SHORT RESEARCH AND DISCUSSION ARTICLE



Leaching of triphenyl phosphate and tri-*n*-butyl phosphate from polystyrene microplastics: influence of plastic properties and simulated digestive fluids

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Abstract

Microplastics have gained considerable attention as a growing environmental problem owing to their potential to serve as vectors for harmful chemicals. However, the leaching of these chemicals from microplastics is unclear. In this study, we investigated the leaching of two organophosphate flame retardants, triphenyl phosphate and tri-*n*-butyl phosphate, from polystyrene microplastics in simulated digestive fluids and water, and polypropylene microplastics were simultaneously used for comparison with polystyrene microplastics. The results indicated that the first-order kinetic model best explained the leaching process, suggesting that leaching was related to the release of organophosphate flame retardant molecules at the polymer surface. Additionally, the size and crystalline state of the microplastics had a significant effect on the leaching to a different extent, and under these influencing conditions, leaching percentages from polystyrene microplastics did not exceed 0.51%. Therefore, leaching from PS microplastics may not be an important source of OPFRs in the environment. However, the release of organophosphate flame retardants can be considerably enhanced with the breakdown of polystyrene microplastics.

Keywords Polystyrene microplastics · Organophosphate flame retardants · Leaching · Kinetics · Simulated digestive fluids

Introduction

Plastics are extensively used across industries owing to their strength and durability. In 2020, the global production of plastics reached 367 million tons, out of which

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only 10.2 million tons of post-consumer plastic waste was collected and processed at the recycling facilities and then reused (Europe 2021). This disposed plastic waste eventually enters the environments and is decomposed into microplastics under physical, chemical, and biological processes. Microplastics have been detected worldwide in ocean, freshwater, soil, and the atmosphere (Ajith et al. 2020; Kasmuri et al. 2022; O'Brien et al. 2023), and this has recently attracted considerable public and regulatory attention in recent years.

Microplastics are easily ingested by aquatic organisms, who suffer their toxic effects (Vo and Pham 2021). The toxicity of microplastics can be primarily attributed to chemical contaminants. These chemical contaminants include both exogenous contaminants, which are adsorbed onto the polymer surface from the environment, and endogenous contaminants, which are additives distributed in the polymer matrix. The primary purpose of additives is to enhance the performance of the plastics. Typically, additives include plasticizers, flame retardants, and antioxidants. The content of plastic additives is 10–70% for plasticizers, 0.7-25% for flame retardants, and 0.05-3% for antioxidants (Hahladakis et al. 2018). Most additives are physically doped in plastic matrices. There are no permanent covalent or ionic bonds between additives and plastic matrices. Consequently, additives can be easily leached; plasticizers, antioxidants, and flame retardants are the most commonly detected additives in the leachate fraction (Catarci Carteny et al. 2023; Qiu et al. 2022; Xu et al. 2023). Reportedly, microplastics might serve as a long-term source of phthalic acid esters (PAEs); the leaching of PAEs from microplastics into oceans has been estimated to range from 57.8 to 16,100 kg annually (Cao et al. 2022). In addition, when microplastics are ingested by marine organisms, the leaching of additives is facilitated in the digestive tract owing to digestive fluids (Chen et al. 2022b; Liu et al. 2020). Digestive fluids greatly increase the exposure risks of additives. Therefore, the leaching of additives from microplastics in the digestive tract should warrant greater attention.

In recent decades, organophosphate flame retardants (OPFRs) have gained popularity in the market as the main substitutes for limiting polybrominated diphenyl ether (PBDE) flame retardants. The global consumption of OPFRs increased from 186 thousand tons in 2001 to 759 thousand tons in 2017 (Dou et al. 2022). The content of OPFRs in consumer products could be as high as 10% (Carlsson et al. 2000; Kajiwara et al. 2011; Wang et al. 2019). OPFRs can leak from plastic products during use or disposal; the concentrations of OPFRs in the natural environment have reached $\mu g \cdot L^{-1}$ and $\mu g \cdot k g^{-1}$ levels (Pantelaki and Voutsa 2019). Chen et al. (2022a) found that triphenyl phosphate (TPhP) was the dominant additive in polyvinyl chloride (PVC) leachates and the main reason for inhibition of enzyme activity. Microplastics have larger surface areas per unit volume and smaller particle sizes than plastic products. However, only a few studies have reported the behavior of OPFR leaching from microplastics (Xu et al. 2023).

