA). The plasticizer stock solution (100,000 mg/L for DINP and 10,000 mg/L for the other nine plasticizers) was prepared in methanol and stored in a refrigerator at − 20 °C.

As the thin and flexible PVC films containing plasticizers are widely used in various applications, two commercially available soft PVC sheets of thickness 0.2 mm (cPVC-1) and 0.3 mm (cPVC-2) were purchased from an online market (FilmBank, Korea). Both PVCs were cut into 4.5 mm diameter MP_S using a multi-hole puncher. The plasticizers in the PVC MPs were extracted with DCM using an ultrasonication apparatus [20], which was further analyzed by gas chromatography coupled with a mass spectrometer and quantified using plasticizer calibration standards (for details, see Text S1). Polydimethylsiloxane (PDMS) was used as a passive sampler to measure the plasticizer concentration in water. PDMS sheet of 1-mm thickness (HSW Co., Ltd., Korea) was cut into 6-mm diameter disks and cleaned as suggested in the literature [5].

2.2. Plasticizer degradation experiment

Sediment was collected from the surface (up to 20 cm) of the Hyeongsan River, South Korea using a manual grab sampler, which was transported to the laboratory using an ice box and stored at 4 °C in the refrigerator until use. For initial microbial community analysis, sediment samples were stored at − 80 °C. 16 s rRNA gene amplicon sequence analysis of the initial sediment was performed immediately before conducting further microcosm experiments. The sediment was sieved through a 2-mm sieve before the experiment.

Plasticizer degradation experiments were conducted under sterile and non-sterile conditions for abiotic and biotic processes, respectively. For abiotic or sterile processes, the sediment and water were sterilized using an autoclave at 121 °C and cooled at room temperature overnight. This process was repeated two times to ensure complete sterilization. The sediment microcosms mainly comprised three different batch sets as a source of plasticizers: two were prepared by mixing PVC MPs of different thicknesses, named ‘cPVC-1 batch’ (0.2-mm thick) and ‘cPVC-2 batch’ (0.3-mm thick), and the third was prepared by mixing the plasticizers directly into the microcosms, named ‘plasticizer batch.’ In addition, four different environmental conditions were employed for each batch (NR, SR, F, and A); the NR, SR, and F microcosms were used under anaerobic conditions. Thus, 12 different batch sets were prepared, each with four replicates, for a total of 48 microcosms for the non-sterile batch, which employed biotic processes. Four replicates of sterile (or abiotic) microcosms were prepared with 4 replicates using the same liquid medium.

In each microcosm, 30 g of sediment and 105 mL of sterile media were combined in 120 mL serum bottles, except for batch A, which employed 250 mL bottles to provide half of the free headspace. The PVC batches consisted of sediment with 1.2% of cPVC-1 and cPVC-2 MPs. In

the plasticizer batch, 300 μL of plasticizer mixture (containing 10 compounds, including 20,000 mg/L of DINP, and 2000 mg/L of nine others) was added directly to the microcosms. Two clean passive PDMS sampler disks were added to each bottle. The media composition for each condition is summarized in Table S2. The media used for both aerobic and fermentation conditions were consistent. Serum bottles were meticulously packed to ensure minimal headspace, placed in a tumbler, and tumbled for 30 d. After 30 d of incubation, the sediment, water, PVC, and PDMS were separated and each sample was subjected to a comprehensive analysis to assess the changes in phthalate concentration, microbial activity, and community composition.

In addition to the degradation study, a sorption experiment was conducted to evaluate the initial partitioning of plasticizers in the sediment and water using the same sediment described above. Briefly, 5.4 g of fridge-dried sediment was placed in a sterile glass vial and 20 mL of sterile deionized (DI) water was added. The sediment and DI water were autoclaved twice. Plasticizer mixture (250 μL; 10,000 mg/L for DINP and 1000 mg/L for other nines) was added to each vial, capped with Teflon-lined caps, and mixed. The experiment included four replicates at designated time points (3, 6, and 24 h). The vials were placed in a vertical tumbler to facilitate mixing. After each time point, the plasticizers were extracted from the sediment and water phases and analyzed.

The plasticizers in the PDMS, and sediment are extracted ultrasonically using DCM, while liquid-liquid extraction is employed for water sample using DCM and analyzed by gas chromatograph (Shimadzu, Nexis GC-2030, Japan) coupled with a mass spectrometer (Shimadzu, GCMS-QP2020 NX, Japan) and DB-5 capillary column (Agilent, dimensions: 30 m × 250 μm × 0.25 μm, USA). The detailed methodologies used in the extraction and analysis, as well as quality assurance and quality control, are summarized in Text S1 and S2. A good recovery of each plasticizer was obtained using these methods and the extraction efficiencies of different phthalates ranged from 80–113, 88–117, and 101–121% in water, PDMS, and sediment, respectively (Table S3). In addition, there was good recovery of the six phthalates from PVC-certified reference materials, ranging from 84–101% (see Table S4).

2.3. Bacterial community analysis

Genomic DNA was extracted from the sediment samples using NucleoSpin® Soil kit (MACHERET-NAGEL GmbH & Co., Germany). The quality and quantity evaluation of the extracted DNA was performed by 1.0% agarose gel electrophoresis and a Nanodrop spectrophotometer (DS-11 FX Series, DeNovix) techniques. Bacterial community analysis was performed by 16 S rRNA gene amplicon sequencing. The V3–V4 regions of the 16 S rRNA genes were amplified using the Herculase II Fusion DNA Polymerase Kit (Illumina, CA, USA). The amplified products were used to generate paired-end sequence reads on an Illumina MiSeq (PE300) platform (Macrogen, Seoul, South Korea). The generated sequence reads were processed and analyzed using the QIIME manual and EzBioCloud 16S-based MTP pipeline [21].

3. Results and discussion

3.1. Plasticizers release from PVC MPs and their subsequent degradation

This study investigated the release of plasticizer additives from PVC MPs into sediment microcosms and their subsequent degradation via abiotic and biotic processes. The MPs used were prepared from two different types of commercial PVC sheets with different thicknesses (cPVC-1) and (cPVC-2). Note that we monitored the DEHT (non-phthalate) and DINP (phthalate) plasticizers in both MPs; however, two additional peaks in the GC-MS chromatogram from each PVC sample remained unknown and were not considered in this study. This was due to the unavailability of chemicals for qualitative and quantitative analysis of unidentified peaks using their calibration standards. The total mass of DEHT and DINP in pristine PVC MPs added to the sediment, the residual total mass in MPs after 30 d, the total mass leached from MPs into the microcosms, and their subsequent degradation during this period are presented in Fig. 1 and S1 and Table S5.

The results showed that plasticizer release into the sediment microcosm increased with increasing initial content of pristine MPs. The initial concentrations of the two plasticizers in the PVC MPs were in the following orders: DEHT: cPVC-1 < cPVC-2; DINP: cPVC-1 > cPVC-2; cPVC-1: DEHT < DINP; cPVC-2: DEHT > DINP; and total (DEHT + DINP) mass: cPVC-1 > cPVC-2. The release of DEHT and DINP masses from cPVC-1 MPs were 1130 ± 54 and 35,300 ± 840 μg in abiotic or sterile (S) microcosms and 1210 ± 6.0 and 37,400 ± 1200 μg in biotic or non-sterile microcosm, respectively. Similarly, the released plasticizer masses from cPVC-2 MPs were 16,700 ± 460 and 340 ± 55 μg in sterile and 16,500 ± 3100 and 340 ± 110 μg in non-sterile microcosm for DEHT and DINP, respectively. In addition, the release of total (DEHT + DINP) mass from cPVC-1 MPs ranged from 36,400–38,600 μg in sterile and non-sterile conditions from the initial mass of 49,500 μg (in pristine MPs), which was relatively higher than that leached from cPVC-2 MPs of 16,800–17,000 μg total mass released from pristine MPs (initial mass; 35,600 μg). This may be due to the higher concentration gradient between MPs and the sediment-water slurry for PVC with a higher plasticizer content [22]. Moreover, an increase in the plasticizer content in plastic products increases the free volume, which weakens the physical bond between the polymer and the plasticizer, leading to wider channels that facilitate the migration of plasticizer molecules with higher leaching rates [23,24]. This indicates that the plasticizer leaching from the products is directly proportional to the fraction of the initial content. A similar result has been reported in the literature, which showed that the leaching of phthalates from PVC MPs increased with an increase in the initial phthalate content [25]. Furthermore, about 74–79% of plasticizer masses were released into the sediment microcosms from the cPVC-1 MPs (0.2-mm thick), whereas only about 35–48% of plasticizers were lost from cPVC-2 MPs (0.3-mm thick), suggesting the effect of thickness of PVC MPs on leaching of plasticizers. Studies have found that the leaching of phthalate plasticizers varies with the type and thickness of the consumer product [19]. They found that there was a large difference in phthalate leaching between abiotic and biotic processes from a thick PVC cable; however, the difference was not significant for thin polyethene plastic under both processes. Wang et al. reported that the DEHP release rate increased with decreasing film thickness [26].

