



Plasticiser leaching from polyvinyl chloride microplastics and the implications for environmental risk assessment

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ABSTRACT

Microplastics in aquatic environments is a growing concern, particularly due to the leaching of chemical additives such as plasticisers. To develop comprehensive environmental risk assessments (ERAs) of high-concern polymers and plasticisers, an understanding of their leachability is required. This work investigated diethylhexyl phthalate (DEHP) and bisphenol A (BPA) leaching from polyvinyl chloride (PVC) microplastics (average diameter = 191 μm) under simulated marine conditions. Leaching behaviours were quantified using gel permeation chromatography (GPC) and thermal gravimetric analysis (TGA), and the polymer's physicochemical properties analysed using differential scanning calorimetry (DSC), Fourier Transform-Infrared Spectroscopy (FT-IR) and optical microscopy. Experimental data were fitted to a diffusion and boundary layer model, which found that BPA leaching was temperature-dependent (diffusion-limited), whereas DEHP leaching was controlled by surface rinsing. Model predictions also highlighted the importance of microplastic size on leaching dynamics. These data contribute towards greater accuracy in ERAs of microplastics, with implications for water quality and waste management, including decommissioning of plastic infrastructure.

1. Introduction

Plastics are pervasive and ubiquitous environmental pollutants that have been detected in terrestrial, aquatic and biological matrices worldwide (Bakir et al., 2020; Reichert et al., 2022; Eriksen et al., 2014a; Blettler et al., 2018). Microplastics (<5 mm in diameter) are an especially hazardous by-product of the plastics industry, which can enter the environment as either primary (i.e., purposefully manufactured at microscopic size) or secondary debris (i.e., formed during fragmentation of larger items) (Andrady, 2017). Microplastics are diverse in their polymeric origin, with polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyvinyl chloride (PVC) comprising the bulk of all microplastic contamination detected in oceanic environments (Eriksen et al., 2014b; Lebreton et al., 2018). The chemical composition of microplastics dictates their density and determines their position in the water table (i.e., buoyancy), thus influencing their interaction with different biota (e.g., benthic or pelagic). PVC is one of the most prevalent high density commodity plastics ($\rho = 1.38 \text{ g/cm}^3$), and as such is one of

the few negatively buoyant plastics detected in the ocean (Turner, 2020; Yu et al., 2016; Henkel et al., 2022). Sinking and sedimentation of PVC microplastics can enhance their bioavailability to low trophic level and benthic organisms (Karami, 2017; Miller et al., 2020; Fauvelle et al., 2021), and has an influence on the leaching behaviours of their additives (Henkel et al., 2022; Mortula et al., 2021; Yan et al., 2021). Plasticisers leaching from PVC microplastics represents a significant environmental stressor (Henkel et al., 2022; Yan et al., 2021; Henkel et al., 2019), and given the unique position of PVC in the water table, this may accelerate the introduction of toxic leachates into unique compartments of the ocean (Karami, 2017; Miller et al., 2020; Fauvelle et al., 2021). These leachates can also act synergistically with other environmental stressors to amplify toxicity response(s), e.g., by decreasing surrounding water quality and altering microbiomes (Teuten et al., 2009; Kühn et al., 2020; Gulizia et al., 2023; Suhrhoff and Scholz-Böttcher, 2016; Hermabessiere et al., 2017; Lear et al., 2021; Schrank et al., 2019). However, to fully reveal the ecological impact of PVC microplastics and their leachates, a comprehensive understanding of the leaching properties is required.

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Owing to their excessive annual production and high additive composition (10–70 % by weight (wt%)) (Yan et al., 2021; Hahladakis et al., 2018)), PVC leaching is a significant pathway for additives into aquatic environments (Yan et al., 2021). While the unique carbon-chlorine backbone gives virgin PVC high tensile strength and rigidity suitable for application in building and construction sectors (Czogala et al., 2021), including subsea infrastructure (Davis et al., 2007; Wang et al., 2017; Saeed et al., 2023), most PVC products require flexibility and malleability that can only be achieved through the incorporation of plasticisers (Lithner et al., 2009; Sampson and De Korte, 2011). Common phthalate acid ester (PAE) and diphenol plasticisers such as diethylhexyl phthalate (DEHP) and bisphenol A (BPA), respectively, are produced annually in high concentrations (>10 million tonnes) mainly for the manufacturing of flexible PVC products (80–95 %) (Walters et al., 2020; Marturano et al., 2019). Moreover, they are known as endocrine-disrupting chemicals (EDCs) with severe toxic consequences for wildlife (Wams, 1987; Qiu et al., 2019), thus the leaching of these plasticisers from PVC is an ongoing ecotoxicological concern (Bridson et al., 2021). Leaching studies of PVC have been conducted on aged and degraded microplastics having different thermal and morphological properties (Suhrhoff and Scholz-Böttcher, 2016; Yan et al., 2021), as well as from plastics exposed to fluctuating abiotic conditions such as solution pH and agitation (Henkel et al., 2022; Yan et al., 2021; Suhrhoff and Scholz-Böttcher, 2016). With these data, factors impacting molecular diffusivity (e.g., polymeric free volume), as well as the plastic surface-water boundary layer properties (e.g., plasticiser solubility), have been identified as the rate-limiting steps of plasticiser leaching from PVC (Henkel et al., 2022). However, unlike other major microplastic polymers, i.e., PS (Gulizia et al., 2023), leaching behaviours of PVC into environmentally relevant matrices has seldom been investigated. Thus, predictive leaching models are not yet applicable for PVC microplastics present in aquatic environments (Gulizia et al., 2023; Suhrhoff and Scholz-Böttcher, 2016).

