

# Effects of pH and Temperature on the Leaching of Di(2-Ethylhexyl) Phthalate and Di-n-butyl Phthalate from Microplastics in Simulated Marine Environment

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**Abstract:** This study aims to examine the influences of pH and temperature on the leaching of bis(2-ethylhexyl) (DEHP) and di-n-butyl phthalate (DBP) from microplastics in pseudo-seawater. This study consisted of two parts. In the first part, DEHP and DBP in three common microplastics (polyethylene (PE), polyethylene terephthalate (PET), and polyvinyl chloride (PVC)) were experimentally leached into pseudo-seawater at pH values of 5, 7, and 9 respectively with simulated waves. High-performance liquid chromatography was used to detect the leached DBP and DEHP in the samples. The concentrations of DBP leached from PE, PVC and PET from Day-4 to Day-16 were in the ranges of 0.558 – 0.711 mg/L, 0.518 – 0.760 mg/L and 0.540 – 0.791 mg/L respectively. The effect of pH on the amount of DBP leached could not be concluded with different polymers having different optimal pH of leaching. In the second part, DEHP and DBP in six common microplastics (PE, PET, PVC, plastic wrap, disposable gloves, disposable plastic bag) were leached into pseudo-seawater at 25°C and 45°C. DBP and DEHP were not detected at 25°C, and a small amount of DBP was detected at 45°C. Higher temperatures promoted the leaching of DBP. This study provides important insight into the leaching behaviors of phthalates from microplastics in the marine environment, which is currently understudied.

**Keywords:** microplastics; seawater; plasticizer; polyethylene; polyvinyl chloride; environment.

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## 1. Introduction

Reports on marine plastic debris have been increasing since the 1970s. Large marine plastic debris and microplastics have been found in large quantities in the Pacific Ocean, Indian Ocean, Atlantic Ocean, and other coastal areas, even in remote and extremely deep ice layers and oceans. Their traces can be found in all regions [1]. In 2016, global plastic production reached 335 million tons. It is estimated that by 2035, global plastic production will double, and by 2050 it will double again, reaching 1.14 billion tons [2]. As society's demand for plastic products grows, 6.3 billion tons of waste plastics have been produced globally, but the recycling rate has not reached 10%. The remaining 90% of the waste can only be processed in landfills or enter different pathways and eventually end up in the marine environment [3]. A study that analyzed 192 coastal countries and regions worldwide revealed that 4.8 to 12.7 million tons of plastic waste find their way into the ocean every year [4]. According to the United Nations Environment Programme's (UN-EP) estimation, about 8 million pieces of garbage enter the ocean daily, and more than 13,000 pieces of garbage float in the ocean per

square kilometer [5]. Using a data-calibrated oceanographic model of float dispersion, Eriksen *et al.* estimated that approximately 5.25 trillion plastics are floating on the global offshore, oceanic, deep-sea, and polar ocean surfaces with a total weight of  $2.7 \times 10^5$  tons [6]. Microplastics end up in aquatic organisms' bodies through metabolic activities and accumulate in tissues [7, 8].

Microplastics in the marine environment include input from land sources, coastal tourism, ship transportation, marine aquaculture and fishing, and atmospheric deposition [9]. Land-based input is estimated to be the major source of marine microplastics and accounts for about 80% of all sources of marine debris [10]. Due to the small microplastic particles, microplastics from different sources (daily chemical products, industrial production, and textile fiber shedding) enter the sewage treatment system [11]. It is difficult to effectively filter and remove them, resulting in many microplastic particles being discharged into the marine environment [12]. Another terrestrial source of microplastics is soil. Microplastics in soil enter the marine environment through erosion or loss. Coastal tourism and ship transportation have caused numerous plastic products and waste to enter the beach or ocean, adding to marine plastic pollution [13].