In this study, TPhP and tri-*n*-butyl phosphate (TnBP) were selected as representative OPFRs. Their leaching behaviors from polystyrene (PS) microplastics were investigated because OPFRs have been widely detected in PS consumer products (Carlsson et al. 2000; He et al. 2022). Polypropylene (PP) microplastics were selected for comparison with PS microplastics, as they have different crystalline states. The primary objectives of this study were to investigate the leaching mechanism and the impact of the plastic properties (microplastic size, OPFR content, and crystalline state) and simulated digestive fluids on the leaching of OPFRs from PS microplastics. Finally, the results were compared with other studies to determine if PS microplastics were the main source of OPFRs in the environment.

Materials and methods

Materials

TPhP (>99%), bovine serum albumin (66 kDa, >98%), and pepsin (35 kDa, \geq 500 U/mg) were purchased from Sigma-Aldrich, Germany. TnBP (>99.5%) was purchased from Macklin, China. PS powder (250 µm) and PP powder (400 µm) were purchased from Shanghai Guanbu Electromechanical Technology Co., Ltd. and Alfa Aesar Chemical Reagent Co., Ltd., respectively. Sodium taurocholate (>97%) was purchased from Shanghai Yuanye Bio-Technology Co., Ltd.

Microplastics containing TPhP and TnBP were prepared as follows: TPhP and TnBP were dissolved in 200 mL of ethanol in a beaker, and plastic powder was added. The mixture was placed in a fume hood until the solvent evaporated. A twin-screw extruder device (Model LRM–M–100, Labtech Engineering, Thailand) was used to prepare bulk plastics with specific contents (2 wt% and 5 wt%) of TPhP and TnBP. Then bulk plastics were ground into microplastic powder using a pulverizer under liquid nitrogen. Microplastic powder in the size range of 70–120 mesh (0.125–0.200 mm) and below 120 mesh (<0.125 mm) was collected using different stainless-steel sieves. Finally, the microplastics were named as microplastics-2% (0.125–0.200 mm), microplastics-5% (<0.125 mm), and microplastics-5% (0.125–0.200 mm).

Leaching kinetics experiments

The leaching kinetics experiments were performed in a 250mL conical flask with a stainless-steel wire cage (pore size of 80 μ m), each containing 1 g of microplastic powders and 200 mL of ultra-pure water. The conical flasks were placed in an orbital shaker with the temperature and rotation speed set to 25 °C and 150 rpm. Leaching kinetics experiments were performed in triplicate for 8 days and analyzed on 2 h, 21 h, 27 h, 53 h, 77 h, 101 h, 118 h, 143 h, and 190 h. Aliguots (1 mL) were collected for follow-up analysis.

Four models were used to describe the leaching kinetics of TPhP and TnBP from PS microplastics.

First – order kinetic model : $\ln (C_e - C_t) = \ln C_e - k_1 t$ (1)

Second – order kinetic model : $1/(C_e - C_t) = 1/C_e + k_2 t$ (2)

Elovich model :
$$C_t = a + b \ln t$$
 (3)

Power model :
$$C_t = at^b$$
 (4)

where C_e (mg·L⁻¹) and C_t (mg·L⁻¹) are the leaching concentrations of PS microplastics at equilibrium and at time t (h), respectively; t (h) is the leaching time; k_1 (h⁻¹) and k_2 (L·mg⁻¹·h⁻¹) are the rate constants of first-order and secondorder kinetic models, respectively; and a and b are constants for the Elovich and power models, respectively.

Leaching capacity analysis in simulated digestive fluids and water

Leaching capacity analysis in simulated digestive fluids and ultra-pure water was performed in 40-mL amber EPA vials equipped with a polytetrafluoroethylene-lined screw cap. Each vial contained 200 mg of microplastics and 40 mL of the aqueous solution. The compositions of simulated gastric fluid (SGF) and simulated intestinal fluid (SIF) of marine invertebrates were prepared according to a previous report (Liu et al. 2020). SGF was prepared by dissolving 3.2 g pepsin in 1 L of 10 mM NaCl solution, and SIF was composed of 5.0 g·L⁻¹ bovine serum protein and 10 mM sodium taurocholate in 100 mM NaCl solution. The pH of gastric and intestinal fluids was adjusted to 2.0 and 7.0, respectively, to simulate acidic gastric and neutral intestinal environments. The samples were shaken at 150 rpm for 24 h at 18 °C. Briefly, 2 mL of the aqueous solution was collected, and then 2 mL of acetonitrile and 1 g of NaCl were subsequently added to the centrifuge tubes and centrifuged at 2000 rpm for 5 min. Thereafter, the supernatant was collected for follow-up analysis.

