



Kinetics of plasticiser release and degradation in soils[☆]

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ABSTRACT

Despite the increasing use of emerging phthalate and non-phthalate plasticisers as replacements for restricted phthalates, few studies have investigated their rates of entry and persistence in soils. We investigated release of the emerging plasticiser diethyl hexyl terephthalate (DEHTP) from polyvinyl chloride microplastics (PVC; 4 mm diameter; 21% DEHTP w/w) in soils in a 3-month laboratory study. DEHTP was released rapidly, with 6.6–12.1 ng DEHTP released per mg PVC within <2 h, although this was a small proportion of the amount in the pellets (<0.006%). Degradation rates of 8 phthalate plasticisers and 4 non-phthalate emerging plasticisers in the soils were measured in a separate 3-month laboratory study. For 7 of the 12 plasticisers, pseudo-first order half-lives were <30 days, suggesting relatively low persistence. 5 higher molecular weight plasticisers, including the emerging trioctyl trimellitate and DEHTP, were more persistent, with half-lives >100 days. Plasticiser half-lives in soils were significantly positively correlated with logK_{OW}. Degradation was typically slower in acidic heathland (pH 3.8; organic matter 3.7%), than in alkaline grassland (pH 7.3; OM 16%) or sandy loam agricultural (pH 5.3; OM 5%) soils. Rapid release and potential persistence of some emerging plasticisers in soils indicates that presence of these contaminants may increase in the future.

1. Introduction

The presence of plastics (including microplastics – particles with diameters <5 mm) in soils has been linked to negative impacts on soil organisms. For example, microplastic contamination of soil has been shown to reduce the growth, reproduction, and fitness of terrestrial species such as earthworms and plants (Boots et al., 2019; Cao et al., 2017; Lahive et al., 2019). These negative impacts arise in part from the particulate nature of microplastics resulting in physical harm to organisms, e.g. inflammation and cell deformation (Jiang et al., 2020; Möhrke et al., 2022).

However, in addition to the physical effects of the plastic particles themselves, the effects of microplastics on soil organisms are also driven by chemical exposures. For example, Kim et al. (2020) found that the acute effects caused by microplastic exposure on a soil nematode were absent following removal of the additive content of the microplastics. Plasticiser additives in particular appear to be associated with negative impacts, such as genotoxicity and oxidative damage in earthworms (Gao et al., 2023; Li et al., 2023), growth inhibition in wheat (Yang et al.,

2023), negative impacts on reproduction and oxidative stress in nematodes (Viljoen et al., 2025), and changes in soil bacterial community structure (Zhu et al., 2018). In order to evaluate the impacts of microplastics on soil ecosystems, it is vital to study both the release of additives such as plasticisers from plastics, and the subsequent persistence of these additives in soils.

Despite the widespread presence of microplastics in soils (Billings et al., 2021; Büks and Kaupenjohann, 2020), studies of the release of additives from plastics have focussed on aqueous media (Henkel et al., 2022; Kwon et al., 2017; Suhrhoff and Scholz-Böttcher, 2016; Viljoen et al., 2023; Yan et al., 2021). One recent study did investigate the terrestrial release of phthalate plasticisers from soil-surface macroplastic films (Viljoen et al., 2023), but release profiles of plasticisers from microplastics have yet to be investigated. Relatively more data is available on the persistence of phthalates in soils than their release rates (Billings et al., 2021). However, phthalate plasticisers have been phased out in Europe and have been replaced by emerging plasticisers, the use of which is increasing (CEFIC, 2021). The rates of degradation of emerging plasticisers and soil property controls on these rates have yet

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to be investigated. The lack of empirical data on the factors controlling plasticiser release and degradation rates in soils limits our knowledge as to the sources, fate, and potential impacts of plasticisers in the terrestrial environment.

The overall aim of our study was to address these knowledge gaps by: 1) assessing the effects of soil properties on the release of plasticisers from microplastics in soils; 2) establishing soil degradation rates of legacy and emerging plasticisers; 3) comparing the soil degradation rates of legacy and emerging plasticisers across different soil types. In order to achieve this, we conducted experimental studies to measure the release of an emerging plasticiser from PVC microplastics, and the degradation of a range of phthalate and emerging plasticisers, in three soils spanning a relatively wide range of different pH (3.8–7.3) and organic matter (%OM) values (3.7–16%), over 3 months. Soil properties such as organic matter and pH have also been associated with changes in rates of phthalate degradation (Chang et al., 2009; Cheng et al., 2019; Tang et al., 2020; Tao et al., 2020; Xu et al., 2008; Zhu et al., 2018). In addition, plasticisers representing a range of properties (e.g. chain length, molecular size, compound class) were selected, as these properties have been shown to be primary drivers of relative degradation rates between phthalate compounds (Cartwright et al., 2000; Tang et al., 2020; Xie et al., 2010).

This is the first study we are aware of to investigate degradation rates of both phthalates and emerging plasticisers in soils, and examine the release of an emerging plasticiser directly from microplastics into soils. Our study aimed to test the following hypotheses: 1) The release rate of the plasticiser diethyl hexyl terephthalate (DEHTP) from PVC microplastics in soils is influenced negatively by soil pH and water holding capacity (WHC), and positively by organic matter; 2) Plasticisers degrade more rapidly in soils with higher pH and WHC, and more slowly in those with higher organic matter content; 3) Degradation rates of emerging plasticisers in soils will be similar to those of analogous phthalate congeners, with increasing persistence of emerging plasticisers observed with increasing molecular weight and $\log K_{OW}$.

2. Materials and methods

2.1. Test soils

Three natural soils were selected to provide a range of major soil properties within the study. Physicochemical properties of these soils were determined prior to experimental work, specifically pH, water holding capacity (WHC) and organic matter content (%OM) (Appendix S1 and Appendix Table S1). Two soils were collected in southern England, UK; an alkaline grassland (Chiltern; pH 7.3; WHC 73%; OM 16%) and an acidic heathland (Dorset; pH 3.8, WHC 41%; OM 3.7%). The third soil was a commercially sourced sandy loam agricultural soil (Lufa Speyer, Germany; pH 5.3; WHC 56%; OM 5.0%). This latter soil is widely used as a medium for studies of chemical fate and effects, including regulatory toxicity testing (OECD, 2010).

