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Leaching of phthalate acid esters from plastic mulch films and their degradation in response to UV irradiation and contrasting soil conditions

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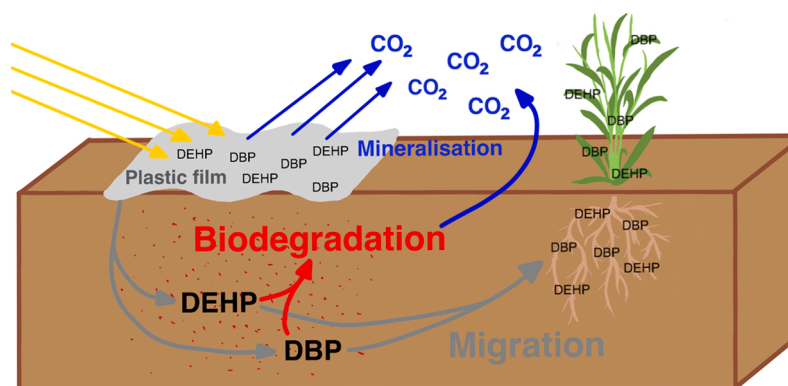
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HIGHLIGHTS

- Method developed to study in-situ breakdown of phthalate acid esters (PAEs) in soil.
- DBP migrated from the PVC plastic matrix and degraded much faster than DEHP.
- Migration of DBP and DEHP from plastic is a key rate limiting step in degradation.
- PAE degradation was accelerated by UV exposure and addition of some biosolids.
- PAEs can persist in soil for longer than previously thought.

GRAPHICAL ABSTRACT



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ABSTRACT

Phthalate acid esters (PAEs) are commonly used plastic additives, not chemically bound to the plastic that migrate into surrounding environments, posing a threat to environmental and human health. Dibutyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP) are two common PAEs found in agricultural soils, where degradation is attributed to microbial decomposition. Yet the impact of the plastic matrix on PAE degradation rates is poorly understood. Using ¹⁴C-labelled DBP and DEHP we show that migration from the plastic matrix into soil represents a key rate limiting step in their bioavailability and subsequent degradation. Incorporating PAEs into plastic film decreased their degradation in soil, DBP (DEHP) from 79% to 21% (9% to <1%), over four months when compared to direct application of PAEs. Mimicking surface soil conditions, we demonstrated that exposure to ultraviolet radiation accelerated PAE mineralisation twofold. Turnover of PAE was promoted by the addition of biosolids, while the presence of plants and other organic residues failed to promote degradation. We conclude that PAEs persist in soil for longer than previously thought due to physical trapping within the plastic matrix, suggesting PAEs released from plastics over very long time periods lead to increasing levels of contamination.

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1. Introduction

The use of plastic has become an integral part of intensive agriculture with current consumption by the agricultural industry estimated to be 12.6 million tonnes annually (FAO, 2021). The most common uses include: (i) mulch films (Wang et al., 2016; Shi et al., 2019; Qi et al., 2020; Yu et al., 2021); (ii) greenhouses and tunnels (Espí et al., 2006); (iii) packaging and storage (Chen et al., 2021); and (iv) irrigation piping (Li et al., 2020a; Qi et al., 2020). With an increased focus on food security and sustainability, plastic mulch films are being increasingly used worldwide to promote crop yields by increasing soil temperatures, lowering soil water evaporation, preventing soil erosion and minimising the use of herbicides, pesticides and fertilisers (Steinmetz et al., 2016; Gao et al., 2019; Serrano-Ruiz et al., 2021). Currently, with little economic incentive to remove plastic films from fields, many are typically ploughed into the soil leading to an inevitable legacy of plastic contamination (Liu et al., 2014). After incorporation, this legacy plastic progressively breaks down and fragments leading to the formation of microplastics (MPs; particles < 5 mm in size; Qi et al., 2020). Although the relative importance of the different breakdown pathways on MP formation is not known, it is known to involve both biotic and abiotic chemical weathering alongside mechanical breakdown of plastic residues during tillage events (Shi et al., 2019).

A field study carried out over a single cropping season, showed MP loading rates up to 10 t ha⁻¹ had no major effect on soil and plant biological health (Brown et al., 2022b). Yet, a wide range of laboratory- and mesocosm-based studies have reported that MPs can have negative effects on earthworm physiology (e.g. reduction in growth, mortality), soil physical properties (e.g. bulk density, water holding capacity) and plant health (Huerta Lwanga et al., 2016; De Souza MacHado et al., 2018; Boots et al., 2019; Zhang et al., 2019; Guo et al., 2020; Zang et al., 2020). The difference in responses may be due to the different polymer compositions, size and shape of the MPs created, soil loading rates and the chemical additives added alongside the plastic polymer (Qi et al., 2020).

The migration of hazardous and toxic chemical additives such as phthalate acid esters (PAEs) from plastic films represents a major cause for concern for both short- and long-term environmental health outcomes (Qi et al., 2020). Plasticisers are additives used to increase the flexibility, durability, and stretchiness of plastic and are present in almost all agricultural plastics. Typically, these additives have a low molecular weight (Mw 190 – 450; (Zhang et al., 2015a) and work by disrupting the polymer crystalline lattice and forming gaps between the polymer chains. Plasticiser concentrations typically range between 10% and 70% of the plastic's total weight depending on polymer type and intended function, with mulch films typically containing 20 – 60% (Wang et al., 2016; Giuliani et al., 2020). The most common plasticiser used across all polymer types are PAEs due to their low cost, low volatility, elastic nature and durability (Chakraborty et al., 2019). As PAEs are not chemically bound to the polymer they can migrate into contact materials (Rastkari et al., 2018; Wang et al., 2020) and are now considered a priority pollutant by the European Union and United States Protection Agency (Qi et al., 2020). The concern surrounding PAEs present in soil, stems from their potential to migrate into food crops, soil mesofauna and the wider food chain, where they can then affect public health (Li et al., 2020b). Di(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP) and three other PAEs have been identified as carcinogenic environmental toxins and endocrine disruptors, with the ability to affect human reproductive health (Liu et al., 2020). Despite this, the long-term impact of PAEs on soil health has scarcely been explored.

While there is evidence of PAEs being present in agricultural soil (Zhang et al., 2015b), research between the quantity of agricultural plastic and resultant PAE concentration in soil is limited. Li et al. (2021b) demonstrated a positive correlation between the concentration of plastics and PAEs in the Xuzhou region of China. However, they also concluded that the plastics and PAEs may not always possess a close

relationship, as the concentration of plastics relies primarily on input, whereas PAEs rely on both input and removal (Li et al., 2021b). The removal of PAEs from soil has been attributed to the migration into crop and removal through irrigation and runoff (Li et al., 2020a; Li et al., 2020b), but most often is the result of microbial degradation (Xie et al., 2010) with both PAE-degrading bacteria and fungi being identified (Wang et al., 2017; Tang et al., 2020; Das et al., 2021; Tran et al., 2022). The initial stages of PAE degradation relies on hydrolysis of the ester bond by enzymes, which is substrate-specific to the enzyme systems (Wang et al., 2017; Ren et al., 2020); thus variations between bacteria and fungi enzyme systems and promotion of microbial activity could result in different degradation rates. The potential for PAE degradation via phytoremediation, however, has scarcely been explored, as the majority focusing on PAE removal from soil through uptake and translocation by various plant species (Liao et al., 2019; Cheng et al., 2021; Das et al., 2021; Wang et al., 2021b). Yet, it has been reported that microbial degradation of PAEs can be accelerated in the rhizosphere due to the change in the microbial community (Wang and Chi, 2012; Li et al., 2014). Environments that optimise plastic degradation, such as high levels of UV exposure, have to our knowledge also not been used to monitor PAE degradation in soil. Exposure to UV has already been shown to cause major molecular changes to the plastic surface and can also increase phthalic monoesters and phthalic acid concentrations, which are both formed from the radical hydrolysis of PAEs (Fig. S1; (Hankett et al., 2013).