Analytical methods

The crystalline state and surface functional groups of microplastics were characterized using X-ray diffractometer (XRD) (D8ADVANCE, Bruker, Germany) and Fourier transform infrared spectroscopy (FTIR) (Nicolet IS50, Thermo Fisher, USA), respectively. The concentrations of TnBP and TPhP in the aqueous phase were measured using the following procedure: an ultra-high performance liquid chromatography (UHPLC) system (Ultimate 3000, Thermo Scientific, USA) equipped with a triple quadrupole mass spectrometer (TSQ

Endura, Thermo Scientific, USA) was used to determine TPhP and TnBP. A sample of 3 uL volume was injected into a Hypersil Gold C18 column (100×2.1 mm, 1.9μ m, Thermo Scientific) at 40 °C. For gradient elution, a binary mobile phase of an aqueous solution of 0.1% formic acid (A) and methanol (B) at a flow rate of 0.3 mL min⁻¹ was applied. The gradient was set as follows: 0 min (40% B), 2 min (40% B), 8 min (98% B), 11 min (98% B), 12 min (40% B), and 15 min (40% B). Quantitative analysis of TPhP and TnBP was performed in multiple reaction monitoring (MRM) mode. The UHPLC-MS/ MS detection parameters, including m/z transitions, collision energy, and radio frequency lens, are presented in Table 1. The electrospray ionization (ESI) was run in the positive ion mode, and the optimal conditions were set as follows: spray voltage, 3500 V; sheath gas pressure, 35 units; auxiliary gas pressure, 10 units; and ion transfer tube, 325 °C.

Quality assurance and quality control (QA/QC)

For quality assurance and quality control, all experiments were performed in triplicate. Data are represented as mean \pm standard deviation. Plastic apparatus was not used to prevent background contamination in the experiment. All glasswares were triple-rinsed with methanol and ultra-pure water before use. TPhP and TnBP were not detected in the procedural blank samples. The limit of detection (LOD) and the limit of quantification (LOQ) were estimated at a signal-to-noise ratio (S/N) of 3:1 and 10:1, respectively. For TPhP, the LOD and LOQ were 0.016 mg·L⁻¹ and 0.053 mg·L⁻¹. For TnBP, they were 0.004 mg·L⁻¹ and 0.013 mg·L⁻¹, respectively. A sevenpoint standard calibration curve was used for the quantification of TPhP and TnBP with correlation coefficient (R^2) values greater than 0.995. Recoveries for the proposed method were performed in triplicate by spiking 31 µg of TnBP and 20 µg of TPhP standards into 40-mL amber EPA vials containing simulated digestive fluids. The average recoveries for TPhP and TnBP leaching were $80 \pm 2.38\%$ -130 $\pm 0.12\%$ in simulated digestive fluids. The precision (<5%) was evaluated by continuously performing five replicates using spiked samples with TnBP at 0.782 mg·L⁻¹, and TPhP at 0.517 mg·L⁻¹.

Table 1Compound name,water solubility, $log K_{OW}$, andUHPLC-MS/MS detectionparameters

Compound	Water solubil- ity, $(mg \cdot L^{-1}, 25 \circ C)^a$	$\log K_{OW}^{a}$	Parent ion (m/z)	Daughter ion (m/z)	Collision energy (V)	Radio fre- quency lens (V)
TnBP	280	3.82	267.1	155.0	10.3	74
				98.9 ^b	15.9	74
TPHP	1.90	4.70	327.1	214.9 ^b	25.7	97
				152.1	35.8	97

^aPantelaki and Voutsa 2019

^bQuantitative ion (m/z)

Results and discussion

Leaching kinetics

The leaching kinetics of TPhP and TnBP from PS microplastics are shown in Fig. 1. Leaching was fast during the first 27 h, and then the concentration showed little change in the remaining time. The leaching results were in line with previous findings on the release of brominated flame retardants (BFRs) and PAEs from microplastics, which reached steady-state levels in a single day when the microplastics were finer than 2 mm (Guo et al. 2020; Rani et al. 2017; Yan et al. 2021).