The soils were chosen as they are broadly representative of the range of typical soils types in temperate environments (Griffiths et al., 2011; Henrys et al., 2012) and span a number of common environments which may be particularly sensitive to plastic and plasticiser contamination based on typical concentrations (Billings et al., 2021; Büks and Kaupenjohann, 2020) and/or sensitive species (Boots et al., 2019; Li et al., 2023). Additionally, there is some evidence that organic matter, pH, and water content are factors controlling phthalate degradation in soils (Chang et al., 2009; Cheng et al., 2019; Tang et al., 2020; Tao et al., 2020; Xu et al., 2008; Zhu et al., 2018). Prior to use, soils were air-dried at room temperature, sieved to 2 mm and stored in polypropylene tubs at 20 °C in the dark. Tubs were lined with aluminium foil to prevent migration of additives from the polypropylene into the soils.

2.2. Test materials

2.2.1. Microplastic pellets used in the plasticiser release experiment

White pre-production virgin PVC microplastic pellets were selected for the release experiment. The pellets were plasticised with DEHTP and had a diameter of 3.9 ± 0.2 mm (mean and standard deviation of $n = 10$ pellets) and mass of 33.8 ± 3.4 mg ($n = 10$). DEHTP content in the pellets was determined in-house and was found to be $21.1 \pm 0.2\%$ w/w ($n = 3$; see Appendix S2 for further details). As the microplastics would need to be manually removed from the soils at the end of the experiment, pellet size and colour were partly dictated by the need for visual distinction from the soil (i.e. a white pellet). PVC was chosen as the majority of plasticisers are used in PVC plastic formulations (CEFIC, 2021), and in some cases plasticiser loads account for up to 70% w/w of the plastic (Hansen et al., 2013).

2.2.2. Plasticisers used in the degradation experiment

A suite of eight legacy (phthalate) and four emerging plasticisers (96–99.5% purity; all from Sigma-Aldrich, USA) were chosen for the degradation experiment (Appendix Table S2). All plasticisers were selected based on production quantities (CEFIC, 2021) and, where available, detection frequencies and abundances in soils (Billings et al., 2021). The phthalate plasticisers (dimethyl phthalate, diethyl phthalate, di-iso-butyl phthalate, di-n-butyl phthalate, benzyl butyl phthalate, diethylhexyl phthalate, di-n-octyl phthalate, and di-iso-decyl phthalate) were chosen to span a range of values for a number of physicochemical parameters potentially relevant to fate including molecular weight, $\log K_{OW}$, solubility in water, and degree of chain branching. A single exemplar compound was chosen from each of the following classes of emerging plasticisers: adipate (diethylhexyl adipate), terephthalate (diethylhexyl terephthalate), citrate (acetyl tributyl citrate), and trimellitate (trioctyl trimellitate).

2.3. Experimental design for the release and degradation experiments

Soils in the release experiment were amended with PVC microplastic pellets to give a concentration of 25 mg g^{-1} dw soil (~ 0.74 pellets g^{-1} dw soil; Fig. 1; see Appendix S3 for details of experimental setup). Although few field soils will contain concentrations of PVC as great as 25 mg g^{-1} dw, the test concentration in this mechanistic study was a compromise between environmental relevance and analytical thresholds for the subsequent analysis of any components released from the plastics into the soil. Soils in the degradation experiment were spiked with a solution of the 12 plasticisers to give a nominal concentration of each plasticiser of $100 \mu\text{g g}^{-1}$ dw (Fig. 1; Appendix S3). Each soil was wetted to 50% water holding capacity (WHC; Spurgeon and Hopkin, 1995). In each experiment, three test replicates and three controls were carried out for each soil.

Vessels were kept in the dark at 20 °C and sampled at regular intervals over three months (Appendix S3). For the release experiment soils, PVC microplastics were carefully removed from each sample using stainless-steel tweezers. All samples were transferred to glass vials and stored immediately at -20 °C in the dark. Soil moisture and pH were monitored throughout, with moisture levels kept constant (Appendix S4).

2.4. Plasticiser extraction and analysis

Plasticisers were extracted from each sample according to a method described in a previous study (Billings et al., 2023). In brief, 3.5–4 g ww (release experiment) or 0.1–0.15 g ww (degradation experiment) of soil was homogenised, dried with anhydrous sodium sulfate, and spiked with deuterium-labelled recovery standards (d4-DnBP and d4-DnOP, Sigma-Aldrich, USA). Plasticisers were extracted in 9:1 dichloromethane (DCM):acetone for 30 min using an Ethos X microwave extraction system (Milestone, Italy). Supernatants were dried with

