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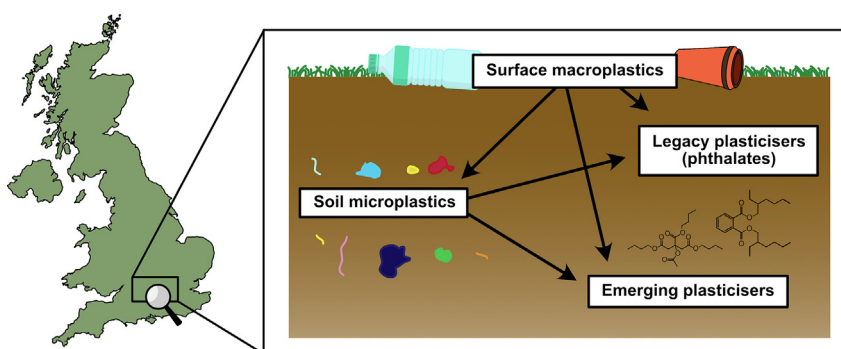
Co-occurrence of macroplastics, microplastics, and legacy and emerging plasticisers in UK soils

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HIGHLIGHTS

- Macroplastics, microplastics and plasticisers were quantified in UK field soils.
- Urban roadside and landfill-adjacent soils were hotspots for macroplastics.
- Microplastics detected in urban and landfill-adjacent soils, but not woodlands.
- Plasticisers were detected in every sample, and most abundant at urban roadsides.
- Emerging plasticisers are widespread and at similar levels to legacy phthalates.

GRAPHICAL ABSTRACT



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ABSTRACT

Despite a theoretical link between plastic and plasticiser occurrence in the terrestrial environment, there are few empirical studies of the relationship between these contaminants in soils. We carried out a field study to assess the co-occurrence of plastic waste, and legacy and emerging plasticisers in UK soils ($n = 19$) from various land uses (woodlands, urban roadsides, urban parklands, landfill-associated). Surface plastics and soil microplastics were quantified and characterised using ATR-FTIR and μ -FTIR. Eight legacy (phthalate) and three emerging (adipate, citrate, trimellitate) plasticisers were quantified using GC-MS. Surface plastics were found at higher prevalence at landfill-associated and urban roadside sites, with levels significantly (2 orders of magnitude) greater than in woodlands. Microplastics were detected in landfill-associated (mean $12.3 \text{ particles g}^{-1} \text{ dw}$), urban roadside ($17.3 \text{ particles g}^{-1} \text{ dw}$) and urban parkland ($15.7 \text{ particles g}^{-1} \text{ dw}$) soils, but not in woodland soils. The most commonly detected polymers were polyethylene, polypropylene and polystyrene. Mean Σ plasticiser concentration in urban roadside soils ($3111 \text{ ng g}^{-1} \text{ dw}$) was significantly higher than in woodlands ($134 \text{ ng g}^{-1} \text{ dw}$). No significant difference was found between landfill-associated ($318 \text{ ng g}^{-1} \text{ dw}$) and urban parkland ($193 \text{ ng g}^{-1} \text{ dw}$) soils and woodlands. Di-n-butyl phthalate (94.7% detection frequency) and the emerging plasticiser trioctyl trimellitate (89.5%) were the most commonly detected plasticisers, with diethylhexyl phthalate ($493 \text{ ng g}^{-1} \text{ dw}$) and di-iso-decyl phthalate ($96.7 \text{ ng g}^{-1} \text{ dw}$) present at the highest concentrations. Σ plasticiser concentrations were significantly correlated with surface plastic ($R^2 = 0.23$), but not with soil microplastic concentrations. Whilst plastic litter seems a fundamental source of plasticisers in soils, mechanisms such as airborne transport from source areas may be as important. Based on the data from this study, phthalates remain the dominant plasticisers in soils, but emerging plasticisers are already widespread, as reflected by their presence in all land uses studied.

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1. Introduction

Many plastic additives (substances added to plastics to modify their properties and/or performance) are not chemically bound to the polymer matrix, and so can enter the environment over the lifetime of a plastic item (Hansen et al., 2013). Historically, some additives have been associated with harmful effects in humans and wildlife, e.g. concerns surrounding the bioaccumulation and endocrine disruption of PBDE flame retardants and bisphenols led to legislation restricting their production and use in the 1990s and early 2010s respectively (European Union, 2011; Oakdene Hollins, 2010). More recently, attention has been given to phthalate plasticisers, due to their suspected endocrine disrupting activity (ECHA, 2022), with limits on the use of certain congeners recently introduced in the EU (ECHA, 2018). Phthalates are ubiquitous contaminants of marine and freshwater environments (Gao and Wen, 2016; Hermabessiere et al., 2017) and have also been commonly detected in the relatively small number of studies conducted for soils (Billings et al., 2021). The occurrence of phthalates in soils has been linked with specific sources such as the use of plastic in agriculture (Kong et al., 2012; Wang et al., 2021; Zeng et al., 2020), application of sewage sludge to agricultural land (Rhind et al., 2013b; Tran et al., 2015; Vikelsoe et al., 2002), and the incineration and processing of electronic waste (Chakraborty et al., 2019; Zhang et al., 2019). However, the role of these point sources compared to diffuse input from more dispersed plastic use have not yet been determined.

The concerns and restrictions surrounding the use of some legacy phthalates has led to an increase in the use of non-phthalate plasticisers over the past 15 years (CEFIC, 2018). Emerging plasticisers such as trimellitates, citrates and adipates may be used in plastic applications as replacements for phthalates. Although knowledge of their environmental occurrence and fate is less well known than for phthalates, in the few studies conducted to date these compounds have been detected across a range of environmental media including air, dust, and sewage sludge (Fromme et al., 2016; Lee et al., 2019). The terrestrial occurrence of these emerging plasticisers remains almost entirely unknown. Given the prevalence of phthalates and the major use of plastics on land and sources of plasticisers to soils, there is the potential for these next-generation chemicals to be widely present in terrestrial ecosystems.

Terrestrial systems are recognised as a major route of plastic entry into the environment (Horton et al., 2017b). Larger plastic items (macroplastics) may break down over time into microplastics (traditionally defined as plastic particles <5 mm). Photodegradation of the polymer surface through the action of UV light, in addition to fluctuations in temperature, are thought to be the dominant processes controlling the fragmentation of plastics and thus formation of microplastics in terrestrial systems (Horton et al., 2017b). This plastic litter may result in the input of plasticisers into soils through direct leaching from large items of plastic on the soil surface or after breakdown into microplastics that have a larger surface area. Leaching occurs through diffusion of the plasticiser molecules to the surface of the plastic item followed by direct desorption into the soil, or through sorption to, and subsequent release of, soil components bound to the surface of the plastic item (Billings et al., 2021). The plasticiser content of a plastic item is partly governed by polymer type. For example, some polymers (e.g. polyethylene) rarely contain high levels of plasticisers, while others may contain high concentrations (e.g. over 80% of plasticisers are used in polyvinyl chloride (PVC; CEFIC, 2018)). Thus, the leaching potential of a plastic item will vary with both polymer type and physical form. Understanding the links between surface and soil-incorporated plastic levels and plasticiser concentrations will grant insights into the inputs of plastic-associated chemicals in the soil environment.

No study has yet looked at the co-occurrence of both above- and below-ground plastic contamination with plasticisers in field soils and we are aware of only two very recent studies that have attempted to quantify microplastic and phthalate co-occurrence, both focussed on agricultural soils (Li et al., 2021; Xu et al., 2022). Both studies carried out extensive sampling, although were not without some technical limitations. For example,

both studies employed microplastic extraction procedures incapable of recovering PVC (the polymer in which the majority of plasticisers are used). Further, neither appeared to use procedural blanks for microplastics to allow assessment of limits of detection, thereby potentially limiting the accuracy of quantification data. Studies that use robust quantitative methods to assess the co-occurrence of surface and soil-incorporated plastics and legacy and emerging plasticisers are needed to close this knowledge gap.