To better understand the ecological impacts of PVC leaching on the environment, factors impacting molecular diffusion (e.g., water temperature, microplastic size, polymeric free-volume) and boundary layer properties (e.g., water agitation, plasticiser hydrophobicity/solubility) need to be investigated in combination (Gulizia et al., 2023; Heezen and Hollister, 1964). Moreover, when applying the diffusion and boundary layer model to plasticiser leaching, consideration should also be given to the size of the microplastic, as well as the specific polymer-plasticiser chemical interactions, as this will impact molecular diffusivity and microplastic leachability (Henkel et al., 2022; Mortula et al., 2021; Gulizia et al., 2023; Garde et al., 2001; Sun et al., 2019). Current studies predominately assess and quantify leaching from plastics with unknown chemical compositions and profiles (i.e., commercially available plastics (Yan et al., 2021)), or under specific experimental conditions (i.e., infinite-sink approach (Henkel et al., 2019)). Implementing both a controlled experimental and mathematical modelling approach using a combined diffusion and boundary layer model under environmentally relevant conditions will allow for kinetic assessment of PVC leaching behaviours relevant to the environment. This will enable predictions of plasticiser leaching from microplastics into different waterways (i.e., seawater (Gulizia et al., 2023)), under fluctuating conditions (e.g., global warming (Rowlands et al., 2021; Zhang et al., 2020)) and of different size classes (i.e., fragmentation (Gigault et al., 2018)).

Therefore, this study applied a diffusion and boundary layer approach to characterise the leaching kinetics of DEHP and BPA from PVC-based microplastics in marine environments, to reveal the impact of the specific polymer-plasticiser interactions (i.e., glass transition temperature; T_g (White and Lipson, 2016) and microplastic size distribution (Gulizia et al., 2023; Garde et al., 2001) on plasticiser leaching rate and concentration. PVC microplastics with known plasticiser concentrations were prepared and characterised, and then exposed to simulated marine conditions known to affect both the boundary layer (agitation: 200 rpm) and molecular diffusion (increasing temperature:

26–60 °C) (Gulizia et al., 2023). Leaching behaviours were quantified using gel permeation chromatography (GPC) and thermal gravimetric analysis (TGA), and the results applied to a numerical model to explain the leaching kinetics of PAE and diphenol plasticisers from PVC (Henkel et al., 2022; Gulizia et al., 2023). These data and model outputs will allow for the prediction of aqueous plasticiser concentration in waters contaminated with PVC microplastics and provide novel insights into the behaviours of non-buoyant and plasticised-polymers in unique compartments of the aquatic environment (e.g., benthic ecosystems (Cheang et al., 2018)), as well as during laboratory exposure studies (Bagel et al., 2011). Ultimately, this will contribute to the generation of a more comprehensive and accurate environmental risk assessment of plasticised microplastics from various point sources (Teuten et al., 2009; Saeed et al., 2023; Francis, 2015).

2. Experimental section

2.1. Materials

PVC (weight-average molecular weight; $M_w = 55,980$ g/mol, 389,239–500 g), DEHP (D201154–500 mL) and BPA (13,3027–500 g) were sourced from Sigma Aldrich and tetrahydrofuran (THF; HPLC grade) was sourced from Unichrom. All were used as received. Filtered seawater (0.5 μm ; pH = 8.10, salinity ≈ 35 ‰) was collected from the Australian Institute of Marine Science National Sea Simulator (AIMS SeaSim).

