Lancaster Environment Centre

Lancaster University

Plasticisers in terrestrial and estuarine environments: sources, occurrence and fate

Alex Billings

Submitted for the degree of Doctor of Philosophy

February 2024

Abstract

Plastics not only have physical effects on organisms, but there is also a chemical burden associated with their presence in the environment. Plasticisers are one of the most widely used classes of chemical additive in plastic items, and thus there is widespread potential for the release of these compounds into the environment over the lifetime of the plastic, where they may pose a risk to organisms. Despite this, there have been very few studies of the occurrence and fate of plasticisers in the UK environment. To address this knowledge gap, field surveys were carried out to assess the occurrence of multiple classes of legacy and emerging plasticiser in UK terrestrial and estuarine environments. The occurrence of macroplastics, and microplastics in the UK terrestrial environment was also investigated. In addition to these field studies, laboratory experiments were also carried out to investigate plasticiser release rates from microplastics into soils, and the persistence and degradation kinetics of multiple classes of plasticiser. Laboratory and field studies in this project were designed to investigate differences and similarities in the occurrence and fate of legacy phthalate and emerging non-phthalate plasticisers, many of which are increasing in use in response to legislative pressure. The results from these studies suggest that plasticiser contamination of UK terrestrial and estuarine environments is widespread, with phthalates the most abundant class of plasticiser in both soils and sediments. Multiple classes of emerging plasticiser were also detected in these environments. In some instances, concentrations of emerging compounds were greater than or equal to restricted phthalate plasticisers, although levels were generally relatively low. The laboratory mechanistic studies indicated that plasticiser release from microplastics into soils can proceed rapidly, and that some emerging plasticisers are among the most persistent plasticisers in soils. Overall, the results from this project suggest that future monitoring of plasticisers, in addition to investigations of the impacts and fate of emerging and legacy plasticisers in organisms, would be warranted in order to assess and manage the risk of these compounds in the UK and wider environment.

Acknowledgements

First and foremost, I'd like to acknowledge my supervisory team. Kevin, thank you for your continued positivity, encouragement, and thoughtful insights. Gloria, thank you for your expert guidance and reassurance that even when things weren't going quite to plan, they would turn out okay in the end. Dave, thank you for the stimulating discussions and ideas, and for helping to steer the project through the challenges of 2020. I'm very grateful for the support and mentorship that the three of you have provided over the course of the project.

I'd like to thank everyone in the Ecotoxicology and Analytical Chemistry groups at UKCEH Wallingford and Lancaster for being so welcoming, approachable, and helpful. Thanks also go to Rich Cross and Dan Read for their useful discussions around all things microplastics, and to Heather Carter for her advice on method development and troubleshooting the instruments. Thank you to all my fellow students past and present, and in particular Holly, Elmer, and Katie for your friendship and support. Huge gratitude also goes to Katharine and Sasha for the use of their flat during the Great Flea Crisis.

Finally, thank you to my parents, Chris and Nuala, whose love and support allowed me to pursue a career in science.

This work was supported by the Natural Environment Research Council NE/S007423/1, with Alex Billings's studentship through the ENVISION Doctoral Training Partnership. The work to collect the sediment samples used in Chapter 6 was supported by the Natural Environment Research Council NE/T003596/1.

Contents

Statement on publications

This thesis contains papers which have been published in, or have been submitted to, appropriate journals. These papers are listed below, with a brief description of the contribution made by the candidate and co-authors.

- **Billings, A.**, Jones, K.C., Pereira, M.G., Spurgeon, D.J., 2021. *Plasticisers in the terrestrial environment: sources, occurrence and fate*. Environ. Chem. 18, 111–130. doi.org/10.1071/EN21033. **(Chapter 2)** *AB proposed the review topics, collated the research and wrote the manuscript, with supervision, guidance, and reviewing from KJ, GP, and DS*.

- **Billings, A.**, Carter, H., Cross, R.K., Jones, K.C., Pereira, M.G., Spurgeon, D.J., 2023. *Co-occurrence of macroplastics, microplastics, and legacy and emerging plasticisers in UK soils*. Sci. Total Environ. 880, 163258. doi.org/10.1016/j.scitotenv.2023.163258. **(Chapter 3)** *AB designed and carried out the field sampling, performed all chemical and physical analyses, and wrote the manuscript. Supervision, guidance, and reviewing was provided by KJ, GP, and DS. HC and RC assisted with initial analytical method development.*

- **Billings, A.**, Jones, K.C., Pereira, M.G., Spurgeon, D.J., 2023. *Emerging and legacy plasticisers in coastal and estuarine environments: A review*. Sci. Total Environ. 908, 168462. doi.org/10.1016/j.scitotenv.2023.168462. **(Chapter 5)** *AB proposed the review topics, collated the research and wrote the manuscript, with supervision and reviewing from KJ, GP, and DS.*

- **Billings, A.**, Jones, K.C., Pereira, M.G., Spurgeon, D.J., 2023. *Kinetics of plasticiser release and degradation in soils*. Submitted to *Environmental Science and Technology* in January 2024. **(Chapter 4)** *AB designed and carried out the experiment, performed all* *chemical and physical analyses, and wrote the manuscript. Supervision, guidance, and reviewing was provided by KJ, GP, and DS.*

Statement on research collaborations

The sediment samples in Chapter 6 were collected by a team at the UKCEH Edinburgh site comprising Alanna Grant, Amy Pickard, Justyna Olszewska, and Francis Daunt. Subsamples were kindly made available for the analysis in Chapter 6. These samples were collected as part of the CLEWS project (Natural Environment Research Council NE/T003596/1), investigating the uptake of chemicals from legacy waste sites in coastal food webs and the effects on higher predators.

1

Introduction

1.1 Background and rationale for the study

1.1.1 Plastic production and the scales of plastic waste in the environment

Modern life is increasingly dependent on plastics. Due to their durability, relative ease of production, and diversity in physical and chemical properties, plastics have found a wide range of applications in society. In 2020, global production of virgin plastics alone (i.e. not including recycled plastic manufacturing) exceeded 367 million tonnes, an increase of almost 10% from 2016 (Plastics Europe, 2021). European production of virgin plastics is estimated to be over 55 million tonnes, with the most widely produced polymers being polyethene (PE), polypropene (PP), polyvinylchloride (PVC), and polyethene terephthalate (PET) (Hansen et al., 2013; Plastics Europe, 2021). Although these four polymers combined represent the majority of plastic demand in Europe (~68%), the European plastic market contains over 30,000 distinct polymeric materials (Horton et al., 2017b; Plastics Europe, 2021). Furthermore, there are hundreds of chemical additives which may be included in the formulation of plastic items, although the exact composition depends on the intended use and characteristics required of the plastic (Hansen et al., 2013). Due to this diversity in the chemical composition of plastics (both base polymer and additive content), these items represent a complex mixture of potential environmental contaminants.

Over the past decade, there has been an increased focus on the occurrence and ecotoxicological impacts of plastics, particularly microplastics, in the environment (Horton et al., 2017b; C. Wang et al., 2021). Microplastics, typically defined as plastic particles smaller than 5 mm (Arthur et al., 2009), may be classified as ‘primary’ or ‘secondary’. Primary microplastics are those that are intentionally manufactured as products of the polymer industry (Horton and Dixon, 2018), such as pre-production ‘nurdles’ that are used as precursors in the production of industrial or consumer plastic goods. These primary microplastics may enter the environment through e.g. accidental release during transport or improper disposal, and can contain plastic additives which themselves may be released into the environment following the entry of the microplastic into e.g. terrestrial or freshwater ecosystems (Horton et al., 2017b; Chapter 2). Secondary microplastics are produced through the fragmentation of larger plastic items present in the environment, through a combination of mechanical, chemical, and biological pathways. Given the mass and quantity of macroscopic plastic items produced globally, secondary microplastics are thought to represent the vast majority of the microplastic burden in the environment, relative to primary microplastics (Horton et al., 2017b). Secondary microplastics, like primary microplastics, will also contain a number of chemical additives, either added intentionally during manufacturing, or potentially through sorption from the surrounding environment on to (or within) the surface of the microplastic particle following initial fragmentation (Horton et al., 2017b; Chapter 2). Given that the rate of release of a chemical additive from a plastic will depend largely on the relative surface area of the item, the exponential increase in relative surface area associated with secondary microplastic generation may increase the potential of a plastic fragment to release chemical additives into the environment. Thus, the study of the relationships between different scales of plastic waste (from macroscopic to microscopic) and the occurrence and release of plastic additives is necessary if the source pathways and ultimate fate of plastics and their chemicals additives in the environment are to be understood.

Given that almost all plastics are produced, used and disposed of on land, the study of the potential impacts of these contaminants on the terrestrial environment is vital. For example, it has been shown that microplastic contamination can have negative impacts on the survival and fitness of terrestrial organisms (Boots et al., 2019; Cao et al., 2017; Huerta Lwanga et al., 2016). To date, these assessments of the impact of plastic waste on organisms have typically focussed on the physical impacts of the particles themselves on e.g. dermal or respiratory surfaces within the organism. In addition to these physical impacts, the chemical load associated with microplastic particles also contributes to the potential toxicity of such particles (Chapter 2; S. W. Kim et al., 2020). Work to assess the levels of microplastics in different environmental matrices, and thus the environmental relevance of such toxicological studies, is ongoing. Nevertheless, the weight of evidence indicates that the risk posed by plastic waste to terrestrial and estuarine organisms arises not only from physical impacts of such contamination (e.g. ingestion of microplastic particles), but also the burden of chemicals that may have been released prior to, or during, interactions between organisms and environmental plastic contamination.

1.1.2 Plasticisers as plastic additives and environmental contaminants

A plastic item typically comprises a polymer matrix (for which the plastic is named, e.g. polyethene, polystyrene) doped with a number of plastic additives (compounds associated with, but not chemically bound to, the polymer matrix). As the vast majority of plastic additives are not chemically bound to the polymer matrix, it is possible that these compounds may be released from the plastic into the environment over the lifetime of the plastic item (Chapter 2). Plasticisers are one such family of chemicals associated with plastics. Plasticisers are added to many plastics during the manufacturing process to increase the flexibility of the final product. Annual demand for plasticisers in Europe alone exceeds 1.3 million tonnes, with the global market estimated at 7.5 million tonnes (CEFIC 2018). The majority of plasticisers (approximately 85%) are used in polyvinyl chloride (PVC) formulations (CEFIC 2018), thus this polymer may be expected to be most closely associated with the occurrence of plasticisers in the environment. Plasticised items are most commonly used in urban areas, e.g. wires, cabling, flooring and wall coverings account of almost half (45%) of plasticiser use in Europe (CEFIC 2018), and a significant proportion of plasticisers are also used in consumer goods and industry (13%). Therefore, it may be expected that urban areas and plastic litter associated with such areas could act as considerable inputs of plasticisers into the wider environment.

Plasticisers typically constitute 10-60% w/w of the item in which they are used, although this percentage is dependent on the application of the item, and they may also be only minor components (<1% w/w; Hansen et al., 2013). The most widely used class of plasticiser, the phthalates (aka. phthalic acid esters), have historically dominated the European and global plasticiser markets (e.g. phthalates alone accounted for 60% of the European plasticiser market in 2017; CEFIC 2018). However, a number of the most commonly used phthalates have demonstrated, or are suspected of, endocrine disrupting activity, which has led to their restriction for use in the EU in many applications (ECHA, 2022, 2018). This legislative pressure has been linked to a decline in the use of phthalates in Europe, e.g. phthalate market share decreased by over 25% between 2005 and 2017 (CEFIC 2018; Chapter 2). The decline in the use of these restricted phthalates has led to an increase in the use of so-called ‘emerging’ plasticisers, which may be higher-molecular weight phthalates not yet on the restriction list, or non-phthalate alternatives (CEFIC, 2021; Chapter 2). The most commonly used class of non-phthalate alternative are the terephthalates (12% of European market), although a diverse range of compounds are also used as replacements, e.g. citrates, trimellitates, and adipates (Chapter 2).

Despite suspected endocrine disrupting activity and genotoxicity of phthalates, there is little information concerning the occurrence, fate, and potential impacts of emerging plasticisers in the terrestrial environment (Chapter 2). Given that the function of plasticisers is identical, plasticiser compounds have many similar properties irrespective of chemical class, and thus the challenges surrounding the fate and impact of phthalates in the environment may also be relevant to some emerging non-phthalate alternatives (Chapter 2). Thus, one of the overarching focuses of this study was to evaluate the differences and similarities in the occurrence and behaviour of legacy (i.e. phthalate) versus emerging plasticisers. Additionally, there is almost no empirical information regarding the occurrence of plasticisers in the UK environment. Thus, two environmental studies were carried out during this project to begin to narrow these knowledge gaps. The rationale and background behind each study is discussed in detail in the respective chapters.

1.2 Selection of plasticiser analytes

It is through the lens of changing patterns of use of ‘legacy’ phthalate and ‘emerging’ plasticisers that the analytes in this study were selected. A literature review was conducted which identified the major classes of plasticiser based on production volumes and significance from an environmental pollution perspective (Chapter 2). This informed the selection of a suite eight phthalate and four non-phthalate plasticisers that were the focus of the majority of analyses in this project (Table 1.1).

Table 1.1: The eight phthalate and four emerging plasticisers selected for investigation in this project, including associated physiochemical properties.

Name and acronym		Class	CAS	Formula	Log K_{OW}	S_{H2O} (mg L^{-1})
Dimethyl phthalate	DMP	Phthalate	131-11-3	$C_{10}H_{10}O_4$	1.61 [A]	4000 [B]
Diethyl phthalate	DEP	Phthalate	84-66-2	$C_{12}H_{14}O_4$	2.54 [A]	1080 [B]
Di-iso-butyl phthalate	DiBP	Phthalate	84-69-5	$C_{16}H_{22}O_4$	4.27 [A]	6.2 (24 °C) [B]
Di-n-butyl phthalate	DnBP	Phthalate	84-74-2	$C_{16}H_{22}O_4$	4.27 [A]	11.2 [B]
Benzyl butyl phthalate	BBP	Phthalate	85-68-7	$C_{19}H_{20}O_4$	4.7 [A]	2.69 [B]
Diethylhexyl phthalate	DEHP	Phthalate	117-81-7	$C_{24}H_{38}O_4$	7.73 [A]	0.27 [B]
Di-n-octyl phthalate	DnOP	Phthalate	117-84-0	$C_{24}H_{38}O_4$	7.73 [A]	0.022 [B]
Di-iso-decyl phthalate	DiDP	Phthalate	26761-40-0	$C_{28}H_{46}O_4$	9.46 [A]	0.28 [B]
Diethylhexyl adipate	DEHA	Adipate	103-23-1	$C_{22}H_{42}O_4$		0.78 (22 °C) [B]
Diethylhexyl terephthalate	DEHTP	Terephthalate	6422-86-2	$C_{24}H_{38}O_4$		4.0 (20 °C) [B]
Acetyl tributyl citrate	ATBC	Citrate	77-90-7	$C_{20}H_{34}O_8$		1.7 [B]
Trioctyl trimellitate	TOTM	Trimellitate	3319-31-1	$C_{33}H_{54}O_6$		3.9×10^{-4} [B]

[A](Net et al., 2015); [B]PubChem online database.

1. Introduction

The suite of plasticisers was designed to cover a wide range of physiochemical properties (e.g. $\log K_{OW}$, chain length, degree of chain branching, molecular size and functional groups), to enable us to investigate intra- and inter-class variations in occurrence and fate. The emerging non-phthalate plasticisers were selected as exemplars of four different classes of plasticiser, namely trimellitate, adipate, citrate and terephthalate.

A method for the simultaneous extraction and analysis of these 12 plasticisers was developed. Briefly, soils of similar type to the test soils were spiked with known concentrations of all target plasticisers. Microwave-digest was used in conjunction with a variety of solvents and solvent mixtures (e.g. DCM, hexane, DCM:acetone 9:1 v/v) to test the extraction efficiencies of the different solvents and the microwave-digest on the spiked test soils. Minimum recovery values of target plasticisers were compared to identify the optimal extraction method and solvent. For most samples, clean-up through automated size-exclusion chromatography was also used prior to instrumental analysis. Clean-up was necessary in order to minimise matrix interferences during analysis which could reduce sensitivity and specificity of the method. Plasticisers were analysed using gas chromatography-mass spectrometry (GC-MS). Optimisation of instrument parameters such as inlet temperature, detector gain, GC oven temperature ramps, dwell time, injection volume, and injection type (split/splitless), was carried out in order to give optimal combination of chromatographic separation and signal intensity across all compounds. All samples were spiked with deuterium-labelled recovery standards to enable routine monitoring of extraction efficiencies. Plasticiser concentrations were recovery-corrected based on the recovery of labelled plasticisers. At least one procedural blank was carried out with each extraction of plasticisers, and plasticiser concentrations were blank-corrected using the value in the blank (or mean value if multiple blanks were carried out). Deuterium-labelled phthalate internal standards were used to correct for e.g. differences in analyte response due to matrix effects in all samples and calibration standards. All target plasticisers and labelled recovery plasticisers were quantified using multi-level external calibration using standard calibration solutions (Sigma-Aldrich, USA). Only regression lines with $R^2 > 0.99$ were used for quantification (minimum 5 calibration levels). The precise details of the methods used for each study (e.g. extraction and clean-up procedures, instrumental parameters, quality assurance, contamination controls) are described in each chapter.

1.3 Research aims and objectives

The overarching aims of this project were to investigate the sources, occurrence and fate of plasticisers in the UK, and examine how the environmental profiles and fate of ‘emerging’ plasticisers compare to those of ‘legacy’ phthalate plasticisers. Field studies of UK terrestrial and estuarine environments were used in conjunction with laboratory studies to achieve these aims. Specifically, the project involved the following objectives:

- Identify knowledge gaps concerning the input rates, sources, concentrations, persistence, and ecological impacts of phthalate and emerging plasticisers in terrestrial, estuarine, and coastal environments.

- Examine the sources, occurrence, and profiles of macroplastics, microplastics, and phthalate and emerging plasticisers in the English terrestrial environment under different land uses, and the relationships between these contaminants.

- Investigate the effects of soil type and soil properties on the rate and extent of release of a plasticiser from microplastics directly into soil.

- Quantify and compare the degradation kinetics of phthalate plasticisers and emerging non-phthalate plasticisers in soils and investigate the effects of soil type on the persistence of these plasticisers in soils.

- Investigate sources and spatiotemporal variation of plasticiser occurrence in sediments in the Firth of Forth estuary and neighbouring coastal area in Scotland, UK.

1.4 Thesis outline

This PhD project was carried out in conjunction with the UK Centre for Ecology and Hydrology (UKCEH) between October 2019 and June 2023. The author spent 15 months at the UKCEH site at Wallingford, UK, where the majority of the evidence collation, experimental work, field sampling, and microplastic analysis was carried out (including during multiple periods of coronavirus lockdown). The remaining 30 months were spent at UKCEH Lancaster, where method development for the extraction and analysis of plasticisers from soils and sediments was conducted, in addition to the measurements of plasticisers in all samples collected during the project. The sediment samples discussed in Chapter 6 were collected by colleagues at the UKCEH site at Edinburgh as part of a wider project (see *Statement on research collaboration*s).

Chapter 2 is a literature review with a detailed discussion of the sources of plasticisers and micron-scale plastic pollution in soils and how this may be linked to plasticiser occurrence. Data from over 40 published studies on the occurrence of plasticisers in soils was collated to provide a systematic assessment of total plasticiser abundance as well as occurrence data for over 20 individual plasticisers. In addition, the factors affecting the persistence of plasticisers in soils and their fate in soil organisms are discussed. The review finishes with a synthesis of information to identify knowledge gaps in the field. This chapter serves to provide background detail and context for Chapters 3 and 4.

Knowledge gaps concerning the sources of plasticisers in soils that were identified in Chapter 2 are investigated in **Chapter 3**. This chapter details the results of a field study investigating the presence of soil-surface plastics, and soil-interred microplastics and plasticisers in soils from a variety of land uses. In quantifying plasticisers in soil samples, this study focuses not only on established compounds such as phthalates, but also considers emerging (non-phthalate) plasticisers. The relationships found between the various measured contaminants are also discussed, to provide insights into the sources of plasticisers and microplastics in the soil environment.

The relationship between plasticiser occurrence and soil microplastics is then investigated further in **Chapter 4**. This chapter discusses the findings of a laboratory experiment of the rate of release of an emerging plasticiser from microplastic pellets into natural soils spanning a range of chemical and physical properties (e.g. pH, organic matter content). The kinetics of the degradation of a suite of phthalate and non-phthalate emerging plasticisers are also compared. Chapter 4 ends with a discussion of the implications of the rapid release and persistence of some emerging plasticisers in the terrestrial environment.

Chapter 5 provides a detailed discussion of the current knowledge of the sources and entry pathways of emerging and legacy plasticisers in estuaries and near-shore environments. This is followed by a thorough overview of the chemical behaviour of plasticisers in these environments, specifically the mechanisms controlling the release of plasticisers from plastic items (e.g. microplastics), and their partitioning between water and sediment. This chapter synthesises information regarding the occurrence of both legacy and emerging plasticisers to provide a detailed picture of the overall plasticiser contamination in estuarine and coastal waters and sediments. The state of the field concerning the persistence of these compounds in sediments and water, and their uptake and effects in biota, is examined. Chapter 5 finishes by bringing together the available information to highlight important knowledge gaps and recommend key research needs.

The results from an environmental study of the levels of plasticisers in sediments of the Firth of Forth estuary are presented in **Chapter 6**. This chapter, in conjunction with Chapter 5, provides an insight into the fate of plasticisers in sediments compared to the soil environments studied in Chapters 2-4. The patterns and profiles of plasticisers in the sediments are discussed, alongside analysis of variations in spatial and temporal plasticiser occurrence within the estuary. These patterns are explained through discussion of plasticiser sources and wider estuarine chemical and physical processes. Consideration is also given to the implications of plasticiser contamination on the estuarine and coastal organisms resident in the Firth of Forth.

The results discussed in Chapters 2-6 are synthesised and placed in a wider context in **Chapter 7**. This chapter draws together the conclusions from the project as a whole. Further, areas for future study arising from the findings in the project are also discussed.

2

Plasticisers in the terrestrial environment: sources, occurrence and fate

2. Plasticisers in the terrestrial environment: sources, occurrence and fate

Abstract

Modern society is widely dependent upon plastic. Therefore, it is unsurprising that macro- and microplastic pollution is found in every environmental compartment on earth. Plasticisers are chemicals added to plastics to increase their flexibility. Like plastics themselves, plasticisers are also widely present in the environment. Plasticisers and plastic debris may undergo long-range transport in the atmosphere and the oceans, contaminating even the most remote areas of land. In addition, although plasticisers typically degrade in a matter of weeks-months, they can persist in soil for decades and have been shown to occur in all land uses studied. Some plasticisers are genotoxic and can be taken up by soil organisms, which may pose a risk to ecosystem and human health. To date the majority of data on plasticisers exists for phthalates. However, plasticisers are a diverse range of chemicals and with the increasing transfer to non-phthalate alternatives, research into the fate and effects of emerging plasticisers is required in order to determine their environmental risk and management options. Data on the occurrence and ecotoxicity of emerging plasticisers, in addition to the impacts of all plasticisers on terrestrial ecosystems, therefore, remains a key research need within the wider plastics debate.

2.1 Introduction

Ever since the mass production of consumer plastic goods began in the mid-20th century, large items of plastic litter have left a clear visible legacy in the landscape. However, the true extent to which plastic pervades the environment came with the recognition of the microscopic fraction of plastic waste that had, until the early 21st century, remained largely unstudied. The term microplastic was coined in 2004 (Thompson et al., 2004), and formally defined as ‘plastic particles smaller than 5 mm’ (Arthur et al., 2009). The additional terminology of nanoplastics was later added, with a size range of 1-100 nm being recognised as a definition (Koelmans et al., 2015; Potočnik, 2011). The usage of these terms has evolved as the diversity in chemical and physical properties of microscopic plastic waste has become apparent, and there is an ongoing debate about how best to define and categorise these contaminants (Hartmann et al., 2019; Rochman et al., 2019). This emerging additional fraction of plastic waste adds to the visible burden of macroplastics as sources of plasticisers in the environment.

Research has shown that almost every environmental compartment on earth is contaminated with plastic (Bergmann et al., 2017; Büks and Kaupenjohann, 2020; Hendrickson et al., 2018; Horton et al., 2017a; Howell et al., 2012). The majority of research to date has focussed on aquatic, particularly marine, environments, whilst the occurrence of microplastics in soils has only recently started to generate research interest. The scarcity of soil studies is partly due to the analytical challenges associated with the extraction and identification of microscopic particles from such a heterogeneous matrix (Möller et al., 2020). Despite this, there is growing evidence of widespread microplastic contamination of the terrestrial environment (Scheurer and Bigalke, 2018; Zhang and Liu, 2018; Zhou et al., 2020b).

Assessment of the impact of plastic waste on the terrestrial environment has tended to focus on the ecotoxicology of microplastic particles themselves. Laboratory studies have reported that microplastics can adversely affect soil fauna. For example, negative impacts on survival (Cao et al., 2017; Huerta Lwanga et al., 2016), biomass (Boots et al., 2019; Cao et al., 2017;

D. Zhu et al., 2018) and reproduction (Kim et al., 2019; D. Zhu et al., 2018) have been reported for terrestrial species including earthworms *(Eisenia fetida, Eisenia andrei, Lumbricus terrestris)*, collembola (*Folsomia candida*) and nematodes (*Caenorhabditis elegans*). The exposure doses used in many studies likely represent ‘worst case scenario’ environmental concentrations, although direct comparisons are uncertain due to a relative scarcity of environmental concentration data and inconsistencies in how such data is reported (Büks and Kaupenjohann, 2020). Some of these negative effects likely arise due to the physical damage caused by the microplastic particles to dermal surfaces or within the organism itself. However, in addition to these physical impacts, the chemically inert nature of polymers (da Costa et al., 2016) means that some of the toxicity indicated may not be due to the plastics themselves, but due to plastic-associated chemicals such as additives or other substances which may have become bound to the plastic following its release to the environment.

Plastics are typically composed of the base polymer doped with additives – compounds associated with, but not themselves part of, the polymer structure. These additives may be released from the polymer matrix over the lifetime of the plastic. Whilst there are many additives which may be incorporated in plastics, e.g. plasticisers, flame retardants, UV and heat stabilisers, pigments and colourants, biocides etc., plasticisers and flame retardants are used in the largest quantities. Plasticisers typically constitute 10-70% w/w of the plastic item in which they are used (Hansen et al., 2013), with flame retardants constituting 3-25% (Hahladakis et al., 2018). However, given that flame retardants are not exclusively used in plastics, making the attribution of their presence to plastics challenging, plasticisers are the focus of this review.

Given the vast and complex nature of the polymer industry, there are many plastics and additives which fill niches for very specific applications. As such, it is beyond the scope of this review to discuss every plasticiser produced on a commercial scale. Instead, we focus on the plastics and plasticisers that have environmental significance due to e.g. high production volumes, occurrence, toxicity, or likelihood for future use as replacements for legacy plasticisers such as phthalates. We begin by providing an overview of plasticiser compounds. This is followed by a discussion of the mechanics of plasticiser release into the terrestrial environment, in addition to the sources and occurrence of plasticisers in soils. We then discuss the persistence of plasticisers in soils, in addition to their uptake by soil fauna and flora. Finally, we discuss existing knowledge gaps and provide recommendations for future research.

2.2 Overview of plasticisers

2.2.1 Introduction and physiochemical properties

Plasticisers are substances added to plastics to increase their flexibility. In Europe, 1.35 million tonnes of plasticiser are consumed each year, whilst the global market is estimated to be 7.5 million tonnes (CEFIC, 2018). The vast majority (~85%) of plasticisers are used in polyvinyl chloride (PVC) (CEFIC, 2018), and typically account for 10-70% w/w of the plastic item (Hansen et al., 2013). Physiochemical data and chemical structures of 6 major classes of plasticiser are shown in Table 2.1 and Appendix Table S2.1 respectively.

Table 2.1: Physiochemical data for the 21 phthalates and 5 emerging plasticisers discussed in this review. Solubility in water is at 25 °C unless otherwise stated.