The primary objective of this study was to investigate the role of diffuse litter as a source of plastics and plastic associated chemicals in terrestrial ecosystems. To address this, we used an attenuated total reflectance-Fourier transform infrared (ATR-FTIR) and scanning-FTIR (μ -FTIR) spectroscopy-based method to measure site-surface macroplastics and soil-interred microplastics, and a GC-MS (gas chromatography-mass spectrometry) method to quantify multiple legacy and emerging plasticisers in soils collected from a range of terrestrial sites associated with land uses expected to have different profiles of plastic inputs, primarily from littering and poor waste management. Conducting these collated measurements of both plastic and plasticiser levels allowed us to test three hypotheses: 1) The occurrence and profile of terrestrial plastic waste and plasticiser contamination will vary between land uses, with areas associated with landfill and urban activity having elevated plastic and plasticiser levels relative to background (woodland) concentrations; 2) Microplastic concentrations and polymer types will reflect a similar profile to those associated with site-surface macroplastics; 3) The occurrence of phthalates and emerging plasticisers in soils will be higher in soils with higher surface plastic litter and microplastic levels.

2. Materials and methods

2.1. Environmental sampling

Sampling took place in central and southern England (UK) in January and February of 2020. Soil and surface plastic samples were collected from 19 sites covering a range of land uses: woodland ($n = 7$), downwind of landfill ($n = 6$), urban parkland ($n = 3$), and urban roadside ($n = 3$). Woodland sites were selected from areas which have had continuous tree cover since at least 1600 CE (Natural England, 2021) that were not in the vicinity of industry, urban areas, or existing or legacy landfill sites. These measures were taken to ensure that the woodland sites were as free from human interference as possible, although due to the relatively high population density in southern England, these sites are likely to see recreational use. In order to minimise this impact, woodland sites were sampled as far away from footpaths as possible. These woodlands, therefore, represent a set of locations with relatively low anthropogenic influence and provide a background measure of plastic and plasticiser contamination to which other sites can be compared.

To assess the influence of landfill sites on plastic and plasticiser occurrence in the surrounding terrestrial environment, public land downwind of sites was sampled as close as possible to the perimeter of the facility. Urban parkland and urban roadside sites were all located within the urban area of the city of Oxford. Parklands were sampled as far away from the boundary of the site and footpaths as possible. Roadsides were sampled where the verge was at its widest point. All sites were sampled in areas representative of the wider site (i.e. not in the vicinity of point sources of plastic such as a litter bins). Site-specific information for all sampled sites is shown in Appendix Table S1.

At each site, a 25 m² grid was marked out. The area within the grid was carefully searched for 10 min to collect any macroplastic visibly present on the soil surface into a clear low-density polyethylene bag. A stainless-steel trowel was then used to collect approximately 200 mL of soil from each corner and the centre of the marked grid. Soil samples were taken to a depth of approximately 15 cm and combined in a 1 L glass jar to provide a representative soil sample for the site. Glass jars were pre-rinsed 3 times with de-ionised (DI) and reverse-osmosis (RO) water. In order to minimise cross-contamination between sites, the trowel was thoroughly cleaned between sites using RO water and covered with aluminium foil

during transit. At each new site, the trowel was pushed into the soil three times before being used for sample collection. Soil samples were not dried and sieved prior to storage, in order to reduce airborne microplastic and plasticiser contamination, and potential loss of some lighter molecular weight plasticisers through vapourisation (e.g. DMP). Soil and surface plastic samples were transported to the laboratory on the day of collection and immediately stored in the dark at -20°C and 4°C respectively. All operators wore cotton clothing where possible.

2.2.1. Plastic sample processing

2.2.1.1. Surface macroplastics. Collected plastic items were cleaned with DI water, gently wiped with a lint-free wipe, and left to dry (n.b. it was not possible to fully clean some particularly fragile items, e.g. polystyrene foams or degraded films). The mass and morphology of each sample were recorded, and each item was sub-sampled for analysis by ATR-FTIR spectroscopy.

2.2.1.2. Soil microplastics. Soil samples were thawed at 4°C for 24 h and gently homogenised using a stainless-steel spatula. 50 g ww (wet weight) of soil was sub-sampled and stored at 4°C in a sealed glass container, with the remaining sample re-stored at -20°C for later plasticiser analysis.

Microplastics were extracted from each 50 g sample according to a method adapted from protocols previously applied to complex solid matrices (Horton et al., 2021; Horton et al., 2017a; Hurley et al., 2018). A sample of 10 g dry weight (dw) equivalents of soil was digested with 30 mL of Fenton's reagent (a 1:1 mixture of 30% H_2O_2 (Honeywell, USA) and 0.05 M aqueous Fe(II) solution (Honeywell, USA)). Samples were kept in an ice bath to avoid temperatures exceeding 50°C . After an hour, a further 20 mL of Fenton's reagent was added, and the reaction left overnight. Remaining solids were captured on a $10\ \mu\text{m}$ stainless-steel filter (Bridgewater Filters Ltd., UK), sonicated in 15 mL of $1.7\ \text{g mL}^{-1}$ ZnCl_2 (aq) (Honeywell, USA) for 15 min, and brushed into the beaker using a natural fibre brush (Daler-Rowney Ltd., UK). Samples were then density separated in a 100 mL measuring cylinder. After a minimum of 20 h quiescence, 50 mL of ZnCl_2 (aq) was added to the measuring cylinder to overflow floated material into a beaker. The top 20–50 mL of ZnCl_2 (aq) in the cylinder was then also poured into the beaker. The solid material recovered by floatation was collected onto a $10\ \mu\text{m}$ stainless-steel filter, sonicated in 50% ethanol (aq) (Honeywell, USA) for 15 min, and brushed into a glass jar. The 20-h density separation was repeated on the remaining material. Solid material from the supernatants was combined and fractionated to 10–178 μm (fine), 178–567 μm (medium) and $>567\ \mu\text{m}$ (coarse). The fine fraction was subject to a 1-h organic matter digestion with 20 mL of Fenton's reagent. The fine and medium fractions were then stored in 50% ethanol. The coarse fraction was stored in a petri dish and dried for 72 h at 50°C prior to analysis. All samples were stored at room temperature in the dark.

2.2.2. Plastic sample analysis

2.2.2.1. Preparation of in-house polymer FTIR spectra library. ATR-FTIR spectra of 41 consumer plastic items representing 15 common polymers were collected in a library (see Appendix Table S2 for item descriptors). Spectra were obtained on a Nicolet iS10 FTIR spectrometer with a Smart iTX ATR accessory (Thermo Fisher Scientific, USA) operating in absorbance mode. Spectra were collected in the range 450–4000 cm^{-1} , with data spacing of 1.93 cm^{-1} and resolution 4 cm^{-1} . A total of 32 scans were collected per spectrum. The ATR diamond was cleaned between each sample with 70% isopropanol and a background spectrum collected before each sample. Sample spectra were background- and baseline-corrected.

2.2.2.2. ATR-FTIR of surface macroplastics. ATR-FTIR spectra were obtained with the same instrumentation and parameters used for in-house library collection. A scalpel was used to cut the sample and expose a clean surface of plastic on each item if necessary. Spectra taken from each item were then compared to the in-house library using the OMNIC 9 software (Thermo

Fisher Scientific, Horsham, UK), using a 0.7 match as the threshold for polymer assignment (Cho et al., 2019; Wu et al., 2021). In the 13 instances (3.6% of all spectra) where multiple polymer types returned matches >0.7 and there was a difference of <0.1 between the most probable identified polymers, the final polymer identification was manually assigned using characteristic absorption bands within the spectra (Jung et al., 2018). Items with multiple plastic components were assigned if all components had a >0.7 match with the same polymer. Otherwise, the item was classified as 'mixed'. Samples with no spectral matches >0.7 were not assigned a polymer type, but were still treated as surface plastic in data analysis if they were large enough to be identified as 'plastic-containing' from visual and physical inspection.