While degradation of high concentrations of PAEs has been monitored through the addition of PAEs directly into soil (Yang et al., 2018; Tang et al., 2020), this approach does not reflect the lower rates of PAE migration into soil which may be expected to occur during plastic degradation (Ye et al., 2020). Further, it does not reflect the physical trapping of PAEs in the polymer matrix which may limit microbial access and enzymatic attack. Moreover, degradation has been monitored via extraction and quantification of PAEs from soil (Wang et al., 2016; Li et al., 2020a), which only determines the depletion in the initial PAE concentration and not accounting for the formation of intermediates, e.g. phthalate monoesters or the complete decomposition to carbon dioxide and water. Furthermore, PAEs have the potential to adsorb to soil particulates inhibiting the extraction recovery, resulting in the elevated degradation rates (Li et al., 2014). Thus, potentially accelerating the timeframe to complete PAE degradation. In this study, we use ¹⁴C-labelled PAEs to directly monitor the complete degradation of PAEs.

Our laboratory-based study aims to assess the effect of different soil environments on the migration and degradation of PAEs from plastic films, using ¹⁴C-labelled DEHP and DBP to determine the complete PAE degradation cycle. We hypothesised that (i) the migration of PAEs out of the plastic and into the soil environment is a rate limiting step in their degradation, and (ii) migration and degradation of PAEs is accelerated under varying UV exposure, (iii) degradation is promoted by upregulating microbial activity in soil via organic substrate addition (accelerated bioremediation), and (iv) rate of degradation will be increased in the rhizosphere due to a root-mediated stimulation of microbial activity.

2. Materials and methods

2.1. Soil

A free draining, sandy clay loam textured Eutric Cambisol was collected from the Henfaes Agricultural Research Station, Abergwyn-gregyn, North Wales (53°14'N, 4°01'W) in February 2021. The soil was collected from five plots at random (at least 10 m apart) (n = 5) within a field under a long-term grass-cereal rotation (*Lolium perenne* L., *Triticum aestivum* L.). The site has a temperate oceanic climate with a mean annual temperature of 11 °C and average annual rainfall of 1060 mm. After collection, the soil was passed through a sieve (< 4 mm) to remove large stones and plant material and subsequently stored fresh at 5 °C until use. Soil pH and electrical conductivity (EC) were measured on 1:5

Table 1

Influence of substrate amendments on soil properties. The soil was sampled after a 7-day pre-incubation period. Results are expressed on a mean dry soil weight basis \pm SEM ($n = 5$). Superscript letters denote significant differences between treatments ($p < 0.05$).

	Control	Grass	Straw	Biosolid
Soil moisture (%)	32.4 \pm 2.1 ^{ab}	31.7 \pm 2.7 ^{ab}	30.2 \pm 2.8 ^a	42.8 \pm 3.4 ^b
pH	5.64 \pm 0.06 ^a	5.60 \pm 0.10 ^a	5.78 \pm 0.07 ^a	8.20 \pm 0.27 ^b
EC (μ S cm ⁻¹)	26 \pm 4 ^a	84 \pm 8 ^b	95 \pm 13 ^b	365 \pm 77 ^c
NO ₃ ⁻ (mg N kg ⁻¹)	9.2 \pm 0.9 ^{ab}	26.4 \pm 6.4 ^a	5.6 \pm 1.8 ^{ab}	7.0 \pm 6.8 ^b
NH ₄ ⁺ (mg N kg ⁻¹)	2.8 \pm 0.7 ^a	27.4 \pm 5.3 ^b	3.4 \pm 0.4 ^a	64.8 \pm 9.9 ^c
DOC (mg C kg ⁻¹)	150 \pm 14 ^a	216 \pm 42 ^a	186 \pm 2 ^a	750 \pm 112 ^b
TDN (mg N kg ⁻¹)	22 \pm 2 ^a	72 \pm 7 ^b	19 \pm 2 ^a	835 \pm 41 ^c
Bacterial: Fungal ratio	0.14 \pm 0.01 ^a	0.14 \pm 0.02 ^a	0.15 \pm 0.03 ^a	0.15 \pm 0.02 ^a
Microbial biomass (mg PLFA kg ⁻¹)	9.13 \pm 0.79 ^a	7.93 \pm 0.73 ^a	7.14 \pm 1.08 ^a	14.90 \pm 2.70 ^a
C:N ratio	9.19 \pm 0.17 ^a	9.46 \pm 0.16 ^a	11.48 \pm 0.16 ^b	8.59 \pm 0.06 ^c

EC, electrical conductivity; DOC, dissolved organic C; TDN, total dissolved N; PLFA, phospholipid-derived fatty acids.

(w/v) soil-to-distilled water suspension using standard electrodes. Soil moisture was measured after oven drying (105 °C) for 72 h. Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were determined using a Multi N/C 3100 analyser (Analytik Jena, Jena, Germany) after samples were extracted in a 0.5 M K₂SO₄ solution (1:5 soil: K₂SO₄ solution; w/v). Ammonium (NH₄⁺) and nitrate (NO₃⁻) concentrations were both determined colorimetrically according to (Mulvaney, 1996) and (Miranda et al., 2001), respectively. Sub-samples of soil were air-dried, ground using a stainless steel ball mill, and the total carbon (C) and nitrogen (N) content determined with a TruSpec CN analyzer (Leco Corp., St Joseph, MI). Soil characteristics are summarised in Table 1.

2.2. Preparation of ¹⁴C-labelled plastic mulch film

Polyvinyl chloride (PVC; Mw 62 000, in pellet form), tetrahydrofuran (THF; \geq 99.9% purity), DBP (99% purity) and DEHP (\geq 99.5% purity) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and these chemicals were used as received. ¹⁴C-radiolabelled DBP (ring-¹⁴C (U); 2.03 GBq mmol⁻¹) and DEHP (ring-¹⁴C(U); 2.72 GBq mmol⁻¹), were purchased from American Radiolabelled Chemicals Inc., St. Louis, MO, USA. Chemical and physical properties of the two PAEs are provided in Table S1.

Plastic films were formed through dissolving PVC resin in THF (1:30 PVC:THF, w/v), at room temperature. Subsequently, the PVC-THF solution was mixed with a plasticiser solution (PAE ratio of 1:1 (v/v); using either ¹⁴C-labelled DEHP or DBP) to form a PAE bulk concentration of 30 wt% of PVC. The solution was mixed for 15 mins, cast onto a 40 cm² glass plate and placed in a fume hood for the THF to evaporate (approximately 4 h). The resultant ¹⁴C-labelled film (~200 μ m thickness) was then cut into squares \geq 1 cm² for use in the experiment. The specific activity of 5 mg of the active film was 0.11 kBq mg⁻¹ (¹⁴C-labelled DBP film) and 0.13 kBq mg⁻¹ (¹⁴C-labelled DEHP film). The equivalent amount of ¹⁴C-labelled DEHP or DBP added to the plastic films was also added to a solution such that the specific activity of 1 mL of the phthalate solution was 0.11 kBq mL⁻¹ (¹⁴C-labelled DBP solution) and 0.13 kBq mL⁻¹ (¹⁴C-labelled DEHP solution).