Microplastics can adsorb organic pollutants in the environment. Pollutants take microplastics as carriers and are transported into organisms or released into unpolluted ecological environments, thus threatening human safety [14, 15]. Marine plastic waste has gradually entered the food chain, endangering the marine ecosystem by leaching chemicals into and adsorbing harmful chemicals from the surrounding [16]. Phthalic acid esters (PAEs), a group of common plasticizers, exist in large quantities in plastic products. Plasticizers may diffuse into the ocean from plastic particles and enter the food web directly through seawater [17]. In plastic products, the compatibility of PAEs with plastic molecules is excellent. There is no covalent bond between PAEs and plastic molecules. They are linked by hydrogen bonds or van der Waals forces and maintain their independent chemical properties [18]. During the aging process of plastic items in the ocean, PAEs may escape from the plastic products and endanger marine life [19, 20]. A study found that phthalate was detected in the corals polluted with microplastics from the Faafu Atoll, Maldives. Appreciable levels of PAEs were detected in the Scleractinian coral samples taken from inside the atoll rim near an inhabited island [21].

PAEs account for about 70% to 80% of the market share of plastic additives [22]. PAEs are prepared by the esterification reaction of phthalic anhydride and alcohol. They mainly comprise dioctyl phthalate (DOP), dibutyl phthalate (DBP), and o-benzene diisodecyl dicarboxylate (DIDP), bis(2-ethylhexyl) (DEHP), etc. [23]. It is believed that macromolecular plasticizers such as DIDP have low toxicity and will not harm public health, and can be used in conventional plastic products [24]. However, small-molecule plasticizers such as DBP and DEHP are highly toxic and are not allowed to be used in toys, children's products, and items that could come into close contact with humans [25]. The study by Zhang *et al.* reported that DBP and DEHP contributed 33.2% and 33.3% to the total PAE concentrations in the Bohai Sea and the Yellow Sea [26]. Fourteen PAEs were detected in the seamount area of the Tropical Western Pacific Ocean, and the sum of the fourteen PAEs' concentrations in the seawater ranged from  $12.13 \text{ ng.L}^{-1}$  to  $60.69 \text{ ng.L}^{-1}$  (av.  $28.86 \text{ ng.L}^{-1}$ ). DBP (20.66%) and DEHP (19.75%) were the predominant PAEs detected [27]. In studying the leaching of DBP and DEHP from microplastics, Net *et al.* reported that DBP and DEHP are the most prevalent phthalates in seawater [28].

Currently, most of the research on microplastics is about the characterization of microplastics in the soil or marine environment. For instance, Zhou studied the types, particle size, abundance, and distribution of microplastics in the North Yellow Sea and the typical tidal flat areas of the Bohai Sea and preliminarily determined the accumulation status of microplastics on the surface of the Bohai Sea and in some marine organisms [29]. The interaction between microplastics and the surrounding environment is also a research hotspot. For example, Chai *et al.* studied the e-waste dismantling area and explored the relationship between microplastics and the surrounding soil environment from the perspectives of ecotoxicology and microbiology [30]. Yu studied the distribution and enrichment of microplastics in the main organs of *Eriocheir sinensis* (Chinese mitten crab) after being ingested by the organism and their effects on the growth of *Eriocheir sinensis*. The study analyzed the oxidative stress resulting from the accumulation of microplastics in various tissues of *Eriocheir sinensis* [31]. With 50% of plastics containing plasticizers, the leaching of plasticizers from microplastics into the seawater and their subsequent entry into marine organisms through the food chain is a concern [32]. However, there has not been enough research to examine the leaching of plasticizers from marine microplastics into the seawater. The closest studies are those related to the leaching of plasticizers from plastic items such as containers and packaging. For instance, the migration of plasticizers from PVC and tri-laminate PE-polyamide-polypropylene under various controlled conditions has been investigated [33]. Another recent study reported the leaching of phthalates and other plasticizers from medical devices, particularly DEHP, followed by bis(2-ethylhexyl) adipate (DEHA) [34].

This study is a relatively novel attempt. It quantifies the PAEs, particularly DBP and DEHP leached from microplastics in a simulated marine environment. It specifically examines the effects of pH and temperature on microplastics' leaching of DBP and DEHP. It also quantifies the DBP and DEHP leached from different plastic items which are reduced to the sizes of microplastics in the laboratory. This study provides significant information on the leaching behaviors of DBP and DEHP from commercial microplastic particles and fresh microplastics generated from plastic items. It quantifies the extent of leaching of PAEs from microplastics into pseudo-seawater to better assess their ecological risks.