2.2. Microplastic preparation

PVC microplastics containing BPA and DEHP were prepared according to methods modified from Gulizia et al. (Gulizia et al., 2023) as follows. Pure PVC beads were dissolved in THF (1:7 w/v) under ambient conditions with constant stirring, after which, a plasticiser solution (DEHP and BPA in THF; 1:10 w/v) was added (85:15 PVC:plasticiser) with constant stirring for a further 4 days to ensure complete dissolution and homogeneity of the solution. Solutions were then cast on a watch glass and the residual solvent removed through evaporation under reduced pressure and high temperature (65 °C) for 3 weeks. Solvent removal was confirmed using TGA (TA SDT 650) with a heating rate of 10 °C/min up to 500 °C and under constant flow of nitrogen (50 mL/min) (Fig. S1). The dried membranes were then processed using a Magic Bullet – Nutribullet® 900 Series blender and sieved over a stainless-steel screen sieve (Glenammer Sieves) to afford irregularly shaped microplastics $\lesssim 200$ μm in diameter (mean size = 159–223 μm). Particle sizes were analysed using optical microscopy (Leica MZ26A; 4 images per plasticiser) and Matlab's Colour Threshold application (v R2022b) according to methods described in Gulizia et al. (Gulizia et al., 2023). The microscope images, corresponding binary image masks and particle size statistics are presented as Figs. S2–S4 and Table S1. These PVC-plasticiser compositions represent the minimum average concentration of plasticisers incorporated into PVC products (15–50 wt% (Chaudhary et al., 2016)) and their morphology is representative of the dominant plastic contamination detected in aquatic and biological matrices worldwide, i.e., DEHP and BPA leachates (Sampson and De Korte, 2011; Tsai, 2006). Their irregular shape and approximate size, 150 μm in diameter, is representative of microplastic fragments found in the marine environment globally (Eriksen et al., 2014b; Gigault et al., 2018; Bermúdez and Swarzenski, 2021; Tanaka and Takada, 2016).

2.3. Chemical characterisation of prepared plastics

The chemical profiles and properties of the plastics pertaining to leaching (i.e., plasticiser concentration and thermal properties) were characterised using GPC, TGA, differential scanning calorimetry (DSC) and Fourier Transform-Infrared spectroscopy (FT-IR). GPC was used to measure the concentration (wt%) of plasticiser incorporated into the

microplastics, and was calculated using prepared calibration curves of PVC, DEHP and BPA in THF from 0.515 to 8.24 mg/mL ($r^2 = 0.99$). For these analyses, microplastics (1.5–3 mg) were dissolved in THF (1.5 mL), filtered through a 22 μm MS® polytetrafluoroethylene (PTFE) filter (Membrane Solutions), and 50 μL aliquots injected into a 1260 Infinity II Multi-Detector GPC (Agilent Technologies) equipped with an ultraviolet (UV) absorbance and refractive index detector. Two PLgel 5 μL MIXED-C columns (300 \times 7.5 mm; Agilent Technologies) were calibrated using PS narrow standards (Agilent EasiVial PS-M). GPC confirmed successful incorporation of plasticisers with an average of 13.75 ± 2.48 wt%. TGA was also used to confirm plasticiser concentration, using methods described above. The relevant thermal properties of the plastic and the polymer-plasticiser interactions pertaining to leaching (T_g (Gulizia et al., 2023; Wypych, 2012; Phetwarotai et al., 2019; Jacobsen and Fritz, 1999)) were characterised using DSC (TA DSC250). Plastics (2–6 mg) were subjected to two cooling and heating cycles from -20 °C to 250 °C at a rate of 10 °C/min under a constant flow of nitrogen (50 mL/min). The thermograms generated after the second heating step are presented in Fig. S5. Infrared profiles of the neat plasticisers, virgin PVC and plasticised-PVC microplastics were obtained using FT-IR (ThermoFisher) equipped with an attenuated total reflected (ATR) crystal Diamond Head attachment (Fig. S6).

2.4. Leaching experiments

PVC leaching dynamics were investigated under agitated seawater conditions to reveal the mechanisms driving plasticiser leaching from microplastics in marine environments. Surface plasticiser concentration (i.e., plasticiser not chemically associated with the polymer and thus not impacted by diffusion/boundary layer properties), the polymer-plasticiser chemical properties (i.e., T_g) and surrounding abiotic conditions (i.e., agitation and temperature) are significant parameters impacting the leaching dynamics of plasticisers from microplastics (Yan et al., 2021; Gulizia et al., 2023; Suhrhoff and Scholz-Böttcher, 2016; Marturano et al., 2019; Sun et al., 2019). Therefore, plasticised-PVC microplastics were rinsed for 1 min in filtered seawater to ensure complete removal of all surface plasticiser (Gulizia et al., 2023). Rinsed plastics (10 mg) were then immersed in excess filtered seawater (10 mL) and exposed to constant agitation (200 rpm) at 26, 43 and 60 °C using a Syncore® vortex evaporator (Buchi). Concurrent exposure to agitated seawater and various temperatures allowed for assessment of the dominant leaching kinetics driving plasticiser leaching from PVC (i.e., diffusion or boundary layer limited). After leaching, microplastics were filtered (0.5 μm filter paper; Whatman), rinsed with deionised water to remove residual leachate and allowed to air dry under ambient conditions. Leachate solutions were stored in airtight glass vials. Leaching behaviours were quantified by calculating the plasticiser concentration remaining in the microplastics (wt%) using GPC, as described above.