2.3. Leaching of PAEs out from PVC films

The leaching kinetics of plasticisers into solution was characterised by placing 5 mg of either ¹⁴C-labelled DEHP or DBP PVC film in 5 mL of KCl (1 mM; (Henkel et al., 2019)) in a sealed vial and maintenance at 20 \pm 1 °C. The ionic strength of KCl was used to reflect that in soil solution. Sampling of the external bathing medium occurred after 1, 4, 7, 11, 16, 28, 42, 60, 78, 91, 108, and 120 d by removal of the film and placing in a new solution. A liquid Wallac 1404 liquid scintillation counter with automated quench correction (Wallac EG&G, Milton Keynes, UK) and alkali compatible scintillation fluid (Optiphase HiSafe 3; PerkinElmer, Waltham, MA) was used to determine the amount of ¹⁴C-PAE leached into the external solution.

2.4. Mineralisation of PAEs in soil

Field-moist soil (5 g) was placed in sterile polypropylene tubes (115 mm height \times 30 mm diameter) and ¹⁴C-labelled plasticiser added either by: (i) 5 mg ¹⁴C-labelled DEHP or DBP PVC film applied directly to the surface of the soil (82 kg ha⁻¹; (Huang et al., 2020)), (ii) 1 mL of DEHP or DBP phthalate solution evenly applied directly to the surface of the soil ($n = 5$, total samples = 20). Following addition of ¹⁴C-labelled plasticisers, a trap containing 1 mL of 1 M NaOH was suspended above the soil surface to capture evolved ¹⁴CO₂, and the tubes sealed and stored at room temperature. The NaOH trap was previous tested to be > 98% efficient by collecting ¹⁴CO₂ generated from adding excess 0.1 M HCl to 0.001 M NaH¹⁴CO₃ (Brown et al., 2022a). The NaOH traps were changed after 1, 4, 7, 11, 16, 28, 42, 60, 78, 91, 108 and 120 d and ¹⁴C determined as described above. Degradation of PAEs was determined as cumulative mineralised ¹⁴CO₂ as a percentage of the starting ¹⁴C activity in the PVC film.

2.5. UV-mediated mineralisation of PAEs

Field-moist soil (5 g) was placed into UV-transparent quartz tubes and PVC film containing ¹⁴C-labelled DEHP or DBP (5 mg) added directly to the soil surface, with control treatments covered in aluminium foil to prevent UV exposure ($n = 4$, total samples = 16). For all treatments, NaOH traps covered with aluminium foil to prevent exposure to UV were used to collect respired ¹⁴CO₂. Samples were then placed in the Atlas SUNTEST XXL (Atlas Material Testing Technology, Mount Prospect, IL, USA) with the irradiance set at 65 W m⁻² continuously and temperature controlled to 25 °C. The NaOH traps were changed after 20, 50, 90, 130, and 180 h, and the ¹⁴C concentration in the NaOH determined as described above.

2.6. Microbial promotion of PAE mineralisation

Mineralisation of ¹⁴C-labelled DEHP or DBP was also assessed as described above in the presence of three organic substrates used to promote soil microbial activity: (1) soil (5 g) amended with 2% (w/w) (2 t ha⁻¹) of ryegrass shoots (*Lolium perenne* L.) collected from a sheep-grazed field at the same location as the soil; (2) soil (5 g) amended with 2% (w/w) (2 t ha⁻¹) of maize (*Zea mays* L.) crop residues; (3) soil (5 g) amended with 1 g (20 t ha⁻¹) of biosolids (wet weight; Five Fords urban wastewater treatment plant; Dŵr Cymru-Welsh Water, Wrexham, UK). Substrates were added to soil at levels reflecting typical agricultural practices (van den Berg et al., 2020; Li et al., 2021a) and preincubated for 7 d. After preincubation, 5 mg of PVC film containing either ¹⁴C-labelled DEHP or DBP were buried to a depth of 1 cm in all treatments, including a substrate-unamended control ($n = 5$, total samples = 40). After treatment, an NaOH trap was suspended above the soil and changed at regular intervals, and ¹⁴C determined as described previously.

Properties of the substrates and amended soil characteristics after preincubation are summarised in Table 1. Total C and N in the substrates was determined with a TruSpec analyzer (Leco Corp., St Joseph, MI, USA).

Phospholipid fatty acid (PLFA) profiling was used to assess changes in size and structure of the soil microbial community in response to the organic amendments. Briefly, soil samples were collected after preincubation and at the end of the 91-d experiment and stored at -80°C . Lyophilisation was performed using a Modulyo Freeze Dryer with an RV pump (Edwards Ltd., Crawley, UK). Samples were shipped to Regen Ag Lab (Pleasanton, NE, USA) for subsequent PLFA analysis. After extraction, fractionation, and transesterification, analysis was performed on a 7890 gas chromatograph (GC; Agilent Technologies, Wilmington, DE, USA) equipped with a 7693 autosampler, split-splitless inlet, and flame ionization detector (FID). Agilent ChemStation and MIDI's Sherlock software were used to control the GC-FID system and assign PLFAs to different microbial groups.

2.7. Plant promotion of PAE mineralisation

Maize seeds (*Zea mays* L. cv. Calvini; KWS SAAT SE & Co. KGaA, Einbeck Germany) were placed in aerated distilled water for 18 h and then allowed to germinate on damp tissue paper at room temperature. When the seedling roots were ca. 5 cm long, one seed was planted in a 280 cm³ plastic pot containing 100 g of field-moist soil (packed to half the pot height). Then.

0.01% (w/w) of PVC film containing either ¹⁴C-labelled DEHP or DBP was placed within the soil containing the roots. Controls consisted of unplanted pots where the PVC film was buried at the same depth of the seed (ca 2 cm). In total there was four treatments with four replicates. Pots were then placed into individual 2.4 L sealed containers that contained a 10 mL NaOH (1 M) trap. Soil moisture levels were maintained by weight at NaOH trap changes and water added when necessary (ca. 1 mL per day). The traps were changed on days 2, 7, 10, 14, and 21 and ¹⁴C concentration as described above.

After 21 d, plants were collected, and roots washed using distilled water to remove soil adhering to the root surface. Plant components (roots, stem/leaves) were separated, weighed (wet), freeze-dried and stored at -80°C until processing. Processing of plant samples was undertaken by grinding all plant residuals in a ball mill at 23 Hz for 90 s. Subsequently, 0.05 g of the ground sample was treated with 1 mL of acetone: hexane (1:1 v/v) in a 1.5 mL microfuge tube, mixed on a vortex for 1 min and kept overnight at room temperature. The supernatant was collected after centrifugation (14,000 g, 5 min) and combined with two further extracted supernatants (0.5 mL acetone: hexane mixed for one minute and left for 40 min). The amount of ¹⁴C present in 1 mL of supernatant was determined by liquid scintillation counting as stated above.