## 2. Materials and Methods

### 2.1. Chemicals and apparatus.

Polyethylene (PE), polyethylene terephthalate (PET), and polyvinyl chloride (PVC) microplastics were commercially sourced. PE, PET, and PVC were chosen in this study because they are the microplastic types commonly reported in the literature [14, 29, 35]. The PE, PET, and PVC microplastics have uniform shapes and sizes. The diameter of the microplastic particles is 106  $\mu\text{m}$ . Standard methanol solution with a concentration of 20  $\mu\text{g/L}$  was used for detection in HPLC runs. The size of the filter membrane was 0.45  $\mu\text{m}$ , and the size of the syringe filter was 0.2  $\mu\text{m}$ .

### 2.2. Preparation of standard series solutions.

500  $\mu\text{g/ml}$  stock solutions of DBP and DEHP were prepared. In the first set of experiment, 50  $\mu\text{g/ml}$ , 20  $\mu\text{g/ml}$ , 10  $\mu\text{g/ml}$ , 5  $\mu\text{g/ml}$ , 2  $\mu\text{g/ml}$  and 0.5  $\mu\text{g/ml}$  standard solutions of DBP and DEHP were constituted respectively from the stock solutions. 20  $\mu\text{g/ml}$ , 10  $\mu\text{g/ml}$ , 5  $\mu\text{g/ml}$ , 2  $\mu\text{g/ml}$ , 0.5  $\mu\text{g/ml}$  mixed standard solutions (DBP + DEHP) were prepared [36].

### *2.3. Preparation and pH adjustment of pseudo-seawater solutions for leaching.*

As seawater contains a myriad of ions and it is challenging to produce pseudo-seawater solutions with the same contents as seawater, salinity was used as the main criterion for preparing pseudo-seawater. Sodium chloride was used to adjust the salinity of pseudo-seawater. The average salinity of seawater is 35 [37]. Therefore, to prepare 1 L of pseudo-seawater, 35 g of NaCl solid is required. 18 pseudo-seawater solutions were prepared by adding 7 g NaCl to 200 ml pure water in separate beakers. The pH of six pseudo-seawater solutions was adjusted to 5, another 6 solutions to 7, and the last 6 solutions to 9. The pHs of natural seawater range from 7.5 to 8.5 and average at 8.2. Increasing ocean acidification due to rising carbon dioxide emissions and dissolution of carbon dioxide in seawater is likely to lower the pH. Besides, soil disturbance caused by coastal development can reduce the pH of coastal waters [20, 38]. As such, a pH range of 5 to 9 covers the worst case of ocean acidification and regional pollution, and the upper limit of ocean pH was selected. HNO<sub>3</sub> stock solution was added to the pseudo-seawater solutions to obtain a pH of 6, while NaOH stock solution was added to obtain a pH of 9.

1 g of PE, PVC, and PET microplastics were weighed separately with analytical balance, and the microplastics were transferred to separate beakers with pseudo-seawater solutions. The beakers were placed on a constant temperature shaker (THZ-24-L). The temperature was set to 25°C, and the rotation speed was 150 r/min. The overall duration of leaching was 16 days. Samples were taken on Day 4, Day 8, Day 12, and Day 16. After sampling, 1 ml of settled solutions were pipetted from the test tubes to sample bottles through a syringe filter for filtration. The samples were stored in a refrigerator at 4°C for subsequent analysis with high-performance liquid chromatography (HPLC 1260).

### *2.4. Experimental design under different temperatures.*

24 pseudo-seawater solutions were prepared where 12 solutions were used for leaching at 25°C and the other 12 for leaching at 45°C. This temperature range represents the most common sea surface temperature in the tropical and subtropical regions [39]. 1 g of PE, PVC, and PET microplastics was weighed and transferred separately to beakers with pseudo-seawater solutions. In addition, disposable gloves, disposable garbage bags, and plastic wrap were cut into dimensions of 4 mm x 4 mm pieces (in the size range of microplastics) by scissors. 1 g of each type of plastic fragment was weighed, transferred to a beaker, and stirred evenly.

Half of the beakers were placed on a constant temperature shaker (THZ-24-L) with the temperature set to 25°C and the rotation speed to 150 r/min. Another half of the beakers were also placed on a constant temperature shaker. The temperature was set to 45°C, and the rotation speed was 150 r/min. Samples were taken on Day 4, Day 8, Day 12, and Day 16, filtered through a syringe filter described above, and stored at 4°C. All the tests were conducted in triplicate.