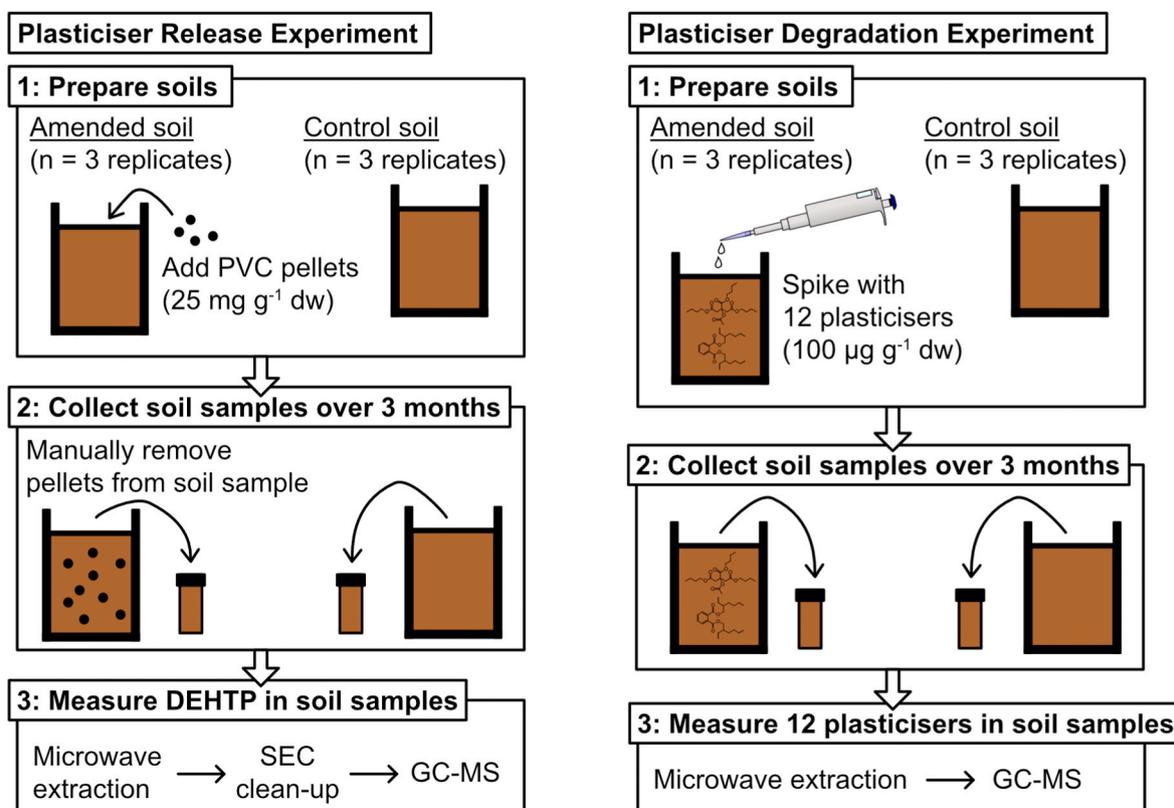


Fig. 1. Design and setup of plasticiser release and degradation experiments.

anhydrous sodium sulfate and passed through a 0.45 μm PTFE filter. Release experiment extracts were cleaned further using automated size-exclusion chromatography (Agilent 1200 series HPLC, Agilent, USA).

All samples were spiked with deuterium-labelled internal standards (d4-DEP and d4-DEHP, Sigma-Aldrich, USA) prior to instrumental analysis. Plasticisers were analysed using a gas chromatograph (6890N, Agilent, USA) fitted with an HP-5ms analytical column (30 m length, 0.25 μm film thickness, 0.25 mm internal diameter, Agilent, USA) coupled to a single-quadrupole mass spectrometer (5975B, Agilent, USA) operating in electron ionisation mode (see Appendix S5 for operating parameters). Plasticisers were quantified using internal standards and calibration curves of plasticiser standards (Sigma-Aldrich, USA). All plasticiser concentrations were recovery-corrected using the % recovery of one of the two deuterium-labelled recovery standards (d4-DnBP 83% \pm 10; d4-DnOP 83% \pm 11). Plasticiser concentrations were blank-corrected and are reported in ng g^{-1} dw. The mean limit of detection (LOD) of DEHTP in the release experiment was 8.5 ± 1.6 ng g^{-1} dw soil. Method LODs for the degradation experiment ranged from 0.5 to 99.4 ng g^{-1} dw soil (see Appendix Table S2 for individual compound LODs). Appendix S5 and Table S2 contain further details of quantification and quality control. Contamination controls were based on those used in a previous study (Billings et al., 2023; Appendix S6).

2.5. Statistical analysis

2.5.1. Estimation of plasticiser half-lives

To investigate comparative rates of plasticiser loss, the degradation time series concentration data for each compound in each soil was fitted to pseudo-zero, pseudo-first, and pseudo-second order kinetic models (hereafter referred to as zero, first and second order). First order models were generally the best fit across all soils and compounds, based on residuals and model outputs (fit parameters for all models can be found in Appendix Tables S4–S6). Zero, first and second order models produced

increasingly long half-lives. Thus we have chosen to report and discuss all values with respect to the first order models. Additionally, first order models are the most common model used in the literature (Cheng et al., 2008; Wang et al., 1997; Xie et al., 2010), thus the use of first order models allows comparison of relative differences in half-lives between the plasticisers across the soils.

2.5.2. Effects of soil and plasticiser properties on release and degradation

Multiple linear regression models (MLRMs) and generalised linear models (GLMs; gamma family and a log link) were used to assess effects of soil and plasticiser properties on initial released DEHTP concentrations (release experiment), and plasticiser half-lives estimated using first order kinetic models (degradation experiment). See Appendix S7 for further details.

3. Results and discussion

3.1. Release experiment

A fraction of the total DEHTP associated with the plastic particles was released rapidly into the soil, reaching detectable concentrations in all test soils in less than one day (Fig. 2). Initial samples collected within 2 h of first introducing the microplastics to the soils showed measured concentrations well above the background DEHTP concentrations present in the unamended soils. Thus, after 2 h of incubation, the mean DEHTP concentrations in the soils were 165 ± 8.8 (alkaline grassland), 302 ± 48.2 (acidic heathland) and 282 ± 63.4 (sandy loam agricultural) ng g^{-1} dw (Fig. 2). This corresponds to non-temporal release rates, i.e. mass of DEHTP released per mass of PVC, of 6.6, 12.1 and 11.3 ng mg^{-1} respectively for alkaline grassland, acidic heathland and sandy loam agricultural soils.

Despite rapid release of DEHTP from the pellets, mass balance calculations using the measured value of 21.1% DEHTP (w/w) in the PVC pellets indicated that only <0.006% of the total DEHTP mass in the

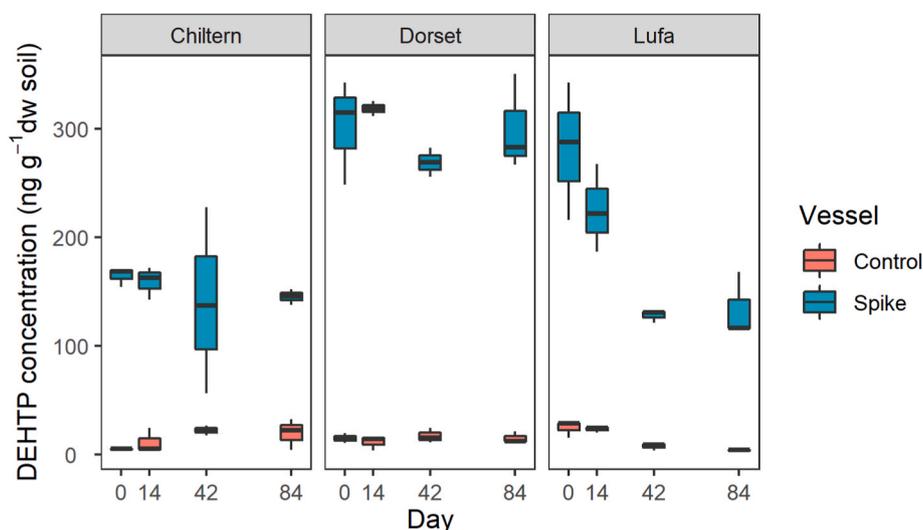


Fig. 2. DEHTP concentration over time in control soils and soils amended with PVC microplastics: alkaline grassland (Chiltern), acid heathland (Dorset), and sandy loam agricultural (Lufa); samples with a DEHTP concentration below the limit of detection were assigned a value of $0.5 \times \text{LOD}$; 2 outliers in acidic heathland (Dorset) soil day 14 and 42 have been removed, as these samples were $\sim 200\%$ the concentration of the other values in the replicates.