Interestingly, significant abiotic and biotic degradation was observed for both compounds in all the microcosms during the degradation study (Fig. 1). After 30 d, about 4–6 μg DEHT was detected in the cPVC-1 and cPVC-2 batches after the abiotic process, whereas the biotic process employing all four conditions (i.e., NR, SR, F, and A) resulted in very low masses (<1 μg). However, a slightly higher mass was observed for DINP after 30 d in the cPVC-1 and cPVC-2 batches, at 103 and 61 μg after abiotic degradation and 4–7 and 5–7 μg after the biotic process. The biotic process exhibited a higher degradation efficiency (>99.9% removal) in both PVC batches; however, degradation was not limited to biotic conditions, as evidenced by the large mass decrease in abiotic conditions.

This study also analyzed the DEHT and DINP concentrations in the sediment and water phases after 30 d of degradation. The results are presented in Fig. 2. The residual concentrations of both plasticizers in all abiotic microcosms were significantly higher than those in the biotic microcosms for both PVC batches, suggesting higher degradation by the biotic process. In addition, the efficiency of biotic degradation was more pronounced in the sediment phase than in the water phase, suggesting that the abiotic degradation of plasticizers via hydrolysis is comparable to biotic degradation in the water phase. This was attributed to the very low mass or concentrations of DEHT and DINP in the water phase because of the higher K_{sw} values of hydrophobic plasticizers, resulting in a low but similar aqueous concentration owing to constant leaching

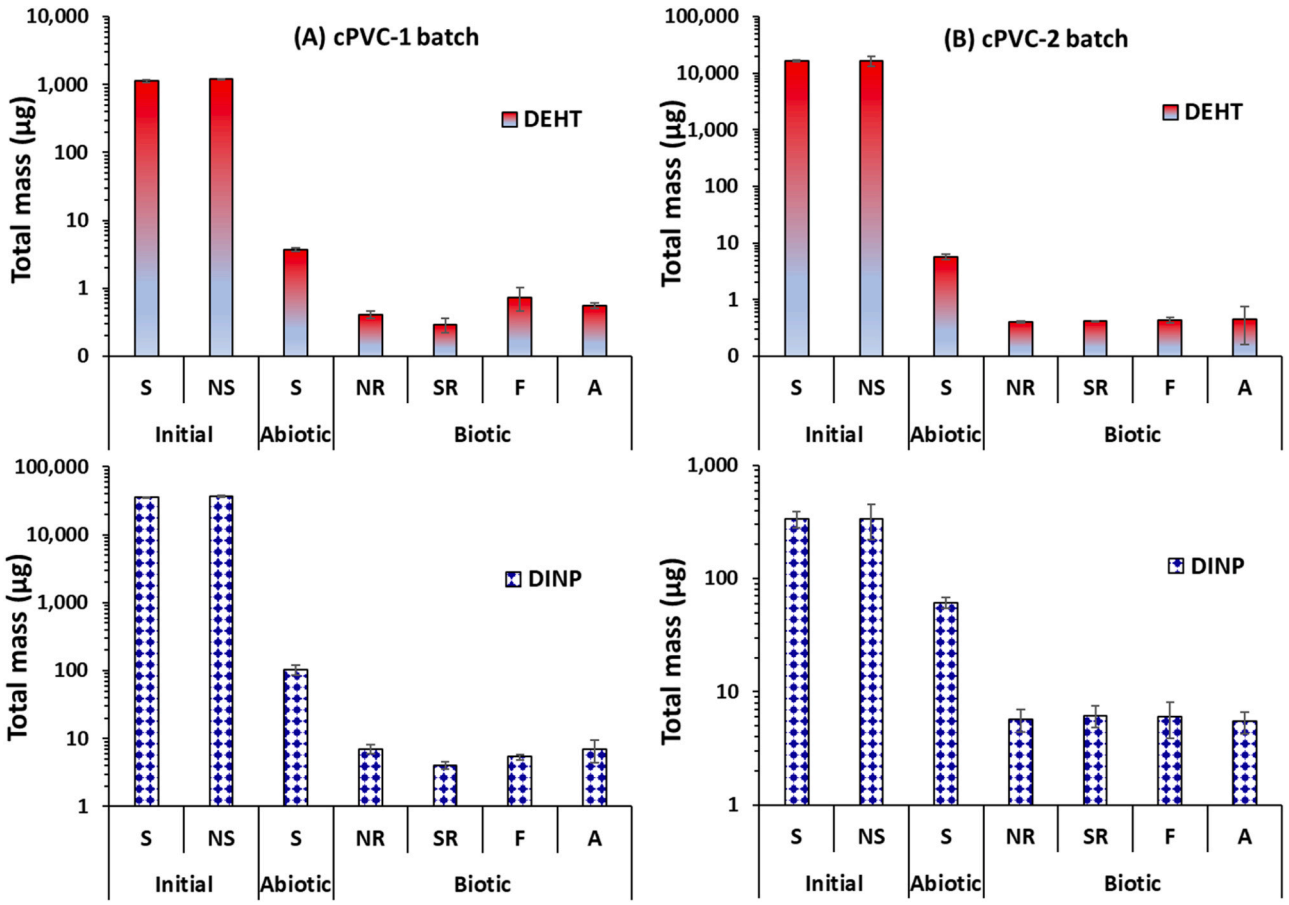


Fig. 1. Change in mass of DEHT and DINP in cPVC MPs mixed batches during 30 d of abiotic and biotic processes (Initial = mass leached from PVC MPs to microcosms, S = sterile, NS = non-sterile, NR = nitrate reduction, SR = sulfate reduction, F = fermentation, A = aerobic).

from PVC MPs. In the cPVC-1 batch, the measured residual DEHT and DINP concentrations in sterile microcosms were 124 and 3440 µg/kg, while those in non-sterile microcosms (i.e., NR, SR, F, A) were 5–25-fold smaller than in sterile microcosms, ranging from 10–25 and 134–236 µg/kg, respectively. Similarly, the residual DEHT and DINP concentrations in sterile microcosms of the cPVC-2 batch were 190 and 2030 µg/kg and those in non-sterile microcosms ranged from 13–15 and 181–205 µg/kg, respectively, showing 10–15 fold differences.

Although there was less variation in the residual aqueous concentrations among the biotic and abiotic microcosms, there was a distinct variation in the DEHT and DINP concentrations among the PVC types. The aqueous concentrations in the sterile cPVC-1 and cPVC-2 batch were 3.30 and 9.10 ng/L for DEHT, and 31.5 and 16.3 ng/L for DINP, respectively (Fig. 2). After biotic degradation, the DEHT and DINP concentrations in water reached 1.00–2.30 and 17.1–23.0 ng/L in cPVC-1 batch and 0.60–7.60 and 9.10–12.7 ng/L in cPVC-2 batch, respectively. This shows that the higher the initial plasticizer content in PVC MPs, the higher the leaching into the microcosms, thereby increasing biotic degradation. Furthermore, the DINP degradation efficiency of DINP is affected by the MP thickness, which was lower in the thicker cPVC-2 batch than in the thinner cPVC-1 batch.