### *2.5. Detection of plasticizers with HPLC.*

High-performance liquid chromatography was used to detect DBP and DEHP. The chromatographic separation was performed on a C18 column with a column temperature of 30°C, a flow rate of 0.6 mL/min, an injection volume of 10 µL, a detection wavelength of 225 nm, and a system pressure of about 55 bars, using gradient elution with acetonitrile and water. In the first three minutes, the ratio of acetonitrile to water was 85% to 15% (v/v). From 3

minutes to 6.5 minutes, the ratio of acetonitrile to water changed from 85%/15% to 0/100% (v/v). After 6.5 minutes, the mobile phase was 100% acetonitrile. The analysis time was 25 minutes, and the run time was 30 minutes [40].

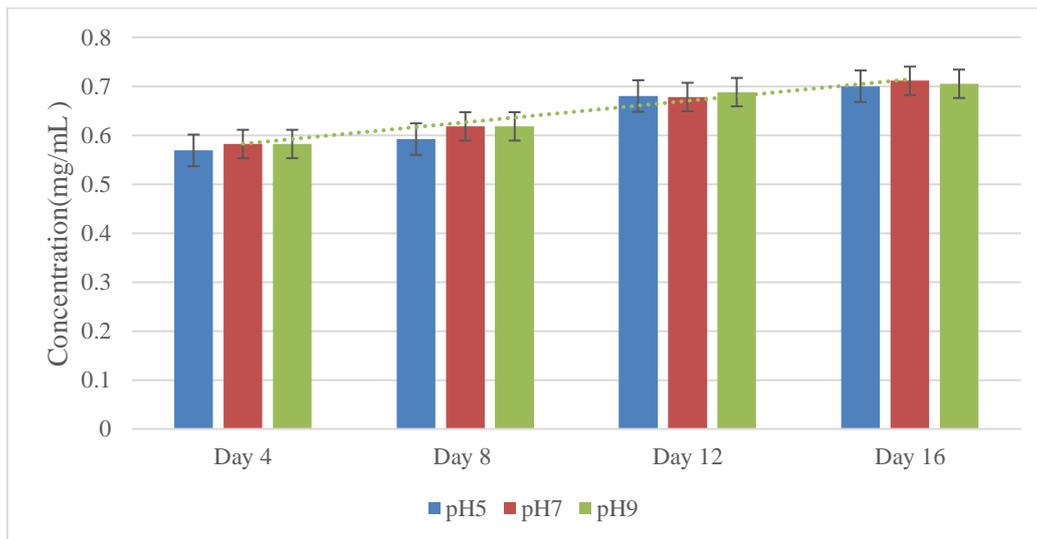
### 3. Results

#### 3.1. Effects of pH on the leaching of DBP and DEHP from microplastics.

The concentrations of DBP leached from PE microplastics are shown in Table 1 and Figure 1. The concentrations of leached DBP in PE did not change significantly under different pH conditions. In the case of pH 5, pH 7, and pH 9, the leaching concentrations of DBP gradually increased with time, showing a trend of continuous increase. However, DEHP was not detected.

**Table 1.** The average detected concentrations of DBP leached from PE microplastics under different pH.

pH	Average concentration (mg/L)			
	Day 4	Day 8	Day 12	Day 16
pH 5	0.558 ± 0.0047	0.592 ± 0	0.680 ± 0.0117	0.700 ± 0.0071
pH 7	0.582 ± 0.0094	0.618 ± 0.0141	0.678 ± 0.0376	0.711 ± 0.0047
pH 9	0.582 ± 0.0094	0.618 ± 0.0047	0.688 ± 0.0282	0.705 ± 0.0047