microplastics was released during the initial release phase. The fact that the mass balance was weighted strongly towards the pellets suggests that rapid initial release of DEHTP may represent mobilisation of molecules on the pellet surface (or near-surface), with subsequent releases via migration of plasticiser from the particle core to surface occurring much more slowly. Recent studies of the release of plasticisers (DEHP, DEHTP, DiNP, and DnBP) from PVC microplastics into aqueous media have also reported rapid initial release preceding a sharp decline in release rates (Henkel et al., 2022; Yan et al., 2021). Thus it appears that, under certain conditions, microplastic deposition in aqueous and terrestrial media may result in both a rapid “acute” and longer-term “chronic” input of plasticisers into these environments. Studies of additive release over longer time scales (e.g. 12–24 months), using plastics representative of a range of surface area:volume ratios and known plasticiser compositions (e.g. a range of percentage w/w and plasticiser properties), would be warranted to provide mechanistic insight on the factors controlling the rapid release and longer-term input of plasticisers observed in our study and those of Henkel et al. (2022) and Yan et al. (2021).

The maximum DEHTP concentrations reached in the acidic heathland and sandy loam agricultural soils were 83% and 71% greater than in the alkaline grassland soil. This difference was not due to differences in added PVC concentration between soils, as the masses of PVC microplastics added to each soil were measured to within 2 decimal places (31.25 g of microplastics were added to each batch of soil). Furthermore, there was no significant difference in the number of PVC particles removed at the first sampling time point across the three soils (Dunn’s test, Benjamini-Hochberg adjusted $p < 0.05$), implying that the sampling method was representative. Instead, the initial release rate of DEHTP will likely depend primarily on abiotic factors (e.g. soil properties; see section 3.1.1).

Differences in DEHTP fate were observed between the three soils. After the initial release period there was only a marginal decrease in DEHTP concentration over the 3-month test period in alkaline grassland (12% reduction) and acidic heathland (0.6% reduction) soils. In contrast, the decrease in DEHTP concentration in the sandy loam agricultural soil over the 84 days of the experiment was much greater, reaching $\sim 50\%$ of initial concentration within 42 days and remaining at this level in later samples (Fig. 2). The nature and abundance of the microbial communities present in the soils and their role in plasticiser degradation are likely to play a key role in the difference in plasticiser fate between the three tested soils. This aspect will be discussed further

in section 3.2.2.

3.1.1. Relationships between soil properties and extent of plasticiser release

The initial released DEHTP concentrations across the three soils were negatively correlated with %OM, pH, and WHC. A GLM of the initial released DEHTP concentrations in the three soils ($n = 3$ replicates per soil) with %OM, pH, and WHC as predictors (section 2.5.2) confirmed the negative associations between these soil variables and initial plasticiser release, although no statistically significant relationships were found ($p < 0.05$). However, it should be noted that the statistical power and interpretation of the model was limited by co-correlation of soil properties (e.g. linear model of WHC vs %OM, $R^2 = 0.85$; linear model of %OM vs pH, $R^2 = 0.86$) and the small number of tested soils (i.e. three). Therefore the initial indication from the results here, that soil properties potentially influence the extent of DEHTP release into soils, requires further studies to confirm which of the soil properties quantified here (e.g. pH, %OM, water holding capacity) may be acting as the major driver of this initial desorption and transfer into the test soils. That said, however, from the literature it is possible to tentatively identify potential drivers of the differences observed between soils.

Maximum initial DEHTP concentration in the organic-rich alkaline grassland soil (15.8% OM) was around half that of both the acidic heathland (3.7% OM) and sandy loam agricultural (5.0% OM) soils. The higher level of organic matter in the alkaline grassland soil could potentially have limited the release of DEHTP, relative to the other two soils, through formation of an ‘ecocorona’ of organic matter. Ecocoronas occur when polymer surfaces become coated in components derived from dissolved organic matter, a phenomenon which has been shown to affect fate dynamics of polymer-coated nanoparticles (Svendsen et al., 2020). Previous studies have indicated that ecocorona formation on microplastics can occur rapidly (i.e. within 24 h; Summers et al., 2018; Yao et al., 2023) thus it is plausible that ecocoronas could have influenced the initial release of DEHTP. The extent of ecocorona formation on polyethylene microplastics was also found to be greater in a soil with a higher %OM (Yao et al., 2023), although the relative contribution of other soil properties to ecocorona formation remains unclear. Thus, it is possible that ecocorona formation driven by greater %OM can limit the extent to which plasticisers can be released from microplastics, by preventing the formation of local concentration gradients around the microplastic particles, thus explaining the reduced DEHTP release from the pellets in the high-OM alkaline grassland soil.

Furthermore, in the high-OM alkaline grassland soil, the transport of

plasticisers away from sites of release (i.e. the pellets) by diffusion may be slower due to stronger binding of lipophilic DEHTP to OM in the soil immediately next to the microplastic particle which prevents the development of a diffusion gradient. This mechanism may result in a more heterogeneous distribution of DEHTP in the alkaline grassland soil than in the acidic heathland or sandy loam agricultural soils. Any such effect on spatial within-soil transport results in the occurrence of local hotspots of DEHTP around the particles not accounted for by the bulk sampling method. The lack of a clear positive relationship between OM and plasticiser release is in contrast to previous results for other classes of organic contaminant in aqueous environments, whereby dissolved OM acts to increase the release of contaminants from plastics by increasing the affinity of the contaminant for the surrounding medium (Rochman et al., 2013; ter Laak et al., 2009). Thus, it may be that the overall effect of organic matter on the release of plasticisers from microplastics may be medium- and compound-specific.

In addition to a higher organic matter content, the alkaline grassland soil also had the highest water holding capacity and pH of the three soils (Appendix Table S1). The greater volume of water present in the alkaline grassland soil relative to acidic heathland or sandy loam agricultural soils could have potentially inhibited or reduced the release of hydrophobic DEHTP from the microplastic pellets. Such an effect would be consistent with previous findings of the relatively slow release of more

hydrophobic phthalate DEHP compared to the less hydrophobic DnBP (Viljoen et al., 2023).