Overall, the degradation trends for DEHT and DINP in the aqueous phase were quite consistent (except under aerobic conditions); however, there was no clear trend in the residual concentrations of plasticizers in the sediment among the four biotic conditions. The decrease in aqueous plasticizer concentration in the biotic microcosms was also supported by the decrease in total organic carbon (TOC) in the water under biotic conditions (Table S6). Furthermore, Fig. S2 clearly shows the substantial reduction in nitrate and sulfate ions in non-sterile microcosms compared to sterile conditions, indicating the effectiveness of nitrate- and sulfate-reducing microorganisms in degrading plasticizers. These results emphasize that microbial communities work effectively under various environmental conditions, including fermentation and aerobic conditions, as they follow a similar trend for degradation. Changes in the sediment or aqueous concentrations of a given plasticizer using all biotic processes (NR, SR, F, and A) were similar in a batch, suggesting less sensitivity of biodegradation to the given conditions. A previous study reported that the release of the DBP plasticizer is less affected by the ionic strength and pH of the solution, which is due to the non-ionic nature of plasticizers and the ability of PVC to resist salt/acid/alkaline solutions [22].

3.2. Results of plasticizer batch study: Abiotic vs biotic degradation

This study investigated the degradation of 10 plasticizers (9 phthalates and 1 non-phthalate, i.e., DEHT) in a directly spiked 'plasticizer batch' over 30 d and the results revealed diverse responses under abiotic and biotic conditions, which are presented in Table 1 and Fig. S3. Although the mass of each plasticizer decreased in both the sterile and non-sterile microcosms (except for DMP in the sterile microcosms), the residual mass was significantly higher in the sterile microcosm than in the non-sterile microcosm, indicating a higher degradation potential of the biotic process (see detailed description in (Text S3). When compared to the abiotic removal, the plasticizer degradation efficiency of biotic processes was significantly higher under all conditions, which ranged from 93–99% for biotic and 62–84% for abiotic processes, except DMP and DEP (Table S7). Unexpectedly, DMP and DEP showed higher concentrations in the sterile microcosms. A previous study reported the lowest degradation rates for low-molecular-weight phthalates (DMP and DEP) [19]. The decrease in nitrate and sulfate ion concentrations in the

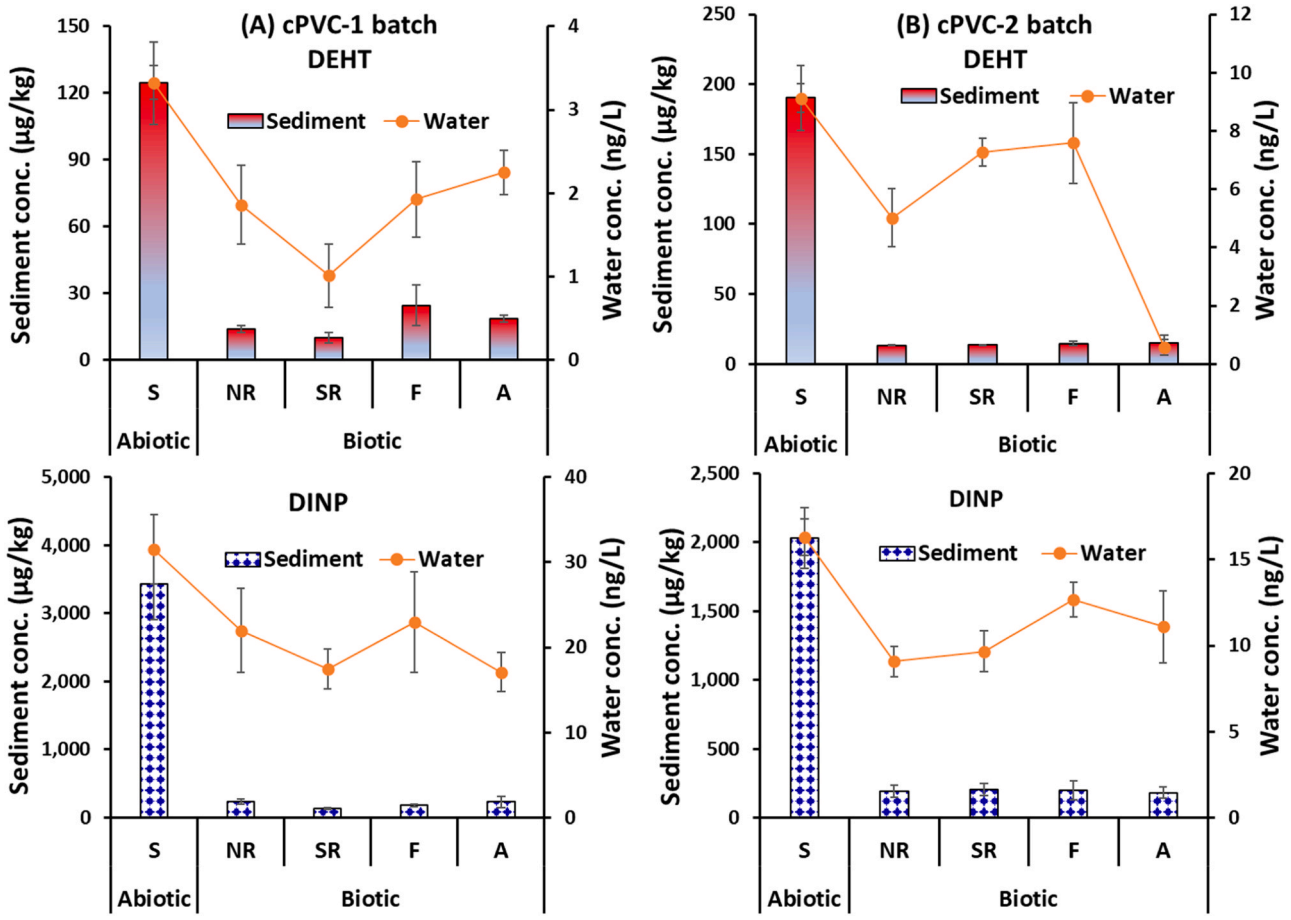


Fig. 2. Residual concentrations of DEHT and DINP in sediment and water in cPVC MPs mixed batches after 30 d of abiotic and biotic processes (S = sterile, NR = nitrate reduction, SR = sulfate reduction, F = fermentation, A = aerobic).

Table 1
Change in the total mass of each plasticizer in plasticizer batches during the 30-d period.

Conditions	Residual mass of plasticizers in microcosms (µg)						
	Spiked mass	Abiotic overall	Biotic overall	Biotic individual batch			
Compounds	Initial	S	NS	NR	SR	F	A
DMP	600	683 ± 44	9 ± 2	7 ± 0.6	4 ± 0.8	20 ± 5	5 ± 0.6
DEP	600	583 ± 48	282 ± 61	272 ± 32	261 ± 31	291 ± 11	336 ± 18
DIBP	600	128 ± 27	34 ± 5	32 ± 5	29 ± 6	40 ± 12	26 ± 5
DBP	600	138 ± 16	9 ± 2	10 ± 0.7	10 ± 3	10 ± 2	11 ± 2
DNPP	600	174 ± 17	14 ± 4	16 ± 5	8 ± 2	16 ± 4	12 ± 5
BBP	600	119 ± 14	7 ± 2	7 ± 0.3	6 ± 2	5 ± 0.8	8 ± 3
DEHP	600	109 ± 36	22 ± 8	31 ± 9	26 ± 7	16 ± 6	17 ± 4
DCP	600	64 ± 17	9 ± 3	4 ± 0.6	9 ± 2	13 ± 1	5 ± 0.8
DEHT	600	227 ± 60	22 ± 7	23 ± 5	24 ± 6	8 ± 2	19 ± 8
DINP	6000	961 ± 252	327 ± 55	426 ± 15	289 ± 40	298 ± 53	202 ± 35
∑Plasticizers	**11,400**	**3190 ± 533**	**735 ± 90**	**828 ± 75**	**665 ± 98**	**719 ± 96**	**640 ± 72**

biotic processes was higher than that in the abiotic processes, showing the ability of nitrate- and sulfate-reducing microbes to degrade plasticizers (Fig. S2). The overall plasticizer (∑Plasticizers) removal efficiency in non-sterile microcosms is about 22% higher than abiotic removal (72% by abiotic vs 94% in biotic overall), which is attributed primarily to the degradation by the indigenous microbial community in sediment.