2.2.2.3. Light microscopy and ATR-FTIR of coarse microplastics from within the soil. The coarse ($>567\ \mu\text{m}$) fraction collected on stainless-steel filters was analysed using a Stemi 2000-C stereo light microscope (Carl Zeiss, Germany) with $50\times$ zoom, equipped with an external light source. Samples were searched for 25 min for plastic particles. Blanks were searched for a minimum of 10 min, and until every particle with longest dimension $>567\ \mu\text{m}$ had been appraised or 25 min had passed. Potential microplastics were identified based on commonly used physical and visual criteria, and categorised by their morphology (Horton et al., 2017a; Primpke et al., 2020a) (see Appendix S3).

It was not possible to perform ATR-FTIR analysis on any fibres due to their small size and insufficient 2D area. However, all other microplastic particles found within the coarse fractions were analysed using a Nicolet iS5 FTIR spectrometer with an iD7 ATR accessory (Thermo Fisher Scientific, USA) using the same parameters as for the in-house library. Sample spectra were compared to the in-house library with a 0.65 threshold. This threshold is slightly lower than that used to characterise surface plastic polymers, as the small size of the particles meant that it was not possible to clean or expose a fresh area of plastic. One sample was manually assigned as multiple polymer types returned matches >0.65 with <0.1 between the most likely polymers.

2.2.2.4. μ -FTIR of fine and medium microplastics from within the soil. High particulate content in the fine (10–178 μm) and medium (178–567 μm) fractions limited the amount of material that could be analysed by μ -FTIR (with the exception of blanks). Therefore, samples were vortexed for 10 s, and a subsample deposited within a 10 mm diameter circle on a 5 μm silver filter (with 25 mm diameter) (Sterlitech Corporation, USA). Optical and infra-red images of each filter were collected on a Spotlight 400 FTIR spectrometer (PerkinElmer, USA). IR scans were collected in the range 700–4000 cm^{-1} , with resolution 8 cm^{-1} , pixel size of 25 μm , 4 scans per pixel, and interferometer speed 2.2 cm s^{-1} . A background spectrum of the silver filter was collected before each sample. The pixel size of 25 μm represents the lowest particle size possible to resolve in the analysis. Thus, whilst the extraction method captured fine microplastics of 10–178 μm , the fine fraction analysed was in the 25–178 μm size range. IR spectra of the sample area were collected in grids with dimensions of 11.6 mm^2 and 9.5 mm^2 for fine and medium fractions respectively. IR output was background- and atmospheric-corrected and processed using siMPle version 1.1.β (Primpke et al., 2020b; Primpke et al., 2018). We used a version of siMPle library 1.0.1 (Primpke et al., 2018) which had been adapted by Roscher et al. (2022) to reduce false positives arising from the presence of natural polymers in microplastic sample extracts. Polyacrylamide assignments were excluded from the results due to unsatisfactory spectral matching, as recommended by Roscher et al. (2022). Assignments of the category 'acrylates/polyurethanes/varnish' were also excluded for the same reason, i.e. false positives arising from misassignments of natural polymer materials. siMPle output maps of medium fraction samples greater than the limit of detection (LOD) were cross-referenced against the siMPle data list output to reduce false positives arising from the extremities of larger particles being assigned as individual particles. In the case of a mismatch, the particle number as determined manually from the map was used in data analysis.

2.2.3. Microplastic contamination controls and quality assurance

The microplastic control measures used were in line with recent studies (Horton et al., 2021; Johnson et al., 2020). Cotton lab coats were worn at all times. All extraction steps were carried out in a laminar flow cabinet. Stainless-steel filters were muffled at 350 °C for 3 h prior to use. All reagents were filtered through 1.2 µm glass fibre filters. Glassware was scrubbed with only natural fibre brushes, stored, covered with aluminium foil, and rinsed with 3 x DI water and 3 x RO water before use. Glassware and natural fibre brushes were all thoroughly rinsed with reagents during processing to maximise microplastic recoveries. Sample vessels were tightly covered with aluminium foil when exposed to laboratory air. Plasticware was avoided wherever possible. The only exception was a distinctly coloured yellow wash bottle made of polypropylene that was used for rinsing glassware and filters, as it was not possible to source a non-plastic replacement with the properties needed for this purpose.

Procedural blanks ($n = 8$) were analysed in full, with the spectral data used to calculate the limit of detection as the mean of blanks + 3.3 x standard deviation. If a polymer was never detected in any blank samples, then the LOD was set to 1 particle on the filter area. Microplastic counts were blank-corrected using the mean values for polymer occurrence in blanks.

Positive control samples ($n = 4$ soils spiked with 63–90 µm polyamide beads at ~ 100 beads g^{-1} dw) were processed to give an approximation of the efficacy of the extraction and analytical methods. The polyamide beads were found to coagulate when samples were deposited on the silver filters, therefore recoveries were estimated from the total area of polyamide detected on the filter as opposed to particle numbers. Estimated recoveries for the 4 spikes ranged from 5.6 to 51.4% (mean 33.6% \pm 19.7). This is lower than those estimated for the same size range and polymer type in a previous study of extraction of microplastics from sewage sludge (mean 52.4% \pm 14.1) (Horton et al., 2021). However, the method used here consisted of up to three Fenton's reactions, whereas Horton et al. (2021) used a maximum of two. Polyamide is particularly susceptible to degradation during the digestion process, which may partly explain the difference in recovery between our study and the previous study. Thus, the microplastic data present here is likely underestimated (see Section 3.3).

2.3. Plasticiser extraction and analysis

Stored soil samples were thawed at 4 °C overnight. Between 3.5 and 4 g ww of soil was then sub-sampled, homogenised and dried with anhydrous sodium sulfate. Samples were spiked with deuterium-labelled recovery standards (d4-DnBP and d4-DnOP, Sigma-Aldrich, USA) and microwave-extracted for 30 min in 9:1 dichloromethane (DCM):acetone (Ethos X microwave extraction system, Milestone, Italy). Supernatants were removed, further dried with anhydrous sodium sulfate and reduced to 0.3 mL on a parallel evaporator (Büchi Syncore, Switzerland). Extracts were made to 2 mL in DCM, filtered through a 0.45 µm PTFE filter, and cleaned with an

automated size-exclusion chromatograph (Agilent 1200 series HPLC, Agilent, USA) with a DCM mobile phase. Deuterium-labelled internal standards (d4-DEP and d4-DEHP, Sigma-Aldrich, USA) were added prior to instrumental analysis.

We analysed 8 phthalate plasticisers and 3 emerging plasticisers (Table 1) using an Agilent 6890N gas chromatograph coupled to an Agilent 5975B single-quadrupole mass spectrometer operating in electron ionisation mode. A volume of 1.7 µL of sample was injected in splitless mode onto a 30 m HP-5ms analytical column (0.25 µm film thickness, 0.25 mm internal diameter, Agilent, USA). The inlet temperature was set to 300 °C, the MS source was set to 230 °C, and the carrier gas was helium (flow rate 1.5 mL min^{-1}). The oven temperature was held at 50 °C for 2 min, followed by ramps at 45 °C min^{-1} to 215 °C, 2 °C min^{-1} to 225 °C, 10 °C min^{-1} to 282 °C, 120 °C min^{-1} to 300 °C, and held at 300 °C for 7.5 min.

To reduce potential plasticiser contamination of samples, all glassware was soaked overnight in Decon 90, non-volumetric glassware was heated in a muffle furnace at 450 °C for a minimum of 2 h (Fankhauser-Noti and Grob, 2007), and all glassware was rinsed 2 x with DCM immediately prior to use. Plasticware was avoided wherever possible, all operators wore cotton lab coats and solid reagents were heated in a muffle furnace at 450 °C overnight.

Analytes were quantified using internal and recovery standards and calibration curves of plasticiser standards (Sigma-Aldrich, USA). For quality control and assurance, two procedural blanks were included in each batch. Recoveries of d4-DnBP and d4-DnOP were in the range 69–106% (mean 86% \pm SD 12) and 60–115% (mean 84% \pm SD 13) respectively. The method limits of detection (LODs) (Table 1) were determined from the lowest quantifiable standard in the calibration curve, the mass of soil analysed, and the dilution factor. All plasticiser concentrations are reported in ng g^{-1} dw and were recovery-corrected. Data were also blank-corrected using the mean value for each compound detected in the procedural blanks.