Soil pH is a major factor controlling the biological and biogeochemical processes in soils (Neina, 2019). However, although the alkaline grassland soil also had the highest pH of the test soils, there is no known mechanistic relationship between soil pH and plasticiser release. One possibility is that the pH of the soil could potentially alter the association of organic matter species with particle surfaces, leading to the formation of different surface ecocoronas (Svendsen et al., 2020). However, although the association of microorganisms and other components of soil organic matter with nanoparticle and microplastic surfaces have been studied in soils, knowledge of the soil property determinants of ecocorona formation remains limited (Svendsen et al., 2020; Yao et al., 2023).

3.2. Degradation experiment

3.2.1. Differences in degradation rates between plasticisers

All plasticisers, with the exception of DiDP and TOTM, exhibited a decrease in concentration over the course of the experiment (Fig. 3). There are a number of processes that could lead to apparent removal of plasticisers from soils. In theory, evaporation of plasticisers may occur from the soil surface. However, due to the high boiling points and low

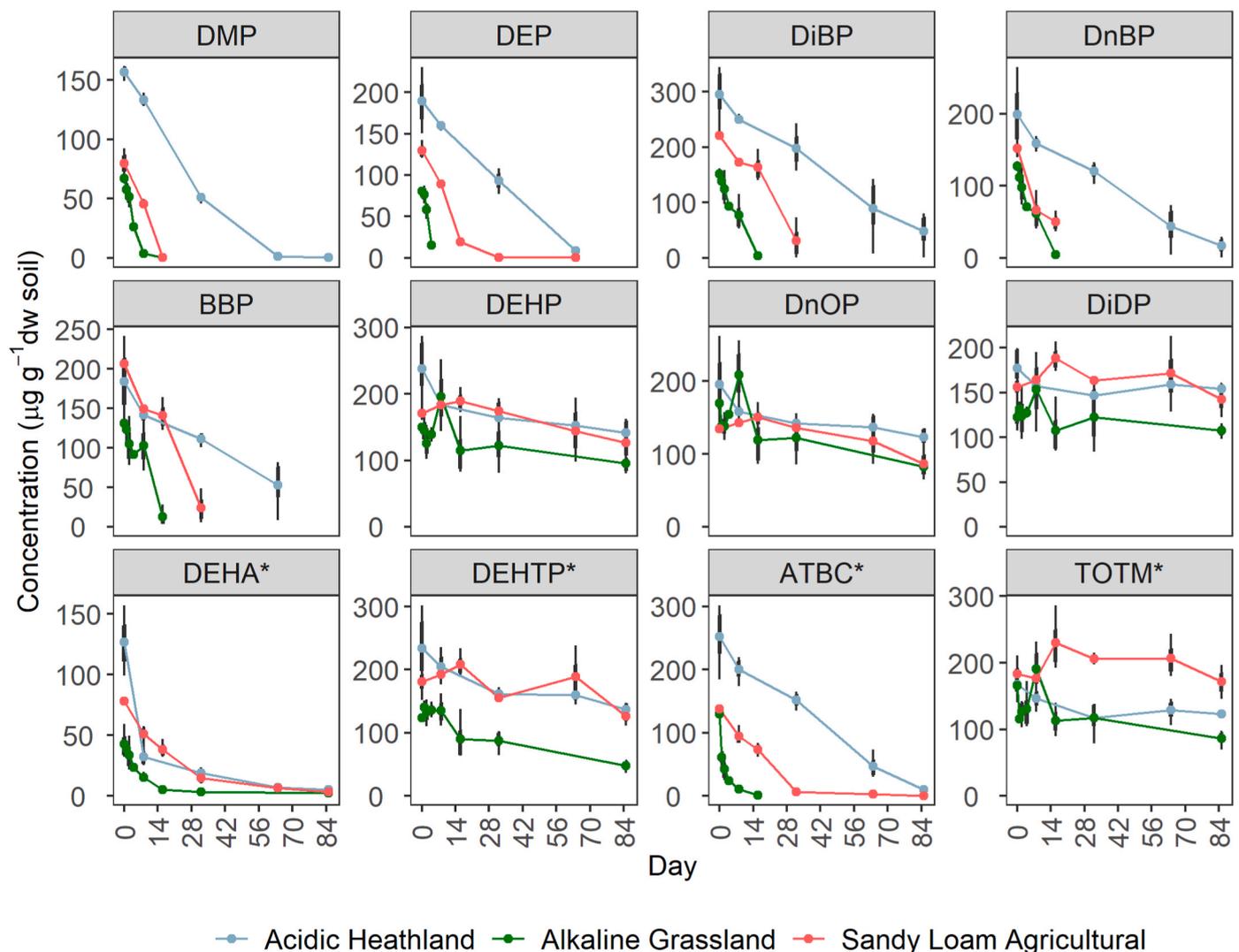


Fig. 3. Plasticiser concentrations over time in spiked soils in the degradation experiment; data points are only shown where all three replicates were >LOD; * indicates an emerging plasticiser.

vapour pressures of the plasticisers used in our study, in addition to a sampling depth of ~8 cm within the soil, it is unlikely that volatilisation made a major contribution to the losses observed in this study. The formation of non-extractable plasticiser residues, through strong binding of plasticisers to organic-rich soil moieties, is a further mechanism that could lead to the apparent removal of plasticisers from the soil. It would be expected that plasticisers with higher affinity for organic matter would be more likely to be affected by this process. However, the concentration of plasticisers with the highest $\log K_{OW}$ values in our study (e.g. DiDP) did not decrease appreciably over time. Additionally, soils were homogenised to a fine grain, and microwave-digested in DCM for 30 min to a temperature of 50°, which further increased the likelihood of extracting all available plasticiser. Given the absence of evidence of a contribution of either non-extractable residue formation or evaporation, microbial biodegradation is most likely to be the dominant mechanism determining the rates of plasticiser concentration losses over time from the test soils, as has been demonstrated in previous investigations of sterilised vs non-sterilised soils (Xie et al., 2010).

Degradation of the majority of the measured plasticisers was found in one or more of the three test soils over the 84 days of the experiment (Fig. 3). The first order model fits (Appendix Table S7) indicated significant degradation in at least one soil for every phthalate except for DiDP, for which concentrations did not appear to change significantly over time in any soils within any model (zero, first, or second order). Each emerging plasticiser was also found to degrade in at least one soil (Fig. 3). Of the four non-phthalate plasticisers, DEHA showed rapid degradation in all soils, while TOTM appeared to be particularly resistant to degradation, especially in the sandy loam agricultural soil (Fig. 3).