Name and acronym		Class	Formula	Vapour pressure (Pa)	Log K_{OW}	Log K_{OA}	Log K_{AW}	S_{H2O} (mg L^{-1})
Dimethyl phthalate	DMP	Phthalate	$C_{10}H_{10}O_4$	2.63 x 10^{-1} [A]	1.61 [A]	7.01 [A]	-5.4 [A]	4000 [C]
Diethyl phthalate	DEP	Phthalate	$C_{12}H_{14}O_4$	6.48 x 10^{-2} [A]	2.54 [A]	7.55 [A]	-5.01 [A]	1080 [C]
Dipropyl phthalate	DPrP	Phthalate	$C_{14}H_{18}O_4$	1.74 x 10^{-2} [A]	3.40 [A]	8.04 [A]	-4.64 [A]	77 (nr °C)
Di-iso-butyl phthalate	DiBP	Phthalate	$C_{16}H_{22}O_4$	4.73 x 10^{-3} [A]	4.27 [A]	8.54 [A]	-4.27 [A]	6.2 (24 °C) [C]
Di-n-butyl phthalate	DnBP	Phthalate	$C_{16}H_{22}O_4$	4.73 x 10^{-3} [A]	4.27 [A]	8.54 [A]	-4.27 [A]	11.2 [C]
Dimethoxyethyl phthalate	DMEP	Phthalate	$C_{14}H_{18}0_6$	3.04 x 10^{-2} [C]	1.11 [B]			8500 (nr °C) [C]
Di-n-pentyl phthalate	DnPP	Phthalate	$C_{18}H_{26}O_4$	1.28 x 10^{-3} [A]	5.12 [A]	9.03 [A]	-3.91 [A]	1.3 (nr °C)
Diethoxyethyl phthalate	DEEP	Phthalate	$C_{16}H_{22}O_6$		2.10 [B]			
Benzyl butyl phthalate	BBP	Phthalate	$C_{19}H_{20}O_4$	2.49 x 10^{-3} [A]	4.7 [A]	8.78 [A]	-4.08 [A]	2.69 [C]
Diphenyl phthalate	DPhP	Phthalate	$C_{20}H_{14}O_4$					
Dicyclohexyl phthalate	DCHxP	Phthalate	$C_{20}H_{26}O_4$	1.16 x 10^{-4} [C]	6.20 [B]			4.0 (24 °C) [C]
Di-n-hexyl phthalate	DnHxP	Phthalate	$C_{20}H_{30}O_4$	3.45 x 10^{-4} [A]	6.00 [A]	9.53 [A]	-3.53 [A]	0.159 (nr °C)
Dimethylpentyl phthalate	DMPP	Phthalate	$C_{20}H_{30}O_4$					
Di-n-heptyl phthalate	DnHpP	Phthalate	$C_{22}H_{34}O_4$	2.76 x 10^{-4} [C]	7.56 [C]			1.83 x 10^{-3} [C]
Hexyl ethylhexyl phthalate	HEHP	Phthalate	$C_{22}H_{34}O_4$		7.65 [B]			
Dibutoxyethyl phthalate	DBEP	Phthalate	$C_{20}H_{30}O_6$	2.89 x 10^{-1} [C]	4.06 [B]			
Diethylhexyl phthalate	DEHP	Phthalate	$C_{24}H_{38}O_4$	2.25 x 10^{-5} [A]	7.73 [A]	10.53 [A]	-2.8 [A]	0.27 [C]
Di-n-octyl phthalate	DnOP	Phthalate	$C_{24}H_{38}O_4$	2.52 x 10^{-5} [A]	7.73 [A]	10.53 [A]	-2.8 [A]	0.022 [C]
Di-iso-nonyl phthalate	DiNP	Phthalate	$C_{26}H_{42}O_4$	6.81 x 10^{-6} [A]	8.6 [A]	11.03 [A]	-2.43 [A]	0.2 (20 °C) [C]
Di-n-nonyl phthalate	DnNP	Phthalate	$C_{26}H_{42}O_4$	6.81 x 10^{-6} [A]	8.6 [A]	11.03 [A]	-2.34 [A]	1.73 x 10^{-5} [C]
Di-iso-decyl phthalate	DiDP	Phthalate	$C_{28}H_{46}O_4$	1.84 x 10^{-6} [A]	9.46 [A]	11.52 [A]	-2.06 [A]	0.28 [C]
Diethylhexyl adipate	DEHA	Adipate	$C_{22}H_{42}O_4$	1.13 x 10^{-4} [C]				0.78 (22 °C) [C]
Diethylhexyl terephthalate	DEHTP	Terephthalate	$C_{24}H_{38}O_4$	2.85 x 10^{-3} [C]				4.0 (20 °C) [C]
Acetyl tributyl citrate	ATBC	Citrate	$C_{20}H_{34}O_8$	4.00 x 10^{-2} [C]				1.7 [C]

Di-iso-nonyl cyclohexanoate	DiNCH	Cyclohexanoate	$C_{26}H_{48}O_4$					
Trioctyl trimellitate	TOTM	Trimellitate	$C_{33}H_{54}O_6$	$5.07 \times 10^{-4\ C}$				$3.9 \times 10^{-4\ C}$

[A](Net et al., 2015), [B](A. Hu et al., 2020), [C]PubChem online database.

The most commonly used class of plasticiser are the phthalic acid esters (aka. phthalates, PAEs). In 2017, phthalates accounted for 60% and 65% of the European and global plasticiser markets respectively. However, the use of phthalates in Europe is declining, with an estimated decrease in market share of over 25% between 2005 and 2017 (CEFIC, 2018). This change has been driven by concerns surrounding the potential endocrine disrupting properties of some phthalates, leading to restrictions on their use in the European Union (ECHA, 2018). The increased regulatory pressure on phthalates is leading to diversification of the market. Terephthalic acid esters (aka. terephthalates) such as diethylhexyl terephthalate (DEHTP) were a minor part of the European market in 2005, but in 2017 accounted for 12% of the European market (and 15% globally) (CEFIC, 2018). Other emerging classes of plasticiser include trimellitates (e.g. trioctyl trimellitate, TOTM), citrates (e.g. acetyl tributyl citrate, ATBC), adipates (e.g. diethylhexyl adipate, DEHA) and cyclohexanoates (e.g. di-iso-nonyl cyclohexanoate, DiNCH) (Table 2.1). Given the growing diversity in the classes of plasticiser being used in plastics, it is becoming increasingly important to assess not only the risk of phthalates in the environment, but the risk posed by emerging plasticisers, the vast majority of which have very little associated ecotoxicology or occurrence data.

Given that the function of all plasticisers is identical, these compounds have similar properties (Table 2.1). Plasticisers are generally viscous, lipophilic (and some highly lipophilic) and have low water solubility. For example, the four phthalates diethylhexyl phthalate (DEHP), di-n-butyl phthalate (DnBP), di-iso-butyl phthalate (DiBP) and benzyl butyl phthalate (BBP) have $\log K_{OW}$, $\log K_{OA}$ and $\log K_{AW}$ in the range 4.27-7.73, 8.54-10.53 and -4.27 to -2.80 respectively (Net et al., 2015). Plasticisers have boiling points >300 ^{o}C, in addition to very low vapour pressures, and therefore the gaseous release of these compounds from their liquid forms should be slow under environmental conditions.

2.2.2 Plasticiser release

Plasticisers are not chemically bonded to the polymer matrix, and so can migrate over time to the surface of the plastic particle, where they can be released in to the environment. The ability of a molecule to migrate is a pre-requisite for some applications, e.g. the controlled release of drug molecules from a polymer matrix (Liechty, 2010). However, unwanted migration of additives also occurs over the lifetime of a plastic item, e.g. into food products from contact material or from medical use materials (Fankhauser-Noti et al., 2006; Welle et al., 2005). The process of plasticiser migration into foodstuffs has been conceptualised as a sequence of 4 steps (Ferrara et al., 2001), but this summary can be generalised for any environmental medium (Figure 2.1).

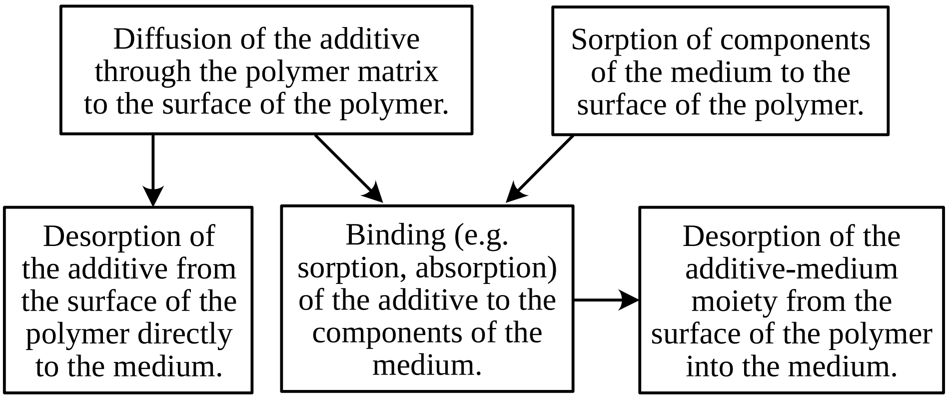


Figure 2.1: Migration and release processes for an additive into a medium.

Despite the apparent ubiquity of plastic in the terrestrial environment, to the authors' knowledge, there are no published studies which assess the release kinetics of plasticisers directly into soil under controlled conditions, although attempts have been made to quantify their release in aqueous media. For example, the effects of plastic weathering on the leaching rates of a wide range of additives, including some plasticisers, from polyethene, PVC and polyethene terephthalate (polyester) into freshwater and saltwater were determined in one study (Suhrhoff and Scholz-Böttcher, 2016). Salinity and UV light were associated with a clear increase in the total additive release in only one instance (a printed polyethene bag), with UV light appearing to reduce additive release in some cases. The effects of salinity were complex and appeared to be compound-specific, whilst the reduction of leached additive in some UV-exposed samples may have been caused by photodegradation of analytes. In contrast, turbulence significantly increased the total additive load in solution for all plastics, which was attributed to the continuous mixing of the solution preventing concentration gradients from forming at the plastic-solution boundary. Of all the target analytes, the plasticiser ATBC showed the highest leaching potential into ambient saltwater relative to its concentration in the test material (4.9% ATBC loss over 78 days from a sample of polyethene). ATBC also appeared to be associated with printed plastic, underlining the composite nature of many items of plastic waste. In contrast to ATBC, the leaching of phthalates from PVC over 57 days was low, e.g. DEHP leached just 0.083% of its initial concentration, although further research is needed to understand leaching kinetics over longer timescales. Whilst it remains challenging to study the aqueous release of inherently hydrophobic plasticisers, recent work has demonstrated that an “infinite sink” approach, which has been previously used to study aqueous release of polychlorinated biphenyls from plastic (Endo et al., 2013), could be applied successfully to the study of DEHP release from PVC (Henkel et al., 2019).

Despite the lack of environmental studies, there is a significant body of research on the release and leaching of plasticisers from food contact materials and medical use plastics. Given that the plastics and plasticisers used in these applications are likely to be similar, if not the same, as those entering terrestrial systems through e.g. mismanaged consumer waste or spent agricultural mulching films, the results of these studies can be used to predict and understand the dominant release processes relevant to the soil environment. In general, substances with lower molecular weights migrate from plastics at a faster rate as they can travel through the polymer matrix more freely to reach the polymer-matrix boundary (Hansen et al., 2013). In addition, plasticisers with a lower affinity for the polymer matrix are likely to have faster migration rates than those whose physiochemical properties are more similar to the polymer. Significant plasticiser migration occurs at higher lipid concentrations in the contact medium, whilst the leaching of plasticisers into aqueous media is very slow. This has been widely observed for phthalates in addition to emerging plasticisers (Bueno-Ferrer et al., 2010; Choi et al., 2018; Coltro et al., 2014; Goulas et al., 2007, 2000; Kastner et al., 2012; Nara et al., 2009; Pedersen et al., 2008). Despite the lack of published studies regarding the rates of plasticiser leaching to environmental media, the lipophilicity of plasticisers suggests that organic matter content and water holding capacity of a soil, in addition to soil water pH and ionic strength, will influence plasticiser leaching kinetics. Furthermore, this pattern has implications for the bioaccumulation and partitioning of plasticisers in animal tissues, although the fate of plasticisers within soil fauna is largely unknown. Leaching also shows a clear positive correlation with temperature (Hanušová et al., 2013), thus plasticiser releases through leaching may show clear seasonal and regional climate-associated trends.

Determining the relative leaching rates of plasticiser classes is made challenging by the absence of reference plastics with known plasticiser formulations and percentage weight concentrations. In addition, concentrations of plasticisers in commercially available plastic items used in kinetic comparison studies are sometimes not reported, despite the fact that plasticiser content is a limiting factor determining leaching rate (Bueno-Ferrer et al., 2010). In the existing food contact and medical use literature, the phthalate DEHP is typically compared with one or more emerging plasticisers, with DEHP often reported as the fastest migrating substance (Bernard et al., 2015; Eckert et al., 2016; Tüzüm Demir and Ulutan, 2013). DEHP may leach relatively quickly because it has a lower molecular weight than emerging alternative plasticisers such as trimellitates (Table 2.1 and S2.1), although further work is required to fully understand which physiochemical properties play the most important role in determining plasticiser migration, and how the relative importance of these properties may be affected by the contact medium or polymer type. Nevertheless, multiple studies have found the high molecular weight trimellitate plasticiser TOTM to leach very slowly in comparison to other tested plasticisers (Bernard et al., 2015; Suhrhoff and Scholz-Böttcher, 2016; Welle et al., 2005), suggesting that molecular weight is indeed an important factor controlling migration rate. For example, TOTM leached just 0.23% of its initial content in PVC into a 1:1 ethanol:water solution after 10 days, and relative leaching rates were in the order DEHP>DiNCH>DEHTP>TOTM (Bernard et al., 2015). An earlier study reported rates in the order ATBC>DEHP>DiNCH>TOTM, with the citrate plasticiser ATBC detected at concentrations exceeding an order of magnitude higher than DEHP, in spite of the fact that ATBC was present in the lowest amounts in the test samples (Welle et al., 2005). In addition, ATBC was detected in a jarred foodstuff at 60 µg g^{-1}, despite being present in the lid at a low concentration (0.9% w/w), which implies high mobility (Fankhauser-Noti et al., 2006). Consequently, this plasticiser was more frequently detected than 4 phthalates in plastic-packaged foodstuffs (García Ibarra et al., 2018). Thus, these studies indicate that some of the emerging plasticisers may have significantly higher leaching capabilities than phthalates, even though the latter group are generally the only plasticiser class targeted in terrestrial occurrence and bioaccumulation studies.

In addition to plasticiser properties, the density and flexibility of the plastic polymer chains themselves can also affect plasticiser leaching rates (Hansen et al., 2013). Polymers with high glass transition temperatures generally have less migration, as the polymer chains are less free to move. In addition, plasticisers within crystalline polymer matrices or those with greater crosslinking and branching will migrate slower than those in polymers with amorphous structures, as there are smaller spaces between polymer chains through which molecules may travel. The effects of plastic properties on plasticiser migration rate have clear implications for understanding how plastics may act as plasticiser sources in the environment. For example, a crosslinked, branched polymer with a high glass transition temperature is more likely to act as a persistent, low-level input of plasticisers than a straight-chain, low glass transition temperature polymer which may produce a more rapid release.

The first step towards resolving the uncertainty surrounding plasticiser leaching in the terrestrial environment should be identifying the plastics which have the greatest potential for plasticiser release, in addition to the fates and sink areas of these plastics in the environment. This could be achieved through a systematic study of common polymers under controlled conditions in order to begin to understand the general trends that could lead to particularly high rates of leaching, thus allowing future work to target plastics or plasticisers which appear to be of particular concern. The vast majority of plasticisers are used in PVC, although this polymer is rarely reported in terrestrial occurrence studies (Büks and Kaupenjohann, 2020). Therefore, the contribution of polymers such as polyethene and polypropene to total terrestrial plasticiser load may be greater than initially expected given their low plasticiser content. Leaching characteristics of a set of common polymers directly into a suite of soils with contrasting properties should be determined, in addition to the influence of plastic particle size and morphology (e.g. film, fibre etc.) on leaching rate. This data, in conjunction with data on environmental plastic waste occurrence, could be used to identify plastics of particular concern to gauge the nature and scale of potential plasticiser sources. In addition, experiments to determine leaching rates of different plasticiser classes and the effects that soil properties, e.g. pH, organic matter content, clay content etc., have on plasticiser leaching rate are critically needed, as the trends observed in the food contact and medical use literature may not hold true for more complex media such as soils. Weathering of polymers through climate (e.g. UV light) or organism-driven processes may also determine the release of plasticisers to the environment, although long-term field experiments are required in order to identify and quantify the nature of such effects.

2.3 Sources of plasticisers in the terrestrial environment

Given the ubiquity of plastic waste in the environment, the leaching of plasticisers from plastic debris likely represents a common, diffuse source of plasticiser into the environment. For example, we estimate that the total annual input of plastic waste to continental (terrestrial and freshwater) environments in the EU and the UK to be 130 kg of plastic per km^2 (Horton et al., 2017b; World Bank, 2017). In addition to this widespread source, input of plasticisers may occur through intensive plastic use and management activities associated with point sources. The relative contribution of these sources to the total terrestrial plasticiser load has yet to be estimated, although given the levels of plastic litter often seen in terrestrial environments, it is reasonable to assume that the diffuse route may account for the majority of plasticiser occurrence in wider soils. Therefore, in order to understand the sources of plasticisers in the terrestrial environment, an understanding of plastic sources and occurrence is necessary given the likely intrinsic link between plastic presence and plasticiser inputs.

2.3.1 Urban areas

Plastic litter represents the most visible and obvious possible source of microplastics and plasticisers in soils. This waste will be generated and concentrated primarily in urban areas, particularly in countries without widespread formal waste disposal networks, and such areas have indeed been identified as hotspots of plasticiser occurrence (Hongjun et al., 2013). The weathering of plastic debris may indirectly increase the input of plasticisers to soils, e.g. consumer goods such as food packaging films become fragmented in the environment, increasing their surface area and leaching potential (Horton et al., 2017b). Whilst plastic items are primarily used and disposed of in urban areas, many items of large plastic waste, and especially primary or secondary microplastics, may be transported long distances to areas without a distinct plastic input by short- and long-range aerial transport, human activities and overland water flows (Horton and Dixon, 2018). Therefore, diffuse plastic litter likely accounts for most of the widespread chronic input of plasticisers in soils at sites away from areas of immediate input (see below - *Multimedia transport as a route to land*).

The majority of plasticised items are used in urban areas. This includes those associated with consumer items and packaging and also larger-scale structural materials. The latter includes wires, cabling, flooring and wall coverings which together account for 45% of plasticiser use in Europe, compared to only 13% of plasticisers that are used in consumer goods and industry (CEFIC, 2018). Many of these plasticised items will be used in a single location for a long period of time prior to disposal, and thus may provide a steady input of plasticisers into the environment. In addition, the vast majority of plasticisers are used in PVC, which is widely used in e.g. building fittings and municipal water pipes, although many of these applications use rigid PVC which has a lower plasticiser content than more pliable PVC-based materials. Transport infrastructure can also act as a significant source of plastics, and therefore plasticisers. Soils in the vicinity of roads receive plastic contamination, e.g. mismanaged plastic litter or particles produced during the mechanical wear of tires against the road surface, known as tire-wear particles (TWPs) (Knight et al., 2020; Wagner et al., 2018). The compositions of TWPs are incredibly complex, although the potential for TWPs to act as sources of plasticisers in soils remains unexplored.

Multiple studies have linked urban activity with increased phthalate concentrations (Hongjun et al., 2013; Škrbić et al., 2016; Sun et al., 2016; Zeng et al., 2008; Zhang et al., 2014). However, not all studies have identified a clear link between urban activity and plasticiser loading. For example, an extensive survey of DEHP in Scottish soils from various land uses found no consistent link between DEHP contamination and distance from urban areas (Rhind et al., 2013a). Many urban areas will see a complex pattern of inputs from many sources, e.g. horticulture, waste disposal and industry. Further work is required to pull apart and enumerate the extent to which these inputs contribute to plasticiser occurrence in urban soils. Studies which measure diverse suites of plasticisers, in addition to exploiting continuing improvements in the ability to extract and identify the microplastic composition of soils (Möller et al., 2020), are needed to better establish the nature of these links.

2.3.2 Waste disposal sites

Landfills are the ultimate disposal site for a large proportion of plastic waste, however the extent to which such sites act as a source of plasticiser contamination to the wider soil environment remains unclear. For example, the mean total phthalate concentration ($\sum_{16}$ phthalates) of soils on a landfill site in China was 4.22 µg g^{-1} [1], but the contamination in adjacent topsoils (0.68 µg g^{-1}) was significantly lower than many agricultural and urban soils in similar study areas (Liu et al., 2010). Thus, plasticisers associated with the landfill seemed to be retained *in situ*. Total mean phthalate concentration ($\sum_{5}$ phthalates) in soils in the vicinity of landfill in 4 Indian cities was also low, at 0.093 µg g^{-1} (Chakraborty et al., 2019), although in contrast the adipate plasticiser DEHA was present at 0.057 µg g^{-1}, suggesting that this substance may have higher mobility than some phthalates. In some instances, intense bacterial activity may cause landfills to act as sinks of plasticiser degradation, rather than being a significant source. For example, the phthalates DEHP, diethyl phthalate (DEP), DnBP and BBP were found in only 29-47% of leachates from primarily municipal landfills in 4 European countries, and dimethyl phthalate (DMP) was not detected at all (Jonsson et al., 2003), but there was widespread presence of phthalate monoesters in the leachates, at significantly higher concentrations. The results of one study suggest that downwards penetration of landfill leachates may act as a source of plasticisers in groundwater. Total phthalate concentration ($\sum_{16}$ phthalates) in groundwater associated with a landfill site was over 3.5 times higher than

---

[1] Plasticiser concentrations discussed in the text have, where possible, been quoted with either dw or ww to indicate whether they refer to dry or wet weight values respectively. However, this information was not reported in all studies.

in the surface water (6.35 µg L^{-1} vs 1.78 µg L^{-1}), despite the fact that the landfill was lined with a geomembrane (Liu et al., 2010). However, this difference may be driven by significantly slower biodegradation of phthalates in groundwater as opposed to surface water, as phthalate degradation is less rapid under anaerobic conditions (Shanker et al., 1985).

Sites of electronic waste (e-waste) processing, particularly in countries with informal e-waste recycling sectors, appear to represent a much greater phthalate input than standard domestic waste landfills in terms of both abundance and diversity of congeners. Mean total phthalate concentrations ($\sum_5$ phthalates) were over 4 times higher at e-waste processing sites than at landfills in 4 Indian cities (0.396 vs 0.093 µg g^{-1}). Plasticiser contamination was especially concentrated at sites where precious metal recovery occurred, which may be attributed to the fact that such sites could be associated with plastic incineration (Chakraborty et al., 2019). A further study of phthalates in soils near a large e-waste processing site by Zhang et al. (2019) also provided clear evidence of airborne transport of phthalates released during plastic-containing e-waste incineration. Soil potentially affected by these inputs exhibited a profile of phthalates not seen in agricultural soils, with the occurrence of dibutoxyethyl phthalate (DBEP, 4.49 µg g^{-1} dw), dimethylpentyl phthalate (DMPP, 2.88 µg g^{-1} dw) and dicyclohexyl phthalate (DCHP, 1.66 µg g^{-1} dw), whilst common phthalates such as DnBP and DEHP were found at concentrations of 1.92 µg g^{-1} dw and 1.05 µg g^{-1} dw respectively. Exceptionally high levels of phthalate contamination ($\sum_5$ phthalates), ranging from 12.6-46.7 µg g^{-1} dw, were also found in soils from 3 e-waste processing sites in China, further indicating the potential of such sites as sources of plasticiser release (Liu et al., 2009).

2.3.3 Plastic use in agriculture

The vast majority of plastic used in agriculture is used in China (Espí et al., 2006), although use is also common in other regions. Of the 23 studies discussed by Büks and Kaupenjohann (2020) in their recent review of terrestrial microplastic occurrence, 11 were for Chinese soils, 6 European, 4 from the Americas, 1 from Iran and 1 from Australia. Of the 14 studies which conducted polymer identification, only 5 detected PVC, the polymer with the highest plasticiser loading. Furthermore, even when identified, PVC was at lower levels than other widely used consumer polymers (Chen et al., 2020; Ding et al., 2020; Fuller and Gautam, 2016; Ljung et al., 2018; Lv et al., 2019). The most commonly detected polymers in soils are polypropene and polyethene, with these two polymers dominating microplastic profiles (Liu et al., 2018; Lv et al., 2019; Yu et al., 2021). A caveat on these results of polymer presence is that microplastic extraction procedures typically employ a density separation step to separate microplastics from soil particles. Of terrestrial microplastic concentration studies, 30% employed a density separation in either water (ρ=1.0 g mL^{-1}) or NaCl solution (ρ=1.2 g mL^{-1}). Density separation can preclude the effective recovery of polymers such as PVC and polyester as these polymers have ρ>1.2 g mL^{-1}. However, even in the studies that used density separation with a media theoretically capable of floating PVC, this polymer was still detected in only 3 out of 8 studies (Büks and Kaupenjohann, 2020). Thus, as polyethene and polypropene, and not PVC, appear to dominate soil microplastic profiles, the majority of plasticiser input from microplastics into agricultural soils will derive from widely dispersed but low-level leaching from these widely used polymer types.

A diverse range of plastic items are commonly used in agriculture, e.g. polytunnels, bale wrappings, irrigation tubing, twine etc, although plastic mulches have received the most interest as a source of microplastics and plasticisers in soils. Mulches often cover entire fields and may contain plasticisers in small proportions (Steinmetz et al., 2016). An individual sheet is typically used for a matter of months and may simply be ploughed back into the field at the end of its useful life. As such, plastics may accumulate in soils where mulch is reapplied on an annual or even-sub annual basis. Studies have reported positive correlations between the mass of plastic mulch used and microplastics recovered from agricultural soils, in addition to higher levels of microplastic abundance at sites with a longer history of mulch use (Huang et al., 2021, 2020; Yu et al., 2021).

Phthalate profiles of mulched agricultural soils are dominated by DEHP, and to a lesser extent DnBP, DiBP and di-n-octyl phthalate (DnOP), although the exact suite of target phthalates differs between studies (Chai et al., 2014; Hu et al., 2003; Kaewlaoyoong et al., 2018; Kong et al., 2012; J. Wang et al., 2013; Zeng et al., 2020). In addition to DEHP, DnOP in particular appears to be linked to agricultural plastic in some cases. E.g. DEHP and DnOP were substantially more abundant than other targeted phthalates in agricultural plastic products on the Taiwanese market (e.g. DnBP was not present in mulch at all), and phthalate profiles of mulched soils resembled those found in the plastic products (Kaewlaoyoong et al., 2018). In addition, DnOP was found to be almost 6 times as abundant in mulched non-vegetable soils than non-mulched, whilst concentrations of DMP, DEP and DEHP were only marginally higher (9.7%-26.9%) (Kong et al., 2012). However, this pattern was reversed in mulched vegetable soils, indicating that the type of mulch used may affect the profile of phthalates found in soils. This indicates the need for greater knowledge of the range and composition of mulched material in order to develop an understanding of the potential inputs of different plasticisers into soils.

Based on widespread use and localised input potential directly to soil, there is strong evidence that plastic mulch is positively correlated with, and likely causes, increased phthalate concentrations in soils (Hu et al., 2003; Kong et al., 2012; Sun et al., 2016; J. Wang et al., 2013; X. Wang et al., 2013; Zeng et al., 2020; Zhang et al., 2015). For example, individual concentrations of all 6 targeted phthalates were between 62%-6439% higher in mulched vegetable soils than in non-mulched soils in one Chinese study (Kong et al., 2012). Similarly, total phthalate concentrations ($\sum_{16}$ phthalates) were significantly higher in Chinese agricultural facilities where mulch was used (2.25 $\mu g\ g^{-1}$ dw) than in mulch-free facilities (1.25 $\mu g\ g^{-1}$ dw) (Zeng et al., 2020). The effect of seasonal mulch use was also investigated in one study (Zhang et al., 2015), with total phthalate concentrations ($\sum_{15}$ phthalates) peaking in the summer. This was associated with a period of increased mulch use, and possibly coincided with greater leaching of phthalates due to higher ambient temperatures. However, although there is a potential association of phthalate release with climate, it is not possible to attribute such seasonal variation entirely to higher temperatures, as summer also sees increased fertiliser application and greater irrigation, both of which may increase phthalate input.

Whilst there is reasonably good evidence linking mulch use to plastic load and soil plasticiser levels, the evidence for the role of other agricultural plastic products in determining plastic associated loading to soils is less well established. For example, the use of polytunnels does not appear to increase either microplastic or plasticiser abundance in soils. For instance, a recent study found that polytunnel use was not associated with a significant difference in microplastic abundance when compared to non-polytunnelled sites (Yu et al., 2021). No significant difference was found between phthalate soil concentrations in greenhouses and open fields (Zeng et al., 2020). Sites which used a combination of mulch and polytunnels had significantly higher phthalate concentrations than sites which used polytunnels alone, although a shorter cultivation history in polytunnel-only sites likely accounted for some of this difference (J. Wang et al., 2013).