2.8. Statistical analysis

Statistical analysis was conducted using R v 4.0.3 (R Core Team, 2021), with graphical analysis being constructed in 'ggplot2'. All the data was subjected to one-way analysis of variance (ANOVA) with a significance level of $p < 0.05$. Normality and homogeneity of variance of the data was assessed using Shapiro-Wilk's test and Levene's test, respectively. For data that did not conform to parametric assumptions, even after using log₁₀ transformation, a Kruskal-Wallis test (stats package; R Core Team, 2019) was used, instead of a one-way ANOVA. The 'vegan' package was used to construct non-metric multidimensional scaling (NMDS) analysis of all PLFA detected communities based on 'bray' dissimilarities. All PLFAs detected were used in the analysis, to represent the whole microbial community. The difference in dispersion between centroids of groups as determined by amendments or sampling time was performed with an analysis of similarities (ANOSIM). Total biomass was calculated by summing the concentration of PLFAs

recovered.

3. Results

3.1. Leaching of PAE from PVC film

After 120 days, $40.4 \pm 1.1\%$ of the ¹⁴C-labelled DBP and $2.1 \pm 1.0\%$ of the ¹⁴C-labelled DEHP had migrated from the plastics into the surrounding solution (Fig. 1). The loss rate of DBP ($1.01 \pm 0.02 \mu\text{g mg}^{-1} \text{plastic d}^{-1}$) was significantly greater than that observed for DEHP ($0.05 \pm 0.03 \mu\text{g mg}^{-1} \text{plastic d}^{-1}$) ($p < 0.0001$). The initial rate of change (weeks 0–2) was significantly higher than the subsequent rates of change (weeks 3–17) for both DBP ($p = 0.002$) and DEHP ($p = 0.008$), indicating an initial fast leaching rate that gradually slowed down through time.

3.2. Mineralisation of free and plastic-bound PAEs in soil

The breakdown of DEHP and DBP directly applied to soil (in solution), versus that embedded in plastic PVC film is shown in Fig. 2. An initial lag in ¹⁴CO₂ mineralisation was observed in the PVC film treatment relative to the non-plastic treatment ($p < 0.0001$). The cumulative percentage of PAE mineralised after 4 months following application directly to the soil, was $78.5 \pm 20.1\%$ for DBP and $8.6 \pm 0.8\%$ for DEHP. In comparison, the total amount of mineralisation for PAE incorporated as a plastic film and added to soil was much lower, being $21.1 \pm 2.6\%$ for DBP and $0.40 \pm 0.04\%$ for DEHP. Mineralisation was significantly lower when the PAE was incorporated into the plastic film (DBP, $p = 0.0008$; DEHP, $p < 0.0001$). For DBP, the degradation kinetics was best described by the first order model as R^2 was greater than 0.95. Therefore, the half-life ($t_{1/2}$) of DBP was determined for free and plastic-bound to be 54.09 d^{-1} and 350.14 d^{-1} . Half lives could not be calculated for DEHP as mineralisation never reached 50%. Additionally, the mineralisation rate of DBP was significantly higher than DEHP ($p = 0.0002$).

3.3. PAE degradation under UV exposure

For both PAEs, UV exposure increased degradation. After 7 d the

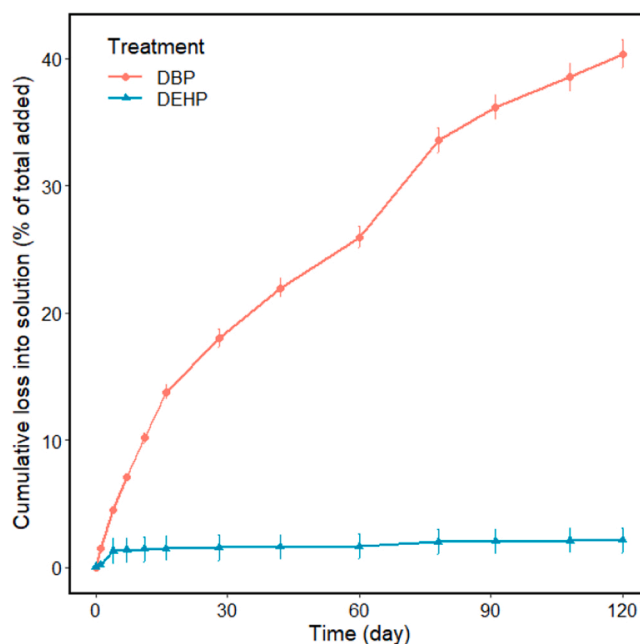


Fig. 1. Migration of ¹⁴C-labelled dibutyl phthalate (DBP) or di(2-ethylhexyl) phthalate (DEHP) from PVC films into a 1 mM KCl solution over 120 d period. Values represent means \pm SEM ($n = 5$).

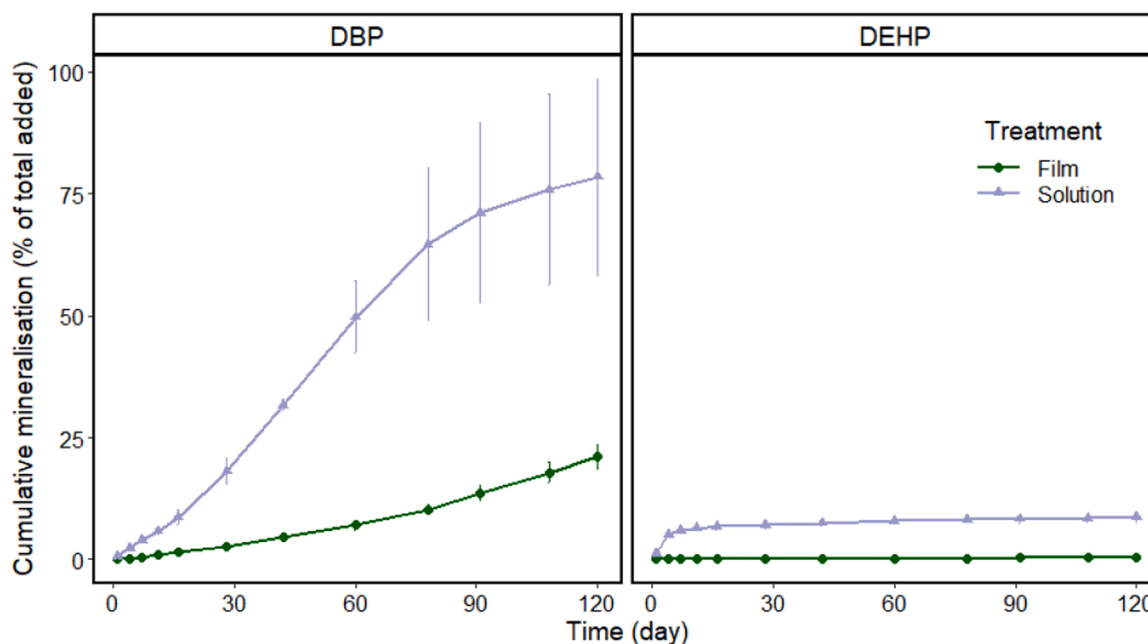


Fig. 2. Degradation of ^{14}C -labelled dibutyl phthalate (DBP) or di(2-ethylhexyl) phthalate (DEHP) in soil when (i) preincorporated into a PVC film before addition to soil (Film), or (ii) added directly to the soil (Solution). The legend is the same for both panels. Values represent means \pm SEM ($n = 5$).

amount mineralised in the presence of UV radiation had reached $2.68 \pm 0.48\%$ for DBP ($p = 0.007$) and $0.89 \pm 0.11\%$ for DEHP ($p = 0.005$), compared to the non-irradiated (control) samples which reached $1.07 \pm 0.15\%$ for DBP and $0.42 \pm 0.03\%$ for DEHP (Fig. 3). Moreover, over the 7-d period, DBP had a significantly higher degradation when exposed to UV than DEHP ($p = 0.0114$). Furthermore, the rate of change between the initial sampling times (0, 20, 40 h) was significantly lower than the later sampling times (90, 130, 180 h) for DBP ($p = 0.005$) and DEHP ($p = 0.011$), indicating the initiation of the biotic hydrolysis in tandem with the abiotic hydrolysis.