To highlight the diffusion and boundary layer kinetics, careful consideration was given to obtain the initial leaching rate and time taken to reach equilibrium for each plasticiser. It was found that DEHP reached equilibrium within 2 h of immersion in seawater, and thus leaching experiments were conducted over 1, 3, 5, 15, 30, 60 and 120 min, and 0.8, 4 and 7 days for these plastics (starting $n = 90$, with $n = 9$ removed at each time point), whereas BPA reached equilibrium after 4 days, and thus leaching experiments were conducted over 30, 60 and 120 min, and 0.8, 4, 7, 14 and 21 days (starting $n = 72$, with $n = 9$ removed at each time). Given that the prepared microplastics encompassed an average size range between 159 and 223 μm , the contribution of each size class (Fig. S7) was also considered when developing a leaching model.

2.5. Numerical modelling

Leaching was modelled using a similar approach to previous work (Gulizia et al., 2023). Briefly, a spherically symmetric microplastic

particle was assumed. The total concentration of plasticiser was partitioned into “free plasticiser”, whose movement is described by the diffusion equation, and “associated plasticiser”, which is bound to the polymer and unable to move under the given experimental conditions. The plastic-water interface was described by a boundary layer model, whereby the concentrations of plasticiser on the water and plastic sides of the interface are related by a partition coefficient. In the boundary layer model, there is an assumed linear decrease in plasticiser concentration with increasing distance into the water, away from the microplastic edge. The bulk water is assumed to have zero concentration of plasticiser. More details are given in Gulizia et al. (2023).

For BPA, the model was extended to consider a distribution of particle sizes. Particle sizes obtained by optical microscopy were grouped into 15 histogram bins based upon their equivalent radius, which is the radius of a sphere whose cross-sectional area is the same as the irregularly shaped microplastic. To account for the distribution of plasticiser mass across the differently sized particles, each histogram bin was weighted in proportion to volume, $V = \frac{4}{3}\pi r^3$, where r is the midpoint of the histogram bin. The results, given in Fig. S7, show the relative proportion of plasticiser in the samples at different sizes. The numerical model was then run for each of these size categories. The overall results are reported as the weighted sum of each individual model run.

For DEHP, the results were independent of temperature, indicating that the rate-limiting step occurs at the boundary layer rather than in the plasticiser bulk. Therefore, the model was simplified to include only the boundary layer step. Under this assumption, the flux of plasticiser leaving the microplastic particle is proportional to its surface area. If the boundary layer is the rate-limiting step, then this implies rapid resupply of plasticiser from within the microplastic back to the edge. Hence, the average plasticiser concentration decreases at a rate inversely proportional to the particle's volume. Therefore, the average free plasticiser concentration p is given by

$$\frac{\partial p}{\partial t} = -\frac{pAD_w}{K_{pw}V\delta}, \quad (1)$$

where A is the surface area of the particle, D_w is the diffusion coefficient of plasticiser in water, K_{pw} is the plastic-water partition coefficient, V is the volume of the plasticiser, and δ is the boundary layer thickness. Assuming spherical microplastic particles and solving the differential equation, an exponential trend is predicted, given by

$$p = p_0 \exp\left(-\frac{3D_w t}{K_{pw}r\delta}\right) = p_0 \exp\left(-\frac{t}{\tau}\right), \quad (2)$$

where p_0 is the initial concentration of free plasticiser and $\tau = 3D_w/K_{pw}r\delta$ is the time constant. If D_w (the diffusion coefficient of plasticiser in water) is approximately independent of temperature within the experimental range, then the entire expression will have negligible temperature variation. Therefore, this model predicts that the time constant τ will be approximately independent of temperature, as was observed for the DEHP data.

Finally, the total plasticiser concentration was measured as the sum of the free and associated plasticiser:

$$p_{total} = p + p_a = p_0 \exp\left(-\frac{t}{\tau}\right) + p_a, \quad (3)$$

where p_a is the concentration of associated plasticiser.

It was found that Eq. (3) was a good fit for DEHP but not for BPA. Therefore, the more sophisticated model that includes the diffusion through the bulk polymer was used for BPA (Gulizia et al., 2023).

The code used for the analysis is published online.¹

¹ <https://github.com/bronsonp/MicroplasticsLeaching>.