2.4. Statistical analysis

For all statistical analyses and the calculation of Σ microplastic and Σ plasticiser concentrations, polymers and compounds <LOD were assigned a zero value to avoid overestimation and included in calculation of mean and median values for each contaminant (Pereira et al., 2021). Due to non-normality of data, non-parametric tests (Kruskal-Wallis ANOVA with a post-hoc Dunn's test) were used to assess the significant of variation of different contaminants between land uses. Data was log_{10} -transformed prior to fitting of simple linear regression models for co-occurrence of different classes of contaminant (e.g. surface plastic vs microplastic). A small constant (0.01) was added to the data for sites with zero values for total surface plastic counts and masses ($n = 6$) and Σ microplastic concentrations ($n = 10$) prior to transformation.

Table 1
Plasticiser analytes targeted in this study.

Name	Abbreviation	Formula	CAS	Mean limit of detection (ng g^{-1} dw)
Dimethyl phthalate	DMP	C ₁₀ H ₁₀ O ₄	131-11-3	0.5
Diethyl phthalate	DEP	C ₁₂ H ₁₄ O ₄	84-66-2	0.3
Di-iso-butyl phthalate	DiBP	C ₁₆ H ₂₂ O ₄	84-69-5	0.3
Di-n-butyl phthalate	DnBP	C ₁₆ H ₂₂ O ₄	84-74-2	0.3
Benzyl butyl phthalate	BBP	C ₁₉ H ₂₀ O ₄	85-68-7	3.8
Diethylhexyl phthalate	DEHP	C ₂₄ H ₃₈ O ₄	117-81-7	0.3
Di-n-octyl phthalate	DnOP	C ₂₄ H ₃₈ O ₄	117-84-0	0.3
Di-iso-decyl phthalate	DiDP	C ₂₈ H ₄₆ O ₄	26761-40-0	50.5 ^a
Diethylhexyl adipate	DEHA	C ₂₂ H ₄₂ O ₄	103-23-1	0.3
Acetyl tributyl citrate	ATBC	C ₂₀ H ₃₄ O ₈	77-90-7	0.3
Triocetyl trimellitate	TOTM	C ₃₃ H ₅₄ O ₆	3319-31-1	0.5

^a DiDP exists as a mixture of isomers and thus had a higher LOD than other analytes (Al-Natsheh et al., 2015; Zou and Cai, 2013). The concentrations of DiDP reported in this study refer to the sum concentration of all DiDP isomers.

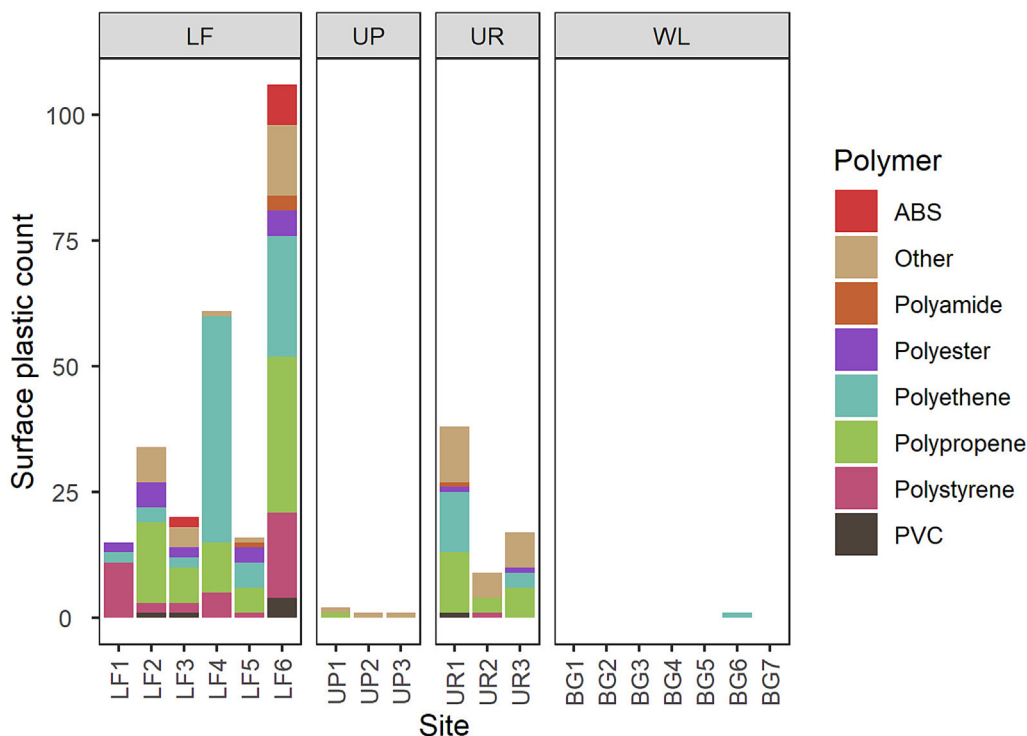


Fig. 1. Counts of surface plastic items collected after 10 min search from a plot of 25 m²; no surface plastic was found at sites BG1–5 or BG7; ABS = acrylonitrile butadiene styrene; PVC = polyvinyl chloride; LF = landfill; UP = urban parkland; UR = urban roadside; WL = woodland; the category ‘Other’ includes all items that could not be assigned a polymer, ethene-vinyl acetate items, nitrile items, and items containing a mixture of polymers.

3. Results and discussion

3.1. Variation of plastic waste with land use

3.1.1. Surface plastic

The number of surface plastic items was significantly different between land uses (Kruskal-Wallis test, $p < 0.005$) (Fig. 1). Specifically, landfill (42.0 items/25 m² ± standard deviation 35.8) and urban roadsides (21.3 items/25 m² ± 15.0) had a significantly higher number of plastic items present when compared to woodland sites (0.1 items/25 m² ± 0.4) (Dunn's test, Benjamini-Hochberg adjusted $p = 0.001$ and 0.03 respectively). In contrast, surface plastic counts at parkland sites (1.3 items/25 m² ± 0.6) were not statistically different from those at the woodland sites (Dunn's test, Benjamini-Hochberg adjusted $p = 0.35$). The mass of surface plastic items followed a similar pattern as for the number of items, with landfill sites significantly higher than woodlands.

The occurrences in woodland and urban parkland sites in this study are comparable to that reported for an agricultural site in Germany (0.52 items/25 m²) (Piehl et al., 2018), indicating that occurrence of surface plastic is mainly centred around hotspots (e.g. landfills and roadsides), with relatively low occurrence in the wider environment.

Increased surface plastic occurrence was associated with sites adjacent to roads. The most polluted urban roadside site (UR1) was located adjacent to a public footpath and the main ring-road around the city. This was duly the third most polluted site in terms of count and fourth most in terms of plastic mass. In addition, highly contaminated landfill sites such as LF6 also occurred near a road. The importance of roads as sources identifies the mismanagement of waste associated with transportation as a source of plastic occurrence in the environment. The differences between surface plastic within urban land uses may partly result from land management in specific locations. For example, the low levels in parklands may reflect the greater amount of litter removal taking place in these locations. The topology of the land is also likely to play a role in the extent to which these sites may act as hotspots for

plastic accumulation. For example, roadside verges are often a depression between the road and adjacent land, and so plastics transported by wind or water processes will build up in these locations.

The majority of collected surface plastic items were films (59%), followed by fragments (26%) and foams (7%). There was 8% of items that did not fall into these three categories and were therefore classified as ‘other’. Although films dominated the total number of plastic items, they represented just 23% of the plastic mass. Fragments and ‘other’ items were 51% and 24% of the total mass, respectively. As the amount of plasticiser depends on the mass of the item (Bueno-Ferrer et al., 2010), it is thus important to report both masses and counts of plastics wherever possible in studies assessing the relationships between plastic and plasticiser occurrence in the environment.