Plasticiser half-lives were found to be significantly correlated with $\log K_{OW}$ (MLRM of $\log_{10}[\text{half-life}]$ with $\log K_{OW}$, pH, %OM, and WHC as predictors; $F = 63.6$, $d.f. = 32$, slope = 0.28, $t = 13.3$, $p < 0.001$, adjusted $R^2 = 0.84$). Whilst previous studies have reported phthalate degradation to be generally slower for those compounds with longer chain lengths and greater $\log K_{OW}$ (Cartwright et al., 2000; Tang et al., 2020; Xie et al., 2010), we also found that this pattern was observed irrespective of plasticiser class (Figs. 3 and 4 and S1). The significant correlation between $\log K_{OW}$ and half-life may be explained by the fact that these substances bind more strongly to organic matter in the soil,

rendering them less available to microorganisms for biodegradation. The modelled first order degradation rates of the emerging plasticisers followed the order ATBC > DEHA > DEHTP > TOTM. Thus although DEHA and ATBC degraded in all soils, concentrations of DEHTP and in particular TOTM changed little over the experiment (Fig. 3). The order of half-lives of the emerging plasticisers generally followed the order of increasing $\log K_{OW}$ (Appendix Table S2), specifically ATBC (4.92) < DEHA (6.83) < DEHTP (8.93) < TOTM (9.3). That ATBC degraded more rapidly than DEHTP and DEHA may also be explained by the difference in the chemical structures of these compounds. Although there is limited knowledge regarding the exact mechanism of biodegradation of these substances, it is possible that the initial step in the degradation of these compounds occurs via the cleavage of the ester groups within their structures, as this is the most easily hydrolysable functional group in their otherwise solely aliphatic or aromatic structures. As DEHTP and DEHA contain two such ester groups compared to four in ATBC, the latter may be more likely to be vulnerable to degradation independent of molecular size.

The calculated half-lives of the 12 plasticisers can be used to broadly separate them into two groups; fast degrading ($t_{1/2} < 30$ days), and semi-persistent or persistent ($t_{1/2} > 55$ days) compounds (Fig. S1). The fast-degrading group contains the lower molecular weight phthalates (DMP, DEP, DnBP, DiBP and BBP), and the emerging plasticisers ATBC and DEHA. The greater susceptibility of these plasticisers to degradation is consistent with the relatively low concentrations of the majority of these compounds (e.g. DMP, DEP, BBP, ATBC, DEHA) reported across monitoring studies conducted in soils (Billings et al., 2023; Zeng et al., 2020; Zhang et al., 2019). The two exceptions for this trend are the two phthalates DiBP and DnBP, which are both commonly found in the environment and account for a significant part of the phthalate load in soils (Billings et al., 2021), despite their relatively rapid potential for degradation. The common presence of DiBP and DnBP indicates that these plasticisers, either through high production volumes or widespread release and transport, may have “pseudopersistence” in soils.

The remaining 5 plasticisers, the higher molecular weight phthalates (DnOP, DEHP, and DiDP) and persistent emerging plasticisers (DEHTP and TOTM), generally had first order half-lives >100 days in all soils (Fig. S1). Occurrence data for TOTM and DEHTP in soils is limited, although these compounds are among the most abundant reported

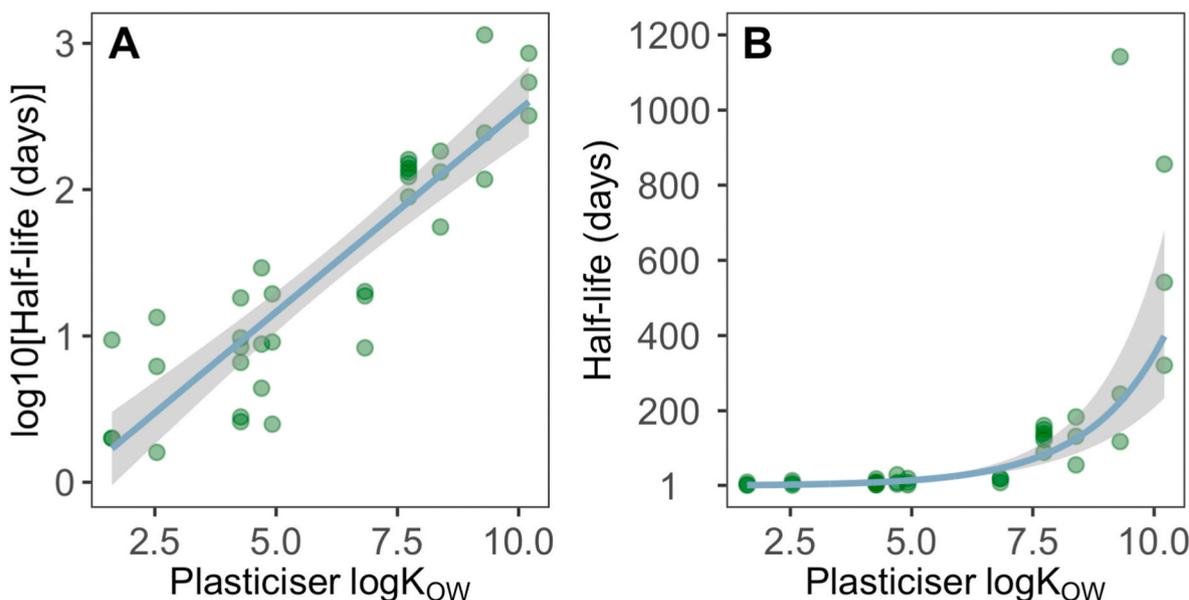


Fig. 4. A and B: Relationships between plasticiser $\log K_{OW}$ and first order half-lives in soils; blue lines indicate predicted values from linear model fit of $\log K_{OW}$ vs \log_{10} -transformed half-life; grey shading indicates 95% confidence interval; green points represent an estimated half-life for a particular plasticiser in a particular test soil based on time-series concentration data (section 2.5.1; Fig. 3; Fig. S1). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

plasticisers in the few available studies of their occurrence in sediment (Jebara et al., 2021; S. Kim et al., 2021; Y. Kim et al., 2021). The fact that DEHTP and TOTM are relatively enriched in some environmental matrices, despite relatively low production volumes relative to phthalates (CEFIC, 2021), may partly be explained by the comparatively slow degradation rates measured here. As such, the loading of these substances that reach soil may remain resident for extended periods.