2.6. Statistical analyses

Data were presented as the mean of triplicates with standard deviation. *t*-Tests performed in Microsoft Excel were used to evaluate the differences between each plasticiser with temperature and over time at a *p*-value threshold of 0.05.

3. Results and discussion

The extent and effect of plasticiser leaching on environmental water quality and biota is influenced by different environmental parameters (e.g., water temperature and agitation) (Fauvelle et al., 2021; Kühn et al., 2020; Gulizia et al., 2023; Suhrhoff and Scholz-Böttcher, 2016) and the chemical properties of the microplastic (e.g., plasticisation efficiency and the proportion of polymer-associated-plasticiser) (Mortula et al., 2021; Gulizia et al., 2023; Marturano et al., 2019; Sun et al., 2019). Under simulated conditions of agitation (200 rpm) and increasing temperature (26–60 °C), differences were observed in the kinetic behaviours of the two plasticisers, DEHP and BPA, as they leached from PVC. Leaching of both plasticisers started within 1 min of immersion in seawater (Fig. 1), however, the leaching rates differed (Table 1). For DEHP, 1.1 wt% (7 % of the total leaching concentration) was leached after 1 min of rinsing at ambient temperature. Following this, after a further 1 min of immersion in agitated seawater, an additional 2.6 wt% was leached (17 % of the total concentration), irrespective of temperature. Overall, 94 % of DEHP leaching occurred within the first 2 min of immersion in seawater, with no significant loss (<1 wt%) observed thereafter for the remainder of the experimental timeframe (*t* = 7 days). This indicates that the bulk of DEHP leaching was controlled by surface rinsing (Gulizia et al., 2023). Combined, the impact of surface rinsing, temperature-independency as well as the hydrophobicity of the plasticiser suggests that molecular diffusion is not a determining factor in DEHP leaching, and instead indicates leaching on this time scale is rate-limited by the boundary layer (Henkel et al., 2022; Gulizia et al., 2023; Suhrhoff and Scholz-Böttcher, 2016; Hermabessiere et al., 2017). In contrast, leaching of BPA was much slower reaching equilibrium between 7 and 10 days, and displayed a strong temperature dependency up to 60 °C (Fig. 1). In line with previous findings, temperature dependency indicates that the leaching of BPA is limited by molecular diffusion within the polymer matrix, and is impacted by changes to temperature (Henkel et al., 2022; Gulizia et al., 2023; Sun et al., 2019). Additionally, microplastic size is also known to play a significant role in leaching dynamics (Gulizia et al., 2023; Garde et al., 2001; Bindow et al., 2017). Given that the leaching rate and leachability of microplastics (i.e., proportion of “associated” plasticiser) are important factors influencing water quality and plastic/plasticiser toxicity, differences in kinetic behaviours of each plasticiser can be used to implicate the hazardousness and ecological fate of plasticised microplastics in aquatic environmental matrices.

3.1. Environmental implications of plasticised PVC leaching

As toxic aqueous contaminants, microplastic leachates can have devastating ecological consequences (Xu et al., 2022). While all investigated microplastic polymers have been shown to leach plasticiser to some degree (Teuten et al., 2009), the different polymer-plasticiser compositions (i.e., density), as well as the size of the microplastic, will impact the leaching rate and concentration (i.e., leachability) (Mortula et al., 2021; Suhrhoff and Scholz-Böttcher, 2016). Previous leaching studies have already demonstrated the leachability of a range of commodity polymers (Mortula et al., 2021), with many attributing these differences to the proportion of polymer-associated-plasticiser (Gulizia et al., 2023; Marturano et al., 2019), the fragmentation pattern of the microplastic (Mortula et al., 2021) and the surrounding hydrostatic pressure (i.e., depth in the water column) (Fauvelle et al., 2021). The rate and concentration of plasticiser released from a microplastic can