Polyethene (PE; mean count 5.1 ± 11.3 items; 47% DF), polypropene (PP; 4.8 ± 8.0 items; 47% DF), polystyrene (PS; 2.1 ± 4.5 items; 37% DF), and polyester (PET; 1.0 ± 1.7 items; 37% DF) were the most commonly detected polymers. Polytetrafluoroethene (PTFE), polyurethane (PU), polycarbonate (PC), polymethyl methacrylate (PMMA), tire-wear particles (TWPs) and polylactic acid (PLA) were not detected in any surface plastic items. Landfill and urban roadsides had the highest mean polymer diversity of the studies land uses (7.3 ± 4.3 and 5.7 ± 3.1 polymer types per site, respectively), and these land uses were significantly more diverse than woodland sites (Dunn's test, Benjamini-Hochberg adjusted $p = 0.002$ and 0.02 respectively). Overall, the nature and diversity of the surface plastic polymer profiles found are comparable with those of Piehl et al. (2018) for an agricultural site and with soil microplastic studies, where PE and PP have also been shown to dominate (Büks and Kaupenjohann, 2020).

Polyvinyl chloride (PVC) plastic items are notable for their frequently high plasticiser load (CEFIC, 2018). Only 7 PVC-containing items were found in total, across 4 sites (3 at landfill sites, 1 at an urban roadside). This reflects the fact that PVC is primarily used in the building and construction sector, and has only a minor use in consumer items such as packaging (Plastics Europe, 2021) that are most likely to enter in to the environment

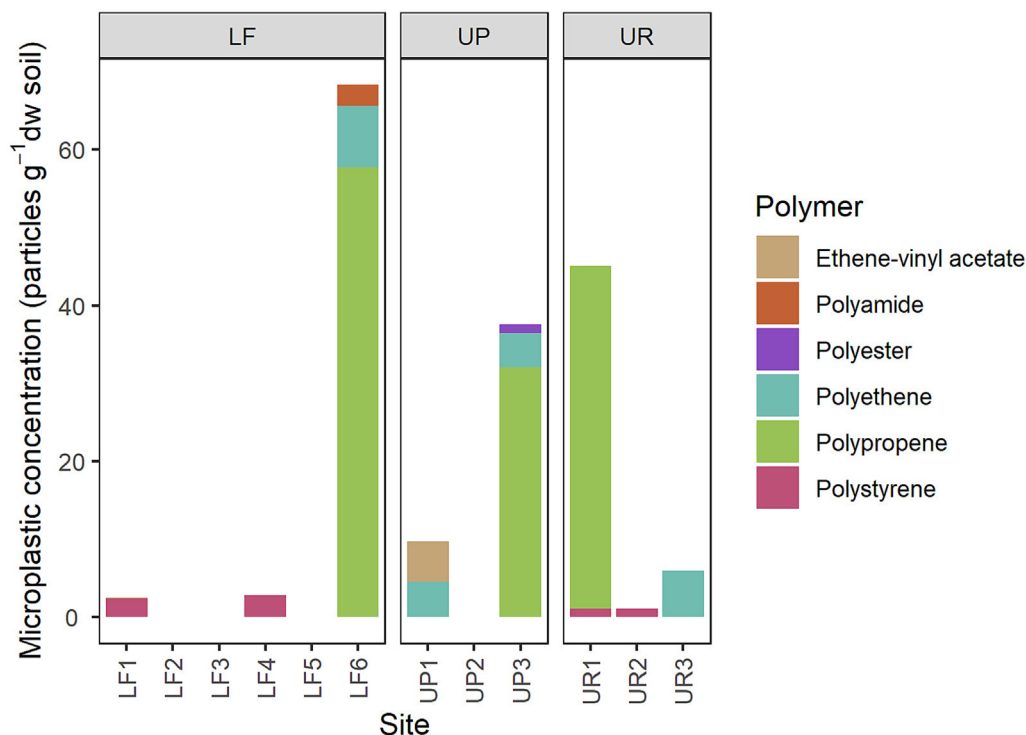


Fig. 2. Σ microplastic concentrations detected in field soils (particles g^{-1} dw) (Appendix Table S5); no microplastics were $>LOD$ at LF2-LF3, LF5 or UP2; no microplastics were $>LOD$ at woodland sites, hence they are not shown on this figure (Appendix Table S4); LF = landfill; UP = urban parkland; UR = urban roadside.

through dispersed releases via littering. Given that the majority of plasticisers are used in PVC (Billings et al., 2021), the absence of PVC items could indicate a low plasticiser input to soils.

3.1.2. Soil microplastics

Microplastics were detected in one or more of the collected fractions at 42% of all sampled sites. Fine (25–178 μm), medium (178–567 μm) and coarse ($>567 \mu m$) microplastics accounted for 97.3%, 2.5% and 0.2% of the total microplastic concentration. Σ microplastic (all size fractions combined) concentrations in field soils ranged from nd-68 particles g^{-1} dw, with a mean of 9.1 particles g^{-1} dw (Fig. 2).

No microplastics were detected at any woodland site, with mean LODs (particles g^{-1} dw) for fine, medium, and coarse fractions of 2.6 (range 1.0–3.5), 2.6 (0.7–5.0), and 0.1 (with the exception of polypropene in the fine fraction; mean LOD 30.7, range 30.1–31.2) (see Appendix Table S4 for a full list of LODs for each microplastic fraction). Thus mean Σ microplastic concentrations in urban roadsides (17.3 ± 24.1 particles g^{-1} dw), urban parklands (15.7 ± 19.5 particles g^{-1} dw) and landfill (12.3 ± 27.5 particles g^{-1} dw) sites indicated that these land uses were contaminated relative to woodlands. This reflects the same pattern for microplastics as surface plastic contamination across these land uses. However, due to the high degree of variation in microplastic concentrations within land uses, no statistically significant differences were found for any individual size fraction or Σ microplastic concentrations between individual land uses (Dunn's test, Benjamini-Hochberg adjusted $p < 0.05$). Thus, whilst surface plastic contamination can be statistically associated to land use, other factors (e.g. local hotspots, distance from footpath, proximity of human settlements) may be responsible for predicting differences in microplastic concentrations.

The most commonly detected polymers in the microplastic samples were polyethene (21% DF), polystyrene (21% DF) and polypropene (16% DF). Ethene-vinyl acetate (10.5% DF), polyamide (5.3% DF), and polyester (5.3% DF) microplastics were also detected. Polypropene had a mean concentration of 7.0 ± 17.2 particles g^{-1} dw and dominated the overall microplastic profile, accounting for 77% of Σ microplastic across all sites. Polyethene (1.2 ± 2.4 particles g^{-1} dw) was the only other polymer

with a mean concentration >1 particle g^{-1} dw, accounting for 13% of Σ microplastic.

The occurrence of polyethene, polypropene and polystyrene as the three most commonly detected polymers in both the surface plastic and soil microplastic profiles reflects the widespread use of these polymers in consumer packaging items. Furthermore, the morphologies (i.e. films, foams) of these products and low polymer densities may facilitate their transport (e.g. by wind and water) in the environment.

The extensive use of surface plastic (film mulch) has been found to determine the generation of microplastics in agricultural soils through incorporation of material into farmland soils during subsequent cultivation (Kundu et al., 2022; Li et al., 2022). To investigate the extent to which surface plastic governs microplastic concentrations in our land use setting (i.e. non-agricultural soils), the relationships between these two contaminants were assessed. For the three most commonly detected polymers (polyethene, polypropene and polystyrene), detection frequencies in soils were 1.8–3 times lower than for surface plastics. Furthermore, polymer diversity was lower for microplastics (6 polymer types) than for surface plastics (10 polymer types), which may reflect differences in the breakdown rate of different polymer types. Given the differences found in detection frequencies and polymer diversity, microplastic concentrations in the soil were only weakly significantly correlated with surface plastic count (simple linear models of \log_{10} -transformed data) ($R^2 = 0.31$; $p = 0.008$) and mass ($R^2 = 0.21$; $p = 0.03$). The relative weakness of these relationships suggests a complex link between surface plastic levels and their rates of breakdown and integration into the underlying soil. In the land uses in this study, surface plastic residence time is likely to be a primary driver of degradation and downwards movement into soils. As both environmental transport and human action may remove plastic litter from site surfaces in a manner that may differ between polymer and plastic form, surface plastics present in a spot-sample may not fully represent either the concentration or polymer composition of microplastics found in soil.