2.3.4 Wastewater treatment products in agricultural soils

The wastewater treatment (WWT) process involves removing particulates and chemicals from the influent before releasing the treated effluent into water courses. Solids removed during this process are referred to as biosolids or sewage sludge, and it is here that plastics and plasticisers entering the WWT plant will generally become concentrated (Ball et al., 2019; Gibson et al., 2005; Y.S. Lee et al., 2019; Simon et al., 2018). A recent study of UK WWT plants found that less than 0.01% of influent microplastic particles were released in the effluent. The remainder partitioned into sludge, with no clear difference in the extent of this separation between polymer types (Ball et al., 2019). Similar removal efficiencies (>99%) of microplastics to sludge have also been reported in Danish WWT plants, indicating the dominance of sludge as the sink for particles during treatment (Simon et al., 2018).

The removal of plasticisers during the WWT process is both better studied and potentially more complex than the partitioning of plastics. Whilst some modern WWT plants use a combination of processes which can degrade phthalates at levels between 80-100% (Gao and Wen, 2016), plasticisers still become highly concentrated in sludge (Gibson et al., 2005; Y.S. Lee et al., 2019; Tran et al., 2015) and may also be present in effluent (Y.S. Lee et al., 2019; Zolfaghari et al., 2014). The partitioning of plasticisers to sludge is strongly influenced by their K_{OW} and molecular weight (M_W), with the majority of low M_W plasticisers (e.g. DMP) released in effluent, but upwards of 90% of higher M_W plasticisers (e.g. DEHP) bound to sludge (Y.S. Lee et al., 2019). This indicates that both effluent and sludge can act as a source of plasticisers to surface water and soil, although the extent may be congener specific.

In many countries, sewage sludge is applied to agricultural land as a soil enhancer in considerable quantities, e.g. 80% of the UK's sewage sludge is spread on agricultural soil (DEFRA 2012). Hence, this route represents a potentially significant source of plastics and plasticisers in the soil environment (Büks and Kaupenjohann, 2020; Tran et al., 2015). Due to challenges and inconsistencies between extraction and analytical methodologies, estimates for microplastic concentrations in sewage sludge vary widely, from 10s to 1000s of microplastics per g dry sludge (Ball et al., 2019; Crossman et al., 2020; Liu et al., 2019; Talvitie et al., 2017; Zubris and Richards, 2005). Polyethene and polypropene, and to a lesser extent polyester and nylon, dominate the microplastic profiles of sewage sludges (Ball et al., 2019; Crossman et al., 2020; Vollertsen and Hansen, 2017). The absence of PVC, which often has a very high plasticiser load, amongst the commonly detected polymers suggests that the plastic burden in sludge may result in lower plasticiser soil inputs than would be expected from a simple assessment based on production volume analysis (CEFIC, 2018).

Historically DEHP and DnBP have been the dominant phthalates detected in sewage sludge. DEHP and DnBP were detected in every sludge sample investigated in a study of German WWT plants, at 28-154 $\mu g\ g^{-1}$ dw and 0.2-1.7 $\mu g\ g^{-1}$ dw respectively (Fromme et al., 2002), and accounted for 79% and 18% of the total phthalate concentration ($\sum_{16}$ phthalates) of sewage sludge from Chinese WWT plants (Meng et al., 2014). DEHP was detected at 62.5 µg g^{-1} and accounted for >95% of total phthalates ($\sum_6$ phthalates) in UK sewage sludge (Gibson et al., 2005) and was also detected at comparable levels (27.54-51.03 µg g^{-1}) in 5 Chinese sewage sludge samples (Cheng et al., 2010). The 3 most abundant plasticisers detected ($\sum_9$ phthalates) in sludge from a French WWT plant were the high M_W phthalates DEHP (~12.5 µg g^{-1} dw), di-iso-nonyl phthalate (DiNP, ~10 µg g^{-1} dw) and di-iso-decyl phthalate (DiDP, ~5 µg g^{-1} dw) (Tran et al., 2015). These levels are consistent with those from both the UK and Chinese studies, indicating a widespread and consistent nature of inputs of the dominant phthalate congeners into wastewater systems.

A recent study of sludge from WWT plants in South Korea ($\sum_{16}$ phthalates, $\sum_5$ emerging) found that emerging plasticisers are present in sludge in comparable levels to phthalates (Y.S. Lee et al., 2019). This demonstrates that sewage sludge may represent an input of emerging plasticisers into soils. DEHP had the highest mean concentration of any plasticiser (71 µg g^{-1} dw), followed by the terephthalate DEHTP (25 µg g^{-1} dw). Mean concentrations of other emerging plasticisers (DiNCH, ATBC, DEHA and TOTM) were considerably lower, ranging from 0.34-1.2 µg g^{-1} dw, although these substances were present in comparable quantities to commonly reported phthalates such as BBP, DnBP and DiBP, indicating their importance to wider plasticiser loading in sludge.

Despite considerable microplastic concentrations in sewage sludge, the extent to which repeated sludge application leads to long-term accumulation of plastics in soils remains unclear. A recent literature review noted that agricultural soils with a history of sludge application generally have microplastic concentrations ~1 order of magnitude higher than soils not receiving sludge inputs (Büks and Kaupenjohann, 2020). However, limited data, analytical challenges and the potential for local-scale factors to influence results precludes a definitive conclusion on the link between repeat input and microplastic loads. For example, a recent study estimated that over 99% of the applied microplastic load was not retained in the soil, and only 1 out of 3 sites demonstrated a net gain of microplastics at ~6 months after the application of sewage sludge (Crossman et al., 2020). This was attributed to a prolonged period of unusually heavy rainfall following sludge spreading, leading to considerable losses of soil microplastics due to e.g. surface runoff. Further work is required to elucidate the effects of climate and land management practices on the long-term accumulation of plastic in sludge-amended soils.

Sewage sludge application has been more clearly linked with both the accumulation and long-term persistence of plasticisers in soils, although evidence to date is limited to phthalates. DEHP levels in soils with a 13-year history of sludge application were ~4 times higher than controls (0.22 µg g^{-1} dw vs 0.06 µg g^{-1} dw) (Rhind et al., 2013b). The same study monitored DEHP concentrations in soils for 10 weeks after applications of sludge in spring and autumn. No clear seasonal difference was found, although DEHP concentrations began to increase about 3 weeks after sludge application and were typically around 3-6 times greater than control soils. Such a lag was not seen in a later study, which found DEHP concentrations in topsoil increased almost 8-fold immediately after application of sludge to agricultural land (0.03 to 0.24 µg g^{-1} dw) (Tran et al., 2015). After 6 months, the mean concentration of DEHP across 4 soil depths (0-20, 20-40, 40-60, 60-80 cm) was 21% higher than after the initial sludge spreading, which was attributed to the release of the plasticiser from bound residues within the soil during re-ploughing. Vikelsoe et al. (2002) measured the concentrations of 7 phthalates at a site with a history of high sludge application. Despite the fact that sludge application had ceased 6 years prior to sampling, individual plasticiser concentrations at this site were at least 1 order of magnitude higher than at neighbouring locations in which fertilisation was through manure, artificial fertiliser or a low-medium level sludge amendment. Such long-term persistence of phthalates in soil was also demonstrated in a study of soil amended with sewage sludge for 18 years, followed by a 12-year period without further addition. DEHP accumulated in the historically treated soil (1.47 µg g^{-1} dw at year 15) and concentrations were over 6 times higher than background levels even after the 12-year application-free period (Patureau et al., 2007). In contrast, one study found no sustained increase in DEHP concentrations in soils amended with sludge for 2.5 years relative to control soils, and DEHP levels remained comparable between the soils for the duration of the experiment (Rhind et al., 2002). Nevertheless, despite some differences between studies that warrant further investigation, the weight of evidence suggests that sewage sludge application to soils can lead to high levels of phthalate contamination which persist long after sludge spreading has ceased, possibly due to a reduction in bacterial bioavailability due to strong partitioning of phthalates to soil organic matter.

2.3.5 Fertilisers and agricultural soils

A recent study has demonstrated that the use of mineral fertilisers in which the active ingredient is coated with plastic microcapsules may lead to significant plastic contamination in farmland soils (144 µg g^{-1} plastic, n=19 sites). Whether this also represents a route of plasticiser input currently remains unclear (Katsumi et al., 2021). Fertilisers themselves have been shown to contain considerable quantities of phthalates. Concentrations in organic fertilisers are higher than in inorganic ones, although reported concentrations vary considerably from trace levels to over 2.5 µg g^{-1} dw (Kaewlaoyoong et al., 2018; Mo et al., 2008; Song et al., 2021). The mass and frequency with which fertilisers are applied, in addition to their water solubility and wide dispersal, has raised questions over their potential as a source of phthalates in agricultural soils and water courses. To date, there appears to be few systematic studies of plasticiser input from fertilisers into soils. Some studies have linked increased fertiliser use with higher phthalate concentrations, although additional inputs such as plastic mulch and irrigation water precluded definitive source apportionment (Song et al., 2021; X. Wang et al., 2013). There is some indication that fertiliser use may not cause a sustained phthalate flux, e.g. increased phthalate concentrations in soils coincided with increased fertiliser application in summer, but by autumn contamination had generally returned to spring levels (Zhang et al., 2015). However, further work on these dynamics would be warranted in studies looking to establish the dominant route of plasticiser inputs into agricultural soils.

2.3.6 Multimedia transport as a route to land

Long-range aerial transport of persistent organic pollutants (POPs) is thought to occur by the process of global distillation, whereby vaporisation, aeolian transport and condensation allow for the movement of chemicals produced in lower latitudes towards the poles. Using an established framework for predicting how a POP travels in the atmosphere (Wania, 2003), plasticisers will likely be subject to similar transport patterns as other types of organic pollutant such as polychlorinated biphenyls (PCBs), e.g. multiple distillations towards the high latitudes (Lohmann et al., 2007). In addition to the conventional transport mechanisms identified to date for organic chemicals, phthalates may also move by their association with plastics that travel in the atmosphere, leading to redistribution worldwide, including to remote soils (Feng et al., 2020). Therefore, long-range aerial transport of plasticisers and plastics of all size ranges can input these contaminants into soils at considerable distances from source areas. Plastics and plasticisers may also move locally within sources areas. For example, wet and dry deposition from a nearby urban area was suspected to account for notable phthalate occurrence ($\sum_{16}$ phthalates = 1.67 µg g^{-1} dw) in woodland soil in a national park (Zeng et al., 2009), and occurrence of a distinct phthalate profile correlated with distance from an e-waste processing site (Zhang et al., 2019).

The transport of plastics and plasticisers from water courses may also lead to inputs into soil. Effluent from WWT plants contains a multitude of plasticisers (Y.S. Lee et al., 2019), and despite the fact that WWT plants can remove the majority of microplastic particles from influent (Ball et al., 2019; Simon et al., 2018), some microplastics will still be discharged in the effluent due to the large volumes of influent that are processed. Flooding events or the extraction of riverine water for irrigation could therefore act as inputs of these contaminants to soils, although this remains largely unstudied. Food webs have also been identified as a route by which organic pollutants (Christensen et al., 2005; Previšić et al., 2021) and microplastics (Al-Jaibachi et al., 2018) can move from water to land, e.g. through predation of aquatic species by terrestrial species, or the emergence of insects from an aquatic larval stages to terrestrial adult stages. To date, however, whether plasticisers can travel by these routes has yet to be definitively established.

2.4 Occurrence of plasticisers in the terrestrial environment

Although an emerging area, there is already a relatively well-developed and growing literature on the presence of plasticisers in soil. A review of published studies identifies over 50 papers that report the concentrations of one or more plasticisers in soil samples. This includes survey studies and studies, such as some of those discussed above, that reported the occurrence of plasticisers in an experimental setting, e.g. studies to assess the effect of sewage sludge additions in field-scale trials. Of the identified papers, 43 have extractable data on concentrations in soils. These data can be assembled to provide an overview of the range of concentrations found based on total measured plasticiser in addition to the number of detected plasticisers and concentration ranges for individual congeners.

To date the large majority of studies of plasticiser occurrence have focussed on phthalates. Hence, the most robust comparative assessment of occurrence can be conducted for this group of substances. Of studies that have measured phthalate concentrations in soil, 86% (n=37) report data for phthalates in Chinese soils (79% of sampling groups, n=82). The remaining studies came from Europe (12% of studies, 17% of sampling groups) and India (2% of studies, 4% of sampling groups). As many papers did not report median concentrations for individual phthalates, mean concentrations were used for comparative data analysis. The bias towards higher values associated with using the mean as opposed to the median may be mitigated by viewing the results from a risk assessment perspective, where one would focus on understanding the upper range represented by worst case high value measurements.

In order to obtain a higher resolution overview of the differences in plasticiser contamination between land uses, data within individual studies were split into discrete sampling groups as primarily urban, agricultural, landfill, rural or mixed. In a minority of cases it was necessary to calculate mean phthalate concentrations manually using the raw data for a sampling group. When such calculations were made, non-detect values were assigned half of the limit of detection (LOD) and included in the mean calculation. Two studies did not give any data for concentrations <1 ng g^{-1}. In these cases, a value of 0.5 ng g^{-1} was assigned. If, for any substance, all analysed samples within a land use group reported concentrations below the detection limit, that group was given a null value for that analyte. A list detailing the data extracted from these 43 papers and the categories assigned to the sampling groups can be found in Appendix Table S2.2, in addition to any notes on whether data had to be treated before analysis. Limits of detection for all 43 studies, where available, are detailed in Appendix Table S2.3.

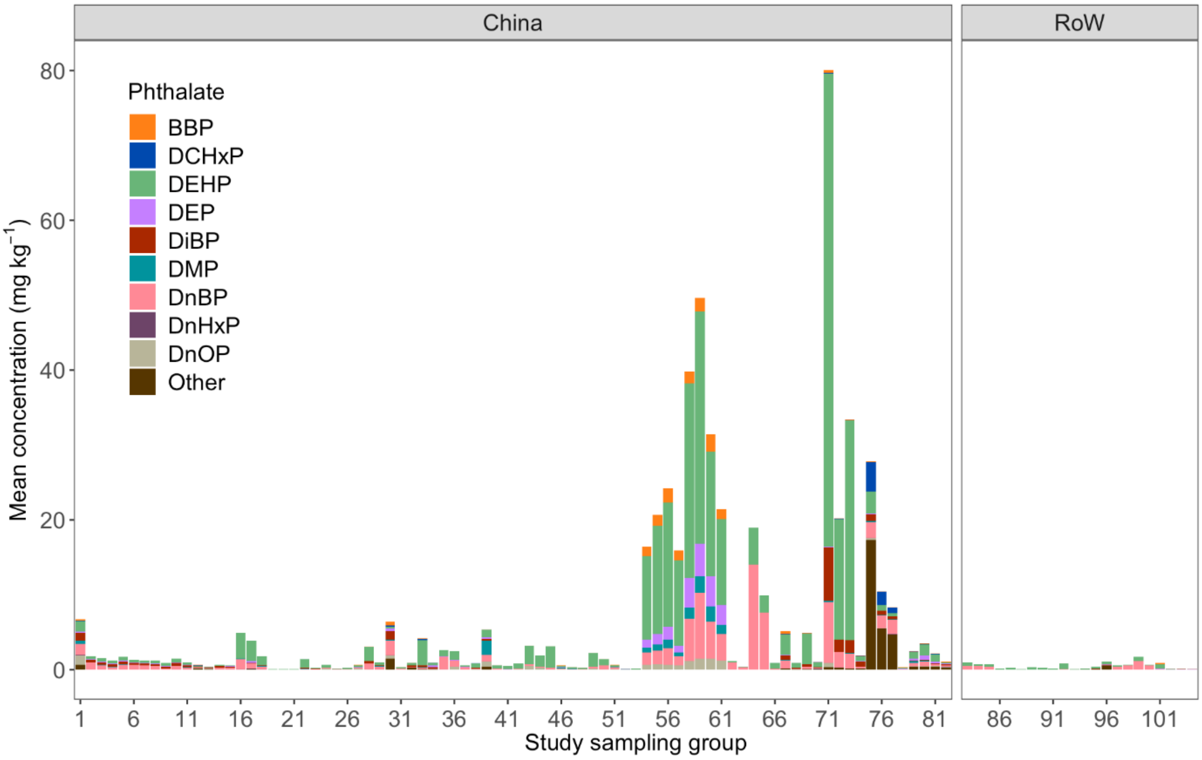


Figure 2.2: Total phthalate concentrations in all land use sampling groups extracted from published literature (n=43 studies, n=104 sampling groups). RoW = rest of world.

Soils with the highest reported total phthalate concentrations are exclusively found in China. Such high levels in Chinese soil may be due to local or regional factors, however, the number of studies of soil plasticiser loads is greater in China than in other regions. Hence, until there is wider geographic investigation of phthalate occurrence, it is not possible to unequivocally establish whether the dominance of high values in China is simply a result of the greater focus on plasticiser measurement or relates to other aspects such as the degree of source intensity. No clear relationship was found between the number of phthalates that were targeted and total phthalate concentration in specific environments (Figure S2.1). This indicates that some soils may have a limited range of phthalate inputs that are well captured by a specific analytical suite that focusses only on a small set, most often of the better known and characterised congeners.

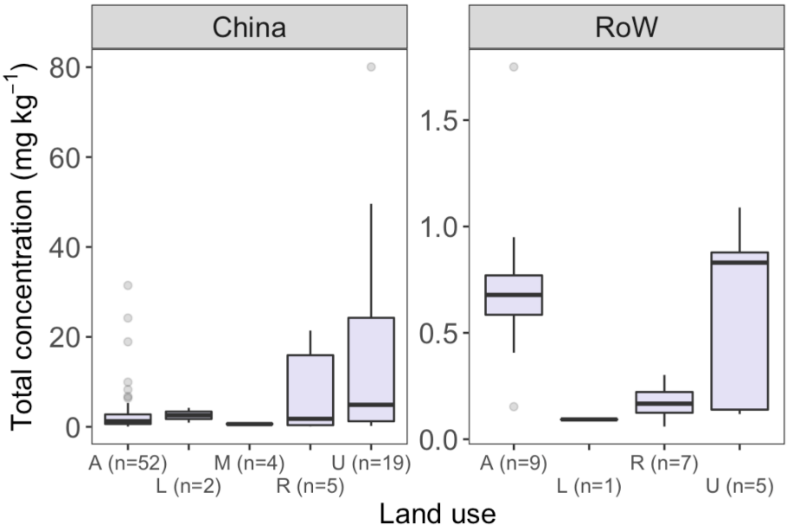


Figure 2.3: Total measured phthalate concentrations in soils worldwide, broken down by land use. n refers to the number of sampling groups in each box. Whiskers represent largest or smallest value less than or equal to upper or lower hinge + 1.5 x interquartile range. A = agricultural, L = landfill, M = mixed, R = rural, U = urban

The variation in total phthalate concentrations between different land uses is shown in Figure 2.3. There is uncertainty in this analysis, as in addition to the variability in number of phthalates targeted, assigning a particular site to a specific land use can be challenging based on the information available for some studies. Despite these challenges, some specific patterns are evident. For example, urban soils represent the land use groups that typically have the highest total maximum phthalate concentrations. Within China, there is relatively low variability of total phthalate concentrations in agricultural compared to urban and rural soils. This may be due to a less complex set of source inputs in agricultural environments that may be subject to similar land management, and to the reduced potential for point source contributions compared to urban sites.

Table 2.2: Detection frequencies (DFs) and limits of detection (LODs) of phthalates in soils (n=43 studies, n=104 sampling groups). LOD means, medians and ranges were calculated from available data (Appendix Table S2.3). Method LODs were used in calculations where possible, otherwise instrumental LODs were used. It should be noted that 60% of studies did not report LOD data for individual phthalates. As such, the LOD summary statistics in this table represent only a subset of studies.

Phthalate	DF (%)	n	Non-detects	Detects	Maximum mean concentration (μg g^{-1})	LOD (ng g^{-1})		
						Mean	Median	Range
DEHP	100	104	0	104	63.20	22.93	10	0.01-130
DnBP	100	98	0	98	14.06	7.96	1.8	0.01-50
DiBP	100	51	0	51	7.15	2.07	2	0.01-4.69
DnHpP	100	3	0	3	0.05	7.79	7.79	-
DMPP	96	26	1	25	3.72	2.16	1.72	0.83-4.34
DMP	94	88	5	83	2.17	5.15	1.6	0.01-30
DEP	93	88	6	82	4.41	15.15	2.5	0.01-110
DiNP	92	13	1	12	0.50	0.26	0.26	0.01-0.5
DnOP	89	72	8	64	1.49	14.18	1.98	0.01-110
BBP	87	71	9	62	2.36	4.03	1.8	0.01-20
DEEP	83	24	4	20	0.20	1.7	1.16	0.67-3.8
DMEP	81	21	4	17	0.25	1.69	1.42	0.59-3.31
DnHxP	81	31	6	25	0.09	1.33	1.08	0.59-2.3
DCHxP	81	31	6	25	3.96	2.39	1.43	0.89-5.8
DBEP	75	24	6	18	12.54	1.77	1.52	0.84-3.2
DPhP	75	12	3	9	0.24	2.63	1.43	1.25-5.2
DiDP	75	4	1	3	0.07	0.01	0.01	-
DnNP	68	22	7	15	0.95	4.83	4.83	3.05-6.6
HEHP	67	18	6	12	0.07	1.02	1.02	-
DnPP	58	26	11	15	0.10	1.58	1.58	0.46-2.7
DPrP	33	3	2	1	0.05	-	-	-

DEHP was the only phthalate that was targeted in every study. A detection frequency (DF) of 100% indicated that this substance is ubiquitously present in soil samples across all studies and land use categories. Other phthalates detected at 100% frequency across all sampling groups, although not necessarily always targeted, were DnBP, DiBP and di-n-heptyl phthalate (DnHpP) (Table 2.2). Indeed, in the case of DnHpP this positive detection related only to a single study (Zhang et al., 2015). Of the 21 phthalates that have been quantified in soils, 17 had a detection frequency of 75% or more, indicating that diffuse sources and long-range transport have caused significant dispersion of these contaminants widely in the terrestrial environment. The limits of detection for individual phthalates tend to fall in the range 0.5-5 ng g^{-1} (Table 2.2), which is generally far below reported soil concentrations, indicating that the results obtained between studies are broadly comparable. However, only 40% of studies reported LOD data for individual phthalates, whilst 12% gave no LOD information at all. Thorough reporting of LOD data in future studies will increase the confidence with which results from different studies can be compared, thereby improving assessments of the risk of phthalates to terrestrial environments.

Statistically significant positive correlations exist between the concentrations of some of the most commonly targeted phthalates in study sampling groups (Table 2.3), indicating similar sources of these congeners in soils. A group of 7 phthalates (DMP, DEP, DiBP, DnBP, BBP, DEHP and DnOP) appear to share common sources, as these compounds show a high degree of correlation across the different sampling groups. Particularly strong relationships are evident between DEHP & DiBP, DnBP & DiBP, and DMP & DEP. DMP and DEP represent the lowest molecular weight phthalate congeners and as such share similar uses, e.g. in cosmetics (Hansen et al., 2013), and potentially similar drivers of post-release fate and transport. Although plastic formulations tend to contain only 1-2 plasticisers, DEHP, DiBP and DnBP share very similar properties so may be used interchangeably, indicating a common potential source through consumer use.

Table 2.3: Pearson correlation coefficients (*r*) of the mean concentrations of the 9 most commonly targeted phthalates in soil study sampling groups. * = p < 0.05, ** = p <0.01

	DMP	DEP	DiBP	DnBP	BBP	DEHP	DnOP	DnHxP
DEP	0.895*							
DiBP	0.075	0.035						
DnBP	0.702**	0.750**	0.952*					
BBP	0.835**	0.900**	0.571**	0.683**				
DEHP	0.485**	0.521**	0.946**	0.608**	0.544**			
DnOP	0.874**	0.845**	0.418*	0.742**	0.830**	0.535**		
DnHxP	0.017	0.230	-0.043	-0.029	0.011	-0.106	0.351	
DCHxP	-0.001	-0.114	0.044	0.203	-0.054	-0.052	0.063	-0.036

When considered as a proportion of total phthalate load, DEHP and DnBP tend to dominate the soil plasticiser profiles (Figure 2.2 and Figure 2.4). Additionally, DiBP, DnOP, BBP and DEP are all commonly present, albeit it in lower concentrations than is the case for DEHP and DnBP. Given that DEHP constitutes 40% of global plasticiser consumption (CEFIC, 2018), its high prevalence and dominance is unsurprising.

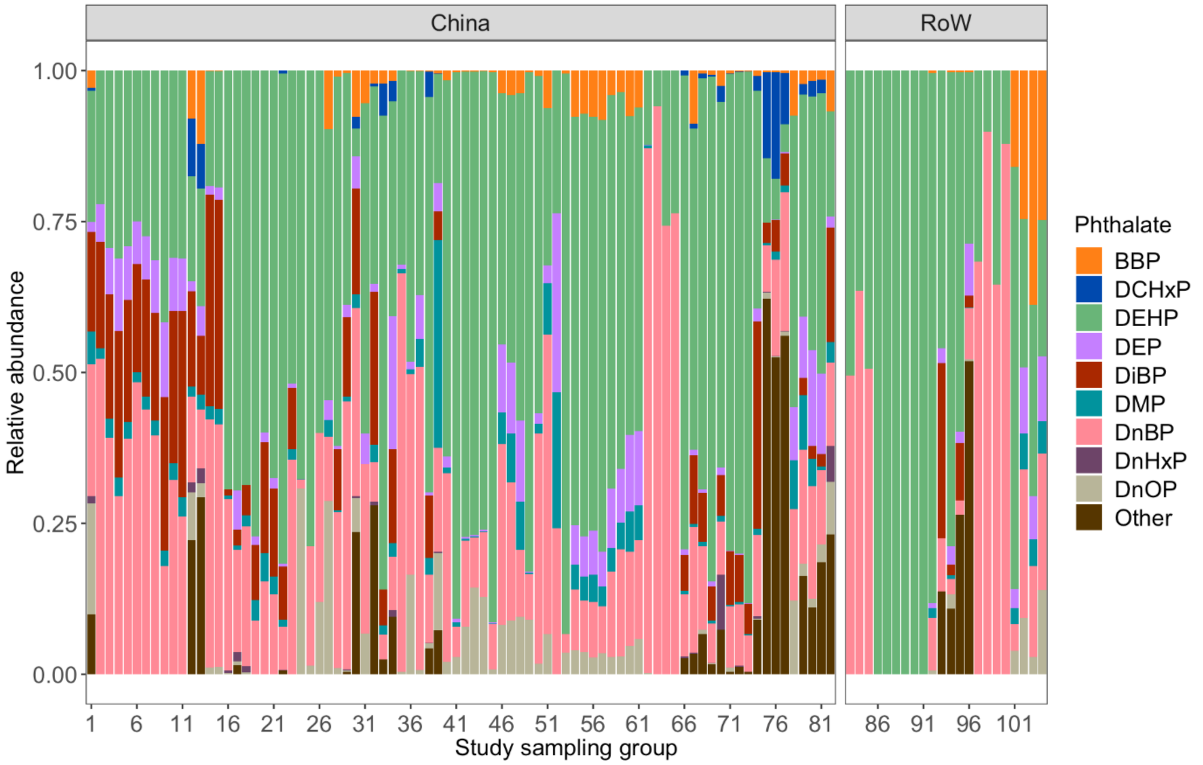


Figure 2.4: Relative abundances of phthalates in all land use sampling groups extracted from published literature to date (n=43 studies, n=104 sampling groups). RoW = rest of world.

Although the profile of phthalate contamination in many sampling groups appears to follow similar patterns, phthalate soil signatures can in some cases be specific to a certain site. For example, notably high concentrations of DBEP (4.49 µg g^{-1} dw), DMPP (2.88 µg g^{-1} dw) and DCHP (1.66 µg g^{-1} dw) were detected in soils in an e-waste processing area, whilst DnBP and DEHP were found at these locations only 1.92 µg g^{-1} dw and 1.05 µg g^{-1} dw respectively (Zhang et al., 2019). The patterns of phthalate contamination seen in soils (Figure 2.2 and Figure 2.4) highlight the importance of diffuse inputs in determining the profiles on a wide scale, but the significant impact that point sources of phthalates can have on local sites. E-waste sites in particular appear to have distinct impacts on local phthalate profiles, possibly due to the specialised use of certain phthalates in electronics. Hence, at any individual site the total burden of phthalates and composition of congeners may be a combination of local, regional and global drivers.

Despite the extensive and widespread analysis of phthalates across land use types, there is to date only one study that the authors are aware of that has quantified the presence of an emerging plasticiser in soil. Whilst it was found in relatively low levels (0.057 µg g^{-1}), DEHA had the highest mean concentration of any of the studied plasticisers in landfill soils in Indian cities (Chakraborty et al., 2019). Emerging plasticisers have been detected in air and dust in Europe, the USA and Japan (Fromme et al., 2016; Larsson et al., 2017; Subedi et al., 2017; Takeuchi et al., 2014), and in sewage sludge at comparable levels to phthalates (Y.S. Lee et al., 2019). Although limited, the data suggest the potential for the occurrence of emerging plasticisers in soil at concentrations on a par with those for phthalates. As use of these chemicals increases in the future, the potential for further emission and release is evident.