Four different models (first-order, second-order, Elovich, and power models) were used to fit the leaching kinetics of PS microplastics. The first-order kinetic model is widely applied to describe the kinetics driven by the concentration gradients between the microplastic external surface and aqueous medium. The second-order kinetic model is used to describe the leaching process, which was controlled by transport across the plastic-medium boundary layer and diffusion in an aqueous medium. The Elovich and power models are empirical equations; the Elovich model is generally suitable for a reaction with a large change in activation energy, and the power model reflects an uneven energy distribution process (Xie et al. 2021). The kinetic rate constants (k) and regression coefficients (R^2) are summarized in Table 2. The R^2 values (≥ 0.960) obtained from the first-order model were higher than those obtained from the other three models in all the tests. Thus, the leaching behaviors of OPFRs can be attributed to the release of additive molecules from the microplastic surface into the surrounding fluids. The effects of OPFR content and microplastic size on the leaching behaviors of OPFRs from PS microplastics were investigated. The leaching kinetics revealed that microplastic size significantly impacts the leaching concentration, whereas OPFR contents had a minimal effect. Smaller PS microplastics strongly promote leaching behaviors because they have a larger surface area in contact with the liquid medium and a shorter diffusion path. The equilibrium concentration of OPFRs that leached from PS-5% (<0.125 mm) was found to be 2-4 times higher than that from PS-5% (0.125-0.200 mm). In contrast, the release of OPFRs showed little variation, with an increase of only 40% when the content was increased from 2 to 5%.





Table 2	Kinetic model	parameters of	TPhP and	TnBP	leaching	from PS	microplastics	,
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Compounds	Microplastics	First-order kinetic model		Second-order kinetic model		Elovich model			Power model				
		$\overline{C_{e}}$	<i>k</i> ₁	R^2	C _e	<i>k</i> ₂	R^2	a	b	R^2	a	b	R^2
		$mg \cdot L^{-1}$	h^{-1}		$mg \cdot L^{-1}$	$L \cdot mg^{-1} \cdot h^{-1}$							
TPhP	PS-2% (0.125-0.200 mm)	0.06	0.08	0.994	0.07	1.21	0.985	0.01	0.01	0.768	0.01	0.44	0.854
	PS-5% (0.125-0.200 mm)	0.08	0.16	0.969	0.09	1.95	0.932	0.01	0.02	0.864	0.02	0.34	0.729
	PS-5% (<0.125 mm)	0.20	0.17	0.992	0.23	0.75	0.987	0.03	0.04	0.952	0.05	0.35	0.856
TnBP	PS-2% (0.125-0.200 mm)	0.12	0.23	0.952	0.13	1.84	0.847	0.03	0.02	0.915	0.03	0.31	0.846
	PS-5% (0.125-0.200 mm)	0.16	0.28	0.985	0.18	1.79	0.972	0.05	0.03	0.918	0.05	0.27	0.846
	PS-5% (<0.125 mm)	0.68	0.23	0.960	0.77	0.30	0.986	0.15	0.14	0.995	0.19	0.32	0.960

Fig. 2 Leaching of TPhP and

TnBP from PS and PP micro-

plastics in SIF, SGF, and water



Leaching capacity analysis in simulated digestive fluids and water

The leaching of TPhP and TnBP from PS and PP microplastics is shown in Fig. 2. The leaching concentrations of TPhP and TnBP from PP-5% (0.125–0.200 mm) microplastics were 1.89–5.97 mg·L⁻¹ and 5.86–6.65 mg·L⁻¹ (Table S1), respectively, which were 10–37 times higher than those corresponding PS microplastic samples. The high leaching capacity of PP microplastics can be attributed to their large free volume in the polymer (Cheng et al. 2020). XRD analysis (Fig. S1) of PS and PP microplastics revealed their crystalline state. PP microplastics displayed both sharp crystallization and amorphous peaks, whereas PS microplastics only displayed amorphous peaks; this suggested that PP and PS microplastics belong to semi-crystalline and amorphous polymers, respectively. In addition, the glass transition temperatures of PS and PP microplastics were 95.6 °C and -6 °C, respectively (De Rosa and Auriemma 2006; Zuo et al. 2019). This implies that PP microplastics consist of crystalline and rubbery subfractions at room temperature, whereas PS microplastics exhibit a glassy state at room temperature. As illustrated in Fig. 3, the molecular chain segments in rubbery subfractions of the PP microplastics are stacked in a more disorderly manner and have larger free volume regions than those of PS microplastics. Thus, the