Like the PVC batches, there was no clear trend for the biotic removal efficiency of each compound among the four conditions tested; however, if the total plasticizer mass is considered, the order of residual mass in different microcosms was NR < F < SR < A, indicating A as the most favorable environmental condition with the highest ∑Plasticizers biodegradation efficiency. In a study conducted by Staples et al. [27] under aerobic conditions using sewage sludge inocula, ≥ 50% of phthalate esters were degraded within 28 d. However, this study showed a significantly better degradation efficiency for most of the plasticizers in sediment using indigenous microbial communities. Higher degradation under biotic conditions may be due to the ability of microorganisms to produce extracellular polymeric substances (EPS), which play a positive role in biodegradation by absorbing and degrading organic pollutants [28]. It has been reported that an optimal pH of 8.0 was suitable for DEHP biodegradation [29]. In this study, the pH of the different microcosms ranged from 7–8, which is favorable for degradation. Several studies have reported that phthalate plasticizers are readily

degraded by biotic methods [6,13,30]; however, their abiotic degradation efficiencies have not been well studied. This study found that the potential for abiotic degradation of plasticizers was also high, which may be due to hydrolysis [31]. Further studies are required to investigate the potential causes of the abiotic degradation of plasticizers. The negligible removal fraction may be attributed to the slight sorption of the plasticizers in the glass bottle [19].

The residual concentrations of different plasticizers in the sediment and water under various environmental conditions are presented in Fig. 3. In general, the concentration of each plasticizer in the sediment was significantly higher in sterile microcosms than in non-sterile conditions, indicating a higher degradation potential of the biotic process (see detail descriptions in Text S4). The total plasticizer (∑10 Plasticizer) concentration in sediment was 121 mg/kg and 10–18 mg/kg under abiotic and biotic processes, respectively, revealing a significant degradation (up to 100 mg/kg more) of plasticizer by indigenous microbes. Furthermore, the results showed elevated degradation of each plasticizer in water under all biotic conditions when compared to abiotic degradation, with a few exceptions for high molecular weight (HMW) compounds, that is, DEHP (in SR), DEHT (NR, SR, F), and DINP (NR, SR, F, A). However, the aqueous concentrations for those HMW plasticizers were very low (<10 μg/L for DINP, and ≤1 μg/L for DEHP and DEHT). In addition, there was significant biotic degradation of the total plasticizer concentration (∑10 Plasticizer) in water, which reached 11.6 and 2.90–3.50 mg/L under abiotic and biotic processes, respectively (see detailed description in Text S5). The higher biotic loss of total aqueous phase plasticizer (∑10 Plasticizer) concentration was supported by the substantial decrease in TOC concentration under the biotic method (see Table S6).

To better understand the degradation of plasticizers, as well as the

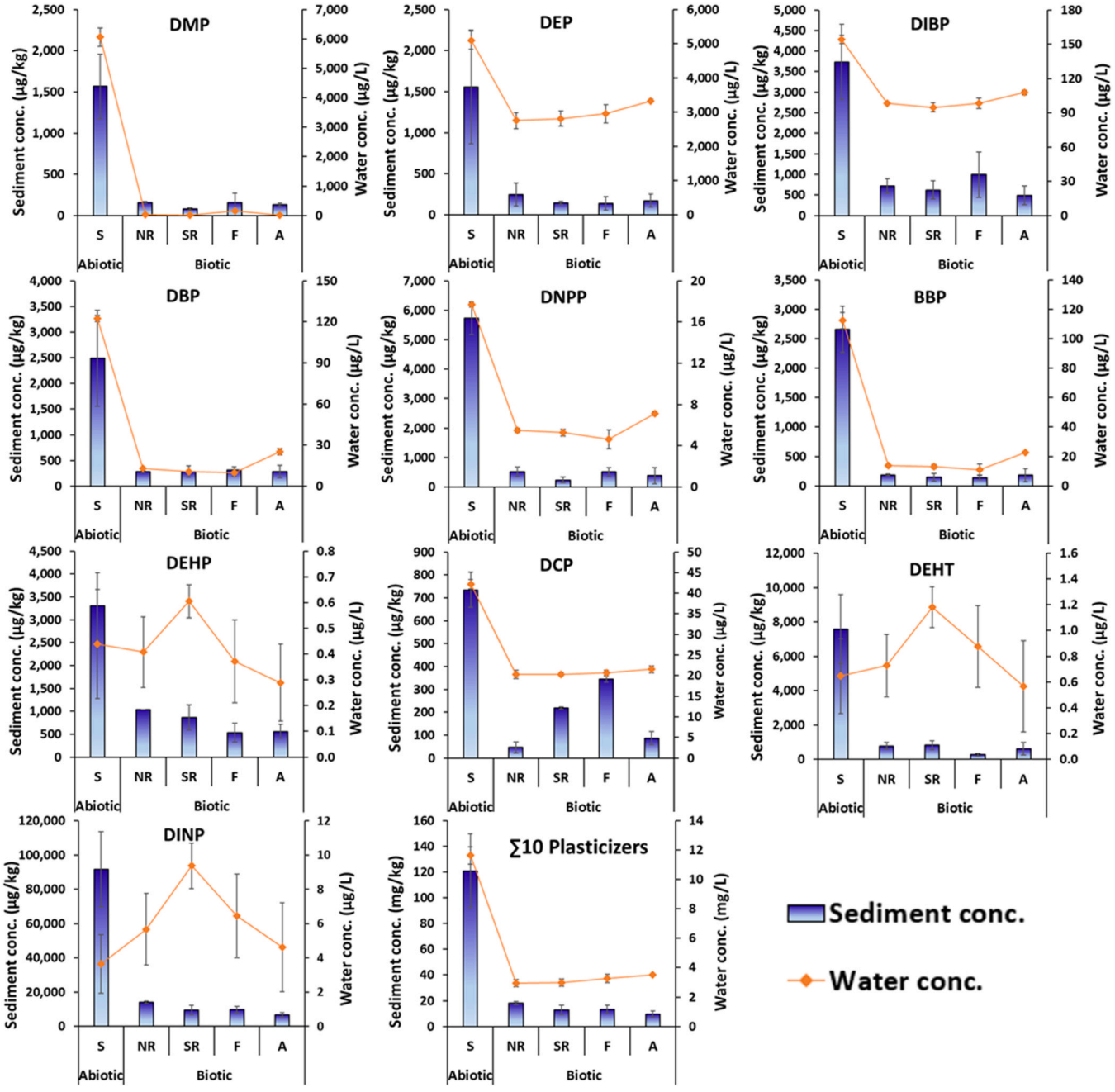


Fig. 3. Residual concentrations of different plasticizers in sediment (bars) and water (lines) in plasticizer spiked batch microcosms after 30 d of abiotic and biotic processes (S = sterile, NR = nitrate reduction, SR = sulfate reduction, F = fermentation, A = aerobic).

changing sorption and desorption processes between the sediment and aqueous phases, the chemical partitioning between the two phases was calculated before and after the 30-d degradation period. It is important to recognize that assessing the partitioning between sediment and water is a crucial process because of the dynamic nature of sediment-water interactions; thus, introducing pseudo-partitioning coefficients or 'equilibrium partitioning constants,' which may better reflect the partitioning behavior of chemicals between these media [32]. Hence, we considered the 'partition constant' of plasticizers between sediment and water at a pseudo-equilibrium state. Potential sorption to glass vials was not considered. The sorption of DMP and BBP onto marine sediments is a rapid process that reaches equilibrium within 6–10 h [33,34]. This study found that the different plasticizers reached their pseudo-equilibrium concentrations in the sediment and water within 24 h (Table S8). Therefore, the sediment and aqueous phase concentrations at 24 h sorption time were used to calculate the initial partition constant, which was used to predict the initial plasticizer concentrations in the sediment and water in the degradation study (see Table S9).