3.2.2. Effects of soil properties on plasticiser degradation

With the exception of DEHA, all the other 11 plasticisers showed fastest degradation in the alkaline grassland soil compared to the two other soils (Fig. S1). The alkaline grassland soil contained a %OM content of 16%, while the acidic heathland and sandy loam agricultural soil had comparable organic matter levels (3.7% and 5%). Thus in this study fastest degradation rates were in the soil with the highest %OM content. In previous studies, organic matter has been negatively correlated with the degradation rates of plasticisers (Kickham et al., 2012; Xu et al., 2008). This effect of organic matter has been linked to the binding of lipophilic plasticisers to this soil fraction, thereby reducing bioavailability to microbes for biodegradation (Kickham et al., 2012; Xu et al., 2008). In contrast to these findings, and in agreement with our results, more recent studies have indicated that the overall effect of organic matter constituents, such as humic acids, can be to promote microbial phthalate degradation (Tang et al., 2020; Tao et al., 2020), potentially via provision of a nutritional source which can prime microbial communities for plasticiser degradation (Billings et al., 2021).

We found that the relative differences in the degradation rates of phthalate congeners between different soils were greater for lower molecular weight and lower $\log K_{OW}$ plasticisers (Appendix Table S7; Appendix Figure S1). This finding suggests that the influence of soil properties, such as organic matter, on degradation rate is congener-specific, with lower molecular weight plasticisers' (e.g. DMP, DEP) degradation more strongly influenced than for the higher molecular weight compounds (e.g. DnOP, DEHP). This effect may be plausibly associated with the increased likelihood of biodegradation for lower molecular weight compounds (Kanaly and Harayama, 2000).

In addition to the highest %OM content, the alkaline grassland soil had the highest pH (7.3 vs 5.3 of sandy loam agricultural, and 3.8 of acidic heathland; Appendix Table S1). That degradation was fastest in the soil with pH closest to 7 is consistent with previous studies (Chang et al., 2009; Zhu et al., 2018). It has been proposed that at high soil pH, the bioavailability of plasticisers to micro-organisms may be increased, as the ability of plasticisers to bind to organic matter is reduced at higher pH levels (Cheng et al., 2019; Yang et al., 2013). This has been attributed to the pH-induced ionisation of organic groups in organic matter leading to reduced hydrophobicity and therefore lower plasticiser binding potential (Cheng et al., 2019). DnBP degradation rates were significantly higher in soils with a higher soil moisture level (Cheng et al., 2018). All the soils in our study were wetted to 50% of their WHC. However, as the alkaline grassland soil had a higher field capacity, the absolute level of water added to this soil was higher than for the other two soils.

Whilst there were clear differences in plasticiser degradation between soils with different properties, $\log K_{OW}$ was the only variable to exhibit a significant relationship with half-life in a MLRM of \log_{10} [half-life] with $\log K_{OW}$, pH, %OM, and WHC as predictors ($F = 63.6$, d.f. = 32, adjusted $R^2 = 0.84$, $p < 0.001$). This may have resulted partly from the fact that limited replicates ($n = 3$ soils) limited the statistical power of the study. Nevertheless, these results suggest associations between plasticiser fate and soil properties that warrant further study. Specifically, investigations of the drivers of degradation, related to soil organic matter content, pH and other soil properties such as the diversity and abundance of bacterial communities, are needed to better understand the controls on plasticiser degradation rates across soil types.

The faster degradation of DEHTP in the sandy loam agricultural soil in the release experiment (section 3.1) was not observed in the degradation study (section 3.2). In the release experiment, total DEHTP

decreases over the time-course were 12% (alkaline grassland), 0.6% (acidic heathland), and ~50% (sandy loam agricultural). This contrasted with the estimated first order half-lives of DEHTP in the degradation study of 56 (alkaline grassland), 132 (acidic heathland), and 183 days (sandy loam agricultural), respectively. The release and degradation experiments were conducted concurrently under similar temperature, UV and soil moisture conditions. The only differences were the initial DEHTP concentrations (~165–300 ng g⁻¹ dw vs ~100–250 μg g⁻¹ dw in the release and degradation experiments) and nature of plasticiser input (associated with PVC microplastics vs direct chemical addition). Thus, it appears that degradation of DEHTP was either subject to a concentration-dependent effect or alternatively was influenced by the presence of PVC microplastics which may have acted to modify relative degradation between the soils.

The fact that faster DEHTP degradation was observed in the sandy loam agricultural soil in the release experiment supports the hypothesis that lower DEHTP concentrations result in shorter half-lives. However, this is not supported by results from the other two soils, which exhibited slower apparent degradation of DEHTP in the release than in the degradation experiment. A previous study also reported that the overall effect of initial DnBP concentration on half-life was soil-dependent (Cheng et al., 2018). Therefore the soil-specific differences between the DEHTP change over time in the release and degradation studies may have arisen from differences in degrader communities between these soils.

Microbial degradation has been demonstrated as a primary driver of phthalate fate in soils (Hurtado et al., 2017; Xie et al., 2010). This can also be expected to be the case for DEHTP, which is a structural isomer of the phthalate DEHP. PVC contains a number of additives in addition to plasticisers, e.g. UV stabilisers and colourants (Hansen et al., 2013), and the presence of PVC in soils has been shown to impact microbial communities (Shen et al., 2023). Thus, release of some of these non-plasticiser constituents concurrent with DEHTP may have acted to alter the degrader communities present in the soil or reduce their functionality. Such effects have been reported by Zhu et al. (2018), who found contrasting impacts of DEHP contamination on different soil bacteria groups, with some groups amplified and others reduced, and the presence of amplified groups correlated with soils exhibiting greater DEHP degradation. In our study, the sandy loam agricultural soil had a more circumneutral pH, so may have a more diverse microbial community than the other test soils, in particular the acidic heathland soil, and so may have a greater multi-functional community (Griffiths et al., 2011). This potentially greater bacterial diversity in the sandy loam agricultural soil may have resulted in greater resilience to non-plasticiser constituents released from the PVC, and could explain why the sandy loam agricultural soil was the only soil in which we saw significant degradation of DEHTP over the course of the release experiment. These results, coupled with the growing evidence for the impacts of microplastic contamination on soil microbial communities, indicate that studies of the impacts of microplastics on the capacity for microbial degradation of plastic additives in soils are warranted. Specifically, given the relatively high concentration of microplastics used in the plasticiser release study (25 mg g⁻¹ dw soil), future investigations of interactions between microplastic presence, plasticiser release, and soil microbial communities over a range of environmentally relevant microplastic concentrations are warranted.