3.4. PAE degradation in organic substrate amended soils

The addition of biosolids caused an increase in soil moisture, pH, EC, ammonium, DOC, TDN, and microbial PLFA biomass (Table 1). There was no change in soil nitrate and the bacterial: fungal ratio as determined by PLFA with the addition of biosolids. A decline in the soil C:N ratio on application of biosolids is primarily a response to the percentage of C and N in the biosolids before addition to soil (Table S2). Biosolid amendment significantly increased the degradation of DBP ($p = 0.009$) and DEHP ($p = 0.002$) four-fold compared to other treatments (Fig. 4).

Organic residue addition to soil did not cause significant changes in the fungal-bacterial ratio or total biomass as determined by PLFA

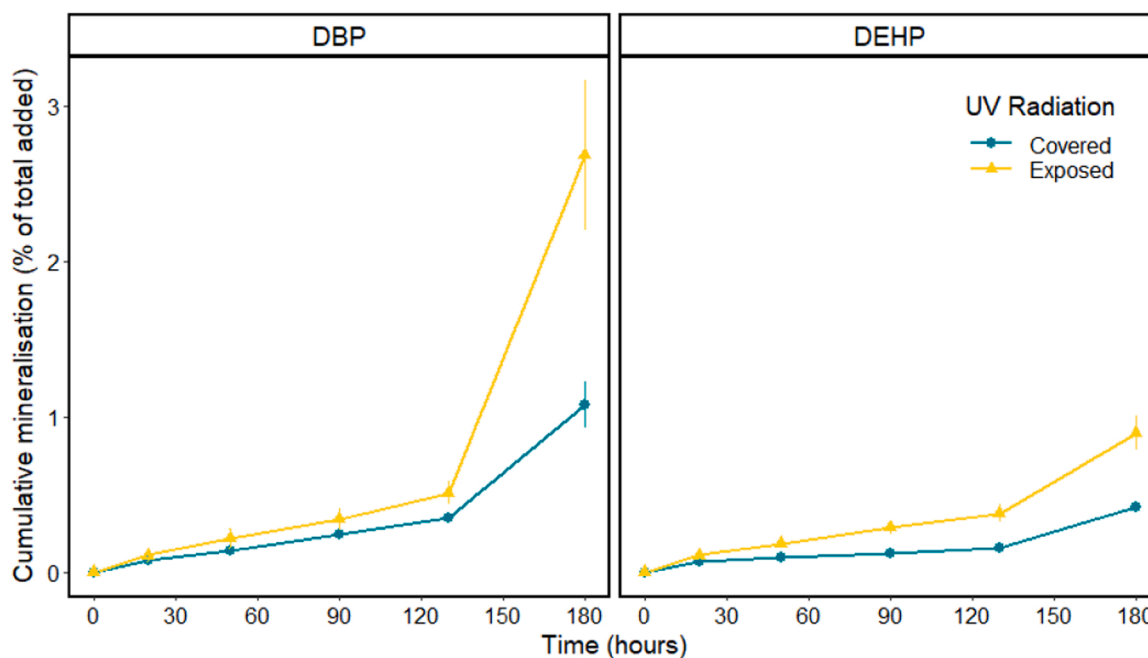


Fig. 3. Degradation of ^{14}C -labelled dibutyl phthalate (DBP) or di(2-ethylhexyl) phthalate (DEHP) incorporated into PVC film in the presence or absence of UV radiation. The legend is the same for both panels. Values represent means \pm SEM ($n = 4$).

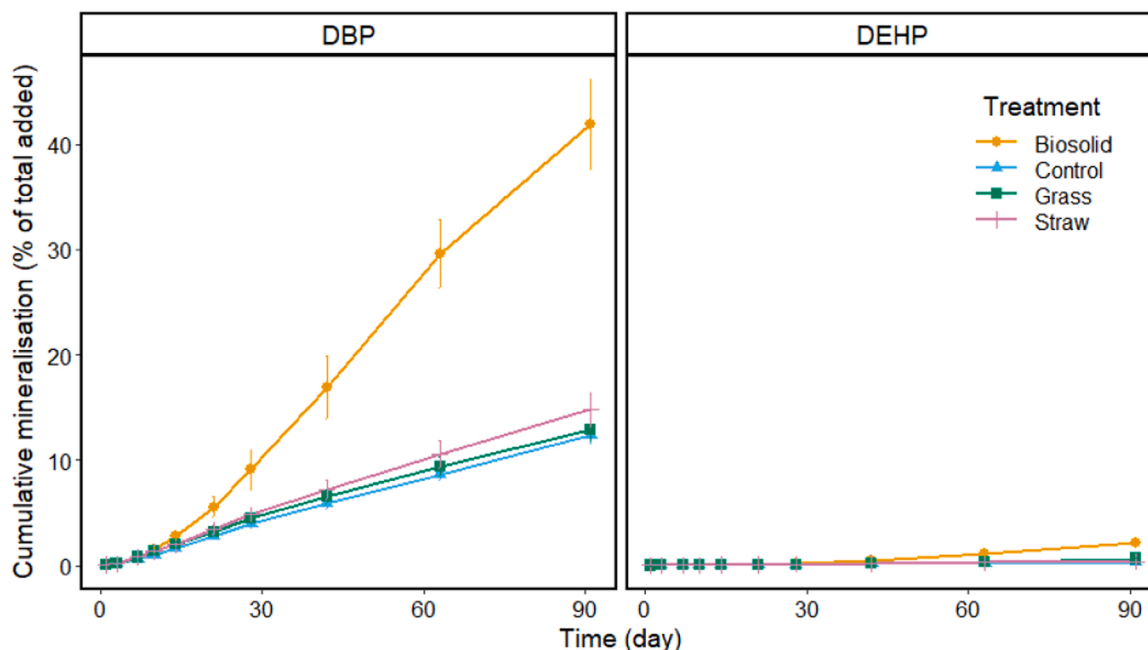


Fig. 4. Degradation of the ^{14}C -labelled dibutyl phthalate (DBP) or di(2-ethylhexyl) phthalate (DEHP) incorporated into PVC plastic mulch film and buried in soil for 3 months in the co-presence of organic amendments aimed at stimulating microbial activity (biosolids, grass residues, cereal straw). The legend is the same for both panels. Values represent means \pm SEM ($n = 5$).

sampled after the 7-day preincubation period (Table 1). When comparing the PLFA sampling dates, samples taken at the end of the 90-day experimental period across all treatments, had significantly higher levels of total PLFA biomass compared to samples taken after the 7-day preincubation period ($p < 0.05$; Table 2). The addition of grass residues and cereal straw did not change the total bacteria or fungal biomass in the experimental samples, yet biosolids addition did significantly increase the total PLFA biomass ($p = 0.006$). Cluster analysis (NMDS) of all soil-derived PLFA compounds showed no grouping evident between the different sampling times ($p = 0.072$); but reflected a significant difference between treatments ($p = 0.0001$), with a change in microbial community structure evident with the addition of biosolids (Fig. 5).