The relationships between the logarithm of the sediment-water partition constant (log K_{sw}) and the molecular weight (MW) or the logarithm of the octanol water partition coefficient (log K_{ow}) of the plasticizers are presented in Fig. 4 and Figs. S4–S5. This shows that a higher fraction of HMW plasticizers is likely sorbed into the sediment, with a lower tendency to be released into the water. Low molecular weight (LMW) plasticizers (mainly DMP and DEP) showed lower K_{sw} values, indicating their strong affinity for water (see detailed explanation in Text S6). The strong hydrophobicity of DEHP (water solubility: ~3 μg/L) increases its adsorption onto sediment particles in aquatic environments [35]. Interestingly, the slope of the linear or logarithmic curves after 30 d of biotic process was lower than that of the 30-d abiotic process and initial partitioning at 24 h. Furthermore, the log K_{sw} of low or moderate molecular plasticizers after 30 d of both biotic and abiotic processes significantly decreased from their initial log K_{sw}. However, 30 d of abiotic processes resulted in an increase in log K_{sw} for the HMW plasticizers (DEHP, DEHT, and DINP) compared to the initial log K_{sw}. This implies that when microbial activity is absent, HMW plasticizers tend to be sorbed onto the sediment rather than being released into the aqueous phase. This is because there is no possibility of forming EPS in sterile microcosms, in which the HMW plasticizers are likely to sorb into sediment from water over time, thereby increasing K_{sw} and slightly lowering the aqueous phase concentration compared to non-sterile conditions. In general, the residual concentration in the sediment increased with an increase in the MW, K_{ow}, and K_{sw} values, and decreased with the water solubility of the plasticizers.

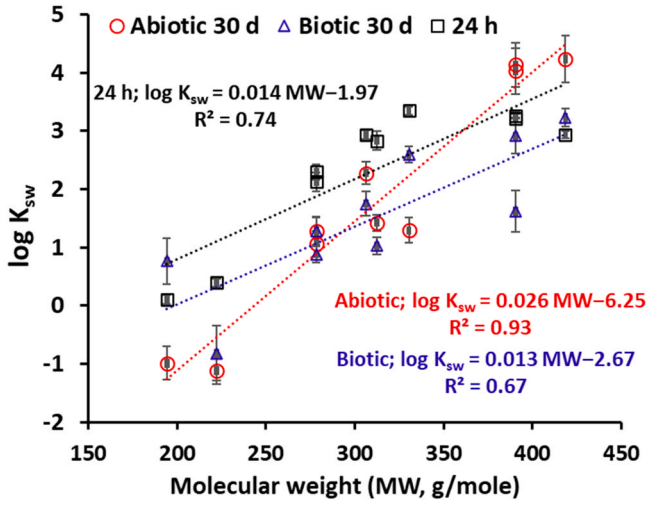


Fig. 4. Relationship between sediment-water partition constant (log K_{sw}) and 1-octanol-water partition coefficient (log K_{ow}) for different plasticizers. The K_{sw} values were obtained from the 24 h sorption study (as initial distribution) and residual concentration in sediment and water after 30 d of abiotic or biotic degradation study.

3.3. Plasticizer release rate and degradation kinetics

The rate of plasticizer release from PVC MPs to the sediment and their degradation in both cPVC and plasticizer batches were calculated by assuming first-order kinetic models (see detailed explanation in Text S7). Several studies have employed this model, which provides a straightforward approach for analyzing degradation processes, [6,16, 19,36,37] including the release of additives from MPs [38,39]. Additionally, Zhong et al. [40] compared the pseudo-first-order model (PFOM) and pseudo-second-order model (PSOM) to describe the DEHP leaching kinetics and found that PFOM effectively describes the leaching kinetic process. The first-order leaching and degradation rate constants under the abiotic and biotic conditions are presented in Table 2 and Figs. S6–S7. The calculated first-order rate constants for the release of DEHT and DINP in the sterile microcosms were 0.448 d^{-1} and 0.044 d^{-1} for cPVC-1 and 0.0215 d^{-1} and 0.0155 d^{-1} for cPVC-2, respectively. Similarly, in non-sterile microcosms the release rate constant of DEHT and DINP are 0.52 d^{-1} and 0.050 d^{-1} in cPVC-1 and at 0.024 d^{-1} and 0.016 d^{-1}in cPVC-2 respectively. The release rate constants decreased significantly under biotic-only conditions, with rate constants of DEHT and DINP of 0.0074 d^{-1} and 0.0061 d^{-1} for cPVC-1 and 0.031 d^{-1} and 0.0008 d^{-1} for cPVC-2, respectively. This study found a faster release of the plasticizer from PVC, with 35–79% of plasticizer mass released into sediment microcosm within 30 d. The calculated half-lives of DEHT and DINP in the sterile microcosms were 15 and 16 d in cPVC-1 and 32 and 45 d in cPVC-2, respectively. Similarly, the half-lives of DEHT and DINP in the non-sterile microcosms were 16 and 14 d in cPVC-1 and 28 and 42 d in cPVC-2, respectively. In the biotic-only condition, the half-life increased for both DEHT and DINP to 94 and 114 d in cPVC-1 and 221 and 822 d in cPVC-2, respectively. This is in contrast to the findings Henkel et al. (2022) [25], who reported desorption half-lives of 9 years for DEHP and 2079 years for DINP, in which the leaching experiment was conducted using the infinite sink method in the presence of activated carbon powder and the aqueous phase concentration was measured.

The rate of plasticizer degradation in all experimental batches was

Table 2
First-order leaching and degradation rate constants (d^{-1}) for each plasticizer in different environmental conditions.

Plasticizers	Abiotic S	Biotic + abiotic **NS**	Biotic only **Biotic**
Release rate: cPVC-1 added microcosm			
DEHT	0.044	0.052	0.007
DINP	0.044	0.050	0.006
Release rate: cPVC-2 added microcosm			
DEHT	0.021	0.024	0.003
DINP	0.015	0.016	0.001
Degradation rate: cPVC-1 added microcosm			
DEHT	0.176	0.262	0.086
DINP	0.195	0.293	0.098
Degradation rate: cPVC-2 added microcosm			
DEHT	0.266	0.352	0.086
DINP	0.046	0.135	0.089
Degradation rate: Plasticizer added microcosm			
DMP	-	0.146	0.146
DEP	0.001	0.024	0.023
DIBP	0.051	0.098	0.047
DBP	0.049	0.136	0.087
DNPP	0.041	0.129	0.088
BBP	0.054	0.150	0.097
DEHP	0.057	0.111	0.054
DCP	0.074	0.150	0.076
DEHT	0.032	0.119	0.086
DINP	0.061	0.101	0.040

higher in the biotic microcosms than in the abiotic microcosms. However, the biodegradation rate constants in some microcosms were similar or smaller when the biotic process alone was compared to the abiotic process. It also shows that the rate of plasticizer degradation (DEHT and DINP) in the PVC batches is higher than that in the plasticizer batch, which is possibly due to biofilm formation on the surface of PVC MPs with the help of EPS, thereby enhancing degradation rates. The degradation rate was in the order DINP > DEHT in the cPVC-1 batch, DEHT > DINP in the cPVC-2 batch, and cPVC-1 > cPVC-2 for DEHT and DINP under all conditions. In addition, when considering the overall results, biotic > abiotic process; however, if biotic alone is considered, the opposite trend is observed, that is, abiotic only > biotic only for both compounds (except for DINP in the cPVC-2 batch). The overall biotic rate constants of the different plasticizers in the plasticizer batches ranged from 0.02—0.15 d^{-1}. The abiotic-only rate constants ranged from 0.001—0.07 d^{-1}, while the biotic-only rate constants ranged from 0.04—0.15 d^{-1}. Interestingly, the rate constant for low-molecular-weight phthalate (DEP) was the lowest, which is consistent with the results of a previous study [19]. Furthermore, with the increasing MW of the compound, the abiotic rate constant increased, whereas the biotic-only rate constant decreased (Fig. S8), implying that abiotic or biotic degradation was strongly related to the hydrophobicity or MW of the plasticizers.