Analytical challenges are very important to take into account when considering plasticiser occurrence data, as they underpin the conclusions that can be drawn from published studies. These challenges are not limited to the issues surrounding the reporting of LODs and underreporting of sum concentrations due to limited analysis suites discussed above. Some studies did not report whether concentrations were reported as dry or wet weights. Such inconsistencies may lead to underreporting of concentrations in soils that measured the concentrations as wet weights, and therefore in order to aid comparability between studies it is preferable that future work focuses on reporting dry weight concentrations. At present, there is no established method for quantifying the relative contribution of microplastic associated plasticisers compared to leached plasticisers. As such, microplastics present in soils may lead to an overreporting of free plasticiser concentrations. The extraction of plasticisers from microplastics will be related to the extraction method used, with less harsh methods likely to lead to less extraction from microplastics but may cause lower extraction efficiencies for targeted phthalates from the soil. Accurate assessments are important for understanding the potential for biological effects of phthalate contamination, as the bioavailability of plastic-interred plasticisers is likely much less than those free in the soil. Additionally, as for other organic chemicals, phthalates can occur as bound residues that can be difficult to extract and analyse, and thus may be underreported (Tran et al., 2015). This has further implications for the reliability of measured values as an assessment of total plasticiser loads.

2.5 Fate

2.5.1 Persistence of plasticisers in soils

A number of studies have demonstrated that biodegradation is one of the dominant processes controlling the persistence of plasticisers that reach the soil environment (Hurtado et al., 2017; Xie et al., 2010). The degradation rates of plasticisers are controlled by a number of factors including environmental conditions (e.g. temperature, moisture, UV light), soil properties and the microbial communities present in soils, sludges and waste amendments. It is well established that anaerobic degradation of plasticisers in soils is significantly slower than aerobic degradation, e.g. half-lives of DMP and DnBP were ~8 times longer under anaerobic conditions (Shanker et al., 1985). The vast majority of studies of plasticiser degradation in soils are aerobic, thus the discussion in this section focuses primarily on aerobic degradation rates, although many of the underlying factors controlling degradation will be the same in both aerobic and anaerobic environments. These studies have focussed exclusively on phthalates (Appendix Table S2.4), with no quantitative data available for emerging plasticisers.

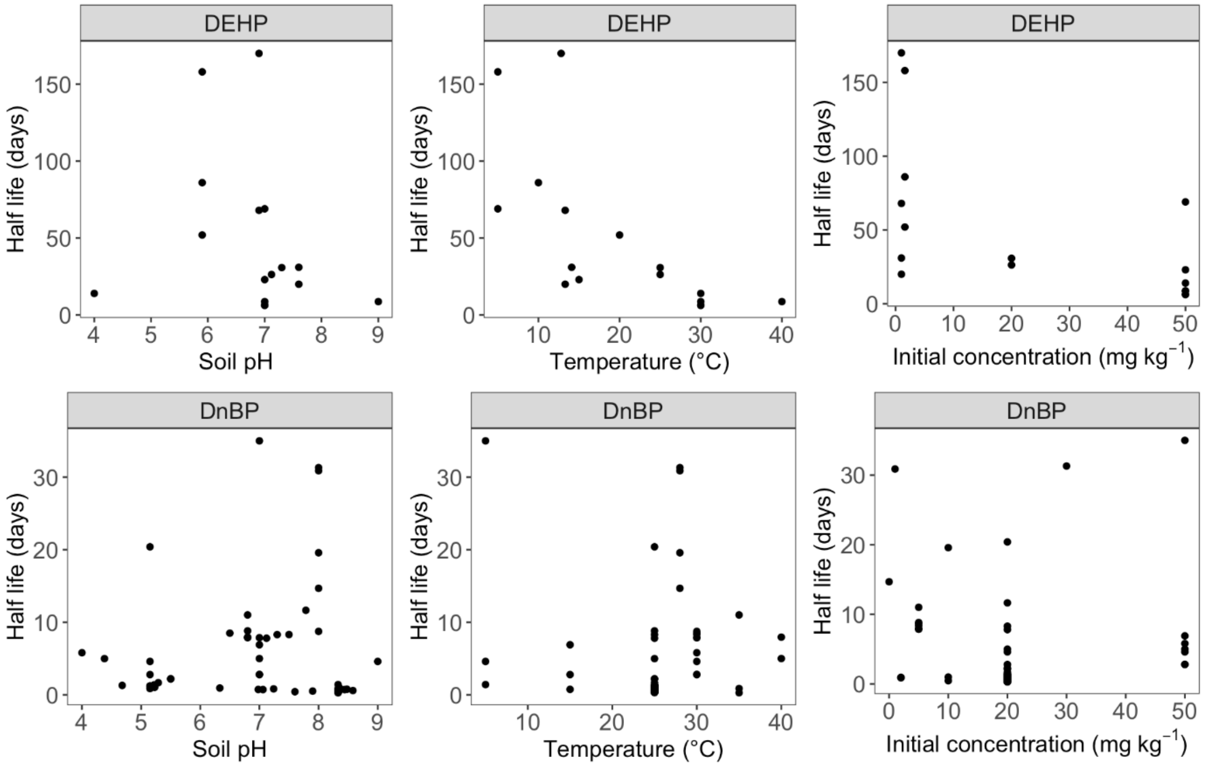


Figure 2.5: Half-lives of the phthalates DEHP and DnBP in soils reported in the literature. Details of all phthalate soil half-life data extracted from the literature can be found in Appendix Table S2.4.

It has been clearly demonstrated that phthalates with longer chain lengths have greater persistence in the environment than shorter chain ones (Cartwright et al., 2000; Tang et al., 2020; Xie et al., 2010; F. Zhu et al., 2018a). This is attributed to the greater hydrophobicity of long chain molecules resulting in stronger soil organic matter (SOM) binding, reducing their bioavailability (Murillo-Torres et al., 2012). In addition, bacterial degradation tends to occur more slowly for larger, more complex organic molecules (Kanaly and Harayama, 2000). No degradation of the more complex, highly hydrophobic DEHP was observed in over 65 days at 20 °C in a field soil, whilst the simpler, more hydrophilic DEP had a half-life of just 0.75 days (Cartwright et al., 2000). Phthalates with branched chains have also been found to degrade more slowly than straight-chained congeners. For example, DnOP degraded more rapidly than DEHP in a marine sediment (DnOP $t_{1/2}$ = 172 days, DEHP $t_{1/2}$ = 347 days) (Kickham et al., 2012). In addition, significantly faster biodegradation of unbranched maleate plasticiser congeners than the equivalent branched congeners has been demonstrated (Erythropel et al., 2015). Conversely, the straight-chain phthalate (DnBP) was found to degrade to a marginally lesser extent than its branched counterpart (DiBP) in two agricultural soils after 42 days (9.6-18.2% DnBP vs. 4.6-6.2% DiBP remaining) (F. Zhu et al., 2018a). A further complexity to understanding phthalate fate in soils is that rates determined in the laboratory may not necessarily reflect those under real field conditions, with some phthalates significantly more persistent than any experimentally determined half-life would suggest. For example, DEHP concentrations in a polluted soil decreased from 1.47 µg g^{-1} dw to 0.88 µg g^{-1} dw over 15 years, a reduction of only 40%, whilst no significant increases were observed in a control soil (Patureau et al., 2007).

The rate of phthalate degradation in soils has been found to be positively correlated with temperature (Figure 2.5), possibly due to increased bacterial activity combined with more rapid physical processes. Thus, even modest temperature changes can have a significant impact on degradation rate. For example, an early study reported a consistent decrease in DEHP soil half-life with increasing temperature ($t_{1/2}$ = 158, 86, 55 days at 5, 10 and 20 °C respectively) (Madsen et al., 1999). DnBP was also degraded quicker at higher temperatures (Cheng et al., 2018). Conversely, other studies have found that overall degradation rates of phthalates actually begin to decrease at higher temperatures. Soil half-lives of DnBP and DEHP consistently reduced from 5 and 30 °C, but rose at 40 °C (Chang et al., 2009). The complexities in the effects of temperature on phthalate degradation may be explained by the distinct profiles of native soil bacterial communities and the temperature sensitivity of metabolic processes controlled by these microbial taxa.

The effects of soil properties (e.g. pH, SOM, clay content, water holding capacity) on plasticiser degradation are complex. Recent results suggest that the principle soil properties affecting degradation of phthalates in soils may differ from those which determine long-term retention. Microbial associated carbon was the most important factor influencing half-life of

DnBP in agricultural soils, followed by pH, then the total SOM (Cheng et al., 2019). This was in contrast to the relative importance of factors affecting the residual DnBP content in the soil, where organic carbon was most influential, followed by microbial carbon. These results compliment conclusions from studies discussed above, where a fraction of phthalate contamination remains persistent in soil for long periods despite the presence of microorganisms.

SOM can reduce the bioavailability of phthalates in soil, which in turn can reduce biodegradation rates as molecules are not accessible to microorganisms for catabolism. This influence is, however, complex as some constituents of SOM, e.g. humic acids, have been shown to increase phthalate degradation rates in soils by providing a nutritional source that can prime bacterial communities to promote phthalate degradation (Tang et al., 2020; Tao et al., 2020). The overall effect of SOM on phthalate degradation, therefore, can have counteracting influences. For example, a recent study observed no significant correlation between phthalate degradation and soil adsorption capacity, and therefore the overall effect of SOM was to increase degradation rate (Tang et al., 2020). In contrast, a pronounced effect of increasing chain length on the phthalate persistence in marine sediment has been observed, which was attributed to organic matter binding (Kickham et al., 2012). The half-lives of DnBP and DEHP in two contrasting agricultural soils indicated that phthalates degraded slower in the soil with higher organic matter (Xu et al., 2008). Such results suggest that the effects of SOM levels on phthalate degradation rates may be congener specific.

Values towards the extremes of the pH values found in soil have been shown to reduce phthalate degradation rates compared to those found in more neutral soils (Figure 2.5). For example, DnBP and DEHP half-lives were longer at pH 4 and pH 9 than at pH 7 (Chang et al., 2009), and faster DEHP degradation occurred in soils with pH 6-8 (F. Zhu et al., 2018b), values that are within the ranges typical for lowlands soils in temperate regions. Phthalate sorption to organic matter was negatively correlated with pH for 4 phthalates (Yang et al., 2013). This finding pre-empted the result of a later study that found DnBP degradation to increase with pH, which was attributed to higher DnBP bioavailability at higher pH due to ionisation of organic groups in SOM that increased hydrophilicity, and potential greater bacterial abundance in higher pH soil (Cheng et al., 2019). In addition, increasing moisture from 20% to 50-80% WHC significantly increased DnBP degradation rates in soils (Cheng et al., 2018) indicating that soil moisture content could be an important controlling factor in some temperate environments.

2.5.2 Uptake of plasticisers by soil organisms

There has been increased interest in the study of the effects of plastics, and in particular microplastics, on soil fauna in recent years, e.g. laboratory and field studies have demonstrated that soil organisms are capable of ingesting microplastics (Huerta Lwanga et al., 2017, 2016; Prendergast-Miller et al., 2019). In addition, laboratory studies have shown that soil microplastic pollution has the capacity to negatively impact growth (Boots et al., 2019; Cao et al., 2017; D. Zhu et al., 2018), reproduction (Lahive et al., 2019; D. Zhu et al., 2018) and mortality (Lahive et al., 2019; D. Zhu et al., 2018), in addition to altering gut microbiota (D. Zhu et al., 2018) of soil fauna, although due to limited data on the occurrence of microplastics in soils, whether these effects are seen at realistic field levels remains unclear. Polymers are inherently inert, and therefore many of the chemical effects of microplastic pollution could result from plastic additives such as plasticisers. For instance, a recent study found that the acute effects caused by microplastics on the soil nematode *Caenorhabditis elegans* were not observed again following the extraction of additives from the plastics (S. W. Kim et al., 2020). Indeed, phthalates themselves have been shown to exhibit genotoxicity to the earthworm *Eisenia fetida* (Du et al., 2015; Ma et al., 2017, 2016; Song et al., 2019; G. Wang et al., 2018), although the impacts on typical sublethal endpoints, such as growth and reproduction, are currently less clear (Feng et al., 2016; Hu et al., 2005).

Despite the evidence of the toxicity of plasticisers in soil organisms, only one study has assessed uptake and bioaccumulation of plasticisers in soil fauna (Hu et al., 2005). The earthworm *E. fetida* was exposed to 5 phthalates (DMP, DEP, DnBP, DEHP and DnOP) at 5, 10, 20, 40 and 50 µg g^{-1} dw soil for up to 30 days. DEHP and DnBP accumulated in worm tissues, although DMP, DEP or DnOP were not detected. At environmentally relevant concentrations of 5 µg g^{-1} dw in soil (Chai et al., 2014; Hongjun et al., 2013; Ma et al., 2019), DnBP and DEHP in worm tissue reached a steady state after around 10 days to ~1-1.5 µg g^{-1} ww and ~0.4-1.2 µg g^{-1} ww respectively. Bioconcentration factors (BCFs) after 15 days of exposure to DnBP ranged from 0.23-0.30 for an agricultural soil (pH 8.3, SOM 1.35%), and 0.18-0.23 for a forest soil (pH 7.6, SOM 4.53%), whilst BCFs for DEHP ranged from 0.13-0.20 for the agricultural soil, and 0.06-0.08 for the forest soil. There was lower phthalate accumulation in the soil with a higher SOM content, possibly due to strong partitioning of phthalates to the organic material in soil, reducing their bioavailability for uptake through either dermal or oral ingestion following patterns observed for other organic chemicals (Kraaij et al., 2001; Sijm et al., 2000).

Phthalates are also capable of inducing ecotoxicity in terrestrial flora, e.g. oxidative stress and negative impacts on growth and germination in multiple vegetable crop species including cucumbers (*Cucumis sativus*), common beans (*Phaseolus vulgaris)* and radishes (*Raphanus sativus)* (Kumari and Kaur, 2020). Phthalate uptake by plants has been demonstrated, although the extent of reported accumulation varies between studies. A recent study reported BCFs of DEHP in *Brassica chinensis* in the range 0.03-2.00, with the highest BCFs found at environmentally relevant DEHP concentrations (Yuan et al., 2020). The concentration of DEHP in rice cultivars in DEHP-spiked soil (20 µg g^{-1} dw) was monitored over the course of the plants' development (Cai et al., 2015). The DEHP concentration of the roots and shoots was very high in some cases, varying from 0.26-11.8 µg g^{-1} dw and 0.40-7.58 µg g^{-1} dw respectively, with no obvious change over the course of the experiment. Although the exposure concentration of 20 µg g^{-1} dw used in this study is significantly higher than most concentrations of DEHP reported in soils, it is representative of the pollution reported in a number of studies (Teng et al., 2015; L. Wang et al., 2018; Wu et al., 2015; Zeng et al., 2008). Very high BCFs (5.8 to 17.9) of 6 phthalates were reported in an earlier field study of plant species cultivated near an e-waste processing site, although the high levels of some phthalates in above-ground tissues may have been due to direct atmospheric exposure rather than through soil uptake and translocation to shoots (Ma et al., 2013). In addition, the composition of sampling and storage materials were not reported, thus it is unclear whether samples may have been contaminated following collection. Nevertheless, the weight of evidence suggests that phthalate uptake by terrestrial flora occurs, although further work is required to determine the relative contributions of different exposure routes.

Despite evidence of bioaccumulation of phthalates in soil fauna and flora, transfer of plasticisers through trophic networks has yet to be clearly demonstrated. There is evidence from both marine and freshwater aquatic studies to suggest that plasticisers can be transferred to species occupying higher trophic levels, e.g. 8 phthalates were detected in 18 species across four trophic levels in a marine aquatic food chain (Mackintosh et al., 2004). A more recent study assessed the concentration of 14 phthalates in multiple freshwater fish species and found total phthalate concentrations ranged from n.d.-1081 ng g^{-1} dw, with DEHP and DnBP again the most commonly detected phthalates (Y. M. Lee et al., 2019). However, the presence of plasticisers in higher trophic levels in these studies could come via direct uptake of phthalates or ingestion of microplastics.

Metabolism likely represents the primary removal pathway of plasticisers within organisms. Although the nature of the various relevant metabolic pathways is complex and beyond the scope of this review, known rates of elimination of phthalates in biota appear rapid (Frederiksen et al., 2007). The nature of these main biotransformation reactions is well studied in some mammals, e.g. humans and rats (Domínguez-Romero and Scheringer, 2019; Frederiksen et al., 2007), and to a lesser extent marine organisms (Hu et al., 2016; Stalling et al., 1973). In contrast, elimination in soil organisms is less understood. However, given that enzymatic metabolic pathways are relatively well conserved between species, pathways for metabolism in soil fauna may reflect those seen in higher organisms. Studies in soil species may therefore initially seek to identify the presence of known metabolites in organisms and the activities of enzymes in families such the cytochrome P450s, esterases and glutathione-S transferases to begin to elucidate the biotransformation pathways for plasticisers in these species.

2.6 Knowledge gaps and future research recommendations

To date, research into the sources, occurrence and fate of plasticisers in the terrestrial environment has focussed on phthalates, with a distinct lack of data for emerging classes of plasticisers. The profiles of phthalates in soils generally reflect their production volumes, with DEHP dominating soil profiles, although knowledge of phthalate occurrence in soils outside of China is limited. Half-lives of phthalates in soils are on the scale of weeks, although in some cases contamination is significantly more persistent. This persistence may result in the prolonged presence of bioavailable phthalate residues that can potentially be taken up by soil organisms. Based on currently available knowledge of the sources, fate, presence and exposure of plasticisers, it is possible to identify a number of the key knowledge gaps that remain for the relevant classes of chemicals and to recommend productive areas for future research.

- The influence of soil properties and weathering of plastics on plasticiser leaching rates are largely unknown and the relative soil leaching potentials across different plastic and plasticiser classes are yet to be determined. Establishing the leaching rates from different plastic types in soils of contrasting properties should be a priority. Longer-term field experiments to establish the effects of weathering and determine environmental leaching rates are especially needed.

- Source apportionment of plasticisers in soils remains unclear, particularly in urban areas. Future work should take a holistic approach by determining not only the occurrence of plasticisers in different land uses, but the presence of plastic pollution both above and below ground, in order to establish the links between polymer and plasticiser soil loadings and the resulting polymer and plasticiser profiles. In addition, studies of sewage sludge amendment as a source of plasticisers in agricultural soils are mainly limited to DEHP, and further work is required to establish whether the long-term accumulation and persistence seen for DEHP is also observed for other phthalates and emerging plasticisers.

- Knowledge of the occurrence of phthalates in soils is limited in areas of the world outside of China. The occurrence of phthalates and emerging plasticisers across different regions should be determined, particularly in areas such as southeast Asia and Africa, where rapid urban expansion may be causing particularly high inputs of plasticisers in the environment as a result of the expansion of plastic use without the development of adequate waste management and recycling networks.

- Inconsistencies in analytical suites and reporting of key data (e.g. limits of detection) are hampering comparisons of plasticiser occurrence between studies. A coordinated approach is required, through the use of a standard suite of commonly detected plasticisers and developing requirements for data reporting. A body of consistent and directly comparable data would be suitable for a meta-analysis approach, which would further address uncertainties in environmental plasticiser distributions and allow for more rigorous analysis of trends in both phthalate and emerging plasticiser occurrence and fate.

- Whilst the degradation of phthalates in soils is well-studied, the persistence of emerging plasticisers in soils is unknown. Degradation kinetics of emerging plasticisers in soils with contrasting properties should be investigated in order to determine whether the factors underpinning phthalate degradation rates are consistent across all plasticisers.

- The fate of phthalates in soil organisms is understudied and is for emerging plasticisers unstudied. Controlled studies across multiple species are required, in order to assess the rates and routes of uptake and elimination, in addition to the potential for bioaccumulation and trophic transfer. Further, the potential for interactive effects of plasticisers with commonly used agricultural chemicals, e.g. pesticides, in terrestrial fauna and flora is a priority, given the abundance of plasticisers in agricultural soils.

2.7 Conclusion

Plasticisers have many sources in the terrestrial environment. These may be diffuse, chronic sources (e.g. microplastics present in soils via the degradation of agricultural plastic film) or point sources (e.g. incineration of electronic waste). Any plastic item which contains plasticisers has the potential to act as an input of plasticiser into the environment, through leaching and migration of additives from the polymer matrix. The ubiquitous occurrence of phthalates in the terrestrial environment has been demonstrated, and these compounds are now distributed across all land uses. However, given the rapidly increasing use of emerging plasticisers as replacements for phthalates, a dearth of studies investigating the occurrence of emerging plasticisers represents a significant knowledge gap. Some plasticiser contamination is degraded in a matter of days or weeks, although local effects can lead to some plasticisers acting as persistent organic pollutants at high levels of contamination, and thus represent a potential threat to terrestrial fauna and flora. Despite this, the terrestrial ecotoxicology of plasticisers is relatively understudied, despite evidence of cytotoxicity, oxidative damage and endocrine disruption. The impacts of emerging plasticisers, and the ecotoxicology of plasticisers in higher vertebrates is unstudied. Plastic is ubiquitous in modern society, and there are increasingly intensive patterns of agriculture requiring even greater use of plastic products. Given this fact, the determination of the impacts of plasticiser contamination on the terrestrial environment is urgently needed from the perspective of environmental management and human and ecosystem health.

2.8 Acknowledgements

This work was supported by the Natural Environment Research Council NE/S007423/1, with Alex Billings' studentship through the ENVISION Doctoral Training Partnership. David Spurgeon was supported by Natural Environment Research Council award number NE/R016429/1 as part of IMP programme delivering National Capability.

3

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

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 particles g^{-1} dw), urban roadside (17.3 particles g^{-1} dw) and urban parkland (15.7 particles g^{-1} dw) soils, but not in woodland soils. The most commonly detected polymers were polyethene, polypropene and polystyrene. Mean ∑plasticiser concentration in urban roadside soils (3111 ng g^{-1} dw) was significantly higher than in woodlands (134 ng g^{-1} dw). No significant difference was found between landfill-associated (318 ng g^{-1} dw) and urban parkland (193 ng g^{-1} 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 ng g^{-1} dw) and di-iso-decyl phthalate (96.7 ng g^{-1} dw) present at the highest concentrations. ∑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.

3.1 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 (Chapter 2). The occurrence of phthalates in soils has been linked with specific sources such as the use of plastic in agriculture (Kong et al., 2012; D. 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; Y.S. 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 (Chapter 2). The plasticiser content of a plastic item is partly governed by polymer type. For example, some polymers (e.g. polyethene) 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; Y. 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.

3.2 Materials and methods

3.2.1 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 AD (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 S3.1.

At each site, a 25 m^2 grid was marked out. The area within the grid was carefully searched for 10 minutes to collect any macroplastic visibly present on the soil surface into a clear low-density polyethene 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 vaporisation (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 were possible.

3.2.2.1 Plastic sample processing

3.2.2.1.1 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.

3.2.2.1.2 Soil microplastics

Soil samples were thawed at 4 °C for 24 hours 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, 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 µm stainless-steel filter (Bridgewater Filters Ltd, UK), sonicated in 15 mL of 1.7 g mL^{-1} $ZnCl_{2\,(aq)}$ (Honeywell, USA) for

15 minutes, 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 hours 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 µm stainless-steel filter, sonicated in 50% ethanol $_{(aq)}$ (Honeywell, USA) for 15 minutes, and brushed into a glass jar. The 20-hour 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 µm (coarse). The fine fraction was subject to a 1-hour 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 hours at 50 °C prior to analysis. All samples were stored at room temperature in the dark.

3.2.2.2 Plastic sample analysis

3.2.2.2.1 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 S3.2 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.

3.2.2.2.2 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.

3.2.2.2.3 Light microscopy and ATR-FTIR of coarse microplastics from within the soil

The coarse (>567 µm) fraction collected on stainless-steel filters was analysed using a Stemi 2000-C stereo light microscope (Carl Zeiss, Germany) with 50x zoom, equipped with an external light source. Samples were searched for 25 minutes for plastic particles. Blanks were searched for a minimum of 10 minutes, and until every particle with longest dimension >567 µm had been appraised or 25 minutes 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 S3.3).

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.

3.2.2.2.4 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 seconds, 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, 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.

3.2.2.3 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 ºC for 3 hours 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 polypropene 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 5.6-51.4% (mean 33.6% ± 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% ± 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.).

3.2.3 Plasticiser extraction and analysis

Stored soil samples were thawed at 4 °C overnight. Between 3.5-4 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 minutes 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.

Table 3.1: 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
Trioctyl 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.

We analysed 8 phthalate plasticisers and 3 emerging plasticisers (Table 3.1) 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 hours (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% ± SD 12) and 60-115% (mean 84% ± SD 13) respectively. The method limits of detection (LODs) (Table 3.1) 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.

3.2.4 Statistical analysis

For all statistical analyses and the calculation of Σmicroplastic and Σplasticiser 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 significance 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 Σmicroplastic concentrations (n=10) prior to transformation.

3.3 Results and discussion

3.3.1 Variation of plastic waste with land use

3.3.1.1 Surface plastic

The number of surface plastic items was significantly different between land uses (Kruskal-Wallis test, $p < 0.005$). Specifically, landfill (42.0 items/25 m^2 ± standard deviation 35.8) and urban roadsides (21.3 items/25 m^2 ± 15.0) had a significantly higher number of plastic items present when compared to woodland sites (0.1 items/25 m^2 ± 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 m^2 ± 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.

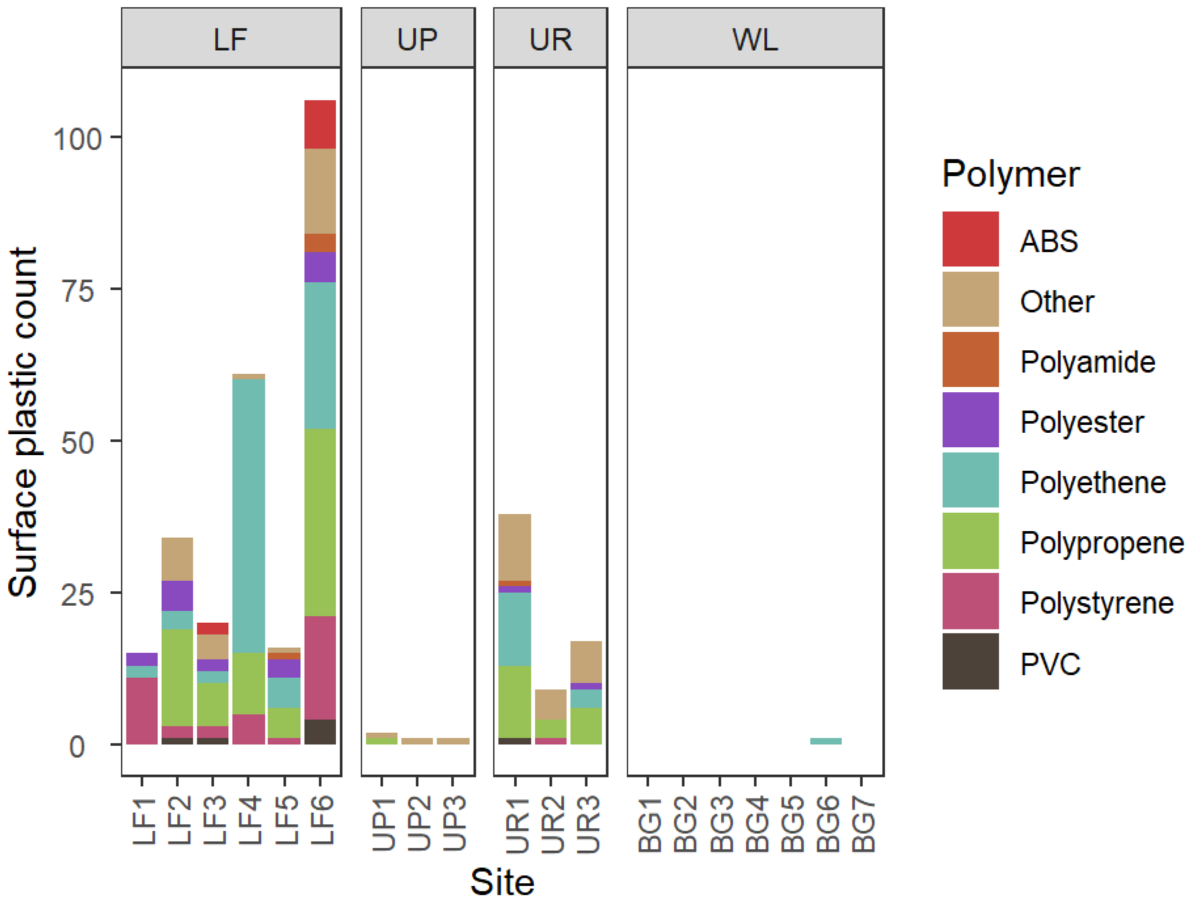


Figure 3.1: Counts of surface plastic items collected after 10 minutes search from a plot of 25 m^2; no surface plastic was found at sites BG1-5 or BG7; ABS = acrylonitrile butadiene styrene; PVC = polyvinyl chloride; LF = landfill; UP = urban parkland; UR = urban roadside; WL = woodland; the category ‘Other’ includes all items that could not be assigned a polymer, ethene-vinyl acetate items, nitrile items, and items containing a mixture of polymers.