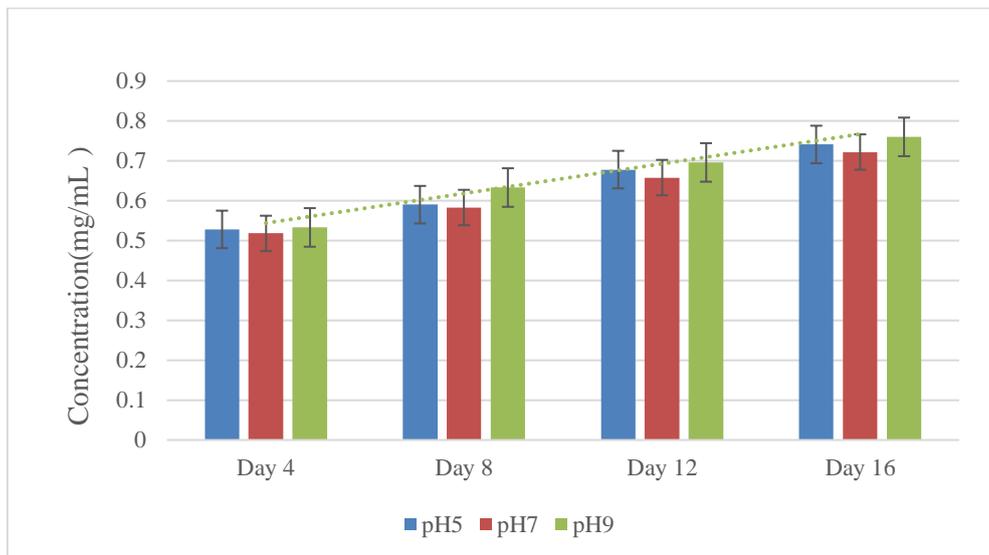


**Figure 1** The concentrations of DBP leached with time from PE.

According to Table 2 and Figure 2, the concentrations of DBP leached from PVC at pH 9 are slightly higher than those at pH 5, and the leached concentrations at pH 7 are the lowest. The leached amount of DBP in an alkaline environment is higher than in an acidic environment. From Day 4 to Day 16, the leached concentration of DBP gradually increased with time, demonstrating a trend of continuous increase.

**Table 2.** The average detected concentrations of DBP leached from PVC microplastics at different pH.

pH	Average concentration (mg/L)			
	Day 4	Day 8	Day 12	Day 16
pH 5	0.528 ± 0.0047	0.590 ± 0.0024	0.678 ± 0	0.741 ± 0.0047
pH 7	0.518 ± 0.0047	0.583 ± 0.0071	0.658 ± 0	0.722 ± 0.0024
pH 9	0.533 ± 0.0118	0.633 ± 0.0118	0.696 ± 0.0024	0.760 ± 0.0071

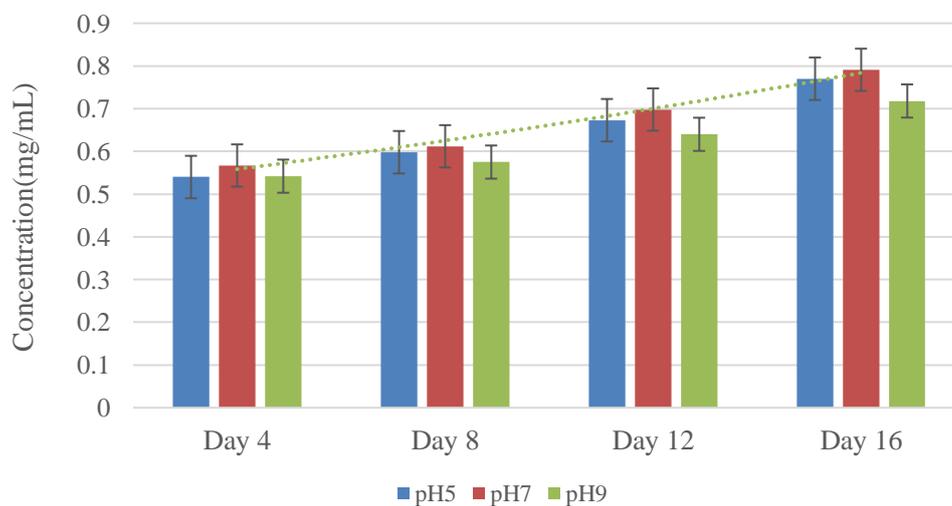


**Figure 2.** The concentrations of DBP leached with time from PVC.

Based on Table 3 and Figure 3, the concentrations of DBP leached from PET at pH 7 are generally higher, and the leached concentrations of DBP at pH 9 are the lowest overall. The amount of DBP leached from PET is the highest in a neutral environment, and the leached amount is the lowest in an alkaline environment. From Day 4 to Day 16, the leached concentration of DBP gradually increased with time, showing a trend of continuous increase.