Thus, our findings highlight the critical importance of acknowledging abiotic degradation as a substantial contributor to the fate of plasticizers and emphasize the necessity of thoroughly investigating and incorporating abiotic processes when assessing plasticizer degradation in environmental contexts. Abiotic degradation can occur rapidly under favorable conditions (temperature, humidity, pH, and exposure to reactive chemicals or light). Compared to polycyclic aromatic hydrocarbons, phthalate or non-phthalate plasticizers have higher solubility in water, causing abiotic degradation of plasticizers, which can occur via physicochemical methods, especially hydrolysis and photochemical oxidation processes [31]. Hydrolysis is the prevalent mechanism governing the abiotic degradation of substances, making it the primary pathway for the breakdown of xenobiotics. Furthermore, the hydrogenation of phthalates is another transformation process that occurs under specific environmental conditions [41]. It has also been reported that the rate of chemical degradation is higher than that of microbial degradation [31]. Thus, plasticizers should not be considered persistent organic pollutants; rather, they are pseudo-persistent because they are readily degraded but their concentration remains high in environmental samples because of the continuous release from the products to the environment.

3.4. Dynamics of bacterial community during phthalate degradation

The diversity of the bacterial community varied among the sediment slurry microcosms. The OTU values declined substantially under all conditions (NR, SR, F, and A) in the plasticizer-added microcosms. Aerobic conditions in all microcosms showed the lowest number of OTU compared with all other conditions and the initial sediment. However, the OTU values under SR and F conditions of PVC-added microcosms (cPVC-1 and cPVC-2) increased relative to those of the initial sediment. The Ace, Chao1, Shannon, and Simpson indices decreased in most microcosms, except under SR and F conditions in the cPVC-1 and cPVC-2 microcosms (Table S10). These observations indicate that the diversity of the bacterial community decreased owing to the addition of the plasticizer to the sediment. Microbial diversity relies on the entire microbial composition, activities, and fate of contaminants in sediments [42]. Here, SR and F conditions in PVC-added microcosms showed higher bacterial diversity than INI and other conditions. This suggests that sulfate reduction and fermentation promote the proliferation of a wide range of bacteria in harsh environments. Furthermore, Principal coordinate analysis and UPGMA cluster tree showed clear discrepancies in bacterial diversity between the initial sediment and other plasticizer-contaminated environments (Figs. S9 and S10). The direct presence of plasticizers or PVC-leached plasticizers influences bacterial abundance and diversity. PVC and various phthalates remarkably alter microbial diversity [43–45], which is consistent with the data obtained in the present study.

A shift in the bacterial community was observed by exploring the taxonomic phyla and family composition (Fig. S11). Proteobacteria was the most dominant phylum in the initial sediment (47.0%), its frequency declined tremendously in most of the plasticizer-contaminated microcosms. The lowest frequency of Proteobacteria was observed in nitrate-supplemented (NR) (9.9%) condition of plasticizer microcosm. Opposite to this trend, the abundance of Proteobacteria surged markedly in A (62–68%) environments of cPVC-1 and cPVC-2 compared to initial sediment. The second most dominant phylum in initial sediment was Firmicutes (12.7%), whose abundance enriched prominently in NR, SR, and F conditions in all microcosms. However, under the aerobic environmental conditions, the dominance of Firmicutes was decreased and reached the lowest 2.7% compared to initial sediment. The inhibitory effect of plasticizers was also observed for the phylum Chloroflexi, which declined from 12.0% (initial sediment) to 1.1% (NR microcosm). Furthermore, the phyla composition recorded that the phylum Bacteroidetes dramatically increased from 7.0% (initial sediment) to 58.0% (NR-plasticizer microcosm). In most microcosms, the phylum Actinobacteria was more abundant than that in the initial sediment. The dominant phyla, Proteobacteria, Firmicutes, Chloroflexi, Bacteroidetes, and Actinobacteria, have been identified in various phthalate-contaminated habitats [45,46]. Species of the enriched phyla Firmicutes, Bacteroidetes, and Actinobacteria play a central role in the mineralization of phthalate-contaminated environments [16,42,46].

The compositional data at the family level showed that Sulfurimonas_f (6.6%), Acidaminobacter_f (4.7%), and Flavobacteraceae (4.3%) were major taxonomic families present in the initial sediments. During 30-d incubation with various plasticizers and PVC, the predominant family domains were altered in each microcosm. The frequency of Rhodobacteraceae and Flavobacteraceae was enriched exponentially in the aerobic treatment of cPVC-1 and cPVC-2 microcosms compared to the aerobic treatment with the plasticizer (Fig. S11). Members of Rhodobacteraceae and Flavobacteraceae are important contributors to biofilm development in PVC- and phthalate-contaminated environments [47]. These families are well-known hydrocarbon degraders that can degrade a wide range of aliphatic and aromatic hydrocarbons [48]. In aerobic treatment with plasticizers, 50% of the bacterial population was accounted for by an unidentified family, EF467588_f, and 10% was covered by Desulfuromonadaceae. The relative abundances of Clostridiaceae, Desulfobacteraceae, and Desulfobulbaceae increased in the anaerobic environments (NR, SR, and F) in all microcosms. Desulfuromonadaceae, Desulfobacteraceae, and Desulfobulbaceae include many sulfate-reducing bacteria. Genomic and metagenomic analyses have shown that sulfate-reducing anaerobic bacteria can degrade phthalates [49]. A notable improvement in the frequency of the Ruminococcaceae family was found in the fermentation environment of the plasticizer microcosms. Clostridiaceae and Ruminococcaceae are generally reported in gut samples and their abundance is influenced by various contaminants, including phthalates [50,51].

Phthalate contamination greatly alters the microbial composition. In biotic environments, the complete degradation of phthalates relies on microbial-mediated processes [43]. Therefore, it is necessary to investigate the microbes responsible for driving phthalate mineralization. Further insights into the dynamics of bacterial communities and phthalate-degrading bacteria can be obtained by conducting genus-level assessments. In the initial sediment samples, the dominant genera were *Sulfurimonas* (4.8%), *Sulfurovum* (4.1%), and *Arcobacter* (3.1%). These genera were almost completely inhibited in PVC- and plasticizer-supplemented microcosms (Fig. 5). An unidentified genus DQ395875_g was highly enriched (26.0–27.0%), followed by *Flavobacterium*, *Hydrogenophaga*, and *Lutibacter* during aerobic incubation of cPVC-1 and cPVC-2 microcosms. Another unidentified genus,

AB189361_g, was significantly high (4.0–53.0%) in plasticizer-added microcosms (A, F, NR, and SR) and PVC-added nitrate-reducing conditions. *Bacillus* and *Clostridium* were notably higher in all anaerobic environments (F, NR, and SR) in both the plasticizer- and PVC-added microcosms. These genera have previously been reported in PVC- and plasticizer-contaminated habitats [17,43–45].