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 m^2) (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 hotpots 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%). 8% of items 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 through dispersed releases via littering. Given that the majority of plasticisers are used in PVC (Chapter 2), the absence of PVC items could indicate a low plasticiser input to soils.

3.3.1.2 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 µm) microplastics accounted for 97.3%, 2.5% and 0.2% of the total microplastic concentration. Σmicroplastic (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 (Figure 3.2).

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 S3.4 for a full list of LODs for each microplastic fraction). Thus mean Σmicroplastic 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 Σmicroplastic 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.

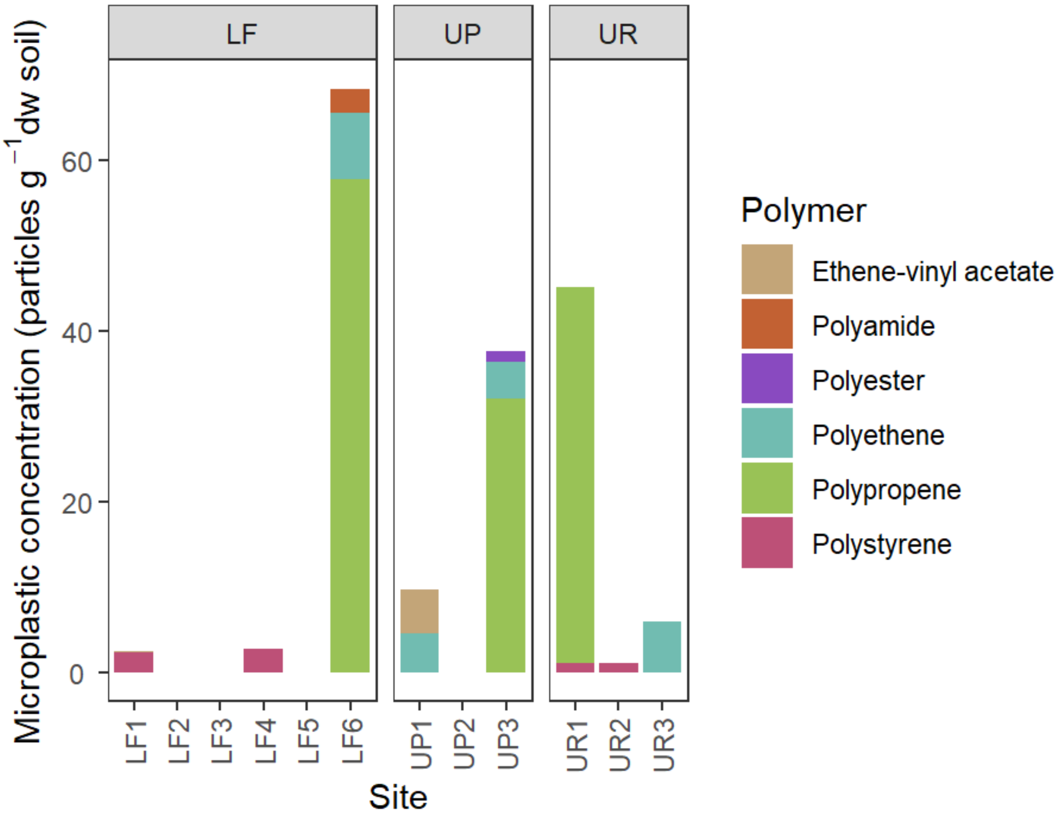


Figure 3.2: Σmicroplastic concentrations detected in field soils (particles g^{-1} dw) (Appendix Table S3.5); no microplastics were >LOD at LF2-LF3, LF5 or UP2; no microplastics were >LOD at woodland sites, hence they are not shown on this figure (Appendix Table S3.4); LF = landfill; UP = urban parkland; UR = urban roadside.

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 Σmicroplastic 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 Σmicroplastic.

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, 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 though 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, where >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 polypropene and polyethene) 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.

3.3.2 Occurrence of plasticisers in soils

3.3.2.1 Phthalate occurrence and variation with land use

Mean Σphthalate 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 Σphthalate 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 (Chapter 2).

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 3.2). 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).

Table 3.2: Plasticiser 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

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. 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 (Chapter 2; 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 (C_8 alkyl chains, 1 branch) and DiDP (C_{10} alkyl chains, minimum of 1 branch) versus e.g. the unbranched DnBP (C_4) or DEP (C_2) 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 (Chapter 2). Thus, this raises questions as to 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, 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.

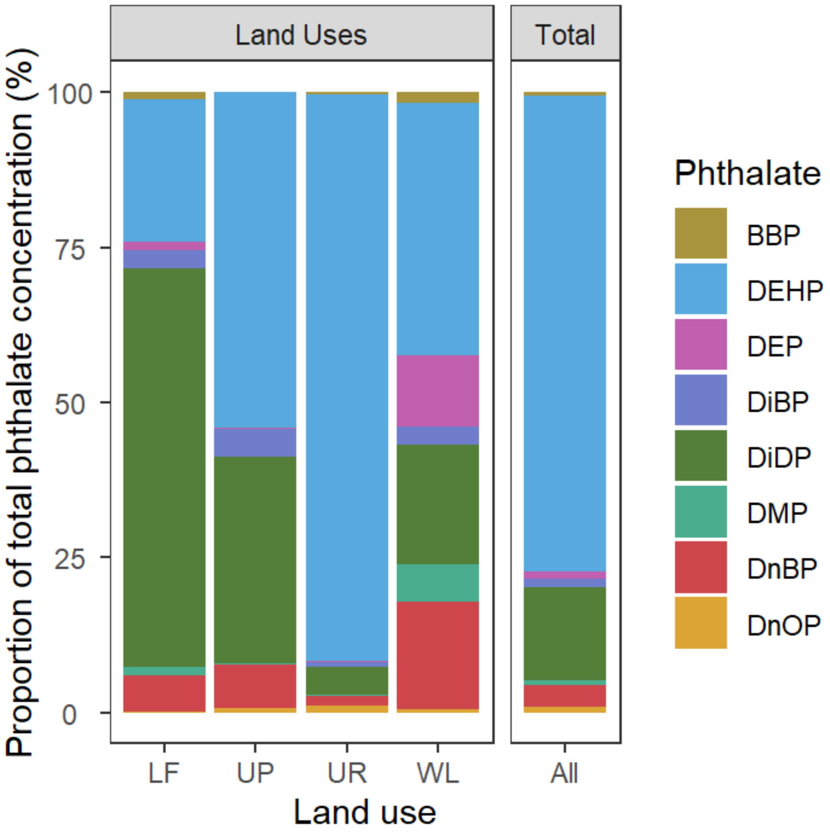


Figure 3.3: Phthalate profiles in soils of the different land uses in this field study; LF = landfill; UP = urban parkland; UR = urban roadside; WL = woodland; All = all sites.

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 (Kaewlaoyoong 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 AD (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 (Chapter 2). Alternatively the milder climate in southern England compared to Scotland may also accelerate phthalate degradation and/or volatilisation from soil.

3.3.2.2 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

(Chapter 2). TOTM and DEHA (both C_8) have longer alkyl chains than ATBC (C_4). 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 (Chapter 2). However, to date there is no published data regarding the half-lives of emerging plasticisers in soils (see Chapter 4). The presence of these emerging plasticisers indicates that their fate in soil warrants further investigation.

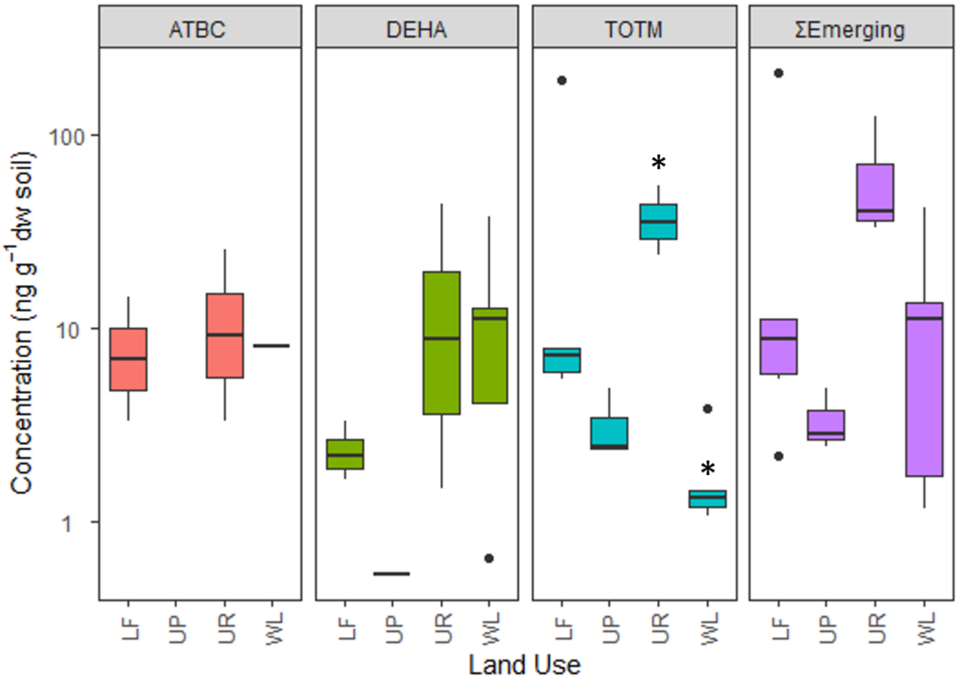


Figure 3.4: ∑concentrations of emerging plasticisers across different land uses; concentrations are plotted on a $\log_{10}$ scale; LF = landfill; UP = urban parkland; UR = urban roadside; WL = woodland; statistically significant differences in ∑concentrations between land uses are indicated by *.

Mean ∑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 ∑emerging concentration at urban parklands was only 30% of that in woodlands (Figure 3.4). No statistically significant differences in the ∑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 ∑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.

3.3.2.3 Relationship between plastic and plasticiser occurrence

∑plasticiser and ∑phthalate concentrations were weakly significantly correlated with surface plastic count (all data $\log_{10}$-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 ∑plasticiser, ∑phthalate or ∑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 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).

3.3.3 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 S3.4), 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 x Fenton’s reagent digestion steps and 2 x 24-hour density separations, a portion of primarily cellulitic 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 positives. 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. Σplasticiser 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.

3.4. 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 polyethene, 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. ∑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.

3.5 Acknowledgements

This work was supported by the Natural Environment Research Council NE/S007423/1, with Alex Billings's studentship through the ENVISION Doctoral Training Partnership.

4

Kinetics of plasticiser release and degradation in soils

Abstract

Despite the increasing use of emerging phthalate and non-phthalate plasticisers as replacements for restricted phthalates, few studies have investigated their rates of entry and subsequent persistence in the terrestrial environment. We carried out two medium-term (3 months) experiments to investigate the release and degradation kinetics of legacy and emerging plasticisers in three natural soils spanning a range of physical and chemical properties. The release of plasticisers from microplastics was investigated in soils amended with polyvinyl chloride (PVC) pellets, with the concentration of the emerging plasticiser diethyl hexyl terephthalate (DEHTP) monitored over the course of the experiment by quantitative GC-MS analysis. DEHTP was rapidly released from the microplastics, reaching maximum concentration within ~2 hours, although the amount released was only a small proportion of the total amount in the pellets (<0.02%). For the degradation experiment, concentrations of 8 phthalate plasticisers and 4 non-phthalate emerging plasticisers in the soils were measured over 3 months by GC-MS, to establish the rates of compound degradation. For 7 out of the 12 plasticisers, estimated pseudo-first order half-lives were <30 days, suggesting relatively low persistence in soils. A group of 5 higher molecular weight plasticisers, including the emerging plasticisers trioctyl trimellitate (TOTM) and DEHTP, were found to be relatively more persistent, with half-life >100 days (i.e. little degradation over the experiment). Di-iso-decyl phthalate (DiDP) was the most persistent plasticiser, followed by TOTM and DEHTP. Plasticiser degradation was typically faster in acidic heathland soil (pH 3.8; organic matter 3.7%), than in alkaline grassland (pH 7.3; organic matter 16%) or sandy loam agricultural (pH 5.3; organic matter 5%) soils. The rapid release and the potential for the persistence of some emerging plasticisers in soils indicates that presence of these contaminants may increase in the future.

4.1 Introduction

The presence of plastic (including microplastics – particles with diameters <5 mm) in soils has been linked to negative impacts on soil organisms. For example, microplastic contamination of soil has been shown to reduce the growth, reproduction, and fitness of terrestrial species such as earthworms and plants (Boots et al., 2019; Cao et al., 2017; Lahive et al., 2019). In addition to the physical effects of the plastic particles themselves, negative effects could also arise due to the chemical additives associated with plastics. Thus, the effects of microplastics on soil organisms may be not only physical but also driven by further chemical exposures. Whilst studies of the release of additives from plastics have focussed on aqueous media (Suhrhoff and Scholz-Böttcher, 2016), to date no study has investigated the release of emerging plasticisers from microplastics directly into soils, as far as we are aware. Whilst comparisons between plasticiser release in the different environmental compartments of freshwaters and the terrestrial environment can be made, the lack of empirical data on direct plasticiser release rates into soils from plastics limits our knowledge as to the sources and rates of plasticiser entry into the environment.

A further knowledge gap of the fate of emerging plasticisers once they reach the soil environment is their persistence. Whilst such data does exist for some phthalates, e.g. previous studies have reported half-lives of DEHP and DnBP on the scales of a few weeks (Chapter 2), these compounds have been phased out in Europe and are being replaced by emerging plasticisers (CEFIC, 2021), for which the degradation rates of many are largely unknown. Factors such as chain length and molecular size have been shown to be primary drivers of the relative degradation rates of phthalates (Cartwright et al., 2000; Tang et al., 2020; Xie et al., 2010). In addition, soil properties such as organic matter and pH have also been found to influence the rates of degradation (Tang et al., 2020; Tao et al., 2020). Furthermore, whilst it appears that phthalates may degrade relatively quickly, some studies suggest that they may be more persistent in the environment than laboratory study results suggest (Patureau et al., 2007). Even though there is some knowledge for phthalates, the rates of degradation of emerging plasticisers and soil property controls on these rates have yet to be investigated. Determining the persistence of these emerging plasticisers in soils is a key research need, as the production and use of these compounds is likely to increase.

Organic matter content and pH have been proposed as major factors controlling phthalate fate and degradation in soils (Chapter 2). Thus, we conducted experimental studies to measure the release of an emerging plasticiser from microplastics, and the degradation of a range of phthalate and emerging plasticisers, in three soils spanning a relatively wide range of different pH (3.8-7.3) and organic matter (%OM) values (3.7-16%). Use of this range of soils allowed us to assess whether there were any clear effects of these variables on the release of plasticisers directly into soil or on degradation kinetics within the soils. Our study investigated the release kinetics of an emerging plasticiser from PVC microplastic particles in the three soils over 3 months. In addition, we monitored the concentrations of a range of legacy (i.e. phthalate) and emerging (i.e. non-phthalate) plasticisers in the same 3 soils over the same period to determine plasticiser degradation kinetics. These studies aimed to test the following hypotheses: 1) Soil properties (pH, organic matter, and water holding capacity) will affect the release and degradation rates of plasticisers in soils; 2) The degradation rates of emerging plasticisers in soils will be comparable to those of analogous phthalates, and these comparisons can be explained based on the physiochemical properties of the different plasticisers. This is the first study we are aware of to investigate the degradation rates of both phthalates and emerging plasticisers in soils, and examine the release of an emerging plasticiser directly from microplastics into soils.

4.2 Materials and methods

4.2.1 Test soils

Three natural soils were selected to provide a range of major soil properties (e.g. pH and organic matter content) within the study. Two soils were collected in southern England, UK;

one from an alkaline grassland (Chiltern) and one from an acidic heathland (Dorset). The third soil was a sandy loam agricultural soil (Lufa) commercially sourced from Germany (LUFA Speyer, Germany). This latter soil is widely used as a medium for terrestrial studies of chemical fate and effects, including for regulatory toxicity testing (OECD, 2009). Prior to use, all soils were air-dried at room temperature, sieved to 2 mm and stored in polypropene tubs lined with aluminium foil at 20 °C in the dark. Bulk properties of these soils determined prior to experimental work are shown in Table 4.1 (see Appendix S4.1 for details of how properties were measured).

Table 4.1: Properties of soils used for plasticiser release and degradation experiments; all values are reported as mean ± standard deviation (n=3); WHC = water holding capacity; %OM = percentage organic matter content.

Soil	**pH**	**%WHC (mL g^{-1} soil)**	**%OM**
Alkaline grassland (Chiltern)	7.3 ± 0.02	73 ± 2.5	16 ± 0.2
Acidic heathland (Dorset)	3.8 ± 0.17	41 ± 0.7	3.7 ± 0.2
Sandy loam agricultural (Lufa)	5.3 ± 0.04	56 ± 1.3	5.0 ± 0.1

4.2.2 Test materials

4.2.2.1 Microplastic pellets used in the plasticiser release experiment

PVC microplastic pellets of diameter 3.9 ± SD 0.2 mm and mass of 33.8 ± 3.4 mg (mean and SD of n=10 pellets) were selected for the release experiment. PVC was chosen as the test polymer as the majority of plasticisers consumed in Europe are used in PVC plastic formulations (CEFIC, 2021), and in some cases plasticiser loads account for up to 70% w/w of the plastic component (Hansen et al., 2013). An initial screening analysis of the amended soil samples confirmed that DEHTP was the only plasticiser in our analytical suite to have been released from the pellets. Given that the majority of plastics are plasticised with a single plasticiser (Chapter 2), and the analytical suite (Table 4.2) included the most widely produced plasticiser compounds (CEFIC, 2021) with relatively low detection limits (Table 4.2), it is likely that DEHTP was the only (or at least major primary) plasticiser used in the pellets.

4.2.2.2 Plasticisers used in the degradation experiment

A suite of eight legacy (phthalate) and four emerging plasticisers (96-99.5% purity; all from Sigma-Aldrich, USA) were chosen for the degradation experiment (Table 4.2). The 12 plasticisers were selected based on production quantities (CEFIC, 2021) and, where available, detection frequencies and abundances in soils (Chapter 2). The multiple selected phthalate plasticisers (Table 4.2) were chosen to span a range of values for a number of physiochemical parameters potentially relevant to fate including molecular weight, Log K_{OW}, solubility in water, and degree of chain branching. A single exemplar compound was also chosen from each of the following classes of emerging plasticisers: adipate (diethylhexyl adipate), terephthalate (diethylhexyl terephthalate), citrate (acetyl tributyl citrate), and trimellitate (trioctyl trimellitate).

Table 4.2: The eight phthalate and four emerging plasticisers used to spike soils in the degradation experiment in this study, including key physiochemical properties (lipophilicity, water solubility at 25 °C) and detection limits for analytes in the degradation study; the limit of detection of DEHTP in the release study was 8.5 ng g^{-1} dw.

Name and acronym		**Class**	**CAS**	**Formula**	**Log K_{OW}**	**S_{H2O} (mg L^{-1})**	**Limit of detection (ng g^{-1} dw)**
Dimethyl phthalate	DMP	Phthalate	131-11-3	$C_{10}H_{10}O_4$	1.61 ^{A}	4000 ^{B}	0.5
Diethyl phthalate	DEP	Phthalate	84-66-2	$C_{12}H_{14}O_4$	2.54 ^{A}	1080 ^{B}	4.9
Di-iso-butyl phthalate	DiBP	Phthalate	84-69-5	$C_{16}H_{22}O_4$	4.27 ^{A}	6.2 (24 °C) ^{B}	4.9
Di-n-butyl phthalate	DnBP	Phthalate	84-74-2	$C_{16}H_{22}O_4$	4.27 ^{A}	11.2 ^{B}	0.5
Benzyl butyl phthalate	BBP	Phthalate	85-68-7	$C_{19}H_{20}O_4$	4.7 ^{A}	2.69 ^{B}	7.4
Diethylhexyl phthalate	DEHP	Phthalate	117-81-7	$C_{24}H_{38}O_4$	7.73 ^{A}	0.27 ^{B}	49.5
Di-n-octyl phthalate	DnOP	Phthalate	117-84-0	$C_{24}H_{38}O_4$	7.73 ^{A}	0.022 ^{B}	4.9
Di-iso-decyl phthalate	DiDP	Phthalate	26761-40-0	$C_{28}H_{46}O_4$	9.46 ^{A}	0.28 ^{B}	99.4*
Diethylhexyl adipate	DEHA	Adipate	103-23-1	$C_{22}H_{42}O_4$		0.78 (22 °C) ^{B}	0.5
Diethylhexyl terephthalate	DEHTP	Terephthalate	6422-86-2	$C_{24}H_{38}O_4$		4.0 (20 °C) ^{B}	9.9
Acetyl tributyl citrate	ATBC	Citrate	77-90-7	$C_{20}H_{34}O_8$		1.7 ^{B}	2.5
Trioctyl trimellitate	TOTM	Trimellitate	3319-31-1	$C_{33}H_{54}O_6$		3.9 x 10^{-4} ^{B}	4.9

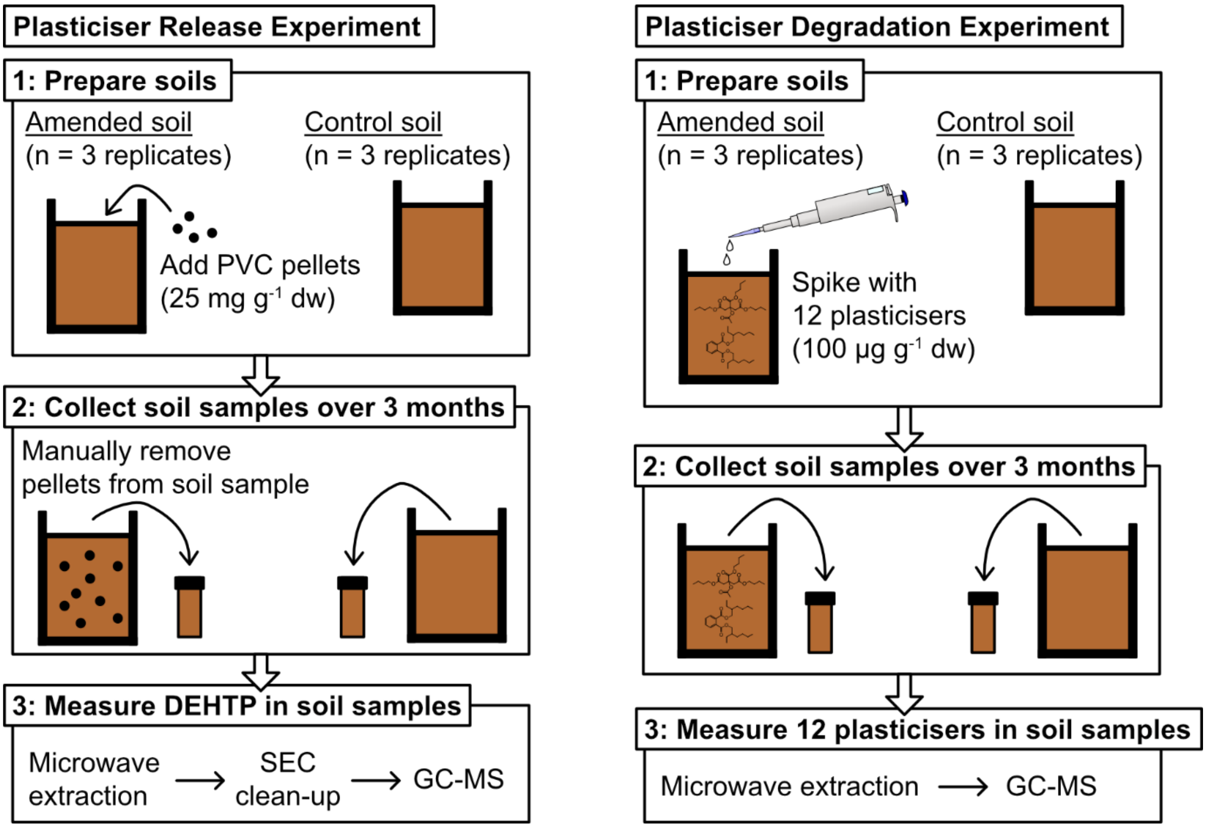
^{A}(Net et al., 2015); ^{B}PubChem online database; *DiDP exists as a mixture of isomers and thus had a higher limit of detection than other analytes (Al-Natsheh et al., 2015; Zou and Cai, 2013). The concentrations of DiDP reported in this study refer to the sum concentration of all DiDP isomers.

4.2.3 Experimental design for the release and degradation tests

4.2.3.1 Plasticiser release experiment

31.25 g of PVC microplastic pellets were added to 125 g dw soil in a metal mixing bowl, and the soil gently homogenised using a metal spoon to evenly distribute the plastic. After the plastic pellets had been added to the initial aliquot of soil, a further 1125 g dw soil was then added to the bowl and the mixture thoroughly homogenised using a metal spoon to give a final microplastic concentration of 25 mg g^{-1} dw soil (~0.74 pellets g^{-1} dw soil; Figure 4.1).

Figure 4.1: Design and setup of plasticiser release and degradation experiments.



Each soil was wetted to 50% water holding capacity (WHC) with reverse-osmosis (RO) water, a standard water content widely used in soil chemical bioavailability and toxicity studies (Spurgeon and Hopkin, 1995). A metal spoon was used to distribute 400 g dw equivalents of soil to each of 3 x 500 mL glass vessels (approximate dimensions 9 x 9 x 18 cm). ~10 g ww (wet weight) soil was sampled from each test vessel to assess pH at day 0. Preparation of a single stock of soil followed by distribution to individual test vessels was used, as the experiment was designed to account for the variability in the release rates between vessels, as opposed to variations in the initial starting concentrations of pellets in the soils. The mass of each test vessel was recorded before and after sampling. Vessels were covered and kept at 20 °C for three-month duration of the study.

4.2.3.2 Plasticiser degradation experiment

Experimental design and setup for the degradation experiment was the same as for the release experiment (Figure 4.1; section 4.2.3.1). However, instead of amending soils with PVC pellets, test soils were spiked with 12 mL of a solution containing the 12 plasticiser analytes in acetone at a concentration designed to give a nominal concentration of each plasticiser in the spiked soils of 100 µg g^{-1} dw (Figure 4.1). The plasticiser spike solution was added in 0.5 mL aliquots to 125 g dw soil in a metal mixing bowl, and the soil gently homogenised using a metal spoon to distribute the plasticisers. The vial was then rinsed with 3 x 2 mL acetone, with each rinse added to the soil in 0.5 mL aliquots. The soil was stirred thoroughly between each rinse. Acetone was also added to the control soils in the same manner as for the spiked soil to control for the presence of plasticisers in the solvent. The solvent was evaporated from all soils through gentle homogenisation in a fume cupboard followed by passive evaporation for at least 15 minutes. All other setup procedures (e.g. soil types, number of replicates) for the degradation experiment were the same as for the release experiment.

4.2.4 Sampling of release and degradation experiments

Samples for the release experiment were taken on days 0, 1, 7, 14, 21, 28, 42, 56, 70, 84 and for the degradation experiment on days 0, 1, 2, 4, 8, 16, 32, 64, 85. For acidic heathland

(Dorset) and sandy loam agricultural (Lufa) soils, a stainless-steel corer was used to take a composite sample (~20 g dw) from multiple locations across the surface of the soil. The alkaline grassland (Chiltern) soils were sampled with a stainless-steel spatula, as the soil texture did not allow for satisfactory core sampling. For consistency, holes from corers in the acidic heathland and sandy loam agricultural soils were gently backfilled with soil from elsewhere in the sampling vessel to mimic the sampling in the alkaline grassland soil. For the release experiment soils, the PVC microplastics themselves were all carefully removed from each sample using stainless-steel tweezers. All were transferred to glass vials and stored immediately at -20 °C in the dark.

Vessel weights were monitored weekly for the first 4 weeks of the experiment, and thereafter fortnightly, and RO water added where necessary to maintain constant soil moisture over the duration of the experiment. Soil pH was measured over the experiment to assess any changes that may affect plasticiser fate. Specifically, 5.0-5.1 g dw soil was sampled fortnightly from each vessel for pH analysis. For this measurement, the sampled soil was shaken thoroughly for 5 minutes in 25 mL 0.01 M $CaCl_{2(aq)}$, left for a minimum of 2.5 hours, and measured using a pH probe (Sartorius PP-25; Sartorius Lab Instruments, Germany). The pH probe was calibrated daily at pH 4, 7 and 10.