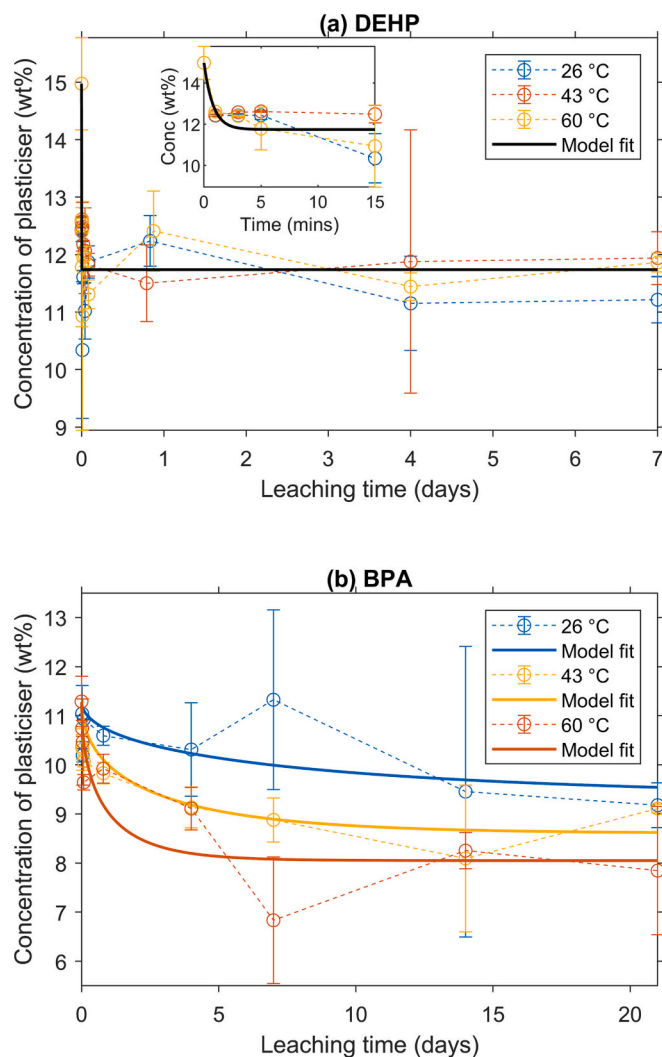


Fig. 1. Leaching behaviours of (a) diethylhexyl phthalate (DEHP) and (b) bisphenol A (BPA) from polyvinyl chloride (PVC) microplastics in seawater at 26 °C (blue), 43 °C (yellow) and 60 °C (orange). The inset in (a) shows the leaching behaviour in the first 15 min. The plots show the change in plasticiser concentration (wt%) after rinsing, whereby the points are the experimental data \pm standard deviation and the lines are the model fits. For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.

Table 1

Parameters obtained by least squares curve fitting.

Plasticiser	Model type	Fitted parameters	
BPA	Diffusion equation and boundary layer	Diffusion coefficient at 26 °C	$1.0 \times 10^{-11} \text{ cm}^2/\text{s}$
		Diffusion coefficient activation energy	53 kJ/mol
		Boundary layer coefficient	< 0.1 mm
		Exponential time constant	48s
DEHP	Exponential (Eq. (3))	Exponential time constant	48s

influence both short and long-term exposure consequences (Mathieu-Denoncourt et al., 2016), therefore the leachability of different polymer-plasticiser blends is an important factor to consider when understanding the fate of microplastics in the environment.

3.2. Size-dependency

Degradative history and microplastic size in the context of additive leaching has been well studied in literature (Yan et al., 2021; Gulizia et al., 2023; Garde et al., 2001; Bandow et al., 2017; Luo et al., 2020; Sørensen et al., 2021). In all cases, decreasing diffusion length (i.e., size or film thickness reduction) accelerated leaching, however, these parameters have yet been to be examined across narrow microplastic size ranges in aquatic matrices. For additives exhibiting diffusion-limited leaching, the size distribution of microplastics will significantly impact leaching behaviours (Gulizia et al., 2023; Sun et al., 2019; Wei et al., 2019; Soto-Cantú et al., 2008), therefore, in this study, the model fit parameters generated from the experimental data (Table 1) were used to predict the leaching dynamics of BPA from microplastics sized between 5 and 136 μm in agitated seawater (Fig. 2 and Figs. S8 and S9). When leaching behaviours are limited by molecular diffusion (as was the case for BPA), model outputs indicated that even 0.5-fold variations in size (52–99 μm) will significantly impact the release rate of plasticisers, i.e., larger microplastics will leach plasticiser at a slower rate (Gulizia et al., 2023; Garde et al., 2001). Moreover, at the smallest microplastic size (<42 μm), the release rate was estimated to be essentially instantaneous upon immersion in water, indicating that small micro- and nanoplastic contamination in the environment has the potential to quickly impact water quality at their source point. However, as larger microplastics (e.g., >136 μm) are transported and dispersed worldwide (Andrady, 2017), they can continue to leach plasticiser for as long as 60 days. At higher temperatures, the process is accelerated: the model predicts that this timeframe reduces to approximately 20 days at 43 °C and 10 days at 60 °C (Figs. S8 and S9). Research into the impacts of microplastics has found size to be a key factor (Lehtiniemi et al., 2018), with the typical size nomenclature (i.e., <5 mm in diameter) refined to categorise the different size classes of microplastics (small: 0.33–1 mm and large: 1.01–4.75 mm³) (Lehtiniemi et al., 2018), however, data here indicates

that even small variations in size can significantly impact microplastic behaviour and leachability. Thus, when investigating the ecotoxicological impacts of microplastics and their plasticisers (both in-situ and *in-natura*), microplastic size distribution and their leachability should be considered during method development.