Based on the Kyoto Encyclopedia of Genes and Genomes (KEGG) database (KEGG modules: M00623, M00624, and M00636) and literature[16–18,43,52], we identified 65 genera that potentially participate in various types of phthalate degradation (Table S11). More precisely, the genera *Arthrobacter, Bacillus, Desulfovibrio, Desulfuromonas, Devosia, Gordonia, Mycobacterium*, and *Sphingomonas* were found in all microcosms (Fig. 6). At the species level, *Arthrobacter globiformis, Hydrogenophaga taeniospiralis, Hydrogenophaga pseudoflava, Pseudomonas aeruginosa, Pseudomonas stutzeri, Sphingomonas sediminicola, Rhizobium tibeticum, Mycobacterium farcinogenes,* and *Mycobacterium intermedium* were notable in all samples (Table S12). Overall, *Bacillus* was a key phthalate degrading genus, with relative abundance ranging from 0.3–4.6%, with *Bacillus subtilis, Bacillus simplex, Bacillus pumilus, Bacillus megaterium, Bacillus benzoevorans* found in higher proportions. This

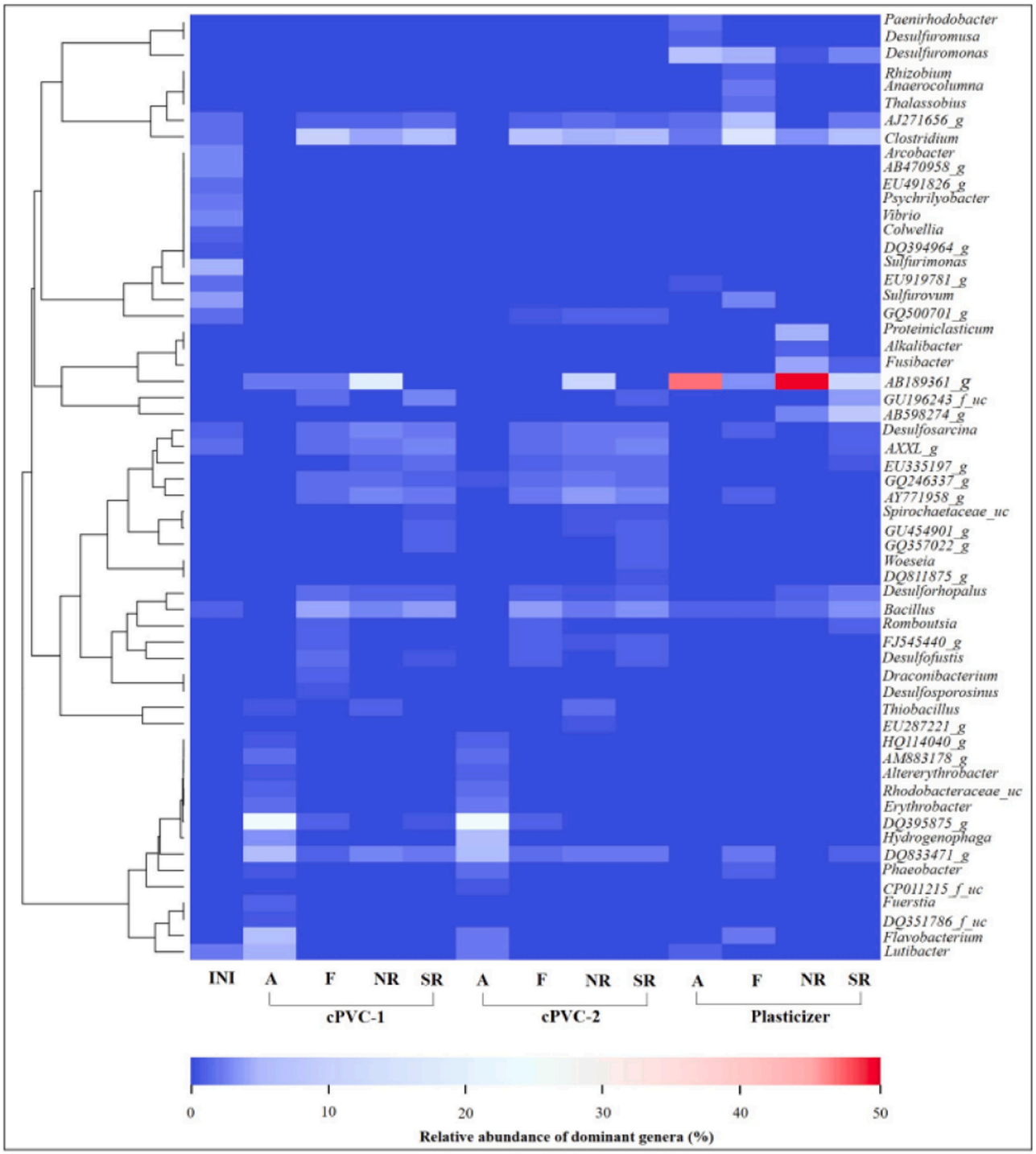


Fig. 5. Heat map of predominant bacterial genera detected in various microcosms during the 30 d incubation period. INI = initial sediment, cPVC = commercial PVC, NR = nitrate reduction, SR = sulfate reduction, F = fermentation, A = aerobic.

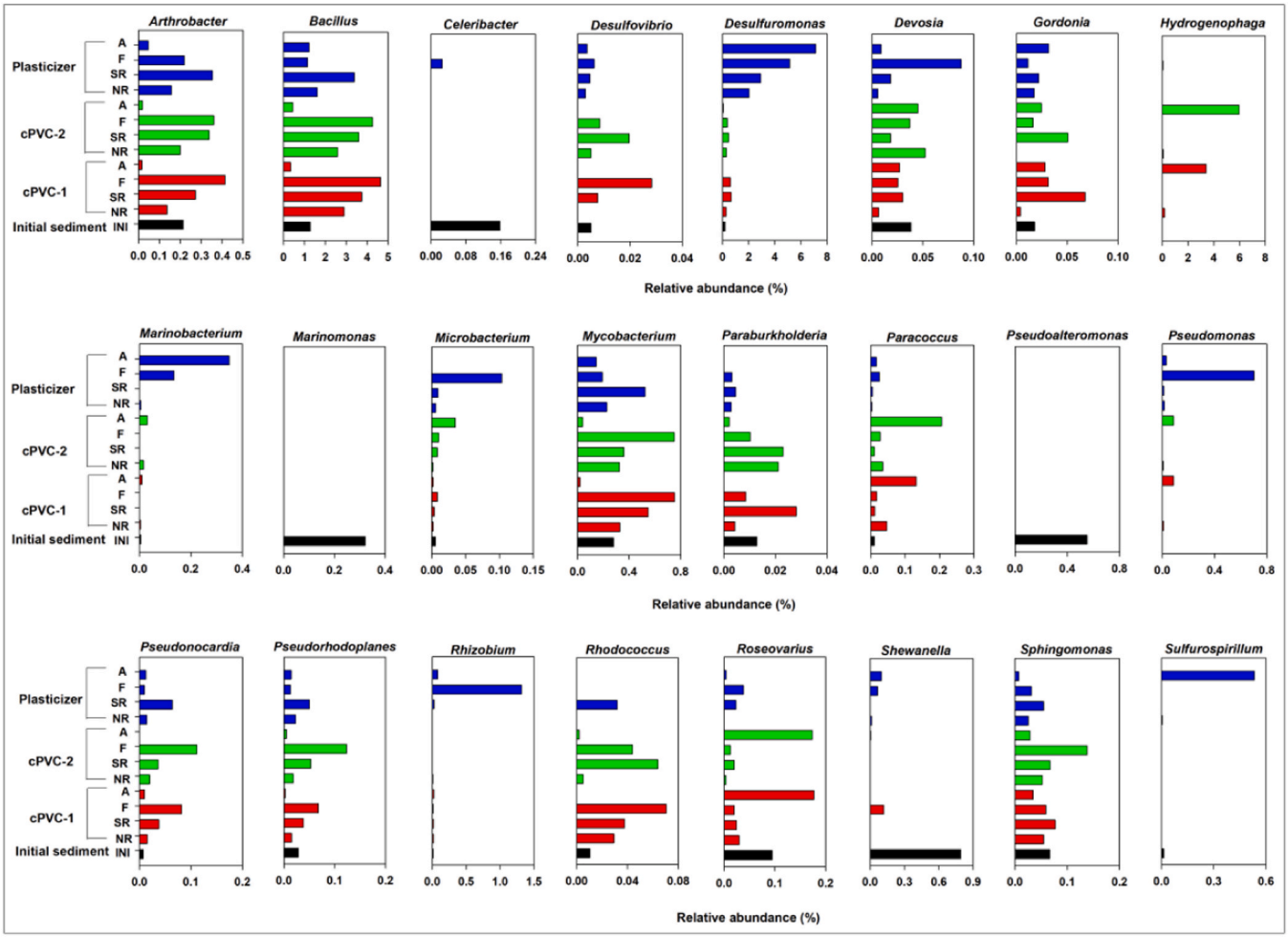


Fig. 6. Variations in the relative abundances of the phthalates-degrading predominant bacterial genera observed in different microcosms. INI = initial sediment, cPVC = commercial PVC, NR = nitrate reduction, SR = sulfate reduction, F = fermentation, A = aerobic.