3.5. PAE degradation in an active rhizosphere

Cumulative mineralisation of ^{14}C -labelled DBP contained in the PVC film in the planted mesocosms was lower than in the unplanted treatments (Fig. 6a, $p = 0.002$), with no differences evident for DEHP ($p > 0.05$; Fig. 6b). Plant root uptake accounted for $0.18 \pm 0.04\%$ of the ^{14}C -label, and the stem and leaves held $0.22 \pm 0.07\%$, resulting in a total plant assimilation including mineralisation (Plants + $^{14}\text{CO}_2$) of $1.76 \pm 0.27\%$ of the ^{14}C -labelled DBP being released from the film. This was significantly lower when compared to the total percentage recovered from unplanted mesocosms at $3.68 \pm 0.34\%$ ($p = 0.005$). In the

planted systems, the equivalent of $0.006 \pm 0.004\%$ of the ^{14}C -labelled DEHP was recovered in the roots and $0.090 \pm 0.004\%$ in the stem and leaves. Thus, the total percentage of ^{14}C -labelled DEHP recovered from the mesocosms (Plants + $^{14}\text{CO}_2$) was $0.59 \pm 0.02\%$. This was not significantly different to the total percentage recovered from the unplanted mesocosms ($0.62 \pm 0.07\%$; $p = 0.77$). In both cases, the relative proportion of ^{14}C -labelled CO_2 evolved from the soil, was significantly greater than the ^{14}C -labelled material recovered in the plant (Fig. 7; DBP, $p = 0.0005$; DEHP, $p < 0.0001$).

4. Discussion

4.1. Loss of PAEs from the plastic matrix

The loss of PAEs from the plastic matrix has been documented in multiple mediums including air, food supplements, seawater and soil (Tüzüm Demir and Ulutan, 2012; Paluselli et al., 2018; Rastkari et al., 2018; Henkel et al., 2019; Li et al., 2020a; Ye et al., 2020). Overall, our results showed a high rate of PAE loss from the PVC film into solution, particularly for DBP. This is supported by other studies showing that PAEs can be readily leached from thin plastic films ($10 \mu\text{m}$ thickness) into seawater, and that this occurs at a much greater rate than from thicker plastic materials (Paluselli et al., 2018). Our results also showed major differences between the capacity of different PAEs to leach from

Table 2

Microbial biomass, total bacteria and total fungi derived from the PLFA profile of the either biosolids, grass residues, or cereal straw amended soils. Samples collected from two different sampling dates: (i) 7-d after amendment addition (Pre-incubation), and (ii) 91-d after amendment addition in soil also containing PVC mulch film (Experiment). The plastic mulch film contained dibutyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP). Values represent means \pm SEM ($n = 5$).

	Microbial biomass (mg PLFA kg^{-1})		Total bacteria (mg PLFA kg^{-1})		Total fungi (mg PLFA kg^{-1})	
	Pre-incubation	Experiment	Pre-incubation	Experiment	Pre-incubation	Experiment
Control	9.1 ± 0.8	10.4 ± 1.0	5.39 ± 0.47	5.60 ± 0.34	0.80 ± 0.09	0.80 ± 0.09
Grass	7.9 ± 0.7	9.1 ± 0.6	4.54 ± 0.39	5.05 ± 0.28	0.68 ± 0.13	0.68 ± 0.13
Straw	7.1 ± 1.1	11.2 ± 1.1	4.16 ± 0.72	6.56 ± 0.65	0.58 ± 0.08	0.58 ± 0.08
Biosolids	14.9 ± 2.7	14.7 ± 1.1	6.86 ± 1.32	7.24 ± 0.47	1.06 ± 0.24	1.06 ± 0.24
p-value	*		*		NS	

* Indicates a significant difference ($p < 0.05$) overall between the Preincubation and Experimental results while NS indicates $p > 0.05$.

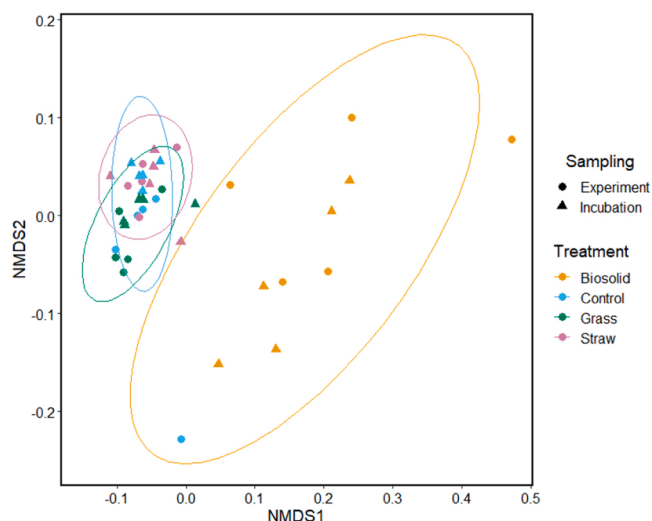


Fig. 5. Non-metric multidimensional scaling (NMDS) ordination plot of the phospholipid-derived fatty acids (PLFA) profile for each organic amendment (Treatments) at two sampling dates; (i) 1 week after organic residue addition to the soil (Incubation), and (ii) 13 weeks after organic residue addition in the presence of a PVC mulch film (Experiment). Ellipses represent 95% confidence intervals for each treatment.

the plastic matrix into the surrounding medium. While DBP was lost rapidly, the low migration of DEHP did not follow the expected trend, especially as it has been reported that DEHP has a greater migration rate than DBP (Rastkari et al., 2018; Wang et al., 2016). However, the length of hydrocarbon chains and the size of the molecule makes DEHP more hydrophobic than DBP. This is supported by the lower $\log K_{OW}$ values for DEHP (7.6) relative to DBP (4.5), and the 40-fold lower reported solubilities for DEHP in water (0.27 mg l^{-1}) relative to DBP (11.2 mg l^{-1}) (Table S1). We speculate that the presence of water in soil will also inhibit the migration of DEHP from the PVC film, resulting in DEHP continually having a lower cumulative mineralisation compared to DBP.

One factor not investigated here, which may accelerate DEHP loss, is the presence of organic matter and associated hydrophobic domains (Magdouli et al., 2013). These domains are commonly found in microbial biofilms, in soil organic matter and root surfaces, and associated with dissolved organic matter (Pan et al., 2008).

Although the two PAE compounds used here are volatile, their Henry's law constants are less than about $5 \times 10^{-5} \text{ atm m}^3 \text{ mol}^{-1}$ and therefore will tend to remain in water (Olson and Davis, 1990; Table S1). Therefore, we hypothesise that the amount of the PAEs lost through evaporation from the leachate trap is negligible.

Previous studies of PAE loss have used commercially available plastic products, and in some cases have reported much lower migration results than observed here (Paluselli et al., 2018). It is possible that these plastics also contained a wide range of other additives which may have influenced PAE solubility and subsequent movement in the plastic matrix. Further work is therefore required to critically test the role of different additives on PAE loss. Our results also showed a rapid release of DEHP into solution, after which the release was very slow. This is supported by (Kastner et al., 2012) who found that $0.79 \pm 0.25\%$ of DEHP was lost into solution over 7 d when PVC films were suspended in deionised water but that this declined with time. Additionally, Zhang and Chen (2014) concluded that almost all DBP molecules will ultimately be lost from PVC/DBP films at DBP bulk concentrations of $\leq 30 \text{ wt}\%$, comparable with our results. Extrapolation of the data in Fig. 1 suggests that the half-time for DBP loss into water was ca. 190 d. Overall, the patterns in DBP and DEHP loss rate were observed in all the later assays performed in soil.