3.3. Leachability of PVC

The concentration of plasticiser released from a microplastic is a key factor impacting the toxicity potential of microplastic contamination. In this study, leaching experiments conducted in turbulent and heated water found only 25–28 % (~4 wt%) of plasticiser was released from PVC microplastics within the experimental timeframe (Fig. 1). This suggests the majority of BPA and DEHP incorporated into PVC will be retained (Yan et al., 2021; Gulizia et al., 2023; Wu et al., 2019; Gavrilă, 2016). Leachability (or the amount of free plasticiser released) of plasticised polymers is impacted by the proportion of polymer-associated plasticiser, which is governed by plasticisation efficiency (T_g) and the bonding interactions between the plasticiser and the polymer backbone (Gulizia et al., 2023; Marturano et al., 2019; White and Lipson, 2016). While both plasticisers investigated in this study have contrasting chemical properties (diphenol and PAE containing functional groups), they had comparable impact on the thermal properties of PVC (T_g of virgin PVC: 80 °C and plasticised PVC: 49–51 °C; Fig. S5) (White and Lipson, 2016). The polymeric free-volume displayed by both BPA and DEHP plasticised PVC microplastics indicates that the plasticisation efficiency and proportion of free plasticiser within PVC is equivalent for both studied plasticisers, and thus explains the similar leaching concentrations (Marturano et al., 2019). However, when comparing the leachability of plasticised PVC to other BPA- and DEHP-polymers exposed to similar aqueous conditions (e.g., PS: 28–56 % leached (Gulizia et al., 2023)), plasticiser release from PVC is substantially lower. This could be due to the bonding interactions between each

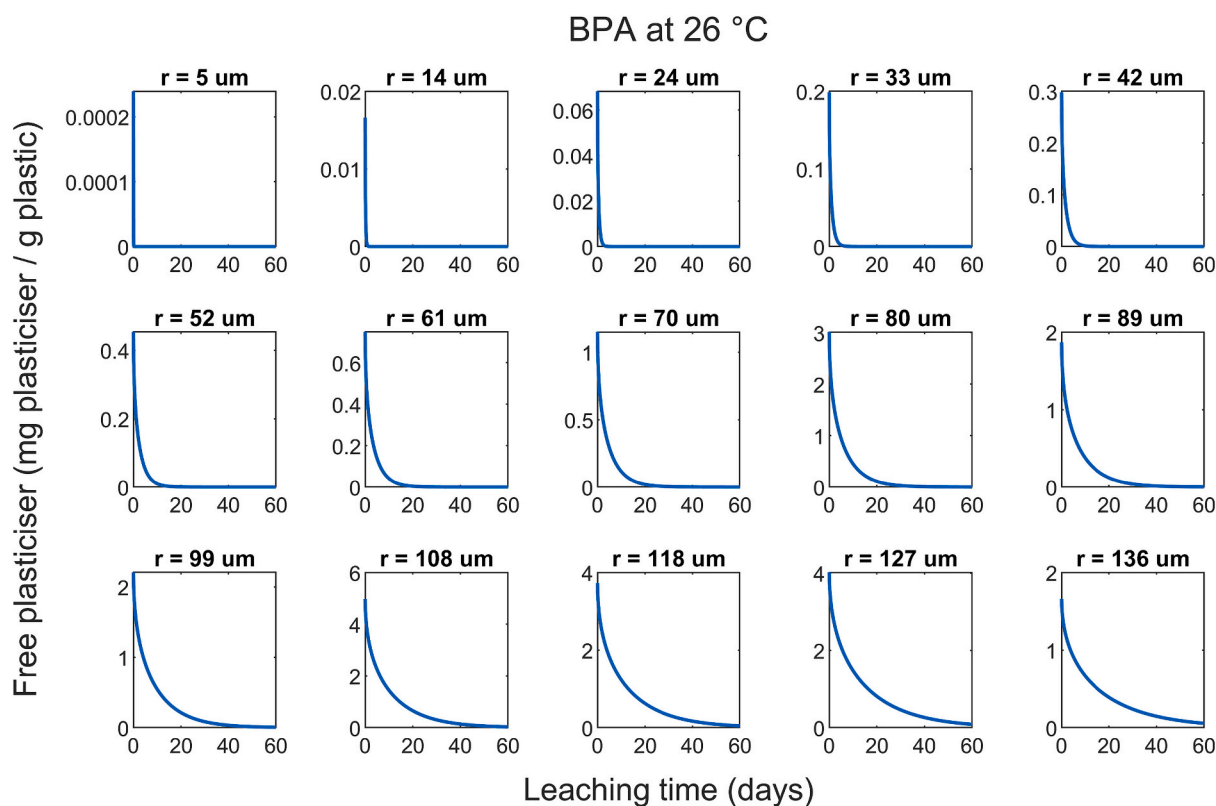


Fig. 2. Size-resolved leaching dynamics of bisphenol A (BPA) from polyvinyl chloride (PVC) microplastics at 26 °C in agitated (200 rpm) seawater over 21 days generated using model fit parameters in Table 1.