diffusion of OPFR molecules into the liquid medium was easy in the case of PP microplastics.

The concentration of TPhP leached from microplastics after 1-day was lower than that of TnBP. Apparently, TnBP is more hydrophilic than TPhP. TnBP had a lower $\log K_{OW}$ and higher solubility than TPhP (Table 1). The leaching concentrations in the three fluids were in the following order: $SIF \ge SGF \ge$ water (Fig. 2). The presence of gastrointestinal components (sodium taurocholate or pepsin) can enhance the solubility of organic contaminants in the liquid phase, thereby facilitating leaching (Liu et al. 2020). Sodium taurocholate in SIF can form critical micelle concentrations with organic contaminants as surfactants and has a stronger solubilization capacity than pepsin. The leaching of TPhP and TnBP in SIF was 2-4 times higher than that in water, except for leaching from PP microplastics. The leaching concentrations of TnBP from PP microplastics were all approximately $6.00 \text{ mg} \cdot \text{L}^{-1}$ in all the three fluids, whereas TPhP concentrations were approximately 6.00 mg·L⁻¹ in SIF, 1.89 mg·L⁻¹ in SGF and water. The latter concentration almost reached the saturation solubility of TPhP in water, which was $1.90 \text{ mg}\cdot\text{L}^{-1}$. In the kinetic section, leaching additive molecules were found to be located on the polymer surface. Therefore, this result can be attributed to the complete leaching of OPFR molecules from rubbery subfractions at the PP microplastic surface. Simultaneously, we observed that SGF was more effective in promoting the leaching of TnBP than that of TPhP. SGF increased the concentration of TnBP by a factor of 1.7–3.2 and that of TPhP by a factor of 1.0–2.3. Pepsin in SGF is an amphiphilic biomolecule, and the solubilization effect of pepsin on hydrophilic substances is stronger than that on hydrophobic substances (Liu et al. 2020).

Environmental implications

In this study, leaching percentages were calculated to determine the leaching potential of additives. The leaching percentages were calculated based on the following equation: leaching percentage = (OPFRs (mg) in fluids/the sum of OPFRs (mg) doped in microplastics) $\times 100\%$. The leaching

Table 3 Comparison of leaching percentages from microplastics with other studies

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Plastic type and size ^a	Leaching parameters (fluids, solid to liquid ratio, time, temperature, mixing)	Leaching percentages (%)	Additives	Reference		
PS; micrometer-sized	Water and simulated diges-	0.02-0.25% in water	TnBP and TPhP	This study		
	tive fluids; 1:200; 18 °C; 1 day; 150 rpm	0.06–0.51% in simulated digestive fluids				
PP; micrometer-sized		0.76-2.51% in water				
		0.71–2.66% in simulated digestive fluids				
PVC; micrometer-sized Water; 1:2000; 2 days; 25 °C; 150 rpm		0.15% Dibutyl phthalate		Yan et al. (2021)		
Polyethylene (PE); millime- ter-sized rpm		0.09–4.5%	PAEs	Dhavamani et al. (2022)		
PS; millimeter- and micrometer-sized	Water; 1:100; 11.5 days; no mixing	0.000181-4.17%	PBDEs	Sun et al. (2019)		
EPS; millimeter- and micrometer-sized	Sea water; 1:500; 1–14 days; room temperature; shaking	37–49%	Hexabromocyclododecanes	Rani et al. (2017)		
EPS; millimeter- and micrometer-sized	Sea water; 1:3333; 30 days; 20 °C; 100 rpm	10.1–49.2%	Hexabromocyclododecanes	Pan et al. (2022)		
PVC; millimeter-sized	Sea water; 1:100; 1-78	3.8%	Bisphenol A	Suhrhoff and Scholz- Böttcher (2016)		
	days; room temperature; 150 rpm	0.00044-0.083%	PAEs and tri-2-ethylhexyl- trimellitate			
PE; millimeter-sized		0.083-5.4%	Acetyltri- <i>n</i> -butyl citrate and its degradation products			
Polyethylene terephthalate (PET); millimeter-sized		0.37%	Dibutyl phthalate			
Acrylonitrile-butadiene- styrene copolymer (ABS); millimeter- and microme- ter-sized	Water and simulated diges- tive fluids; 1:100; 15 days; 42 °C; 250 rpm	<1% in water, 0–8.32% in simulated digestive fluids	BFRs	Guo et al. (2020)		