3.3. Environmental implications of findings

Once in the soil environment, plasticisers are subject to degradation mediated mainly by the actions of the microbial communities present. The rates of such biodegradation differ considerably between compounds, with those compounds with greater $\log K_{OW}$ (and associated higher lipophilicity) compounds showing significantly greater persistence. For example, regression modelling predicts that, for a unit increase in $\log K_{OW}$, half-life increases by a factor of 1.89; (linear

regression of $\log_{10}[\text{half-life}]$ versus $\log K_{OW}$; slope = 0.28, $t = 11.5$, d.f. = 34, $p < 0.001$, adjusted $R^2 = 0.79$). Previous studies have suggested that the rate of release of plasticisers from plastics may be negatively correlated with molecular weight (Hansen et al., 2013), thus the overall fate of plasticisers present within microplastics is a complex process that may be mediated strongly by molecular size. Whilst plasticiser $\log K_{OW}$ was found to be a significant driver of differences in half-life in soils, irrespective of plasticiser class, the effects of soil properties (organic matter, pH, water availability) on plasticiser degradation rates also suggests that soil types, as well as source intensity and underlying soil microbiology, may affect plasticiser fate, and as a result, concentration in soil. Given that local and seasonal differences can be expected in pH, soil %OM content, organic matter inputs, temperature and rainfall, both local-scale and seasonal differences in plasticiser degradation (and resulting concentrations) may be anticipated, which will affect the exposure of organisms to these pollutants.

The release study suggested that some of the additive load associated with microplastic particles can be released very rapidly following entry into the soil environment. However, it is likely that the mass balance will depend on particle size. For instance, our study was limited to using relatively large (4 mm) microplastics, but a smaller particle size may have resulted in greater initial DEHTP release due to a large surface area to volume ratio, with a corresponding reduction in the capacity for chronic release. Thus, given that microplastic size distributions in field soils are typically dominated by smaller fractions, e.g. particles $< 500 \mu\text{m}$ (Billings et al., 2023; Yoon et al., 2024), the initial release rates of DEHTP observed in our study may represent an underestimation of release rates for the majority of microplastics in soils. Therefore, studies investigating plasticiser release rates and particle-soil plasticiser mass balances spanning a range of size fractions (e.g. 1–100 μm , 100–500 μm , 500–1000 μm , 1000–4000 μm) are a key research need, although the use of increasingly small particles in such studies will be associated with challenges in removal of the amended microplastics from the soil matrix prior to plasticiser extraction.

Based on our results, entry of macroplastics or large microplastic items into soils may act as a significant vector for plasticiser entry into the soil environment, given that the majority of the plasticiser load added to these plastics will be retained and may be released only over timescales beyond those used in this study. Under conditions of potentially very slow release of the bulk of the plasticiser fraction, plasticisers that are more resistant to degradation may maintain or even increase in concentration in soils following the input of plastics in which they are present. Plasticisers have been shown to accumulate in a variety of soil taxa, e.g. earthworms (Hu et al., 2005), cereals (Cai et al., 2015), and brassicas (Yuan et al., 2020), although data on accumulation at higher terrestrial trophic levels is lacking. Thus, given that we found that high $\log K_{OW}$ emerging plasticisers (e.g. TOTM) are most persistent in soils, there may be a particular risk of organism exposure, bioaccumulation and subsequent trophic biomagnification of these plasticisers. Given the potential chronic exposure of terrestrial organisms to persistent plasticisers in soils, future studies are warranted to establish whether the uptake of plasticisers observed in soil taxa represents “true” bioaccumulation or a “steady-state”, in addition to the long-term impacts of such accumulation and exposure.

4. Conclusions

This study investigated the release of an emerging plasticiser, the terephthalate DEHTP, from PVC microplastics into three soils with contrasting properties over 3 months. DEHTP was found to migrate rapidly from PVC microplastics into all of the test soils, with maximum concentrations reached within 2 h. Notably less DEHTP appeared to be released from the microplastics in the soil with the highest organic matter content, potentially suggesting that the presence of organic matter associated with the microplastic particles could have acted as a barrier to prevent further sorption of DEHTP into the surrounding soil.

Furthermore, the higher water content in this soil may have further inhibited the release of DEHTP due to the hydrophobicity of this analyte.

Given that our mechanistic study used pristine microplastics of only a single polymer type (PVC), formulation, and size (4 mm), further work regarding plasticiser release from plastics into soils is needed. Such studies should focus on expanding the range of polymer types and particle sizes investigated and compounds considered, as the internal polymer structure and compound properties may affect the movement of compounds within the matrix, thereby affecting release rate. Pristine microplastic pellets will constitute only a minor fraction of the microplastic present in the environment, therefore future studies using ‘aged’ microplastics with altered internal and external polymer structures are warranted. Additionally, the amount and type of additive content depends on polymer type due to the variety of applications for which plastics are used, and different release patterns may be observed for different plasticisers.

We also carried out an experiment to determine the degradation rates of 8 phthalate and 4 emerging plasticisers over 84 days. Significant degradation of all plasticisers in at least one soil was observed, except for the phthalate DiDP. We found that the persistence of phthalates and emerging plasticisers was significantly correlated $\log K_{OW}$, indicating that sorption of plasticisers to organic matter, thus rendering them unavailable for biodegradation, may play a key role in determining relative degradation rates between different plasticisers. The majority of plasticisers were found to degrade relatively rapidly, with half-lives of < 30 days. This included the phthalates DMP, DEP, DnBP, DiBP and BBP, and the emerging plasticisers ATBC and DEHA. However, little degradation over 3 months was observed in a group of significantly more persistent plasticisers, including the emerging plasticisers DEHTP and TOTM.

That $\log K_{OW}$ was found to be a significant factor in determining half-life, irrespective of plasticiser class, suggests that the concentrations of some emerging plasticisers in the terrestrial environment may increase in the future. Such results support the increasing need for determination of fate, bioavailability and potential toxicity of next-generation higher-molecular weight plasticisers in soil organisms, particularly given the increasing production and use of these compounds.

CRediT authorship contribution statement

Alex Billings: Writing – original draft, Visualization, Validation, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Kevin C. Jones:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **M. Glória Pereira:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Funding acquisition, Conceptualization. **David J. Spurgeon:** Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Conceptualization.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2025.125997>.

Data availability

Data will be made available on request.

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