At present, it is challenging to draw meaningful comparisons between studies of soil microplastic concentrations due to differences in extraction and analytical techniques, and the fact that many published studies did not carry out/report blank corrections or apply LODs. Additionally,

Table 2Plasticiser concentrations in land uses sampled in this field study (ng g⁻¹ dw soil); DF% = detection frequency; nd < LOD.

		DMP	DEP	DiBP	DnBP	BBP	DEHP	DnOP	DiDP	ATBC	DEHA	TOTM
All land uses n = 19	Mean	4.8	7.2	8.5	22.0	3.6	493	6.3	96.7	2.9	6.8	18.8
	Median	1.2	2.3	nd	18.3	nd	74.0	nd	72.1	nd	1.5	3.9
	Range	nd-35.6	nd-51.6	nd-29.8	nd-87.8	nd-20.3	nd-4853	nd-70	nd-686	nd-25.6	nd-43.9	nd-195
	DF%	52.6	68.4	47.4	94.7	36.8	63.2	42.1	63.2	26.3	63.2	89.5
Landfill n = 6	Mean	3.9	3.8	8.1	15.8	3.3	63.1	0.5	178	3.0	1.2	37.0
	Median	1.1	2.5	nd	11.7	2.0	58.4	nd	91.3	nd	0.8	6.6
	Range	nd-15.3	nd-13.4	nd-29.8	7.7-34.4	nd-10.9	nd-164	nd-2.9	nd-686	nd-14.7	nd-3.3	nd-195
	DF%	50.0	83.3	33.3	100.0	50.0	66.7	16.7	83.3	33.3	50.0	83.3
Urban Parkland n = 3	Mean	0.4	0.3	8.6	13.2	-	102	1.3	63.1	-	0.2	3.2
	Median	nd	nd	nd	18.3	-	92.9	1.9	85.5	-	nd	2.4
	Range	nd-1.2	nd-1	nd-25.9	nd-21.2	-	nd-214	nd-2.1	nd-104	-	nd-0.5	2.4-4.9
	DF%	33.3	33.3	33.3	66.7	-	66.7	66.7	66.7	-	33.3	100.0
Urban Roadside n = 3	Mean	5.4	5.2	20.7	45.0	11.8	2781	36.2	140	9.6	18.1	38.2
	Median	2.4	2.4	20.5	29.2	15.1	2771	29.6	143	3.4	8.9	35.8
	Range	2-11.8	nd-13.1	15.7-25.7	18-87.8	nd-20.3	719-4853	9-70	87.3-189	nd-25.6	1.5-43.9	24.1-54.6
	DF%	100.0	66.7	100.0	100.0	66.7	100.0	100.0	100.0	66.7	100.0	100.0
Woodland n = 7	Mean	7.3	14.0	3.6	21.2	2.0	49.5	0.5	23.3	1.2	9.6	1.5
	Median	nd	5.0	nd	27.2	nd	nd	nd	nd	nd	4.2	1.3
	Range	nd-35.6	nd-51.6	nd-17.9	8.9-30.7	nd-7.8	nd-199	nd-2.3	nd-90.8	nd-8.2	nd-38	nd-3.9
	DF%	42.9	71.4	42.9	100.0	28.6	42.9	28.6	28.6	14.3	71.4	85.7

suspected microplastics are often spectroscopically verified with only a limited subset of particles (and in some cases purported microplastics are identified through light microscopy alone). To combat these limitations of past studies we spectroscopically verified all particles through analysis of the entire deposited sample, rather than relying on extrapolation from a subset of detected particles. In addition, as particles fragment, the number concentration is also likely to be highly dependent on the minimum detectable size particle, as demonstrated in the differences between the three size fractions evaluated in this study, with >90% of particles were in the smallest size fraction. As such we have clearly reported the lower size limits of each fraction studied, to allow this data to be meaningfully interpreted in the future. To date, the majority of data on soil microplastic concentrations exists for agricultural land (Büks and Kaupenjohann, 2020). The polymer profiles reported here for urban and landfill sites (e.g. the dominance of polypropylene and polyethylene) are broadly similar to those reported for agricultural sites (Liu et al., 2018; Piehl et al., 2018; Vollertsen and Hansen, 2017). This indicates that microplastic profiles may be relatively consistent across land uses and larger regions. This reflects the ubiquity of readily-fragmented plastic films from either agricultural or consumer packaging applications that may be susceptible to windblown dispersal.

3.2. Occurrence of plasticisers in soils

3.2.1. Phthalate occurrence and variation with land use

Mean Phthalate concentrations in the urban roadside soils were significantly greater (25 times) than those at woodland sites (Dunn's test, Benjamini-Hochberg adjusted $p = 0.01$). Mean Phthalate levels were, however, not significantly different between the other land use pairings, although landfill and urban parklands were respectively 2.3 and 1.6 times greater than woodland sites. These results are in agreement with previous studies that have identified that urban soils typically have higher phthalate concentrations than other land uses (Billings et al., 2021).

DnBP (94.7% of sites), DEP (68.4% of sites), DEHP (63.2% of sites) and DiDP (63.2% of sites) were the most commonly detected phthalates (Table 2). BBP had the lowest detection frequency of all phthalates (36.8% of sites) and was consequently the only phthalate not detected in all land uses (being at concentrations <LOD in all urban parkland sites).

DEHP, DiDP and DnBP dominated the phthalate profile in soils, accounting for a mean of 76.8%, 15.1% and 3.4% of the mean total phthalate load across all land uses (Fig. 3). DEHP was present in high concentrations in the roadside soils (mean concentration 2781 ng g⁻¹ dw), accounting for 91.3% of phthalates in this land use. DEHP and DnBP have been previously reported to dominate phthalate profiles in soils and other environmental

matrices (Billings et al., 2021; Hermabessiere et al., 2017). Thus, the dominance of DEHP in particular is consistent with its known widespread use and associated environmental occurrence. Long-chain phthalates with more complex chain structures are also known to have longer half-lives in soils (Tang et al., 2020; Xie et al., 2010). Such increased persistence may further underpin the dominance of DEHP (C₈ alkyl chains, 1 branch) and DiDP (C₁₀ alkyl chains, minimum of 1 branch) versus e.g. the unbranched DnBP (C₄) or DEP (C₂) detected in the sampled soils.

In contrast to the other land uses, DiDP was found to be the most abundant phthalate at landfill-adjacent sites (mean concentration 178 ng g⁻¹ dw, 64.3% of phthalate profile). DiDP is rarely analysed as part of analytical suites of plasticisers (Billings et al., 2021). Thus, this raises questions as to

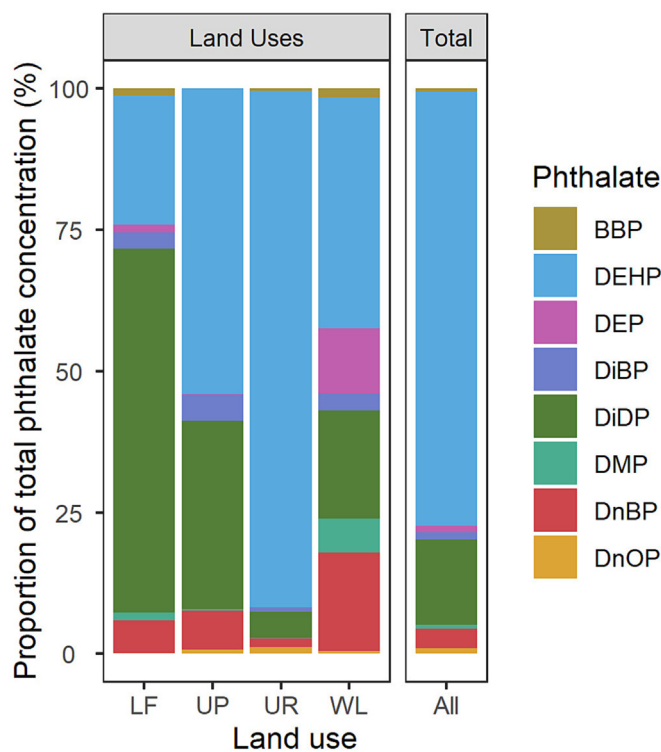


Fig. 3. Phthalate profiles in soils of the different land uses in this field study; LF = landfill; UP = urban parkland; UR = urban roadside; WL = woodland; All = all sites.

whether past analyses may have always captured relevant phthalate occurrence in the environment in cases where plasticisers such as DiDP are not included in the analysis. DiDP was not included in the group of phthalates recently restricted in the EU (ECHA, 2022, ECHA, 2018). As a result, it may be increasing in use as a replacement for restricted phthalates (ECHA, 2013). If this pattern of substitution continues, then it may be possible that concentrations of this plasticiser will increase in the future making it an important candidate for inclusion within analyses.