**Table 3.** The average detected concentrations of DBP leached from PET microplastics at different pH.

pH	Average concentration (mg/L)			
	Day 4	Day 8	Day 12	Day 16
pH 5	0.540 ± 0.0258	0.598 ± 0.0329	0.673 ± 0.0588	0.770 ± 0.0400
pH 7	0.567 ± 0.0118	0.612 ± 0.0282	0.698 ± 0.0235	0.791 ± 0.0235
pH 9	0.542 ± 0.0094	0.575 ± 0.0047	0.640 ± 0.0118	0.718 ± 0.0188



**Figure 3.** The concentrations of DBP leached with time from PET.

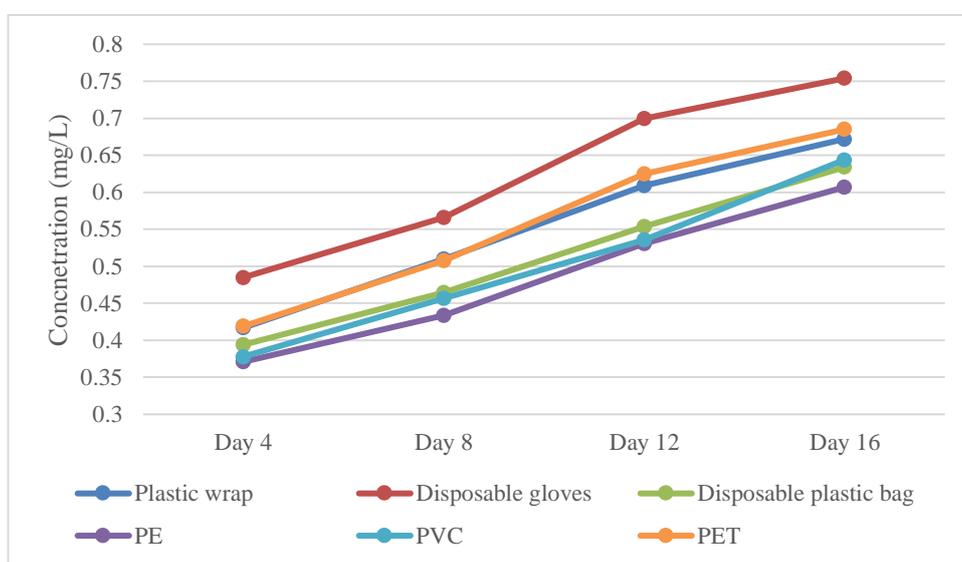
*3.2. Effects of temperature on the leaching of DBP and DEHP from microplastics and micro-scale plastic items.*

At 25 °C, DBP and DEHP were not detected in all the samples on Day-4, Day-8, Day-12, and Day-16. There was no peak of DBP or DEHP.

At 45°C, according to Table 4 and Figure 4, the concentrations of DBP leached from disposable gloves are the highest, and the concentrations of DBP from PE are the lowest. The leached concentrations of DBP from PET and plastic wrap are almost the same, and they are higher than the leached concentrations of DBP from disposal plastics bag, PVC, and PE. From Day 4 to Day 16, the leached concentrations of DBP were continuously increasing.

**Table 4.** The average detected concentrations of DBP leached from microplastics at 45°C.

Types of microplastics	Average concentration (mg/L)			
	Day 4	Day 8	Day 12	Day 16
Plastic wrap	0.417 ± 0.0233	0.510 ± 0.0560	0.609 ± 0.0607	0.672 ± 0.0467
Disposable gloves	0.485 ± 0.0023	0.566 ± 0.0047	0.700 ± 0.0117	0.754 ± 0.0093
Disposable plastic bag	0.394 ± 0.0140	0.465 ± 0.0444	0.554 ± 0.0257	0.634 ± 0.0117
PE	0.371 ± 0.0280	0.434 ± 0.0420	0.531 ± 0.0350	0.607 ± 0.0350
PVC	0.378 ± 0.0280	0.457 ± 0.0373	0.536 ± 0.0560	0.644 ± 0.0070
PET	0.419 ± 0.0023	0.508 ± 0.0350	0.625 ± 0.0187	0.685 ± 0.0187