4.2. Degradation of phthalates in soil

Overall, our findings from the direct application of PAEs to soil are in accordance with previous studies (Xie et al., 2010; Cheng et al., 2018, 2019; Yang et al., 2018; Tang et al., 2020). Critically, however, our study highlights the importance of the film matrix in regulating degradation rate. For both PAE compounds, the film application significantly decreased mineralisation when compared to the direct application, indicating that the shielding properties of the plastic strongly inhibited

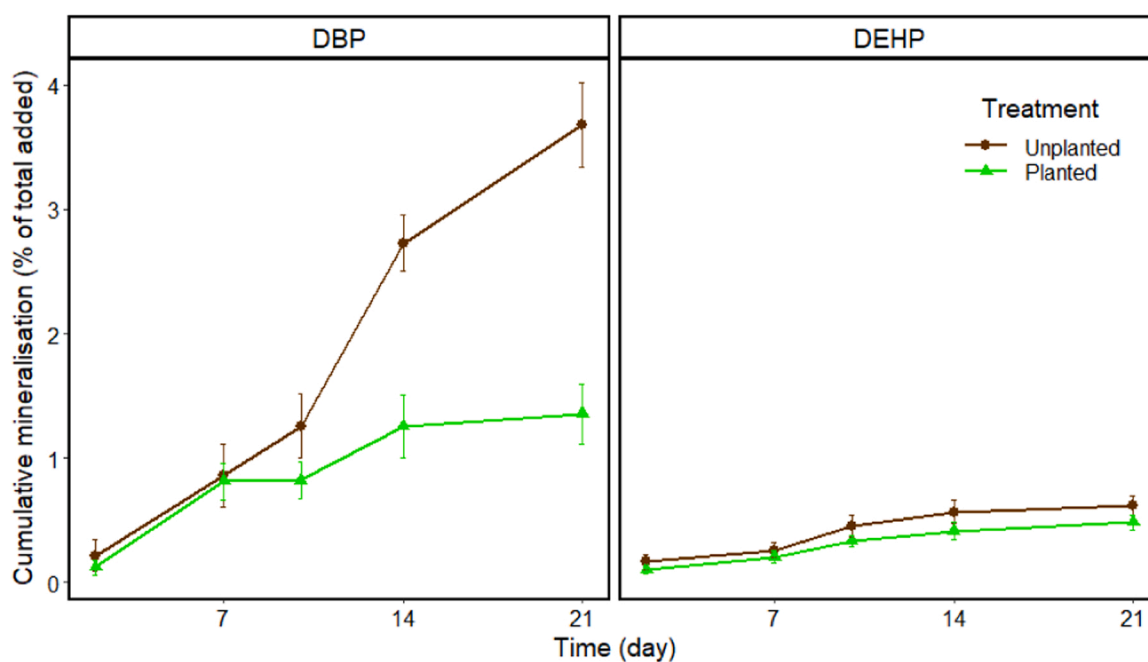


Fig. 6. Influence of maize plants on the degradation of ^{14}C -labelled dibutyl phthalate (DBP) or di(2-ethylhexyl) phthalate (DEHP) preincorporated into a PVC film and then added to the soil. Unplanted controls consisted of plastic mulch film in soil without the presence of plants. The legend is the same for both panels. Values represent means \pm SEM ($n = 4$).

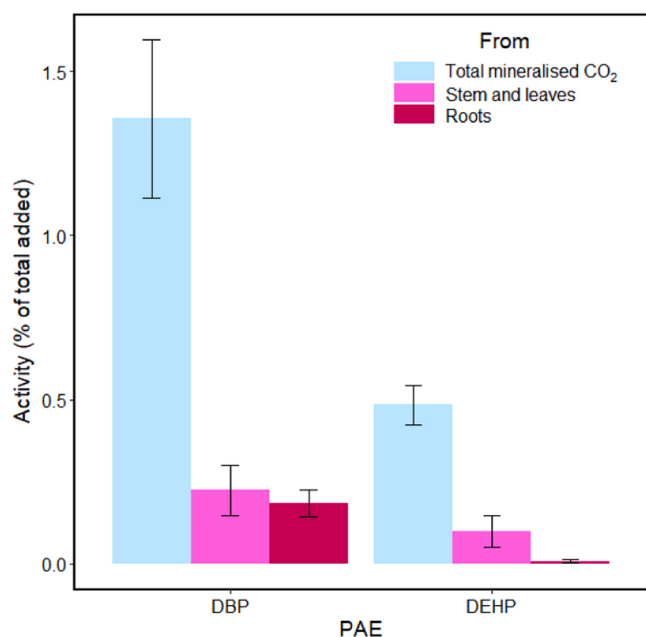


Fig. 7. ¹⁴C recovery in maize plant tissues which was derived from either ¹⁴C-labelled dibutyl phthalate (DBP) or di(2-ethylhexyl) phthalate (DEHP) labelled PVC. The PAEs extracted from the roots and the leaves and stem are represented as a percentage of the starting activity. Additionally, total mineralised ¹⁴CO₂ over the 21-d growing period is shown. Values represent means ± SEM (n = 4).

PAE degradation. The shielding effect of PVC results in PAEs being present in soil for longer than the accepted time of 60 d to achieve complete degradation (Yang et al., 2018; Cheng et al., 2019; Tang et al., 2020).

In this study, the percentage degradation of PAEs from direct application was lower than observed in previous studies which have shown that 96.0% of the added DBP degraded over 60 d, across 20 different soils (Cheng et al., 2019). This could be attributed to the differences in methodology used to monitor degradation: previous studies monitored PAE degradation by determining the decrease in the starting concentration via extraction and analysis (Cheng et al., 2019; Feng et al., 2021). In our study, we monitored complete degradation through the trapping of mineralised radiolabelled ¹⁴CO₂. As the labelled ¹⁴C in both PAEs was present in the benzene ring, we assume that the activity measured in the NaOH traps represents complete degradation, as benzene ring opening, and formation of CO₂ is the final step in the degradation of PAEs (Fig. S1). We feel it is important to capture the complete mineralization process as some of the breakdown products of DBP and DEHP (e.g. butylmethyl phthalate, mono-(2-ethylhexyl) phthalate) are known to be much more cytotoxic than the parent compound and thus may pose a greater risk to soil health (Kim and Lee, 2005; Wang et al., 2012). Further work is required to determine the length of time for all PAEs present in the film, but it is clear from this study that it is longer than previously thought.

4.3. UV mediated PAE degradation

It is well established that PVC-based plastics can break down abiotically when exposed to sunlight (Masry et al., 2021; Yousif and Hasan, 2015). However, as sunlight can only penetrate ca. 200 μm into soil, this breakdown pathway is only relevant to plastic exposed on the soil surface (Ciani et al., 2005). The mechanism for UV degradation of PAEs has been established in multiple mediums, forming the PAEs' monoester and phthalic acid, which further breakdown to form CO₂ and H₂O (Hankett et al., 2013; Barreca et al., 2014; Wang et al., 2019; Berenstein et al., 2022; Feng et al., 2022). In this study, when both PAEs films were

exposed to UV radiation, the rate of degradation was more than double that of those not exposed to UV. We ascribe this to UV-mediated radical hydrolysis of the PAEs, which unlike enzymatic hydrolysis, as seen in microbial degradation, is not hindered by the migration of the PAEs from the plastic. Radical hydrolysis is rapid and difficult to control, so within the plastic film, radicals will also hydrolyse the polymer chain resulting in film fragmentation (Song et al., 2017). Once film fragmentation occurs, PAEs can readily migrate from the film into the soil, which we speculate is responsible for the observed rapid increase in mineralisation at 180 h (Fig. 3). Previous studies have also reported that 39% of the DBP in agricultural film can migrate into soil during 48 h of UV radiation exposure (Berenstein et al., 2022); therefore it is likely that the rapid acceleration in PAE degradation seen in this study at 180 h is a combination of both UV and microbial degradation. The presence of a lag time indicates that the biotic pathways are hindered by the shielding potential of the plastic matrix, therefore it can be assumed that abiotic pathway (UV exposure) is more effective than biotic pathways in PAE degradation as it is not hindered by the plastic matrix. It should also be noted that many commercial PVC and film-based products contain photostabilisers (additives) to minimise UV breakdown (Hadi et al., 2019) and therefore the results presented here may be unrepresentative of some products.