The majority of studies of phthalate levels in soil have been conducted in China. The levels measured in the present study are generally much lower than in the Chinese studies (although in some cases it is difficult to make direct comparisons as literature concentrations may be reported on a dry or wet weight basis). For example, phthalate concentrations in our urban soils were at least ~ 1 order of magnitude lower than those reported in roadside, residential and parkland soils in Chinese cities (Wu et al., 2015; Zeng et al., 2009). However, relative to cities outside of China, DEHP concentrations in the urban roadside soils in our study are an order of magnitude higher than previously reported urban soil values (Kaewlaoyong et al., 2018; Škrbić et al., 2016; Tran et al., 2015). Such a difference may reflect both relative source intensity, as well as the grouping of land uses in previous studies such that urban sites in these studies may represent an urban background average (e.g. of roadsides, parklands, gardens etc.), as opposed to the urban roadside sites in our study, which may represent hotspots for phthalates. The urban parkland soils measured in this study were between ~ 3 – 6 times less contaminated than values for urban soils reported in European cities (Škrbić et al., 2016; Tran et al., 2015). The phthalate profiles in the measured urban soils were similar to those previously reported for other European cities, although differences in analytical suites hamper direct comparison (Škrbić et al., 2016; Tran et al., 2015).

We are aware of only two studies that have reported phthalate concentrations in landfill-associated soils. Individual phthalate concentrations at the landfill sites measured in our study were generally on the same order of magnitude as those reported by Chakraborty et al. (2019) who measured 6 phthalates in soils near open municipal landfill sites across 4 Indian cities. Conversely, concentrations of 7 phthalates in soils near a landfill site in central China were an order of magnitude greater (Liu et al., 2010). It is unclear whether these differences are driven by site management practices, local climatic conditions, or differences in source intensity. Given the high levels of plastics found at the landfill sites in our study, further studies to assess plasticiser concentrations in soils in the vicinity of such sites are warranted given their potential to act as a source of these chemicals into the environment.

As far as we are aware, the only other field study of plasticisers in UK soils is a survey of DEHP in rural Scottish soils (Rhind et al., 2013a). Mean DEHP concentrations in woodlands in our study were over 4 times lower than those reported in the previous study. The woodlands in our study are primarily deciduous broadleaf and have had continuous tree cover since at least 1600 CE (Natural England, 2021), whereas those studied by Rhind et al. (2013a) were forestry plantations of non-native conifers. Differences in DEHP contamination between these two studies could be explained by the faster biodegradation in deciduous woodland due to greater organic matter content, which may promote phthalate degradation by some bacterial communities (Billings et al., 2021). Alternatively the milder climate in southern England compared to Scotland may also accelerate phthalate degradation and/or volatilisation from soil.

3.2.2. Emerging plasticisers occurrence and variation with land use

TOTM was the most frequently detected emerging plasticiser (89.5%), followed by DEHA (63.2%), and both of these plasticisers were detected across all land uses. ATBC was the least commonly detected of the emerging plasticisers (26.3%), although was detected in all land uses except urban parklands. TOTM was found at the highest concentration (nd-195 ng g⁻¹ dw, mean 18.8 ng g⁻¹ dw), accounting for 65.9% of the total emerging plasticiser burden across all land uses. Mean and maximum concentrations of DEHA (nd-43.9 ng g⁻¹ dw, mean 6.8 ng g⁻¹ dw) and ATBC (nd-

25.6 ng g⁻¹ dw, mean 2.9 ng g⁻¹ dw) were an order of magnitude lower than those of TOTM. There is a lack of information available on the current uses of TOTM, both in terms of the quantities used and polymers that it is used with. TOTM was estimated to occupy 3% of the plasticiser EU market share in 2017, versus 7% for aliphatic plasticisers (a class which includes DEHA) (CEFIC, 2018). That TOTM was detected both most commonly and at the highest concentrations suggests that this emerging plasticiser may be growing in widespread use and/or persists longer than DEHA and ATBC in soil. It is well-established that longer-chain phthalates degrade slower than shorter-chain molecules (Billings et al., 2021). TOTM and DEHA (both C₈) have longer alkyl chains than ATBC (C₄). Additionally, TOTM has the greatest molecular mass of any other plasticiser analysed in this study, further suggesting that it may be more resistant to degradation in soils than DEHA or ATBC (Billings et al., 2021). However, to date there is no published data regarding the half-lives of emerging plasticisers in soils. The presence of these emerging plasticisers indicates that their fate in soil warrants further investigation.

Mean Σ emerging plasticiser concentrations at urban roadsides and landfill-adjacent sites were 5.4 and 3.4 times greater than in woodland sites, although the mean Σ emerging concentration at urban parklands was only 30% of that in woodlands (Fig. 4). No statistically significant differences in the Σ emerging concentration between sampled land uses were found. Mean TOTM concentrations were significantly (26 times) greater in urban roadside soils than in woodlands (Dunn's test, Benjamini-Hochberg adjusted $p = 0.014$). This difference between land uses reflects the pattern seen for the Σ phthalate concentrations, which were significantly (25 times) greater in roadside than woodland soils. The common finding between phthalates and TOTM indicates that urban roadsides may be particular hotspots for plasticiser contamination relative to background levels found in the wider urban and, especially, rural environment.

Only one previous study has investigated emerging plasticiser occurrence in soils. Chakraborty et al. (2019) reported a mean concentration of DEHA in landfill-associated soils in Indian cities of 57 ng g⁻¹, this level being greater than for any co-measured phthalate. These findings contrast with the results found here. For example, the mean DEHA concentration measured here of 1.2 ng g⁻¹ dw was only 0.4% of the mean total plasticiser contamination in landfill-adjacent soils, compared to the phthalate DiDP which comprised 56% of the total plasticiser burden these soils.

Across all measured phthalates and emerging plasticisers, TOTM was second most frequently detected and had the third highest maximum concentration in soils. In some local hotspots, TOTM concentrations were comparable to or even exceeded those of the phthalates (e.g. at landfill site LF2, TOTM was the second most abundant plasticiser, accounting for 21.5% of total concentration, behind DiDP at 75.4%). However, compared to DEHP and DiDP (73.5% and 14.4% of total plasticiser concentration across all sites), TOTM accounted for only 2.8% of the total plasticiser load across all sites. Thus, it appears that whilst there may be hotspots of emerging plasticiser contamination, the wider concentration of the plasticisers in soils remains relatively low compared to the more common phthalates.