4.2.5 Plasticiser extraction and analysis

Plasticisers were extracted from each sample according to a method previously described in Chapter 3. In brief, 3.5-4 g ww (release experiment) or 0.1-0.15 g ww (degradation experiment) of soil was homogenised, dried with anhydrous sodium sulfate, and spiked with deuterium-labelled recovery standards (d4-DnBP and d4-DnOP, Sigma-Aldrich, USA). Plasticisers were extracted in 9:1 dichloromethane (DCM):acetone for 30 minutes using an Ethos X microwave extraction system (Milestone, Italy). Supernatants were dried with anhydrous sodium sulfate, reduced to a known volume, and passed through a 0.45 µm PTFE filter. Release experiment extracts were cleaned further using automated size-exclusion chromatography (Agilent 1200 series HPLC, Agilent, USA). All samples were spiked with deuterium-labelled internal standards (d4-DEP and d4-DEHP, Sigma-Aldrich, USA) prior to instrumental analysis.

Plasticisers were analysed using a gas chromatograph (6890N, Agilent, USA) fitted with an HP-5ms analytical column (30 m length, 0.25 µm film thickness, 0.25 mm internal diameter, Agilent, USA) coupled to a single-quadrupole mass spectrometer (5975B, Agilent, USA) operating in electron ionisation mode. For release experiment samples, 1.5 µL of sample was injected in split mode (split ratio 10:1). For degradation experiment samples, 1.7 µL of sample was injected in splitless mode. The inlet temperature was set to 300 °C, the MS source was set to 230 °C, and the carrier gas was helium at a constant flow rate of 1.5 mL min^{-1}. See Appendix S4.2 for oven temperature ramps.

Plasticisers were quantified using internal and recovery standards and calibration curves of plasticiser standards (Sigma-Aldrich, USA). A single procedural blank was included in each batch of degradation sample analyses, whilst two procedural blanks were included in release experiment sample analyses. Recovery of d4-DnOP in the release experiment ranged from 62-118% (mean 82% ± 12). The mean limit of detection (LOD) of DEHTP in the release experiment was 8.5 ± 1.6 ng g^{-1} dw soil. This was determined from the calibration curve, the mass of soil analysed, and the dilution factor. Recoveries of d4-DnBP and d4-DnOP in the degradation experiment were in the range 63-100% (mean 83% ± 10) and 61-104% (mean 83% ± 11). The method LODs for the degradation experiment are shown in Table 4.2. All plasticiser concentrations are reported in ng g^{-1} dw (dry weights were calculated using the initial moisture content in the soil; soil moisture was monitored throughout the experiment and adjusted where necessary in order to maintain constant moisture levels) and were recovery and blank-corrected.

4.2.6 Contamination controls

All glassware used during the experiments and sampling was soaked overnight in a 1% HNO_3 bath, rinsed 3 x with DI water, 3 x with RO water, and muffled at 450 °C for 8 hours. All sampling utensils were rinsed 3 x with DI water and 3 x with RO water before use and cleaned thoroughly with DI water and a natural-fibre lint-free wipe between samples. For each experiment, the same spatula and corers were used for each soil type. In order to capture any effects of cross-contamination during sampling, samples of each soil were collected in the order amended soil 1, control soil 1, amended soil 2, control soil 2, etc. For the release experiment, the actions and time spent removing the PVC microplastic pellets from the amended soil samples was replicated for control samples. Aluminium foil was used to provide a barrier between soil and the plastic lid of screw-top sample vials prior to storage at -20 °C.

All glassware used for the analysis was soaked overnight in Decon 90 and rinsed 2 x with DCM immediately prior to use. Glassware used during degradation sample extraction was also heated in a muffle furnace at 450 °C for a minimum of 2 hours prior to use (non-volumetric glassware only) (Fankhauser-Noti and Grob, 2007) to reduce the contamination of phthalates (primarily DEHP and DnBP). It was not deemed necessary to muffle glassware for the release sample extractions, as the analyte (DEHTP) was <LOD in every blank during the release experiment. The use of plasticware was avoided wherever possible and operators wore cotton lab coats. Solid reagents were heated in a muffle furnace at 450 °C overnight.

4.3 Results and discussion

4.3.1 Release experiment

Measurements indicate that a fraction of the total DEHTP associated with the plastic particles was released rapidly from the microplastics into the soil, reaching detectable concentrations in all 3 test soils in less than one day (Figure 4.2). The initial samples collected within 2 hours of first introducing the microplastics to the test soils showed measured concentrations well above the background DEHTP concentrations present in the unamended soils. Thus, after two hours of incubation, the mean DEHTP concentrations in the soils were 165 ± 8.8 (alkaline grassland), 302 ± 48.2 (acidic heathland) and 282 ± 63.4 (sandy loam agricultural) ng g^{-1} dw (Figure 4.2). Despite the rapid release of DEHTP from the pellets, mass balance assessment indicated that the total proportion of DEHTP released into each soil was estimated to be only very small, at <0.02% of total DEHTP mass in the pellets, based on a w/w value of 10% plasticiser (Hansen et al., 2013). The fact that the mass balance was weighted strongly towards the pellets suggests that the rapid initial release of DEHTP from the pellets may represent the mobilisation of molecules on the pellet surface (or near-surface), with subsequent releases via migration of plasticiser from the particle core to surface occurring much more slowly.

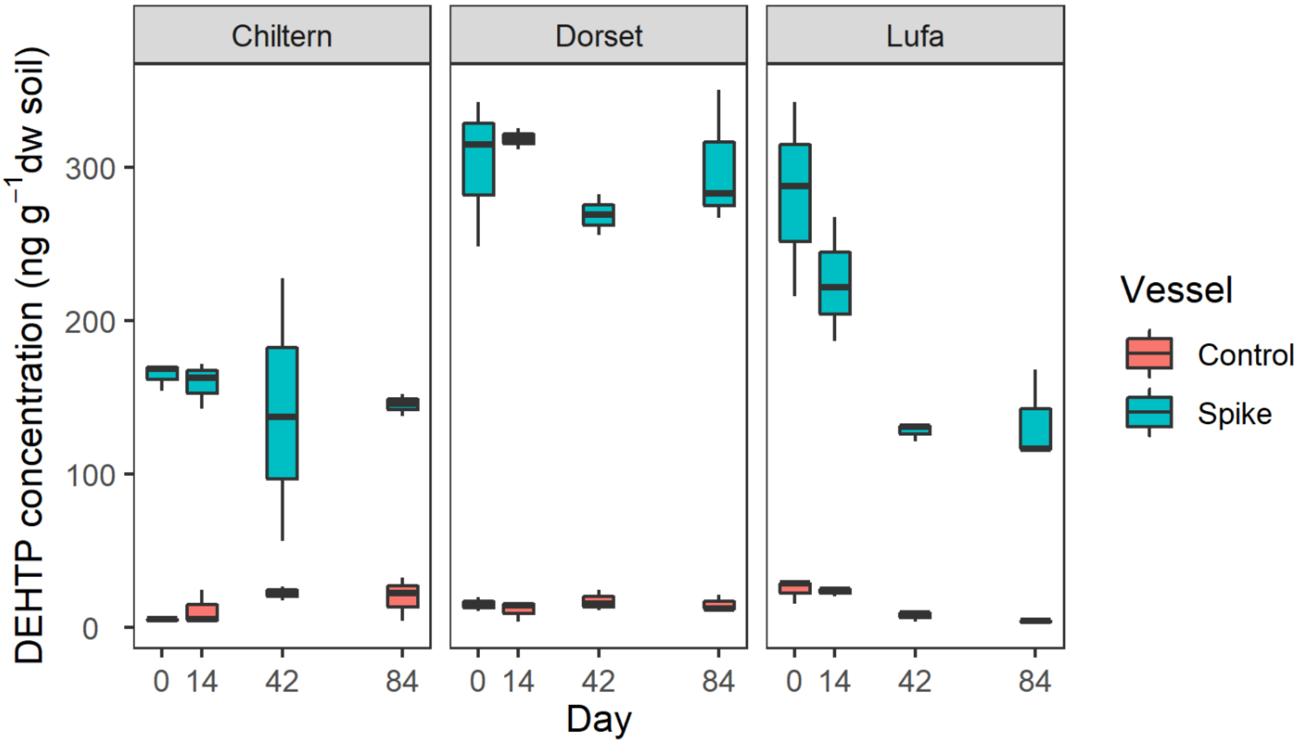


Figure 4.2: DEHTP concentration over time in control soils and soils amended with PVC microplastics: alkaline grassland (Chiltern), acid heathland (Dorset), and sandy loam agricultural (Lufa); samples with a DEHTP concentration below the limit of detection were assigned a value of 0.5 × LOD; 2 outliers in acidic heathland (Dorset) soil day 14 and 42 have been removed, as these samples were ~200% the concentration of the other values in the replicates.

The maximum DEHTP concentrations reached in the acidic heathland and sandy loam agricultural soils were 83% and 71% greater than in the alkaline grassland soil. This difference was not due to the differences in added PVC concentration between soils, as it was possible to measure the mass of PVC microplastics added to each soil to within 2 decimal places (31.25 g of microplastics were added to each batch of soil). Furthermore, there was no significant difference in the number of PVC particles removed at the first sampling time point from each core/sample across the three different soils (Dunn's test, Benjamini-Hochberg adjusted $p <$

0.05), implying that the sampling method adopted was representative. Instead, the initial release rate and subsequent maximum concentration of DEHTP will likely depend primarily on abiotic factors (e.g. soil properties) and their influence on the potential for release.

In addition to variations in the extent of initial release, differences in the DEHTP fate were also observed between the three soils. After the initial release period there was only a marginal decrease in DEHTP concentration over the 3-month test period in alkaline grassland (12% reduction) and acidic heathland (0.6% reduction) soils. In contrast, the decrease in DEHTP concentration in the sandy loam agricultural soil over the 84 days of the experiment was much greater, reaching ~50% of initial concentration within 42 days and remaining at this level in later samples (Figure 4.2). The nature and abundance of the microbial communities present in the soils and their role in plasticiser degradation are likely to play a key role in the difference in plasticiser fate between the three tested soils. This aspect will be discussed further in section 4.3.2.2.

4.3.1.1 Relationships between soil properties and extent of plasticiser release

The initial released DEHTP concentrations in the three soils were negatively related to the organic matter content, pH, and water holding capacity of the three soils. Due to the small number of tested soils (i.e. three) and the potential co-correlation between the different measured soil properties, statistical modelling using linear or non-linear correlation assessment could not be reliably used to investigate the nature of any relationships between soil properties and DEHTP release. Thus the initial indication from the results here, that soil properties potentially influence the extent of DEHTP release into soils, requires further studies to confirm which of the soil properties quantified here (e.g. pH, %OM, water holding capacity) may be acting as the major driver of this initial desorption and transfer into the test soils. That said, however, from the literature it is possible to tentatively identify potential drivers of the differences observed between soils.

Maximum initial DEHTP concentration in the organic-rich alkaline grassland soil (15.8% OM) was around half that of both the acidic heathland (3.7% OM) and sandy loam agricultural (5.0% OM) soils. The higher level of organic matter in the alkaline grassland soil could potentially have limited the release of DEHTP, relative to the other two soils, through formation of an 'ecocorona' of organic matter. Ecocoronas occur when polymer surfaces become coated in components derived from dissolved organic matter, a phenomenon which has been shown to affect fate dynamics of polymer-coated nanoparticles (Svendsen et al., 2020). The extent of ecocorona formation on polyethene microplastics was found to be greater in a soil with a higher %OM (Yao et al., 2023), although the relative contribution of other soil properties to ecocorona formation remains unclear. Thus, it is possible that ecocorona formation driven by greater %OM can limit the extent to which plasticisers can be released from microplastics, by preventing the formation of local concentration gradients around the microplastic particles, thus explaining the reduced DEHTP release from the pellets in the high-OM alkaline grassland soil. Furthermore, in the high-OM alkaline grassland soil, the transport of plasticisers away from sites of release (i.e. the pellets) by diffusion may be slower due to stronger binding of lipophilic DEHTP to OM in the soil immediately next to the microplastic particle which prevents the development of a diffusion gradient. This latter mechanism may result in a more heterogeneous distribution of DEHTP in the alkaline grassland soil than in the acidic heathland or sandy loam agricultural soils. Any such effect on spatial within-soil transport results in the occurrence of local hotspots of DEHTP around the particles not accounted for by the bulk sampling method.

In addition to a higher organic matter content, the alkaline grassland soil also had the highest water holding capacity and pH of the three soils (Table 4.1). The greater volume of water present in the alkaline grassland soil relative to acidic heathland or sandy loam agricultural soils could have potentially inhibited or reduced the release of hydrophobic DEHTP from the microplastic pellets. Such an effect would be consistent with previous findings of the relatively slow release of more hydrophobic phthalate DEHP compared to the less hydrophobic DnBP (Viljoen et al., 2023).

Soil pH is a major factor controlling the biological and biogeochemical processes in soils (Neina, 2019). However, although the alkaline grassland soil also had the highest pH of the test soils, it is not immediately clear why this would act to limit the amount of DEHTP released from the microplastics as there is no known mechanistic relationships between soil pH and plasticiser fate. One possibility is that the pH of the soil could potentially alter the association of organic matter species with particle surfaces, leading to the formation of different surface ecocoronas (Svendsen et al., 2020). However, although the association of microorganisms and other components of soil organic matter with nanoparticle and microplastic surfaces have been studied in soils, knowledge of the soil property determinants of ecocorona formation remains limited (Svendsen et al., 2020; Yao et al., 2023).

4.3.2 Degradation experiment

4.3.2.1 Differences in degradation rates between plasticisers

All plasticisers, with the exception of DiDP and TOTM, exhibited a decrease in concentration over the course of the experiment (Figure 4.3). There are a number of processes that could lead to apparent removal of plasticisers from soils. In theory, evaporation of plasticisers may occur from the soil surface. However, due to the high boiling points and low vapour pressures of the plasticisers used in our study, in addition to a sampling depth of ~8 cm within the soil, it is unlikely that volatilisation made a major contribution to the losses observed in this study. The formation of non-extractable plasticiser residues, through strong binding of plasticisers to organic-rich soil moieties, is a further mechanism that could lead to the apparent removal of plasticisers from the soil. It would be expected that plasticisers with higher affinity for organic matter would be more likely to be affected by this process. However, the concentration of plasticisers with the highest $\log K_{OW}$ values in our study (e.g. DiDP) did not decrease appreciably over time. Additionally, soils were homogenised to a fine grain, and microwave-digested in DCM for 30 minutes to a temperature of 50 degrees, which further increased the likelihood of extracting all available plasticiser.

Given the absence of evidence of a contribution of either non-extractable residue formation or evaporation, microbial biodegradation is most likely to be the dominant mechanism determining the rates of plasticiser concentration losses over time from the test soils. To investigate the comparative rates of loss, the degradation time series concentration data for each compound in each soil was fitted to zero, first, and second order kinetic models. The best model fit for a specific compound was not always consistent between soils (fit parameters for all models can be found in Appendix S4.3-S4.5), and the zero, first and second order models also produced increasingly long half-lives. To allow comparison of relative differences in half-lives between the plasticisers across the soils (something not possible if the half-lives from the best fitting models were used), we have chosen to report and discuss all values with respect to the first order models given that this is the most common model used in the literature (e.g. Cheng et al., 2008; Wang et al., 1997; Xie et al., 2010).

Degradation of the majority of the measured plasticisers was found in one or more of the three test soils over the 84 days of the experiment (Figure 4.3). The pseudo-first order model fits (Appendix S4.6), indicated significant degradation in at least one soil for every phthalate except for DiDP, for which concentrations did not appear to change significantly over time in any soils within any model (0, 1st, or 2nd order). Each emerging plasticiser was also found to degrade in at least one soil (Figure 4.3). Of the four non-phthalate plasticisers, DEHA showed rapid degradation in all soils, while TOTM appeared to be particularly resistant to degradation, especially in the sandy loam agricultural soil (Figure 4.3).

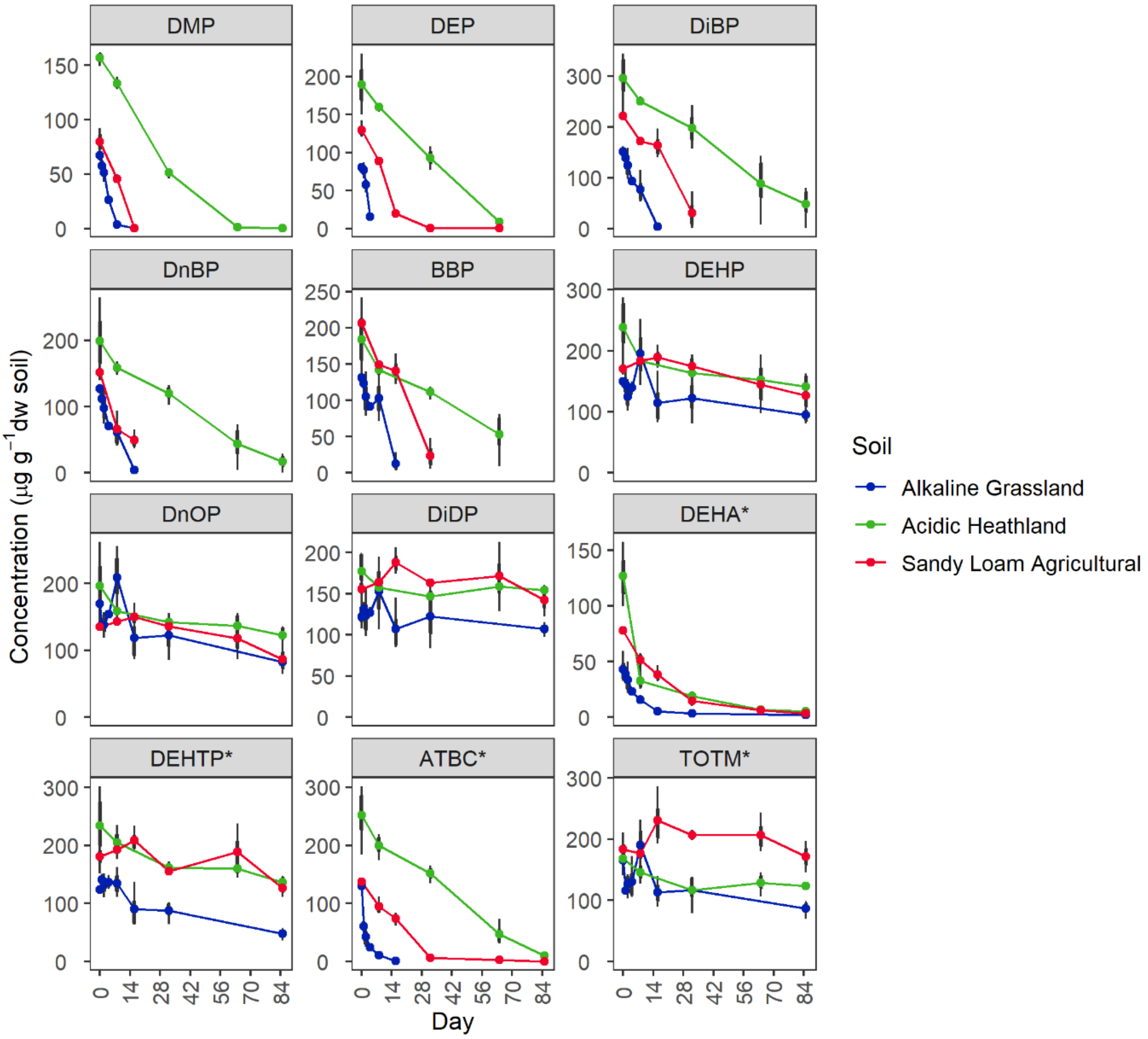


Figure 4.3: Plasticiser concentrations over time in spiked soils in the degradation experiment; data points are only shown where all three replicates were >LOD; * indicates an emerging plasticiser.

Phthalate degradation was generally more rapid for those compounds with lower molecular weights and chain lengths. This finding is in line with previous observations, which have linked the slower degradation of phthalates with longer chain lengths to their logK_{OW}, which means that these substances will bind more strongly to organic matter in the soil, rendering them less available to microorganisms for biodegradation (Cartwright et al., 2000; Tang et al., 2020; Xie et al., 2010). The modelled first-order degradation rates of the emerging plasticisers followed the order DEHA > ATBC > DEHTP > TOTM. Thus although DEHA and ATBC degraded in all soils, concentrations of DEHTP and in particular TOTM changed little over the experiment (Figure 4.3). Although $\log K_{OW}$ data is not readily available for the four emerging plasticisers, the order of half-lives of these plasticisers generally followed the order of increasing molecular masses, specifically DEHA (RMM 371) < ATBC (403) < DEHTP (391) < TOTM (547), thus some association with $\log K_{OW}$ is also likely. That ATBC degraded more rapidly than DEHTP may be explained by the difference in the chemical structure of these two compounds. Although there is limited knowledge regarding the exact mechanism of biodegradation of these substances, it is possible that the initial step in the degradation of both compounds occurs via the cleavage of the ester groups within their structures, as this is the most easily hydrolysable functional group in their otherwise solely aliphatic or aromatic structures. As DEHTP contains two such ester groups compared to four in ATBC, the latter may be more likely to be vulnerable to degradation independent of molecular size.

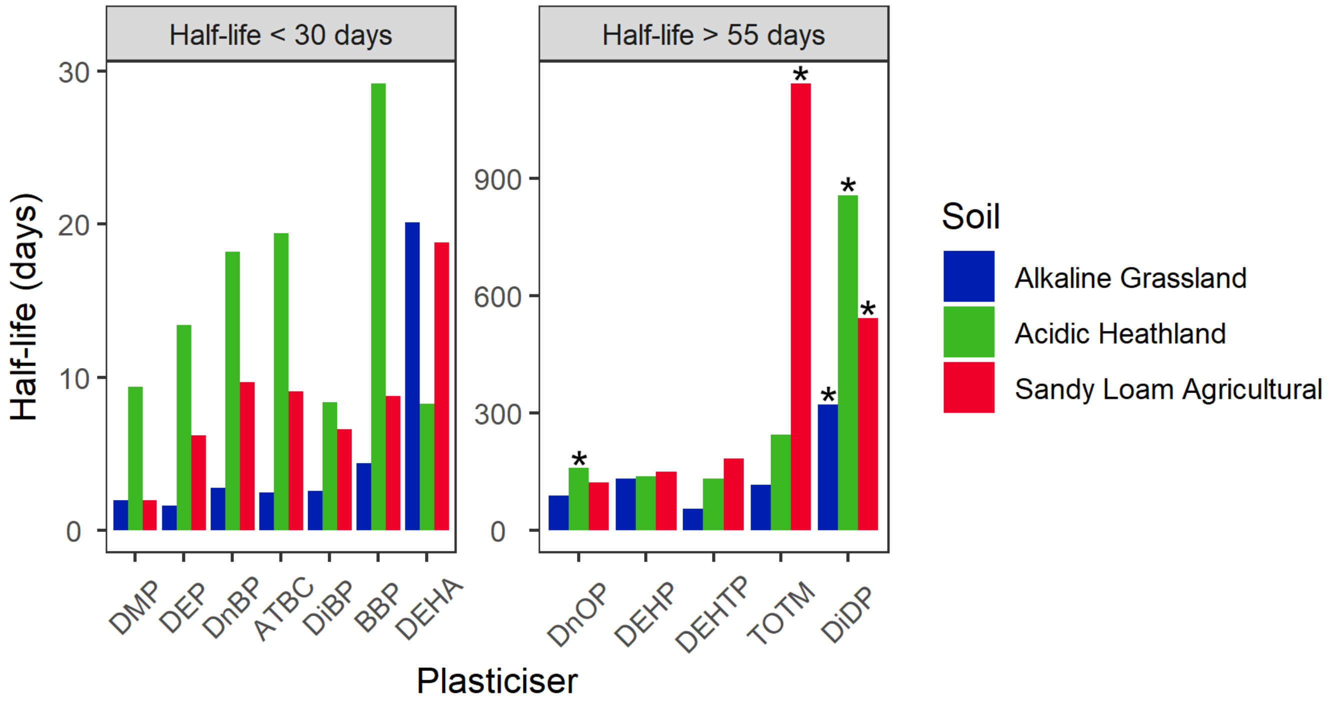


Figure 4.4: Half-lives of plasticisers in soils in the degradation experiment estimated with a pseudo-first order model; * indicates insignificant degradation over the course of the experiment according to model outputs.

The calculated half-lives of the 12 plasticisers studied, broadly separate them in to two groups; fast degrading ($t_{1/2}$ <30 days), and semi-persistent or persistent ($t_{1/2}$ > 55 days) compounds (Figure 4.4). The fast-degrading group contains the lower molecular weight phthalates (DMP, DEP, DnBP, DiBP and BBP), and the emerging plasticisers ATBC and DEHA. The greater susceptibility of these plasticisers to degradation is consistent with the relatively low concentrations of the majority of these compounds (e.g. DMP, DEP, BBP, ATBC, DEHA) reported across monitoring studies conducted in soils (Chapter 3; Zeng et al., 2020; Zhang et al., 2019). The two exceptions for this trend are the two phthalates DiBP and DnBP, which are both commonly found in the environment and account for a significant part of the phthalate load in soils (Chapter 2), despite their relatively rapid potential for degradation. The common presence of DiBP and DnBP indicates that these plasticisers, either through high production volumes or widespread release and transport, may have “pseudopersistence” in soils.

The remaining 5 plasticisers, the higher molecular weight phthalates (DnOP, DEHP, and DiDP) and persistent emerging plasticisers (DEHTP and TOTM), generally had pseudo-order order half-lives >100 days in all soils (Figure 4.4). Occurrence data for TOTM and DEHTP in soils is limited, although these compounds are among the most abundant reported plasticisers in the few available studies of their occurrence in sediment (Jebara et al., 2021; S. Kim et al., 2021; Y. Kim et al., 2021). The fact that DEHTP and TOTM are relatively enriched in some environmental matrices, despite relatively low production volumes relative to phthalates (CEFIC, 2021), may partly be explain by the comparatively slow degradation rates measured here. As such, the loading of these substances that reach soil may remain resident for extended periods.

4.3.2.2 Effects of soil properties on plasticiser degradation

With the exception of DEHA, all the other 11 plasticisers show fastest degradation in the alkaline grassland soil compared to the two other soils (Figure 4.4). The alkaline grassland soil contained a %OM content of 16%, while the acidic heathland and sandy loam agricultural soil had comparable organic matter levels (3.7% and 5%). Thus in this study fastest degradation rates were in the soil with the highest %OM content. In previous studies, organic matter has been negatively correlated with the degradation rates of plasticisers (Kickham et al., 2012; Xu et al., 2008). This effect of organic matter has been linked to the binding of lipophilic plasticisers to this soil fraction, thereby reducing bioavailability to microbes for biodegradation (Kickham et al., 2012; Xu et al., 2008). In contrast to these findings, and in agreement with our results, more recent studies have indicated that the overall effect of organic matter constituents, such as humic acids, can be to promote microbial phthalate degradation (Tang et al., 2020; Tao et al., 2020), potentially via provision of a nutritional source which can prime microbial communities for plasticiser degradation (Chapter 2).

We found that the relative differences in the degradation rates of phthalate congeners between different soils were greater for lower molecular weight and lower $\log K_{OW}$ plasticisers' (Appendix S4.6; Figure 4.4). This finding suggests that the influence of soil properties, such as organic matter, on degradation rate is congener-specific, with lower molecular weight plasticisers (e.g. DMP, DEP) degradation more strongly influenced than for the higher molecular weight compounds (e.g. DnOP, DEHP). This effect may be plausibly associated with the increased likelihood of biodegradation for lower molecular weight compounds (Kanaly and Harayama, 2000).

In addition to the highest %OM content, the alkaline grassland soil had the highest pH (7.3 vs 5.3 of sandy loam agricultural, and 3.8 of acidic heathland) (Table 4.1). That degradation was fastest in the soil with pH closest to 7 is consistent with previous studies (Chang et al., 2009; F. Zhu et al., 2018b). It has been proposed that at high soil pH, the bioavailability of plasticisers to micro-organisms may be increased, as the ability of plasticisers to bind to organic matter is reduced at higher pH levels. (Cheng et al., 2019; Yang et al., 2013). This has been attributed to the pH-induced ionisation of organic groups in organic matter leading to reduced hydrophobicity and therefore lower plasticiser binding potential (Cheng et al., 2019). Cheng et al. (2018) further found that DnBP degradation rates were significantly higher in soils with a higher soil moisture level. All the soils in our study were wetted to 50% of their WHC. However, as the alkaline grassland soil had a higher field capacity, the absolute level of water added to this soil was higher than for the other two soils. Further studies of the drivers of degradation, related to soil organic matter content, pH and potentially other soil physiochemical properties are, however, needed to better understand the controls on plasticiser degradation rates across soil types.