**Figure 4.** Trendlines show the leached concentrations of DBP with time for six types of microplastics at 45°C.

#### 4. Discussion

The leaching of DBP from three different microplastics was different under different pH (Table 1-3; Figure 1-3). The leached amount of DBP from PE was the largest in neutral pseudo-seawater, while the leached amount of DBP from PVC was the largest in alkaline pseudo-seawater. For PET, the leached amount of DBP was marginally higher under neutral conditions. The three different microplastics produced different experimental results. It is, therefore, difficult to conclude the effect of pH on the leached amount of PAEs from microplastics, and it is likely that the optimal pH for the leaching of the same plasticizers from different types of microplastics could be different. Besides, the optimal pH for the leaching of different plasticizers from the same type of microplastics could also differ. There is currently very little literature on the effect of pH on the leaching of PAEs from microplastics in a simulated marine environment. Most existing studies focus on the leaching of PAEs from plastic bottles into the water they contain. These existing studies yielded inconsistent results on the influence of pH on leaching. Annamalai & Namasivayam showed higher leaching of PAEs into the acidic beverage (pH 2.7) than drinking water (pH 6.5) from plastic containers [41], but Bosnir *et al.* revealed a lower influence of orthophosphoric acid on leaching compared to preservatives such as sodium benzoate [42].

Regarding the effect of temperature on the leaching of plasticizers, no DBP and DEHP were detected at 25°C for all the microplastics samples, while a small amount of DBP was detected in the samples at 45°C. The concentration range of DBP from Day 4 to Day 16 is about 0.37 – 0.76 mg/L (Table 4 and Figure 4). As observed in this study, increased leaching of PAEs, particularly DBP, with increasing temperature is consistent with other studies. Liu *et al.* (2022) reported a greater release of microplastics and harmful substances from disposable plastic materials into the water at elevated temperatures (100°C) [43]. The result showed that organic chemicals and heavy metals with maximum concentrations of  $2.1 \pm 0.85 \text{ mg}\cdot\text{L}^{-1}$  and  $4.2 \pm 0.32 \text{ ng}\cdot\text{L}^{-1}$  were detected in the leachate from plastic packing and cups, indicating the potential risk of these materials while holding hot food or drink [43]. Keresztes *et al.* also reported more pronounced leaching of phthalates, including DBP and DEHP, from PET bottles into mineral water at a storage temperature of 60°C compared to 22°C after 44 days [44]. Besides, another recent study revealed an increase in the leaching of PAEs from PET with higher temperatures, and DBP was the most abundant PAE detected, probably because they were present at very high concentrations (62.9 µg/kg to 511.52 µg/kg) in the PET bottles tested [45].

At higher temperatures, there is a tendency for certain PAEs to leach from plastic products particularly plastic wrap and gloves. Among the six plastic items converted into microplastics, the amounts of DBP leached from disposable gloves were the highest. The material of disposable gloves is PVC, and the material of plastic wrap is PE. Phthalate plasticizers are commonly added to PVC products to soften the PVC material and increase its viscosity. The PE material, which is more flexible and less viscous, requires less or no plasticizer. This could result in more DBP being leached out from disposable gloves [23].

The prevalence of phthalates in the coastal and marine environment has been reported. At Solhabad Wharf and Rishahr Park, the highest and lowest mean concentrations of runoff PAEs were 137.54 and 25.32 µg/L, respectively [46]. A total PAEs (sum of di-isobutyl phthalate (DiBP), DBP, and DEHP) concentration of up to 287.2 ng·g<sup>-1</sup> was detected by Liu *et al.* in *Mytilus edulis* from Jiaozhou Bay, China [47]. The study by Natascha *et al.* analyzed the organic plastic additives, including seven PAEs and nine organophosphate esters (OPEs) in microplastics. PAE concentrations ranged from 100 to 527 ng·L<sup>-1</sup> (mean  $191 \pm 123 \text{ ng}\cdot\text{L}^{-1}$ ) in seawater [18]. In surface waters of the Bay of Marseille in the NW Mediterranean Sea, PAEs have previously been reported at concentrations of 130 – 1330 ng·L<sup>-1</sup> ( $\Sigma$  PAEs) [48]. Surface water and storm-water concentrations of seven plasticizers varied between 92.62 and 770 ng/L (mean  $176.1 \pm 104.8 \text{ ng/L}$ ) and 120.9 – 781.5 ng/L (mean  $355.2 \pm 232.5 \text{ ng/L}$ ), respectively [49]. In this study, the leached amounts of DBP were in the range of 371 – 791 ng·L<sup>-1</sup>, similar to the environmental concentrations of PAEs reported.