3.2.3. Relationship between plastic and plasticiser occurrence

Σ plasticiser and Σ phthalate concentrations were weakly significantly correlated with surface plastic count (all data log₁₀-transformed) ($R^2 = 0.23$ and $p = 0.021$; $R^2 = 0.25$ and $p = 0.016$) and surface plastic mass ($R^2 = 0.23$ and $p = 0.021$; $R^2 = 0.25$ and $p = 0.018$). No other significant correlations were observed between Σ plasticiser, Σ phthalate or Σ emerging versus surface plastic count or mass, or microplastic concentration ($p < 0.05$) (n.b. due to a high proportion of non-detects for surface plastic and microplastic polymer types, it was not possible to perform a correlation analysis between individual plasticisers and polymer types). Absence of a strong and consistent correlation between surface plastic or microplastic and plasticiser concentrations indicates that plasticiser occurrence in soils is not strongly explained by in situ plastic occurrence. Due to its potentially transient nature, the surface plastic data for some sites represents a snapshot of contamination, whereas the plasticiser burden in soils may be

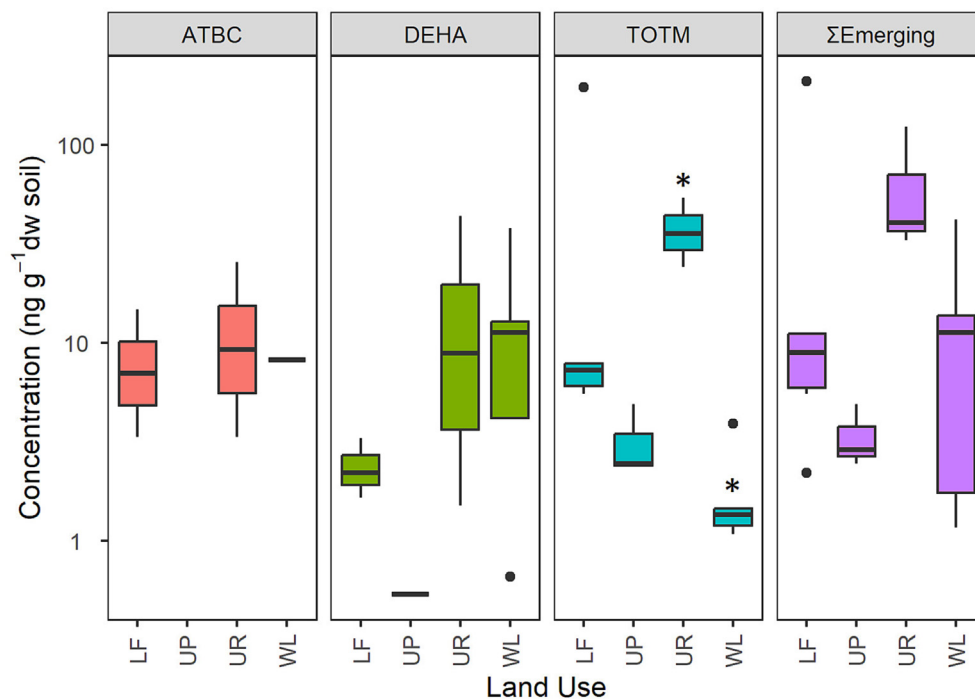


Fig. 4. Σ concentrations of emerging plasticisers across different land uses; concentrations are plotted on a log scale; LF = landfill; UP = urban parkland; UR =₁₀ scale; LF = landfill; UP = urban parkland; UR = urban roadside; WL = woodland; statistically significant differences in Σ concentrations between land uses are indicated by *.

more long-lived. Therefore, soil plasticiser contamination may be related not only to the surface plastics at the time of sampling, but also previous contamination that has been degraded or been removed. Additionally, the fact that plasticisers can be detected in sites with no detectable microplastic or surface macroplastics indicates potential sources through aerial transport alongside direct plastic inputs. This is in line with previous findings, which attributed DEHP contamination in some Scottish rural top-soils to long-range aerial transport and deposition (Rhind et al., 2013a).

3.3. Limitations and uncertainties

The microplastic concentrations reported in this study are most likely underestimated, as demonstrated by the mean of the spiked recoveries. Due to differences in density, morphology etc. between different polymer types, recovery correction of each microplastic polymer type was not feasible. The relatively high limits of detection for some polymers, e.g. polypropene in the fine fraction (Appendix Table S4), have also likely resulted in underestimations in particle numbers, which serves to highlight the importance of publishing LOD data in future microplastic studies. Despite employing up to 3 × Fenton's reagent digestion steps and 2 × 24-h density separations, a portion of primarily cellulosic or root-based degradation-resistant material was retained in many of the microplastic extracts. Such organic matter may obscure microplastic particles during spectroscopic analysis, rendering them undetectable. Conversely, the similarity of the IR spectra of some plant materials and synthetic polymers may lead to false positives which could potentially increase the number of false assignments. By taking advantage of a recent development in microplastic polymer spectra libraries which vastly reduces the number of false positives arising from natural organic matter, we were, however, able to limit the number of such misidentifications (Roscher et al., 2022).

The relatively small number of sampling sites ($n = 19$) limited the power of the statistical tests used to infer relationships between the different classes of contaminant. Thus this may partly explain why only relatively weak correlations were observed between e.g. Σ plasticiser and surface plastic levels. Furthermore, it was not possible to entirely compartmentalise some land uses, e.g. all of the landfill-adjacent sites were also situated

next to roadsides. However, none of the landfill sites were in proximity to large urban areas and thus were largely distinct from urban roadsides. All sites were sampled within two weeks in the winter of 2019/20. Zhang et al. (2015) reported some seasonality in plasticiser occurrence in agricultural soils, but this was tied to farming practices and thus the drivers of these patterns are unlikely to be seen in the non-agricultural soils. However, other seasonal drivers may apply, such as increased use of recreational land in the warmer months and differences in weather affecting transport to and from sink locations. Seasonal differences in environmental conditions such as temperature and soil moisture levels have the potential to alter plasticiser degradation rates and modify leaching from plastic items. For example, temperature may increase degradation, but also accelerate diffusion out of plastics. At present the seasonality of plasticiser concentrations in the wider terrestrial environment remains relatively unknown.

4. Conclusions

This study investigated the co-occurrence of different size ranges of plastic pollution and phthalate and emerging plasticisers in field soils from the UK. Urban roadsides and sites adjacent to landfill were found to be hotspots for surface plastic (macroplastic) pollution, with woodlands and urban parklands least contaminated. Microplastics were detected in landfill and urban soils, although no contamination was detected in woodlands, and microplastic concentrations were weakly positively correlated with surface plastics. Surface plastic and microplastic profiles were both dominated by polyethylene, polypropene and polystyrene, although detection frequencies of microplastics were up to 3 times lower than surface plastics. This indicates that transient surface plastic loads may not reflect soil-incorporated plastics and that the generation of secondary microplastics from these surface plastics and their subsequent incorporation into non-agricultural soils may be a relatively slow process.

Mean plasticiser concentrations in soils were greater in landfill and urban sites compared to woodlands, although plasticisers were found in the latter land use, despite the extensive absence of surface plastics and microplastics in these soils. Such widespread presence suggests that diffuse contamination not directly linked to plastic source inputs may play a significant role in plasticiser occurrence in soils under all land uses, but especially

more rural sites. Urban roadsides were particularly contaminated with plasticisers, indicating a significant input from roadside surface plastics and potential inputs from neighbouring buildings and vehicles. Urban parklands were conversely the least contaminated land use when compared to woodlands. Σ plasticiser concentrations were not significantly correlated with microplastic concentrations, although surface plastic occurrence could explain a quarter of the variation in plasticiser occurrence in a simple linear model. Thus, while plastics play a role in determining soil plasticiser concentrations, other diffuse sources (e.g. from air) are likely contributing factors.

The phthalates DEHP and DiDP dominated soil plasticiser profiles, a result largely consistent with previous studies. The emerging plasticiser TOTM was widespread, being the second most frequently detected plasticiser in this study. Occurrence of TOTM and other emerging plasticisers (DEHA and ATBC) across all land uses indicated that these plasticisers may accumulate in soils, are available for aerial transportation and deposition far from sites of use/production, and are present in soils in comparable quantities to phthalates which have been in use for decades. Hence, an increased focus on these emerging chemicals may be warranted.

CRedit authorship contribution statement

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

Data availability

Data will be made available on request.

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.scitotenv.2023.163258>.

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