The faster degradation of DEHTP in the sandy loam agricultural soil in the release experiment (section 3.1) was not observed in the degradation study (section 3.2). In the release experiment, total DEHTP decreases over the time-course were 12% (alkaline grassland), 0.6% (acidic heathland), and ~50% (sandy loam agricultural). This contrasted with the estimated first order half-lives of DEHTP in the degradation study of 56 (alkaline grassland), 132 (acidic heathland), and 183 days (sandy loam agricultural), respectively. The release and degradation experiments were conducted concurrently under similar temperature, UV and soil moisture conditions. The only differences were the nature of plasticiser input (associated with PVC microplastics vs direct chemical addition) and initial DEHTP concentrations (~165-300 ng g^{-1} dw vs ~100-250 µg g^{-1} dw in the release and degradation experiments). Thus, it appears that degradation of DEHTP was influenced either by the presence of PVC microplastics which may have acted to modify relative degradation between the soils or alternatively be subject to a concentration-dependent effect. Concentration-dependent degradation of DnBP was observed by Cheng et al. (2018), and degradation rate was positively correlated in one soil and negatively correlated in the other. Furthermore, we found no clear link between the initial concentration of DnBP and DEHP and their degradation rates in soils in Chapter 2. Thus the effect of initial concentration on half-life may be soil- and compound-specific. Microbial degradation has been demonstrated as a primary driver of phthalate fate in soils (Hurtado et al., 2017; Xie et al., 2010). This can also be expected to be the case for DEHTP, which is a structural isomer of the phthalate DEHP. The sandy loam agricultural soil had a more circumneutral pH, so may have a more diverse microbial community than the other test soils, in particular the acidic heathland soil, and so may have a greater multi-functional community (Griffiths et al., 2011). This may partly explain why the sandy loam agricultural soil was the only soil in which we saw significant degradation of DEHTP over the course of the release experiment.

4.3.3 Environmental implications of findings

The rapid increase in DEHTP concentrations in the release study suggested that some of the additive load associated with microplastic particles or plastic items can be very rapidly released following entry into the soil environment. An estimate of the mass balance indicates, however, that the rapid initial release may result from the presence of plasticisers on the surface (or near-surface) of the plastic item, followed by much slower migration and release of plasticiser occluded within the polymer matrix. Thus, entry of plastics into soils followed by release may act as a significant vector for plasticiser entry into the soil environment, given that the majority of the plasticiser load added to plastics will be retained and may be released only over timescales beyond those used in this study. Under these conditions of potentially very slow release of the bulk of the plasticiser fraction, plasticisers that are more resistant to degradation may maintain or even increase in concentration in the terrestrial environment following the input of plastics in which they are present.

Once in the soil environment, plasticisers are subject to degradation mediated mainly by the actions of the microbial communities present. The rates of such biodegradation differ considerably between compounds, with the heavy molecular weight (and associated higher lipophilicity) compounds showing greater persistence. The potential effects of soil properties (organic matter, pH, water availability) on plasticiser degradation rates suggests that soil types, as well as source intensity and underlying soil microbiology, may affect plasticiser fate, and as a result, concentration in soil. Given that local and seasonal differences can be expected in pH, soil %OM content, organic matter inputs, temperature and rainfall, both local-scale and seasonal differences in plasticiser degradation (and resulting concentrations) may be anticipated, which will affect the exposure of organisms to these pollutants.

4.4 Conclusions and suggestions for future work

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

Given that our mechanistic study used pristine microplastics of only a single polymer type (PVC) and formulation, further work regarding plasticiser release from plastics into soils is needed. Such studies should focus on expanding the range of polymer types investigated and compounds considered, as the internal polymer structure and compound properties may affect the movement of compounds within the matrix, thereby affecting release (Chapter 2). Pristine microplastic pellets will constitute only a minor fraction of the microplastic present in the environment, therefore future studies using ‘aged’ microplastics with altered internal and external polymer structures may be warranted. Additionally, the amount and type of additive content depends on polymer type due to the variety of applications for which plastics are used, and different leaching patterns may be observed for different plasticisers (Hansen et al., 2013).

We also carried out an experiment to determine the degradation rates of 8 phthalate and 4 emerging plasticisers over 84 days. Significant degradation of all plasticisers in at least one soil was observed, except for the phthalate DiDP. We found that the persistence of phthalates and emerging plasticisers was generally correlated with chain length and $\log K_{OW}$, indicating that sorption of plasticisers to organic matter, thus rendering then unavailable for biodegradation, may play a key role in determining relative degradation rates between different plasticisers. The majority of plasticisers were found to degrade relatively rapidly, with half-lives of <30 days. This included the phthalates DMP, DEP, DnBP, DiBP and BBP, and the emerging plasticisers ATBC and DEHA. However, little degradation over 3 months was observed in a group of significantly more persistent plasticisers, including the emerging plasticisers DEHTP and TOTM. As these emerging plasticisers, in addition to DiDP, are increasingly being used as replacements for phthalates, the concentrations of these compounds in the terrestrial environment are likely to increase as they accumulate in soils in the future. Future work should focus on determining fate, bioavailability and potential toxicity of these next-generation higher-molecular weight plasticisers (e.g. DEHTP, TOTM, DiDP) in soil organisms, as the occurrence of these compounds may increase in the future due to their increasing use and apparent persistence.

4.5 Acknowledgements

This work was supported by the Natural Environment Research Council NE/S007423/1, with Alex Billings’s studentship through the ENVISION Doctoral Training Partnership.

5

Emerging and legacy plasticisers in coastal and estuarine environments: A review

5. Emerging and legacy plasticisers in coastal and estuarine environments: A review

Abstract

The occurrence of plastic waste in the environment is an emerging and ongoing concern. In addition to the physical impacts of macroplastics and microplastics on organisms, the chemical effects of plastic additives such as plasticisers have also received increasing attention. Research concerning plasticiser pollution in estuaries and coastal environments has been a particular focus, as these environments are the primary entry point for anthropogenic contaminants into the wider marine environment. Additionally, the conditions in estuarine environments favour the sedimentation of suspended particulate matter, with which plasticisers are strongly associated. Hence, estuary systems may be where some of the highest concentrations of these pollutants are seen in freshwater and marine environments. Recent studies have confirmed emerging plasticisers and phthalates as pollutants in estuaries, with the relative abundance of these compounds controlled primarily by patterns of use, source intensity, and fate. Plasticiser profiles are typically dominated by mid-high molecular weight compounds such as DnBP, DiBP, and DEHP. Plasticisers may be taken up by estuarine and marine organisms, and some phthalates can cause negative impacts in marine organisms, although further research is required to assess the impacts of emerging plasticisers. This review provides an overview of the processes controlling the release and partitioning of emerging and legacy plasticisers in aqueous environments, in addition to the sources of plasticisers in estuarine and coastal environments. This is followed by a quantitative analysis and discussion of literature concerning the (co-)occurrence and concentrations of emerging plasticisers and phthalates in these environments. We end this review with a discussion the fate (degradation and uptake by biota) of these compounds, in addition to identification of knowledge gaps and recommendations for future research.

5.1 Introduction

Contaminants used in different settings may be transported towards the oceans through entry into rivers via e.g. runoff from agricultural land, leaching from contaminated soils (e.g. landfill) into surface water or groundwater, or discharge from wastewater treatment plants. Additionally, estuarine sediments and waters adjacent to heavily urbanised or industrial areas may see direct contaminant input from surface runoff, or leaching from legacy or current-use waste disposal sites (e.g. landfills). Estuaries have the potential to act as traps for these contaminants, delaying their input into the wider marine environment, although the extent to which this occurs is driven primarily by the hydrophobicity of the chemical as this determines its partitioning between sediment and water (Chapman and Wang, 2001). This is because the so called ‘estuarine filter’ effect occurs, whereby increased salinity associated with the transition from fresh to marine water results in the sorption (‘salting out’) of contaminants to estuarine sediments (Stumm and Morgan, 1996). Within estuaries, the highest levels of contaminants tend to be closer to the shore, as these chemicals become diluted with increasing distance from the estuary mouth and proximity to sources such as industry and coastal landfill (Zhao et al., 2020). Thus it is clear that estuaries and coastal environments will likely exhibit one of the highest burdens of non-polar organic contaminants in the marine ecosystem.

Plasticisers are chemicals added to plastics to increase their flexibility, and chemicals performing this role can account for up to 70% w/w of a given plastic item (Hansen et al., 2013). Historically, phthalates have been the most widely used class of plasticiser. However, recent concerns surrounding the endocrine disrupting properties of phthalates has led to their restriction in the European Union (ECHA, 2022, 2018). Limits on their use have resulted in an increase in the use of non-phthalate (also known as ‘emerging’) plasticisers over the last 20 years (CEFIC, 2021). The most commonly produced emerging plasticiser class in Europe are the terephthalates (~13% market share in 2020) (CEFIC, 2021), followed by the aliphatics (e.g. adipates; 8%), cyclohexanoates (8%) and trimellitates (3%). Despite the recent increase in use of these emerging compounds, phthalates still dominate the European and global plasticiser markets, accounting for an estimated ~55% of overall use in this sector in the year 2020 (CEFIC, 2021).

Studies of plasticiser occurrence in the terrestrial environment have almost exclusively focussed on legacy (i.e. phthalate) plasticisers, with very limited data concerning emerging plasticisers (Chapter 2). In contrast, a greater diversity of plasticiser compounds have been studied in marine environments. However, despite the increasing variety of plasticisers entering the environment, there remains a lack of synthesis of data concerning legacy and emerging plasticisers in estuarine and coastal systems. To provide this overview, this narrative assessment will focus on studies addressing the co-occurrence of multiple classes of plasticiser. Sources, inputs, and fates of plasticisers in estuarine and near-shore environments are also discussed, in conjunction with existing information of their exposure to and ultimately uptake by biota. On the basis of the data available, a summary of key knowledge gaps and recommendations for future research is also provided.

5.2 Sources of plasticisers in estuarine and coastal environments

Plasticisers are synthetic chemicals, therefore their occurrence in the environment stems entirely from human activities. There are a range of potential entry points of plasticisers into the environment, e.g. leaching from plastics used in urban, industrial, and agricultural areas. Plasticisers released in these land uses may be transported to estuarine environments through entry into rivers via surface runoff or entry into groundwater, followed by downstream transport and eventual transport in to estuarine or coastal systems. Alternatively, plasticisers may be released directly into estuarine environments if the source area is in close proximity to the coast. Within the environment, various scales of plastic debris (e.g. macro- and microplastics) act as vectors of plasticiser transport, thus the movement of plastics from source areas to sites of deposition can also result in the ultimate input of plasticisers at these sites.

5.2.1 Urban and industrial areas

Areas associated with plastic manufacturing or associated industries will likely act as point sources of plasticisers into rivers, through e.g. mismanagement of waste during transportation, leaching from the plant or process itself, or unintentional discharges (Liu et al., 2021). The use of plasticisers in urban and industrial infrastructure also leads to the input of these chemicals into the environment. E.g. plasticisers used building and construction materials account for 45% of plasticiser consumption in Europe, whilst consumer items such as packaging materials account for 13% (CEFIC, 2018). Thus, urban areas may provide a passive input of plasticisers into the rivers through leaching from the PVC pipes typically used in drinking or waste water infrastructure, in addition to leaching from waste consumer items.

5.2.2 Waste disposal sites

Waste disposal sites (e.g. municipal or industrial landfills) have been identified as medium-term sinks of plasticisers and plastics in the terrestrial environment (Chapter 2). Numerous studies from a variety of countries have identified the presence of phthalates in landfill (Jonsson et al., 2003; Mohammadi et al., 2022). Many landfill sites, particularly historical legacy sites (e.g. some sites used in the United Kingdom from the 1950s-1990s) or those in developing countries may not be lined. Such sites may act as inputs of plasticisers into rivers through direct runoff, lateral flows into neighbouring soils or water bodies, or vertical movement into groundwater that later recharges rivers.

Even for landfill sites lined with membranes designed to prevent vertical leaching of contaminants, contamination of groundwater with plasticisers may still occur. Liu et al. (2010) reported that the mean Σphthalate concentration (16 congeners) in groundwater associated with a municipal landfill site was almost 4 times greater than in corresponding surface water, although measured concentrations were still relatively low (1.78-6.35 μg L^{-1}) compared to concentrations in leachate collected from the landfill (78 μg L^{-1}). Adjacent soils were, however, contaminated at levels higher than any water sample (681 ng g^{-1}), indicating that the lipophilicity of plasticisers may somewhat limit their transport in the aqueous environment, and thus soils may act as a sink for plasticisers emitted from landfill sites. A recent study detected Σphthalate concentrations (7 congeners) ranging from 1000-6000 μg L^{-1} in surface leachates from a coastal municipal landfill (Mohammadi et al., 2022). These concentrations are greater than those reported by Liu et al. (2010) by a factor of >100. It is unclear whether this difference arises from differences in sampling methods of high intra-site variability, or whether site history and the nature of received waste may influence plasticiser contamination in landfill sites. Thus, some legacy landfill sites in the proximity of the coast likely result in a significant input of plasticisers to estuaries, through e.g. coastal erosion and vertical runoff, whilst sites with a higher degree of lining may act as relatively minor inputs.

5.2.3 Wastewater treatment and sewage effluent

The primary outputs of wastewater treatment plants (WWTPs) are sewage sludge as biosolids that can be transferred to soil, and effluent that is released into surface water or directly into estuarine-coastal systems. Particulates (such as microplastics) and the majority of organic chemicals (including plasticisers) not degraded or removed during the treatment process are dominantly retained in the sewage sludge (Horton et al., 2021; Y.S. Lee et al., 2019). However, even though the majority may be retained in sludge, plasticisers may also occur in the effluent that is released directly into rivers (Y.S. Lee et al., 2019). Effluent may become relatively more concentrated in lower molecular weight plasticisers (e.g. diethyl phthalate, DEP), whilst sewage sludge is relatively more abundant in higher molecular weight compounds (e.g. di-n-octyl phthalate, DnOP). The majority of sewage sludge produced in the UK is spread on agricultural fields as an amendment (DEFRA, 2012), and runoff and direct leaching may result in the input of plasticisers into rivers. Whilst there have been few studies directly assessing the role of wastewater treatment effluent on the occurrence of plasticisers in rivers and estuaries, direct releases of effluent have been linked with elevated levels of plasticisers in river sediments. For example, a nationwide study of sediments from urban rivers in China found that the highest emerging plasticiser and phthalate concentrations were associated with cities with greater discharge from WWTPs owing to higher population densities, in addition to the mismanagement of wastewater or less advanced treatment processes (Liu et al., 2021).

5.2.4 Agricultural land

Agricultural land can act as a source of plasticisers in estuarine environments via leaching of plasticisers from agricultural plastic material, followed by runoff directly into river courses, or from sub-surface lateral flow via field drains to neighbouring water bodies. There is a significant body of evidence that links the use of plastic mulch in farmlands with the occurrence of plasticisers in soils (e.g. Hu et al., 2003; Kong et al., 2012; Sun et al., 2016). Sewage sludge addition to agricultural land has also been shown to result in the long-term accumulation of phthalates in soils, with concentrations remaining significantly elevated for years following application (Rhind et al., 2013b; Tran et al., 2015; Vikelsoe et al., 2002). As the sewage sludge is generally ploughed into the fields, this creates a broken-up and fragmented layer of amended soil on the surface which may be particularly susceptible to transport via overland surface flows following rainfall. There remains a lack of systematic studies of the effects of sludge application on the fluxes of plasticisers in river sediments or water, although a recent catchment-wide field study found no clear link between microplastic contamination in Chinese soils and adjacent riverine sediments (L. Xu et al., 2022), indicating that the transfer of microplastic-associated plasticisers from soils to adjacent riverine sediments may be slow.

5.2.5 Seasonality of river inputs

Given that rivers are the primary vector by which contaminants enter estuaries, seasonality of plasticiser occurrence in rivers may impact the input of plasticisers into coastal environments. A recent study reported the concentrations of 6 phthalates in both water and sediments of an inland river in China were higher in the dry seasons than in the wet season (Dong et al., 2022). These differences were attributed to the increased dilution of river water and sediments during the wet season compared to under low flow conditions. Furthermore, Huang et al. (2008) and Lin et al. (2009), found that the concentration of the phthalates diethyl hexyl phthalate (DEHP), benzyl butyl phthalate (BBP) and di-n-butyl phthalate (DnBP) in river sediments from Taiwanese rivers were also generally greater in the dry than wet season. A more complex seasonal pattern was observed by Wang et al. (2008), who reported Σphthalate (5 congeners) concentration in river water up to 2 orders of magnitude greater in the dry season than the wet season. However, between the two seasons sediment concentrations were broadly comparable, demonstrating that some river sediments can act as a medium-term sink for plasticisers irrespective of variations in river discharge. Converse to these patterns indicating higher concentrations in the dry season, a study of a river in Taiwan found significantly higher concentrations of DEHP in sediments in the wet than dry season (mean concentrations of 28.6 vs 17.8 µg g^{-1} dw) (Chen et al., 2018). An earlier European study across three seasons reported no significant difference in DEHP and DnBP concentrations in Dutch freshwaters across spring, summer and autumn (Peijnenburg and Struijs, 2006). The variations in the extent and patterns of seasonality in plasticiser concentrations between different regions and studies likely arise from differences in channel flow, linked to increased sediment resuspension and transport, and the effects of dissolved vs particle phase plasticiser transport. Furthermore, differences in the magnitude of e.g. temperature and rainfall variations across the annual seasonal cycle between areas with contrasting climates may exacerbate these flow variations.

Overall trends across the range of reported studies suggests that plasticiser concentrations in rivers may be at their highest in drier portions of the year, when flows are lowest and, thus, dilution is lowest. Rivers at this time will therefore provide a more concentrated input of plasticisers into estuaries during these lower flow periods. However, the total plasticiser input to estuaries may ultimately be greater under high-flow conditions (e.g. during the wet season), due to increased flow velocity and input of resuspended sediments and runoff from adjacent land.

5.*2.6 Comparison of plasticiser fluxes associated with different land uses*

Urban, and in particular industrial, land uses appear to be primary sources of plasticisers in estuarine systems. For example, coastal sediments associated with industrial land uses were found to be the most contaminated by Arfaeinia et al. (2019), with Σphthalate (16 congeners) found at greater concentrations in industrial (82 $\mu g\ g^{-1}$) areas than urban (13 $\mu g\ g^{-1}$) or natural rural (6.5 $\mu g\ g^{-1}$) sites. The occurrence of 13 phthalates in sediments collected from a bay fed by multiple rivers provides further evidence for the role of urbanised areas in plasticiser occurrence. B. T. Zhang et al. (2020) found that land use in areas surrounding rivers discharging in to the bay had a strong influence on the concentrations of plasticisers present in the estuarine sediments, irrespective of river discharge. Thus, phthalates were most abundant in the areas of the bay fed by rivers with higher population densities and anthropogenic activities (e.g. industry, wastewater discharges), whilst sediments in the areas of the bay fed by 'agricultural' rivers had lower phthalate concentrations. Wang et al., (2014) measured the occurrence of 6 phthalates in river sediments associated with industrial/commercial, residential and agricultural land uses. Mean Σphthalate concentration was an order of magnitude greater in industrial/commercial sediments (27.8 $\mu g\ g^{-1}$) than in agricultural ones (3.3 $\mu g\ g^{-1}$), and ~3 times greater than in residential area samples (8.8 $\mu g\ g^{-1}$). The primary driver of this difference was the higher relative abundance of DEHP and to a lesser extent DnBP and BBP, indicating that these phthalates may be particularly associated with industrial areas. Thus, whilst there is evidence for the inputs of plasticisers into rivers and coastal environments from agricultural sources (Arfaeinia et al., 2019; Wen et al., 2018), the intensity of these inputs appears to be less than from industrial or residential sources (Arfaeinia et al., 2019; Wang et al., 2014).

There appear to be regional differences in phthalate concentrations in coastal sediments and waters, although data is limited, and these variations suggest local sources may be particularly important in determining phthalate concentrations. For example, Arfaeinia et al. (2019) reported very high concentrations of DEHP (mean 2.0-30.3 µg g^{-1} dw), DnBP (mean 0.9-12.0 µg g^{-1} dw) and di-iso-butyl phthalate (DiBP; mean 0.3-3.6 µg g^{-1} dw) in coastal sediments of the Persian Gulf, values around an order of magnitude greater than those reported in e.g. the northern Mediterranean (Castro-Jiménez and Ratola, 2020; Paluselli et al., 2018a). Concentrations of DEHP (71.7 µg L^{-1}), DnBP (17.2 µg L^{-1}) and DiBP (75.4 µg L^{-1}) in coastal seawater in the Southern Mediterranean were over an order of magnitude greater those reported in the northwestern Mediterranean for coastal and estuarine water (Paluselli et al., 2018a). Thus, the occurrence of phthalates in estuarine and coastal environments may be highly dependent on the nature and intensity of the inputs deriving from river inputs and point sources along the coast.

5.3 Processes controlling plasticiser release and partitioning in aqueous environments

5.3.1 Plasticiser leaching

The majority of legacy and emerging plasticisers exhibit high lipophilicity and poor water solubility, with the exception of some of the lower molecular weight phthalates, e.g. dimethyl phthalate (DMP) and DEP, which are relatively soluble in water (Table 5.1). It is these properties which primarily determine the leaching rates of plasticisers out of the plastics in which they are incorporated and into the surrounding environment. For example, plasticiser release into organic-rich media (e.g. sediments) will likely be faster than into aqueous media (e.g. seawater), as has been widely documented in food-contact literature (Choi et al., 2018; Coltro et al., 2014; Kastner et al., 2012). Thus, the presence of dissolved or suspended organic matter in a water body will also likely increase the rate of plasticiser leaching. The chemical properties of plasticisers may also affect the plasticiser profiles that leach from plastics, due to differences in K_{OW}. For example, higher molecular weight phthalates (e.g. DEHP, C8 chains) may leach more rapidly into sediments than lower molecular weight phthalates (e.g. DEP, C2 chains), and vice versa (Dhavamani et al., 2022). However, whilst there are a number of studies of plasticiser release into seawater (e.g. Cao et al., 2022; Paluselli et al., 2019; Suhrhoff and Scholz-Böttcher, 2016), no such data is available for sediments.

Table 5.1: Physiochemical data for selected phthalate (legacy) and the most frequently studied emerging plasticisers; adapted from Chapter 2; solubility in water is at 25 °C unless otherwise stated.

Name and acronym		Class	Formula	Vapour pressure (Pa)	Log K_{OW}	Log K_{AW}	S_{H2O} (mg L^{-1})
Dimethyl phthalate	DMP	Phthalate	$C_{10}H_{10}O_4$	2.63×10^{-1} ^{A}	1.61 ^{A}	-5.4 ^{A}	4000 ^{B}
Diethyl phthalate	DEP	Phthalate	$C_{12}H_{14}O_4$	6.48×10^{-2} ^{A}	2.54 ^{A}	-5.01 ^{A}	1080 ^{B}
Di-iso-butyl phthalate	DiBP	Phthalate	$C_{16}H_{22}O_4$	4.73×10^{-3} ^{A}	4.27 ^{A}	-4.27 ^{A}	6.2 (24 °C) ^{B}
Di-n-butyl phthalate	DnBP	Phthalate	$C_{16}H_{22}O_4$	4.73×10^{-3} ^{A}	4.27 ^{A}	-4.27 ^{A}	11.2 ^{B}
Benzyl butyl phthalate	BBP	Phthalate	$C_{19}H_{20}O_4$	2.49×10^{-3} ^{A}	4.7 ^{A}	-4.08 ^{A}	2.69 ^{B}
Diethylhexyl phthalate	DEHP	Phthalate	$C_{24}H_{38}O_4$	2.25×10^{-5} ^{A}	7.73 ^{A}	-2.8 ^{A}	0.27 ^{B}
Di-n-octyl phthalate	DnOP	Phthalate	$C_{24}H_{38}O_4$	2.52×10^{-5} ^{A}	7.73 ^{A}	-2.8 ^{A}	0.022 ^{B}
Di-iso-nonyl phthalate	DiNP	Phthalate	$C_{26}H_{42}O_4$	6.81×10^{-6} ^{A}	8.6 ^{A}	-2.43 ^{A}	0.2 (20 °C) ^{B}
Di-n-nonyl phthalate	DnNP	Phthalate	$C_{26}H_{42}O_4$	6.81×10^{-6} ^{A}	8.6 ^{A}	-2.34 ^{A}	1.73×10^{-5} ^{B}
Di-iso-decyl phthalate	DiDP	Phthalate	$C_{28}H_{46}O_4$	1.84×10^{-6} ^{A}	9.46 ^{A}	-2.06 ^{A}	0.28 ^{B}
Diethylhexyl adipate	DEHA	Adipate	$C_{22}H_{42}O_4$	1.13×10^{-4} ^{B}			0.78 (22 °C) ^{B}
Diethylhexyl terephthalate	DEHTP	Terephthalate	$C_{24}H_{38}O_4$	2.85×10^{-3} ^{B}			4.0 (20 °C) ^{B}
Acetyl tributyl citrate	ATBC	Citrate	$C_{20}H_{34}O_8$	4.00×10^{-2} ^{B}			1.7 ^{B}
Trioctyl trimellitate	TOTM	Trimellitate	$C_{33}H_{54}O_6$	5.07×10^{-4} ^{B}			3.9×10^{-4} ^{B}

^{A}(Net et al., 2015), ^{B}PubChem online database.

Given the low vapour pressures (Table 5.1) and relatively high boiling points (>300 ºC) of many plasticisers, their release from the surface of plastics into the surrounding air is likely to be relatively slow when compared to release into e.g. sediments. However, plasticiser release is related to the concentration of the compound in the plastic (Bueno-Ferrer et al., 2010) and the density and flexibility of polymer chains (Hansen et al., 2013). Thus, a plastic item may still exhibit significant leaching into seawater or air, simply due to the fact that it has a high plasticiser content, or has an amorphous low-crosslink structure which allows for relatively unimpeded movement of plasticiser molecules to the item surface (Hansen et al., 2013). Plasticisers with lower molecular weights may exhibit faster migration as smaller molecules can migrate more easily towards the surface of the plastic, from where they can leach into the surroundings. Plasticiser leaching rates are also positively correlated with temperature (Dhavamani et al., 2022), although higher temperatures also serve to increase plasticiser degradation rates, thus the effect of temperature results in competing effects of leaching and degradation, with the balance of these two processes mediating the overall occurrence of plasticisers in the environment.

Empirical data regarding plasticiser leaching rates in seawater is limited, and it appears that to date no studies have investigated leaching kinetics directly into sediments. Cao et al. (2022) measured the effects of pH on the leaching rates of 5 phthalates from microplastics into artificial freshwater over 14 days. Little difference in Σphthalate was observed between pH 3-9, but concentrations of the measured phthalates at pH 11 were less than 50% of those detected at pH 9. This was likely due to the increased hydrolysis of the ester bonds in the within the phthalate molecules at the highly alkaline pH. Comparison of the phthalates present at these two pH values supported this hypothesis as the phthalate profile at pH 11 became relatively enriched in phthalates with greater degradation-resistance (e.g. DEHP), although this sits outside the typical pH range of 7-8.6 for estuarine environments (US EPA, 2006). UV light generally appears to increase leaching rates into seawater, although the effects may be polymer and compound specific. For instance, the leaching of phthalates from polyvinyl chloride (PVC) into seawater was greater in the presence of UV light, whilst no such effect was observed for leaching from polyethene (PE), although concentrations of phthalates in the test plastics were not reported (Paluselli et al., 2019). In contrast to these negative results for PE, Dhavamani et al., (2022) reported that leaching of six phthalates from LDPE, HDPE, and recycled PE into seawater was faster in the presence of UV light. Thus at present there remains some uncertainty as to the precise circumstances under which UV light affects leaching from PE. Contrasting effects of salinity on plasticiser leaching have been reported. Suhrhoff and Scholz-Böttcher (2016) found that salinity was positively correlated with leaching of acetyl tributyl citrate (ATBC), di-iso-decyl phthalate (DiDP) and di-iso-nonyl phthalate (DiNP), negatively correlated with leaching of trioctyl trimellitate (TOTM), but had no effect on the leaching of DEHP over 57 days. More recent studies have reported a negative correlation between salinity and release of phthalates such as DEHP, DnBP, DiBP, and DEP (Cao et al., 2022; Dhavamani et al., 2022). The range of test salinities used within each study is comparable (~0.01-4% w/w), thus the effects of salinity appear complex and are likely to be compound and polymer specific.

5.3.2 Partitioning of plasticisers between sediment and water

The continual movement of water in estuarine and coastal environments results in a constant exchange of particulates and dissolved substances at the boundary between water and sediment. These processes likely play an important role in controlling the partitioning of plasticisers between compartments.