This study indicated that substantial leaching of DBP could occur over a duration as short as 16 days. Leaching has been shown to progress with time, and the concentrations of leached DBP showed a continuous upward trend. This is consistent with the findings of other studies that the concentrations of PAEs leached from plastic containers into the water therein increased with time. However, leaching was usually permitted over a longer time in these studies [41, 44, 45]. Nonetheless, this study shows that leaching of DBP from microplastics could occur over a relatively short time in pseudo-seawater, attributed probably to the larger surface area of contact of microplastics with pseudo-seawater.

In this study, only DBP was detected, while DEHP was not detected. Multiple studies have reported the detection of DEHP in seawater at relatively high concentrations, probably

due to the longer duration of leaching in the natural environment and the presence of other environmental factors which could facilitate leaching [43, 50]. However, DBP was reported as the most abundant PAE leached from PET bottles [45]. Furthermore, the solubility of DBP in water at 25°C is 0.03%, while the solubility of DEHP in water is less than 0.01%. The differences in solubility may be one of the reasons for the non-detection of DEHP in this study [45].

This study encountered certain limitations. In studying the influence of temperature on the leaching of PAEs, it is better for more temperature gradients to be established. A temperature gradient can be set up between 25°C and 45°C to observe the temperature at which DBP starts to leach. The sampling interval for this experiment was once every four days for 16 days to examine if substantial leaching of plasticizers from microplastics could take place over a short term. Taking the leached amount of DBP from PET at 45°C as an example, the leached amounts were 0.419 mg/L (Day 4), 0.508 mg/L (Day 8), 0.625 mg/L (Day 12) and 0.685 mg/L (Day 16). It can be seen that the amount of DBP leached was still increasing from 12 days to 16 days. As this study was designed to examine the leaching of DBP and DEHP from microplastics over a short term, it stopped at Day 16. In the future, the duration of this study could be extended until a relatively constant leached concentration of DBP is attained. As substantial leaching was already observed on Day 4, the sampling interval could be reduced to one day instead of four days. It is noteworthy that the effects of pH on the leaching of PAEs from the microscale plastic items had not been conducted, and the rationale was that the items were mostly made of PE, PET, and PVC, of which the respective microplastics had been tested for PAEs leaching under different pH. This could constitute a constraint of this study as the microscale plastic items could have different PAEs leaching patterns.

Due to the complexity of natural seawater, this study used a simple pseudo-seawater solution with a salinity of 35‰ (35 g per kilogram of seawater) prepared with NaCl. However, the contents of natural seawater are very complicated. Pseudo-seawater in this study did not contain suspended solids, organic matter, and biological matter, which are present in natural seawater. The pseudo-seawater prepared in the laboratory could provide a leaching environment significantly different from the natural seawater.

#### **4. Conclusions**

This study confirms that microplastics leach a small amount of PAEs into the seawater, and leaching tends to increase with time. In addition, leaching of PAEs from microplastics could occur over a short duration. Therefore, this study is crucial in elucidating the potential ecotoxicological effects of microplastics in natural seawater due to the leaching of plasticizers. Plasticizers, particularly PAEs, have been shown to possess endocrine-disrupting effects and potentially cause teratoma, mutation, and cancers [51, 52]. However, the effect of pH on the leaching of PAEs is inconclusive as different types of microplastics seemed to leach PAEs optimally at different pH. The differences in the amounts of DBP leached from the microplastic samples into the pseudo-seawater solutions at 25°C, and 45°C indicate that high temperatures favor the leaching of PAEs from microplastics. This study provides important insight into the leaching patterns of PAEs from microplastics under a simulated marine environment at different pH and temperatures. This is crucial for understanding the risk related to the leaching of PAEs from microplastics in the marine environment. Future studies can be conducted with shorter sampling intervals to examine the leaching of PAEs daily over a longer experimental duration with more refined pH and temperature gradients. Future studies can also investigate

the leaching of other PAEs, such as DIBP, DMP, DOP, DAP, etc., in microplastics. This paper has not studied the establishment of mathematical models, leaching rates, or kinetic models. These could be covered in further studies.

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## Conflicts of Interest

The authors declare no conflict of interest.

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