4.4. Use of soil organic amendments to promote PAE degradation

Generally, microbial biomass increases following the addition of high amounts of labile organic matter to soil (Willers et al., 2015). PLFA analysis revealed a shift in the size and structure of the microbial community between the biosolid treatment compared to other soil substrate treatments, similar to previous studies (Montiel-Rozas et al., 2018). The biosolids-induced increase in the size and diversity of the microbial community resulted in accelerated PAE degradation. As microbial degradation of PAEs occurs through enzymatic hydrolysis, which is substrate-specific, increased diversity of the microbial community will allow for a higher percentage of enzymes that can attack the active site of the PAEs (Wang et al., 2017).

In contrast to biosolids, the addition of grass and straw residues resulted in no major change in the microbial community or increase in DBP and DEHP turnover. Our results are contrary to previous studies where grass and straw addition promoted microbial growth (Sleutel et al., 2012; Wang et al., 2021a). Although we added the substrates at realistic field doses, it is possible that higher doses are needed to promote greater microbial activity and PAE degradation. We did note a significant increase in total dissolved N with the addition of grass (Table 1), however, this change did not affect PAE degradation, suggesting that the breakdown of C-rich PAEs was not N limited. Overall, our results suggest that the addition of cropping residues is unlikely to greatly influence the turnover of PAEs in soil.

4.5. PAE degradation in the rhizosphere

The rhizosphere is a microbial nexus, where roots and soil interact, stimulating the production of microbial enzymes (Bilyera et al., 2021). In the current study, however, the presence of plant roots repressed DBP and DEHP mineralisation when compared to the unplanted treatment. This contrasts with previous studies showing that PAE and other xenobiotic mineralization is promoted in the presence of plants (i.e. rhizoremediation; Gerhardt et al., 2009; Ma et al., 2012; Wang and Chi, 2012; Li et al., 2014; Vergani et al., 2017; Kotoky et al., 2018). We ascribe our results to the plant providing multiple alternative C sources that are readily consumed by the microbial community over PAEs. Moreover, plant excretion of root exudates have been shown to promote DBP adsorption to soil particulates which could further hinder microbial degradation of PAEs (Lin et al., 2018). This could also potentially hinder the migration of PAEs from the plastic matrix, limiting their bioavailability, however further testing is required to support this hypothesis.

Furthermore, some plant species (Ceylon spinach (*Gynura cusimbua*) and leaf mustard (*Brassica juncea*)) significantly decreased DEHP concentration in soil whereas other species (Sunflower (*Helianthus annuus*)) do not (Wu et al., 2019). Indicating, the plant species have a significantly impact the phytoremediation of PAEs. Additionally, within the same species different cultivars can induce different DEHP dissipation, with maize (*Zea mays*) removal rates ranged from 69% to 87% over 40 days compared to a control (unplanted) removal rate of 66% (Li et al., 2014). However, the decrease in PAE concentration of the rhizosphere is a combination of processes e.g. phytoextraction, phytostabilisation and not reliant on rhizobacteria degradation (Wang et al., 2021b; Tran et al., 2022). This indicates that not all plant growth in the soil may accelerate the degradation of PAEs and pose a higher risk of PAEs migrating into the crops and plants. Clearly, the influence of other plant species need testing in this context as we only evaluated the response with maize.

PAEs have been recovered from a wide range of plants and crops that have been cultivated in close contact with agricultural plastics (e.g. mulch films or tunnels; (Du et al., 2009; Ma et al., 2015; Shi et al., 2019; Li et al., 2020a). The migration of PAEs into the plant system was also observed in this study. In the roots of the plant, DBP was more prominent than DEHP, probably reflecting its faster release rate from the plastic and migration through the soil matrix. This is supported by previous work where DEHP was the most abundant PAE present in the soil, but DBP accumulated most in pepper (*Capsicum* spp.) samples (Li et al., 2020b). For both PAEs, their concentration in the leaf and stem was higher than in the roots. We ascribe this to the migration of PAEs in the xylem flow. This is in agreement with previously reported results, as the uptake and translocation results in a larger concentration of DBP and DEHP being present in the stem and leaves over the roots (Ma et al., 2012, 2013; Liao et al., 2019; Cheng et al., 2021). However, it is also possible that small amounts of soil-derived ¹⁴CO₂ not captured by the NaOH traps were photosynthetically fixed by the leaves.

5. Conclusions

This study clearly demonstrates that the degradation of two common PAEs is regulated by the migration rate from plastic into the surrounding soil. It is clear that when PAEs are embedded in the plastic matrix that their degradation is suppressed, leading to their persistence in soil, albeit probably not bioavailable and therefore presumably of low risk. Furthermore, this study demonstrated that exposure to UV radiation accelerated PAE degradation suggesting that some PAE loss from plastic films may occur prior to incorporation into the soil. Contrary to expectation, the presence of plant roots, straw and grass residues failed to promote PAE breakdown suggesting that rhizo- and phytoremediation strategies may not accelerate the cleaning of sites where PAEs are incorporated into a plastic matrix. The enhanced remediation in the presence of biosolids, however, suggests that some microbial consortia can promote PAE turnover in soil. In conclusion, we present a method for tracing the fate and behaviour of PAEs embedded in plastic film residues, allowing studies on additives to be conducted under highly realistic conditions. Furthermore, our study highlights the importance of application method, PAE type, and prevailing soil conditions on the behaviour and fate of individual PAEs in soil.

CRedit authorship contribution statement

Samantha J. Viljoen, David R. Chadwick, Davey L. Jones: Conceived the experiment. **Samantha J. Viljoen:** Conducted the experiments, Analysed the results, Wrote the main manuscript. **Francesca L. Brailsford, Daniel V. Murphy, David R. Chadwick, Davey L. Jones:** Analysed the results and suggested additional analyses. **Samantha J. Viljoen, Francesca L. Brailsford, Daniel V. Murphy, Frances C. Hoyle, David R. Chadwick, Davey L. Jones:** All reviewed and commented on the manuscript.

Environmental Implications

Phthalate acid esters (PAEs) are commonly used plastic additives which are not chemically bound to the polymer matrix and therefore readily migrate to surrounding environments. The manuscript focuses on two common PAEs, dibutyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP), which have been identified as priority pollutants due to their carcinogenic and endocrine disrupting properties. Our work demonstrates that the plastic matrix inhibits PAE degradation, resulting in longer soil residence times than previously thought. Moreover, we present evidence of PAE migration into crops, highlighting a key pathway for PAEs to enter the food chain and impact human health.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2022.130256](https://doi.org/10.1016/j.jhazmat.2022.130256).

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