finding is consistent with several previous studies that reported *Bacillus* as an effective bacterium for phthalate remediation [16,43,52]. *Bacillus* are ubiquitous endospore-forming, facultative anaerobic bacteria that degrade phthalates by releasing hydrolases [53,54]. Hydrolytic enzymes include lipase, esterase, cutinase, and phthalate ester hydrolases [54]. Previous studies have shown that the metabolic pathways of PAE biodegradation typically involve two distinct stages. In the initial phase, PAEs undergo conversion into phthalic acid, primarily achieved through either β-oxidation or the direct hydrolysis of ester bonds [55]. Phthalic acid can subsequently undergo decarboxylation to benzoic acid, a metabolic step commonly associated with anaerobic microorganisms. The subsequent stage involves the cleavage of the benzene ring, which facilitates further metabolic reactions [6].

Furthermore, bacterial composition data showed variations in the abundance of phthalate-degrading bacteria in different microcosms. For instance, *Hydrogenophaga* was enriched sharply in the aerobic conditions of the PVC-supplemented microcosms, whereas *Pseudomonas*, *Mycobacterium*, *Desulfuromonas, Rhizobium*, and *Sulfurospirillum* proliferated highly under anaerobic conditions in all microcosms. The heterogeneous distribution of phthalate-degrading populations may be explained by various environmental conditions (aerobic, fermentative, nitrate, and sulfate reduction). Biotic degradation mechanisms depend on environmental conditions, chemical structure, and MW, which may also determine the abundance of phthalate degraders[16,56]. Overall, the data from various microcosms clearly showed the effects of PVC and phthalates on bacterial community structures. Moreover, the enrichment of phthalate-degrading bacteria implied that indigenous bacterial populations play a significant role in phthalate depletion under various environmental conditions. Indigenous bacteria can mineralize various types of petroleum hydrocarbons, MPs, antibiotics, and other waste materials [57,58]. Indigenous bacteria are more efficient in MP and phthalate degradation than non-indigenous populations because of their adaptive and stress-tolerant features in their native environments [18]. Indigenous bacteria promptly form biofilms after adhering to plastic surfaces. This assists in increasing the efficiency of the degradation of plastic polymers [59]. Furthermore, indigenous bacteria may have evolved mechanisms to target and break down specific types of MPs that are common in their native environments. This specificity can lead to a more targeted and efficient degradation process than that of non-indigenous bacteria [60]. Employing indigenous bacteria for MP degradation may be more cost-effective than introducing or maintaining non-indigenous bacterial populations. Indigenous bacteria are ubiquitous in the environment, eliminating the need for large-scale introduction and the associated logistical challenges [61]. While there are advantages to using indigenous bacteria, it is important to carefully assess each situation and consider factors such as the type of MPs present, characteristics of the local environment, and potential unintended consequences before implementing any bioremediation strategy.

3.5. *Implications of this study and future recommendation*

This study presented a novel investigation into the leaching and degradation of plasticizers from PVC MPs in sediments, considering both abiotic and biotic degradation processes. It evaluated plasticizers

released from PVC MPs and in plasticizer-amended batches and examined the sorption dynamics between sediment and water. The observed alterations in the partition constants of the plasticizers during degradation may have important implications for understanding the environmental behavior and distribution of plasticizers. Additionally, this study identified changes in bacterial communities and potential plasticizer-degrading bacteria in sediments, providing valuable insights into the fate of plasticizers and microbial degradation pathways. Our research fills a critical gap in the existing literature by investigating the often-overlooked aspect of abiotic degradation of plasticizers, which has been less studied before.

One of the limitations of this study is related to the dynamic nature of partitioning during degradation, which is influenced by several environmental factors, such as pH, temperature, organic matter, and microbial activity, which affect the chemical behavior between sediment and water. These fluctuations may not be fully captured by sampling at discrete time points, leading to uncertainties in the interpretation of partitioned data over time. Future studies should employ continuous monitoring or sampling at more frequent intervals to capture temporal variations in partitioning dynamics during degradation and integrate environmental parameters into predictive models to enhance the understanding of the factors driving partitioning behavior and accuracy. Accordingly, the degradation kinetics would be well fitted to the different models. In addition, the mechanistic pathways of abiotic and biotic plasticizer degradation remain significant areas of interest. Furthermore, conducting a life cycle assessment of plasticizer-containing products would provide valuable insights into their overall environmental impact.

4. Conclusions

This study provided valuable insights into the abiotic and biotic degradation of plasticizers in sediment microcosms under varying conditions. It demonstrated the significant roles played by both abiotic and biotic processes in the degradation of plasticizers in sediments. Approximately 35—79% of the DEHT and DINP were released from PVC MPs into sediment, with $>$ 99.9% degradation under various conditions. Although biotic processes resulted in higher degradation rates (94%) in plasticizer-added batches, the noticeable abiotic loss (72%) highlights the importance of considering both mechanisms in plasticizer fate studies. Changes in the partition constants of the plasticizers during degradation may have crucial implications for understanding their distributions. The rate of plasticizer release from PVC and its degradation were influenced by the initial plasticizer content, environmental conditions (abiotic/biotic), and other physicochemical properties.

These results demonstrated that microbial communities can biodegrade phthalates in the environment. This study revealed notable shifts in the bacterial community composition and decreased diversity in all microcosms, indicating the influence of plasticizer degradation on microbial communities. The identification of enriched plasticizer-degrading bacteria, particularly *Bacillus*, suggests their importance in the biodegradation processes and their potential for targeted bioremediation strategies. Future research should focus on further elucidating the mechanisms of plasticizer degradation, investigating the metabolic pathways or enzymes involved in degradation by the identified bacterial genera, and conducting life cycle assessments of products containing plasticizers to better understand their overall environmental impacts. Such studies will aid in the development of more effective mitigation strategies for plasticizer pollution. Proper waste management, recycling, and development of more sustainable materials are crucial for mitigating the potential risks associated with these plasticizers.

Environmental Implication

The study emphasizes leaching of plasticizers from commercial polyvinyl chloride into the sediment and subsequent degradation under abiotic and biotic processes, with microbial communities playing a crucial role. Understanding this is important for evaluating the environmental impact of plastic pollution. While certain bacteria are key in degradation of plasticizers, abiotic processes also play a significant part. This suggests that naturally occurring microbes are capable of mitigate the plasticizers from the environment. Changes in microbial communities and the fate of plasticizers in sediment offer important insights into the lasting environmental effects of microplastic contamination.

CRediT authorship contribution statement

Yongseok Hong: Writing – review & editing, Validation, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. **Jung-Hwan Kwon:** Writing – review & editing, Methodology. **Rishikesh Bajagain:** Writing – review & editing, Data curation, Conceptualization. **Gayatri Panthi:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Pil-Gon Kim:** Methodology. **Dhiraj Kumar Chaudhary:** Writing – original draft, Data curation.

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

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2024.134167.

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