plasticiser and the PVC polymeric backbone (Marturano et al., 2019). Unlike PS and other high concern commodity plastics (e.g., PE), PVC halogen bonds can form with incorporated plasticisers (Wu et al., 2019; Gavrilă, 2016) (Fig. S6), which may contribute to the high proportion of polymer-associated-plasticiser and result in a lower concentration of plasticiser being release into the surrounding water (Mortula et al., 2021). Therefore, when the leachable properties of plasticised PVC are considered in isolation, PVC microplastics may be less hazardous in aquatic ecosystems compared to other polymers, and consequently, benthic and deep sea ecosystems may be less susceptible to the impacts of plasticiser leachates.

3.4. Implications for environmental risk assessment

PVC microplastics are discharged into aquatic environments worldwide from various point sources, including from ineffective waste disposal, municipal wastewater, industrial (e.g., construction and decommissioning of subsea infrastructure (Saeed et al., 2023; Koppel et al., 2023)) and fishery activities (Geyer et al., 2017). Thus an understanding of their leachable properties in different aqueous matrices and under different environmental conditions is important to ensure an all-encompassing risk assessment of microplastics in the environment (Henkel et al., 2022). While DEHP and BPA plasticisers are inherently toxic, the data obtained here for PVC (and previously for PS (Gulizia et al., 2023)) suggests that leaching will be further exacerbated by rising and fluctuating water temperatures, such as those predicted with global warming. Similarly, exposure to water currents, including ocean upwelling from the seabed and high wave action in coastal environments is also expected to accelerate plasticised-PVC leaching (Gulizia et al., 2023; Suhrhoff and Scholz-Böttcher, 2016; Erythropel et al., 2014). However, in the context of leaching, the continual fragmentation and size reduction of microplastics into smaller particles (i.e., nanoplastics (Gigault et al., 2018)) is of the greatest ecological concern, and has the potential to significantly impact water quality at the source point. This highlights the critical need to manage plasticised plastics before they enter aquatic ecosystems, as well as to consider the implications of decommissioning plastic infrastructure already in the environment (i.e., offshore and subsea pipelines (Saeed et al., 2023; Koppel et al., 2023)).

4. Conclusion

Leaching of DEHP and BPA plasticisers from PVC microplastics follows a diffusion and boundary layer model, whereby DEHP is rate-limited by the boundary layer and BPA is rate-limited by molecular diffusion (influenced by water temperature). Exposure to agitated and heated seawater prompted a significant release of both DEHP and BPA plasticisers from PVC, confirming PVC microplastic contamination in aquatic ecosystems contributes to aqueous plasticiser pollution. These findings are in line with previous work (Henkel et al., 2022; Yan et al., 2021; Gulizia et al., 2023; Sun et al., 2019), and suggests accelerated leaching of plasticisers with rising water temperatures (i.e., global warming), in ecosystems with strong water currents (i.e., coastal environments) and during fragmentation of plastics (i.e., decommissioning of offshore/subsea infrastructure (Saeed et al., 2023; Koppel et al., 2023)). These kinetic behaviours impact the rate and concentration of leached plasticiser and suggest that the impacts of PVC leaching are expected to be highly localised, with immediate impacts to water quality before the materials settle on the seabed. Finally, while this diffusion and boundary layer model has successfully described leaching from a number of polymers (e.g., PVC and PS (Henkel et al., 2022; Gulizia et al., 2023)) and additives (e.g., brominated flame retardants (Sun et al., 2019)), models to further improve environmental risk assessment of microplastics leaching should be expanded to include aged and/or degraded polymers as well as from environmental and/or consumer samples (e.g., PVC pipes). Regardless, current kinetic and chemical leaching data allows for a comprehensive assessment and extrapolation

of PVC leaching behaviours in a range of environmentally relevant conditions, which are determinate of the hazardousness of microplastics in the ocean.

CRediT authorship contribution statement

AMG, BP, CAM and GV conceptualised the study. AG prepared and characterised the plastic particles, performed leaching experiments and chemical analyses. JZ obtained microscope images and assisted in preparation of the graphical abstract. BP performed numerical modelling. CAM aided the data analysis. AMG, GV, BP and CAM drafted the manuscript. All authors reviewed and approved the submission of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests of personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data is provided in the Supporting Information and code has been published as outlined in the manuscript

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2023.115392>.

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