^aSize = millimeter (1–5mm), micrometer (0.1–1mm)

percentages of OPFRs are listed in Table 3. Although simulated digestive fluids promoted the leaching process, the leaching percentages of OPFRs from PS and PP microplastics did not exceed 0.51% and 2.66%, respectively. Previous studies have found that microplastics' crystalline state or simulated digestive fluids can affect the sorption–desorption reversibility because all the sorbed compounds are distributed on the polymer surface (Liu et al. 2019; Zuo et al. 2019). In this study, both the crystalline state and simulated digestive fluids could only act on the additives distributed on the microplastic surface, and most additives were distributed homogeneously within the microplastic matrices. Therefore, the crystalline state and simulated digestive fluids had little impact on the leaching percentages.

The comparison of leaching percentages of OPFRs observed in this study and other additives in previous reports are summarized in Table 3. Leaching percentages of OPFRs in this study were in the same range as most additives, including PAEs, BFRs, bisphenol A, citrate ester plasticizers, and trimellitate plasticizers, which did not exceed 10%. In addition, no significant difference in leaching percentages was observed between lab-made (Yan et al. 2021) and commercially available additive-containing microplastics (Dhavamani et al. 2022; Guo et al. 2020; Suhrhoff and Scholz-Böttcher 2016; Sun et al. 2019). Among the additive leaching tests, only the leaching percentage of expanded polystyrenes (EPS) was high (10.1–49.2%) (Pan et al. 2022; Rani et al. 2017). This can be owing to the porous structure of EPS, which provides a greater contact area with the liquid medium. Notably, the particle sizes of the microplastics in the above studies were in hundreds of micrometers. According to Sun et al. (2019), the leaching percentages of PBDEs from PS microplastics with common size (0.1-5 mm) were below 10%, and direct leaching from microplastics revealed negligible contribution to the release and bioaccumulation of PBDEs (Sun et al. 2019; Sun and Zeng 2022). Thus, it is reasonable to conclude that leaching from PS microplastics will contribute little to OPFR release fluxes. However, when the particle size of microplastics is reduced to 10%, the leaching percentage increases to 10 times (Sun et al. 2019). PS microplastics can be broken down into smaller particles by environmental weathering or chewing and gastrointestinal motility of aquatic organisms. The leaching percentages of OPFRs from PS microplastics can be increased greatly when their sizes are reduced to the nanoscale.

Conclusions

This study examined the leaching behaviors of TPhP and TnBP from PS microplastics in simulated digestive fluids and water. The leaching of these compounds was attributed to molecules on the surface of polymer and followed a first-order kinetic model. The PS microplastic size and crystalline state as well as simulated digestive fluids strongly affected the leaching concentration, whereas TPhP and TnBP contents had a minimal effect. Nevertheless, the leaching percentage did not exceed 0.51% regardless of variations in these factors. Overall, leaching from PS microplastics, which are hundreds of micrometers in size, is not an important source of OPFRs in the environment. However, the leaching percentages of OPFRs can greatly increase with the gradual breakdown of microplastics. Therefore, understanding the effects of microplastic breakdown by weathering is critical for assessing the risks of microplastic release into the environment.

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Author contribution LZ: conceptualization, formal analysis, data curation, visualization, writing—original draft, and funding acquisition. YL: methodology and investigation. WH and FW: investigation. YF: supervision. ZZ: writing—review and editing, supervision, and funding acquisition

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Data Availability The data will be provided upon a reasonable request to the corresponding author.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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