Many of the principles that underpin the leaching of plasticisers from plastics into the surrounding media can also be applied to the partitioning of plasticisers between water and sediment. For example, the high hydrophobicity of many plasticisers means that concentrations found in sediments tend to be higher than those in the overlaying water (Jebara et al., 2021; Z. M. Zhang et al., 2020a). The sorption of phthalates to sediment appears to be relatively rapid, e.g. equilibria of phthalates between suspended sediment and water have been found to be reached within 6 hours (Mohammadian et al., 2016; Zhou and Liu, 2000). The hydrophobicity of plasticisers also results in an affinity for the organic matter fraction present both in the water column and sediment (Arfaeinia et al., 2019). For example, organic matter in both water and sediment was significantly positively correlated with total phthalate concentration (6 congeners) in a field study in a river system in central China (Dong et al., 2022), with plasticiser concentrations being overall greater in the more organic matter rich sediment than water. Variations in chemical properties between different plasticiser compounds can also affect partitioning. For example, Mohammadian et al. (2016) and Wang et al. (2021) both reported that phthalates exhibited an increasing affinity for sediment with increasing molecular weight, with lower molecular weight phthalates (e.g. DMP) more prevalent in seawater than higher molecular weight, more lipophilic phthalates (e.g. DEHP).

The size distribution of sediment particles can also influence plasticiser levels. Thus, smaller sediment grains and higher organic matter levels were both associated with greater DEHP concentrations in an urban river-estuary system in Taiwan (Chen et al., 2018). However, the effect appeared to be season-specific, with a significant positive correlation between DEHP concentration and grain size observed in the dry season, but no correlation in the wet season. Sun et al. (2013) also reported no significant correlation between grain size and total phthalate concentrations (16 congeners) in sediment samples collected at the beginning of the wet season in a field study of a river in eastern China. The correlations between DEHP concentration and grain size and organic matter can be explained by the increased organic matter sorption to smaller grains and an increase in charged surfaces which may act as plasticiser binding sites on finer inorganic particles. However, it is possible that the trend is dominated by the association of plasticisers with organic matter, due to their lipophilicity and lack of readily ionisation groups.

In a study of salinity effects, higher salinities were found to be positively correlated with the sediment sorption coefficient of DEHP (Zhou and Liu, 2000). Supporting this finding, the sorption of DEHP to suspended particulates was found to be significantly greater in sea water than river water, after controlling for particulate quantity and size distribution (Turner and Rawling, 2000). The trend for increasing salinity to increase phthalate sorption to suspended sediment can be attributed to greater particulate agglomeration at higher salinity (salting-out), potentially augmented by changes in the structure of particulates at higher salinity which may improve plasticiser uptake (Turner and Rawling, 2000). Not all studies have clearly linked higher salinity to higher sediment phthalate levels. Thus, Sun et al. (2013) found no significant correlation between total phthalate concentration (16 congeners) and salinity in rivers in eastern China. These discrepancies between laboratory studies and field studies suggest that other factors, e.g. sediment composition, grain size, organic matter content etc., may play a relatively larger role in plasticiser partitioning in the environment.

The molecular structures of the vast majority of legacy (phthalate) and emerging plasticisers, e.g. TOTM, ATBC, diethyl hexyl terephthalate (DEHTP), and diethyl hexyl adipate (DEHA), do not contain proton donor (e.g. carboxylic acids) or proton acceptor (e.g. amines) groups. Thus it may be expected that the effects of pH on plasticiser binding will be negligible. Studies to date have suggested that pH has little influence on partitioning of plasticisers in aquatic environments (Arfaeinia et al., 2019; Sun et al., 2013).

5.4 Occurrence of plasticisers in coastal environments

5.4.1 Phthalates in estuarine and coastal environments

A diverse range of phthalates have been studied in the coastal environment. Most of these studies have been conducted in China, in common with the situation for terrestrial environments (Chapter 2), although studies of coastal phthalate levels have also been carried out in other parts of Asia (Heo et al., 2020; Malem et al., 2019), the Middle East (Arfaeinia et al., 2019), and Europe (Paluselli et al., 2018a, 2018b).

Table 5.2: Summary data for selected plasticisers from studies discussed in this review; n = number of studies; DF% = detection frequency; the mean concentration for each plasticiser within each study was calculated and used to calculate median, mean, range and DF%; mean and range were only calculated for plasticisers with n ≥ 3; see Appendix Tables S5.1 and S5.2.

Plasticiser	**Sediment concentration (ng g^{-1})**					**Water concentration (ng L^{-1})**				
	n	**Median**	**Mean**	**Range**	**DF%**	**n**	**Median**	**Mean**	**Range**	**DF%**
DEHP	17	1658	2912	92.9-11965	100	17	317	4612	7.4-71700	100
DnBP	16	253	1194	nd-6398	94	16	271	2030	20.1-17200	100
DEP	16	61.3	314	nd-3213	94	16	40.4	860	3.7-12600	100
DMP	15	29.1	242	nd-2548	87	13	3.7	36.2	nd-238.7	92
BBP	15	8.0	405	nd-5280	93	16	4.0	17.8	nd-90	81
DiBP	14	317	915	1.2-4147	100	12	168	7052	nd-75400	92
DnOP	9	6.2	502	nd-4125	67	12	2.8	21.4	nd-140	67
DiNP	7	116	327	nd-842	86	3	8.8	11.7	5.3-20.9	100
DiDP	5	69.1	143	nd-493	80	1	23.6	-	-	100
DnNP	4	78.2	354	2.9-1258	100	3	1.6	34.5	0.3-102	100
DEHA	7	3.5	459	nd-3080	86	5	8.9	24.1	nd-100	60
DEHTP	5	84.6	532	4.3-2420	100	1	634000	-	-	100
TOTM	4	104	292	3.6-954	100	-	-	-	-	-
DiNCH	4	8.3	8.3	0.9-15.9	100	-	-	-	-	-
ATBC	4	4.5	4.8	0.5-9.8	100	-	-	-	-	-

Phthalate occurrence in coastal and estuarine sediments is broadly comparable to those found in soils (Chapter 2). Profiles are generally dominated by mid to high molecular weight phthalates, specifically DEHP (C8 chains) and to a lesser extent DnBP (C4), DiBP (C4), BBP (C4 and C7) and DnOP (C8). In surface sediments (n=26) sampled along a stretch of coast on the Persian Gulf (Arfaeinia et al., 2019), DEHP (30% of total phthalate abundance), DnBP (16%), BBP (13%) and DnOP (10%) were the most abundant of 16 phthalates. Over 90% of the phthalate profile (6 congeners) of coastal sediments (n=29) of the Yangtze River estuary was accounted for by the 3 phthalate congeners DEHP (74%), DiBP (13%) and DnBP (11%). Further studies have also reported comparable profiles (L. Y. Wang et al., 2021; Zhang et al., 2018b). These patterns of phthalate co-occurrence in sediments reflect the widespread use and high production volumes of these congeners, their higher affinity for organic matter with increasing chain length, and relative resistance to degradation (see Sections 5.3.1 and 5.3.2).

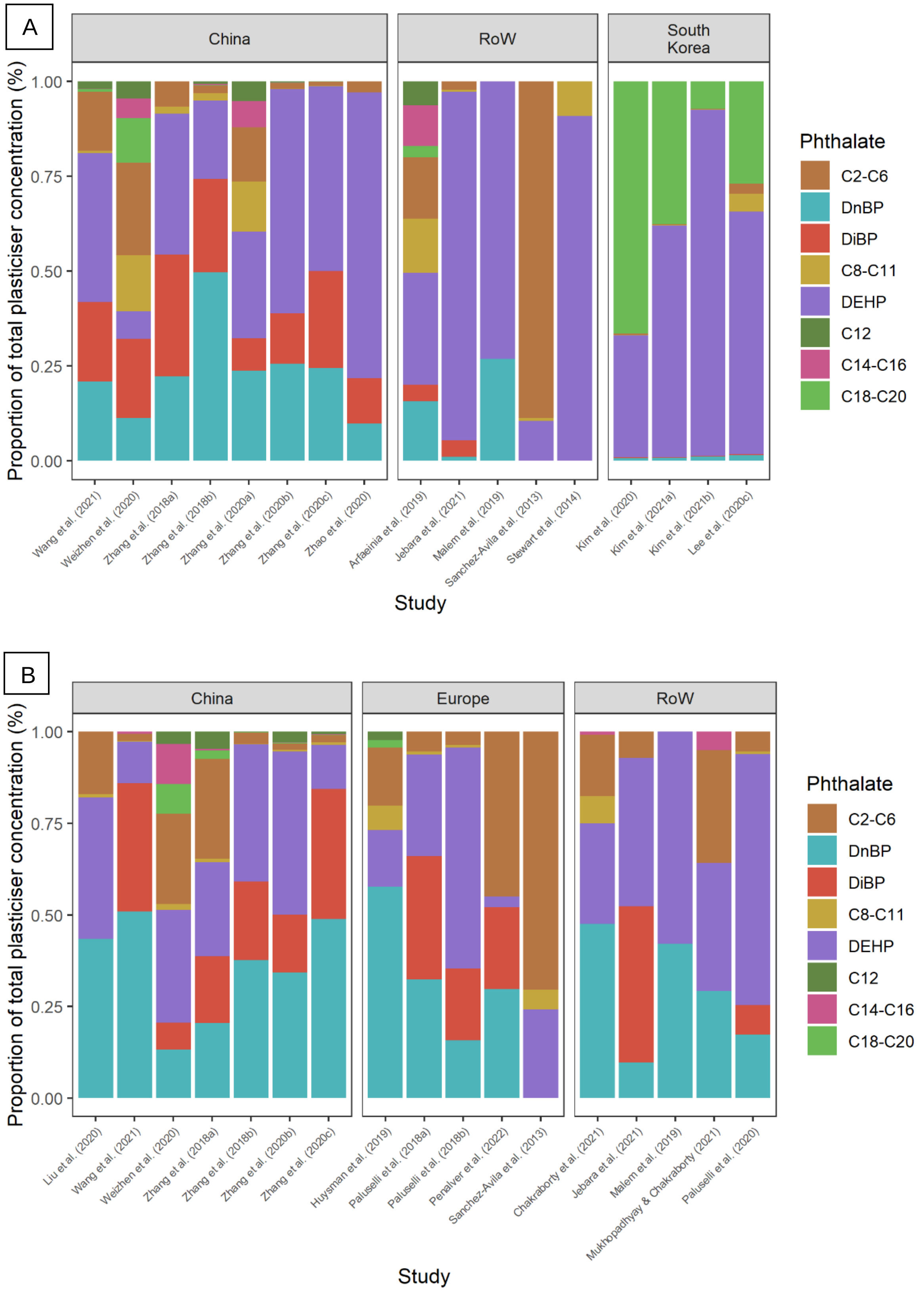


Figure 5.1: Phthalate profiles in estuarine and coastal sediments (A) and water (B) from studies discussed in this review; profiles were calculated using the mean value for each phthalate reported in the study; data has been grouped by region and country where sensible

to do so; RoW = rest of world; phthalates <LOD were treated as 0 to avoid overestimation and included in mean calculation; some phthalates have been grouped by total chain carbon number to minimise biases arising from inconsistencies in analytical suites between studies.

Lower molecular weight plasticisers (e.g. DEP, DnBP) have a higher solubility in water than higher molecular weight plasticisers (e.g. DEHP, DnOP). Consistent with these physiochemical properties, phthalate profiles in coastal and estuarine waters contain a higher proportion of lower molecular weight phthalates than seen in sediments. For example, DEHP was the most abundant phthalate in sediments (n=24) collected from an estuary in eastern China in summer and autumn, (37% and 42% of total phthalate abundance) (L. Y. Wang et al., 2021). However the contribution of DEHP in the corresponding seawater was only 19% and 5%, with the aqueous profile instead being dominated by DnBP and DiBP in both seasons (combined contribution of 79% and 91% in summer and autumn). The higher prevalence of these lower molecular weight phthalates is consistent with the findings of Z. M. Zhang et al. (2020b), who reported relative DEHP concentrations in sediment up to 5.6 times greater than in water, whilst DiBP and in particular DnBP were relatively enriched in the Yangtze River estuary water. Zhang et al. (2018) also found that DEHP, DnBP and DiBP dominated the phthalate profiles of both seawater and sediment in coastal areas of eastern China, although the phthalate profiles in these sediments were in contrast to those reported by Wang et al. (2021) and Z. M. Zhang et al. (2020b). Specifically, the contributions of DEHP, DnBP and DiBP in seawater were between 31-33%, but were 20%, 49% and 25% respectively in the sediment. Despite this, the weight of evidence suggests that DEHP is relatively more enriched in sediments, and DnBP and DiBP dominate profiles in coastal and estuarine waters. It should be noted that the majority of such studies target a limited number of phthalates. This restricted analysis suite means that the true phthalate profiles in estuaries may differ from those reported, e.g. the phthalate DiDP is rarely studied but may be present in the environment in comparable concentrations to abundant phthalates such as DnBP (Chapter 2).

5.4.2 Emerging plasticisers in estuarine and coastal environments

A handful of studies have investigated emerging plasticisers in coastal environments. These studies are mainly from non-targeted analyses concerning multiple classes of organic pollutants (Chakraborty et al., 2021; Peñalver et al., 2022; Sánchez-Avila et al., 2013; Stewart et al., 2014). Such studies have limited specificity for plasticisers and are not fully quantitative. A number of recent studies have provided more detailed quantitative insights into the co-occurrence of phthalates and multiple classes of emerging plasticisers in coastal systems (Jebara et al., 2021; S. Kim et al., 2021, 2020; Lee et al., 2020). The breadth of plasticiser analytes studied in coastal environments is greater than in the terrestrial environment, although there are fewer publications concerning plasticiser occurrence in coastal systems. Studies concerning the leaching and occurrence of emerging plasticisers to date have focussed on the chemicals with the greatest production volumes; the adipates (e.g. DEHA), citrates (e.g. ATBC), terephthalates (e.g. DEHTP), trimellitates (e.g. TOTM) and cyclohexanoates (e.g. DiNCH).

We found 8 studies that have investigated the occurrence of emerging plasticisers in coastal and estuarine sediments. DEHA was analysed in every study, with DEHTP (5 studies), ATBC, DiNCH and TOTM (4 studies each) next most commonly investigated. Half of the identified studies investigated the co-occurrence of DEHA, DEHTP, ATBC, DiNCH, TOTM and multiple phthalate plasticisers in coastal sediments around South Korea, providing a detailed picture of plasticiser contamination in this region (S. Kim et al., 2021, 2020; Y. Kim et al., 2021; Lee et al., 2020). Across this set of studies, TOTM and DEHTP dominated the emerging plasticiser profiles in the majority of cases. For example, the mean concentrations of TOTM and DEHTP in sediments (n=60) from the Masan Bay were 58.9 and 4.29 ng g^{-1} dw respectively, which accounted for 89% and 6.5% of the total mean emerging plasticiser concentration (Σemerging). Mean concentrations of TOTM and DEHTP were 150 ng g^{-1} dw (46% of Σemerging) and 141 ng g^{-1} dw (43% of Σemerging) in sediment samples (n=35) spanning 15 years in an artificial freshwater lake on the Korean coast (Y. Kim et al., 2021). The highest reported mean sediment concentration of TOTM in any study of 954 ng g^{-1} dw (89% of Σemerging) occurred in samples collected from South Korean bays with a history of industrial land use inputs. In these areas, DEHTP was the second most abundant emerging plasticiser, accounting for 8% of the Σemerging load (S. Kim et al., 2021). Mean concentrations of DEHA, ATBC and DiNCH in these 4 Korean studies range from 1.5-16, 0.5-9.8, and 0.8-15.9 ng g^{-1} dw respectively, and were thus minor contributors (0.3-18.5%) to the total emerging plasticiser burden (S. Kim et al., 2021, 2020; Y. Kim et al., 2021; Lee et al., 2020).

The remainder of studies which have reported emerging plasticisers in estuarine or coastal sediments have been carried out in the United States (Jaffé et al., 2006), Spain (Sánchez-Avila et al., 2013), New Zealand (Stewart et al., 2014) and Tunisia (Jebara et al., 2021). A monitoring study of organic contaminants in estuarine and coastal areas in the Bay of Biscay (Northern Spain) reported DEHA concentrations in sediments (n=10) ranging from nd-825 ng g^{-1} dw (mean 107 ng g^{-1} dw) (Sánchez-Avila et al., 2013). Sediments (n=135) from the Tunisian coastline (south Mediterranean) were found to contain mean DEHA and DEHTP concentrations an order of magnitude greater than the other studies discussed in this section. Jebara et al. (2021) (n=165) reported DEHA concentrations ranging from nd-3580 ng g^{-1} dw (mean 3080 ng g^{-1} dw), and DEHTP concentrations ranging from 1700-2860 ng g^{-1} dw (mean 2420 ng g^{-1} dw). The high concentrations found by Jebara et al. (2021) suggest a very strong consistent localised input, e.g. emissions associated with sites of plasticiser manufacture or disposal. In contrast, Stewart et al. (2014) did not detect DEHA in sediments (n=13) from estuaries in New Zealand, although given the very high limits of detection (e.g. LOD of DEHA ranged between 200-500 ng g^{-1} dw) we may assume a possible underestimation of DEHA concentrations.

As expected, emerging plasticisers are less well-studied in coastal and estuarine waters than in sediments. DEHA is again the most commonly studied, with 6 studies reporting DEHA concentrations, while DEHTP and ATBC have been investigated in a single study each. Currently it appears there is no published data concerning the occurrence of DiNCH or TOTM in coastal or estuarine waters. Concentrations of emerging plasticisers in water are generally an order of magnitude lower than in sediments, although complexities arising from differences in composition between these two media make comparisons of absolute concentrations challenging. DEHA was not detected in water samples (n=16) from the Ganges Delta in 2016 (Mukhopadhyay and Chakraborty, 2021), although in 2017 (n=6) concentrations ranging from nd-0.14 ng mL^{-1} were detected (mean 0.1 ng mL^{-1}) (Chakraborty et al., 2021). Lower concentrations of DEHA (0.06-0.26 ng mL^{-1}) and ATBC (0.05 ng mL^{-1}) were reported by Smith et al. (2015) in water sampled from Kuwait Bay (n=16). Similarly, concentrations of DEHA in water (n=11) from coastal areas in Northern Spain were also low, ranging from nd-0.035 ng mL^{-1} (mean 0.012 ng mL^{-1}), in contrast to a mean concentration in sediment of 107 ng g^{-1} dw (Sánchez-Avila et al., 2013). The mean DEHA concentration from a lagoon (n=7) in Southern Spain was 2 orders of magnitude greater that reported by Sánchez-Avila et al. (2013) at 8.9 ng mL^{-1} (Peñalver et al., 2022). Despite concentrations in sediment exceeding 3 µg g^{-1} dw, DEHA was not detected in coastal waters (n=165) from the south Mediterranean by Jebara et al. (2021). DEHTP however exhibited a very high mean concentration in the water (634 ng mL^{-1}), although even at these levels remained an order of magnitude less than the concentration found in the associated sediments.

The variation in the profiles of emerging plasticisers between studies from different regions suggests that, as the move away from phthalates due to legislation, the alternatives that come in to use may not be taken up consistently for product applications between different jurisdictions. To date, data regarding emerging plasticiser use and associated occurrence in environmental compartments remains limited, although the concentrations of these emerging compounds in sediment and water remain low relative to phthalates (see Section 5.4.3). Thus, further studies are required to ascertain the key drivers of emerging plasticiser occurrence in the coastal environment. Based on knowledge for other major high-use classes of organic chemical, the profiles of emerging plasticisers in coastal environments will be dependent not only on the degree and nature of source intensity, but also the relative persistence of the different substances and their physiochemical properties. Currently, degradation rates of emerging plasticisers in the environment represent a major knowledge gap (see Section 5.5.1), meaning that such kinetic parameters cannot be readily integrated into multi-media fate models. Thus, there remains a clear need for studies investigating the degradation kinetics and persistence of emerging plasticisers in the environment.

5.4.3 Relative concentrations and co-occurrence of emerging plasticisers and phthalates

We have identified 11 studies which have quantified the co-occurrence of phthalates with at least one class of emerging plasticiser in coastal environments. The extent to which emerging plasticisers contribute to the total mean plasticiser burden (Σplasticiser) in estuarine and coastal media varies greatly between these studies. Generally, emerging plasticisers represent a relatively minor (<4%) proportion of Σplasticiser in sediments (S. Kim et al., 2020; Y. Kim et al., 2021; Lee et al., 2020), however there are some exceptions to this general trend. For example, DEHA represented 9.2% of Σplasticiser (1 emerging, 4 phthalates) in sediments (n=10) from Spanish estuaries (Sánchez-Avila et al., 2013). In a study in South Korea, TOTM accounted for 21% of Σplasticiser (5 emerging, 8 phthalates) in sediments (n=42) from industrialised bay areas, and was the second most abundant plasticiser in this study, behind the phthalate DEHP. In sediments (n=165) collected from the Tunisian coast in the South Mediterranean, the emerging plasticisers DEHA and DEHTP were the second and third most abundant plasticisers, accounting for 29% and 23% of Σplasticiser (2 emerging, 6 phthalates), with DEHP again the dominant plasticiser (44% of Σplasticiser). Thus, whilst it appears that emerging plasticisers typically represent a relatively small proportion of the plasticiser profile in coastal systems, hotspots of these compounds have been reported, potentially arising from differences in the nature and intensity of source inputs.

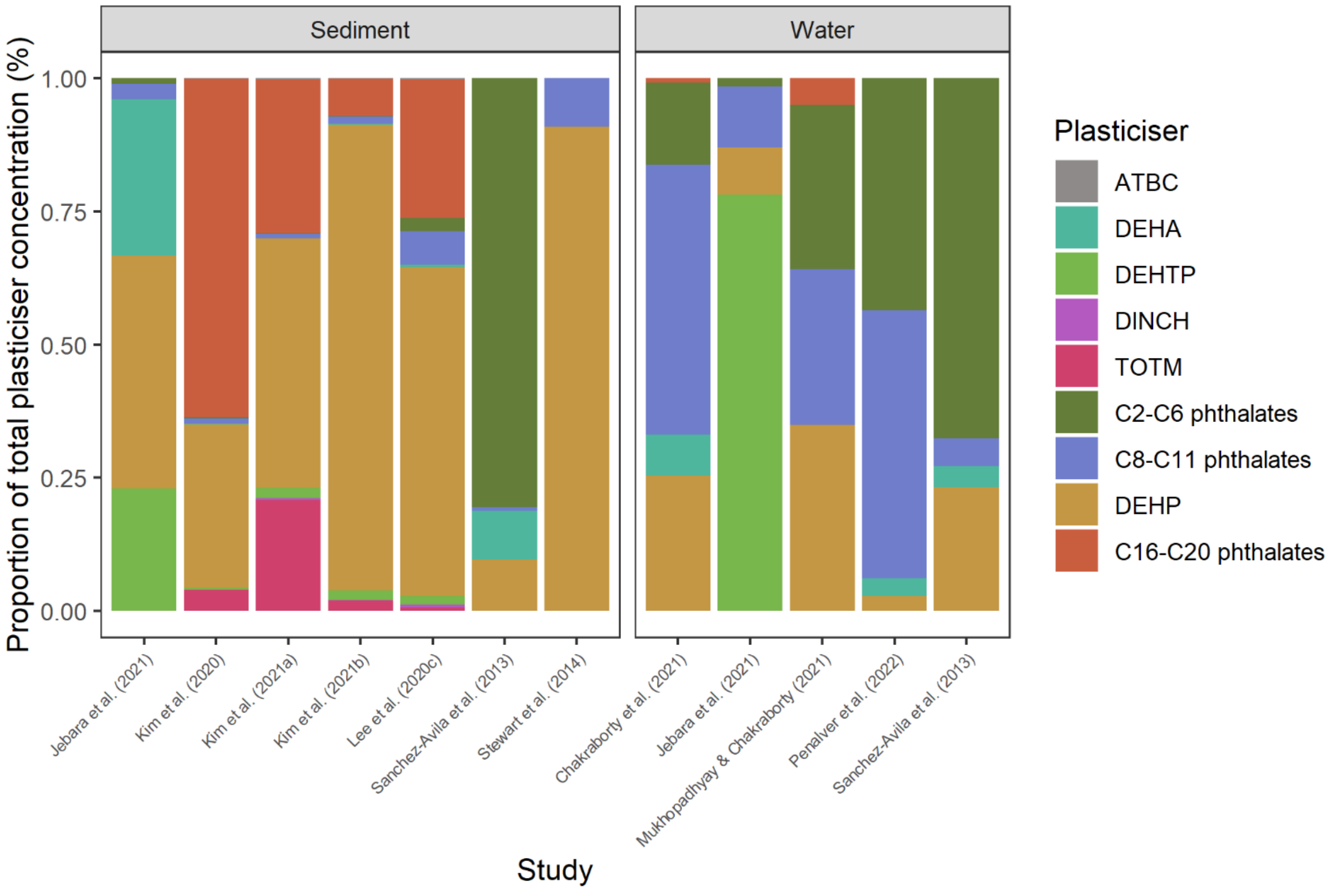


Figure 5.2: Emerging and phthalate plasticiser profiles in estuarine and coastal systems in studies discussed in this review; only studies of co-occurrence of >1 class of plasticiser are shown; profiles were calculated using the mean value for each plasticiser reported in the study; plasticisers <LOD were treated as 0 to avoid overestimation and included in mean calculation; some phthalates have been grouped by total chain carbon number to minimise biases arising from inconsistencies in analytical suites between studies.

Studies of phthalate and emerging plasticiser co-occurrence in coastal waters are more limited than for sediments. DEHA was reported to account for 3.3-7.7% of Σplasticiser (Chakraborty et al., 2021; Peñalver et al., 2022; Sánchez-Avila et al., 2013), although represented a significantly reduced component of the plasticiser burden in water samples (n=16) collected from Kuwait Bay (Smith et al., 2015), and was not detected by Mukhopadhyay and

Chakraborty (2021) in water (n=16) from the Ganges River delta at all. DEHTP was by far the most abundant plasticiser (2 emerging, 6 phthalate) in water (n=165) from the Tunisian coast (78% of Σplasticiser), with the phthalates DiBP and DEHP accounting for only 9.3% and 8.8% of Σplasticiser.

Despite the fact that emerging plasticisers remain a relatively small proportion of the plasticiser market (CEFIC, 2018), the available data suggests that they can contribute significantly to the total plasticiser burden in coastal environments. This likely represents accumulation in the environment due to resistance to degradation, in addition to variations in degree and nature of source inputs. However, a lack of studies and inconsistencies in analytical suites make definitive comparisons challenging, as the majority of studies investigate only one or two emerging plasticisers. As such, the available data may be an underrepresentation of the true contribution of emerging plasticisers to the total plasticiser burden in estuarine and coastal environments.

5.4.4 Effects of seasonality on plasticiser occurrence

A handful of studies have investigated the effects of sampling season on the occurrence of plasticisers in coastal waters and sediments. Rainfall is potentially one of the primary seasonal drivers that may determine changes in input and retention of plasticisers in these environments. Whilst increased rainfall leads to increased dilution of water courses and thus reduction in absolute concentrations of plasticisers in water and sediment, high flow conditions may ultimately increase the flux of plasticisers from rivers into estuaries, due to increased channel flow, resuspension of sediment, and greater leaching and surface runoff from plasticiser sources, e.g. sludge-amended agricultural land. Additionally, storm events may lead to increased input of sewage directly into rivers due to storm drain overflows. Conversely, increases in river discharge may serve to resuspend contaminated estuarine sediments and transport them further away from the coast. Such scouring effects may ultimately reduce concentrations in estuaries, transporting pollutants towards the open ocean. Seasonal trends in human activities, such as industrial production, tourism and shipping may also influence the occurrence of plasticisers across the year (Paluselli et al., 2018b; Z. M. Zhang et al., 2020a). Thus, the effects of increased rainfall and flow on the total burden of plasticisers in an estuarine environment depends on the competing effects of increased river flux into the estuary, and increased scouring and movement of contaminants towards open ocean. This is reflected in the contrasting results observed across studies regarding the nature and extent of seasonality of plasticiser concentrations in estuarine and coastal environments.

The results from a number of studies suggest that plasticiser concentrations in coastal waters can vary throughout the year, although the pattern and extent varies between studies. Paluselli et al. (2018b) reported greater concentrations of six phthalates in the summer in a year-long monitoring study of seawater in Marseille Bay (Northern Mediterranean). These higher levels were associated with increased tourist activity and maritime traffic which could both be identified as potential sources. Z. M. Zhang et al. (2020a) found greater Σphthalate concentrations (16 congeners) in coastal and marine areas in the East China Sea in autumn than in spring. Here, higher concentrations were attributed to increased flux of plasticisers from terrestrial inputs such as agricultural and industrial sources during the autumn months. Σphthalate (16 congeners) concentrations were significantly higher ($p < 0.05$) in the winter (10.2 µg L^{-1}) than in spring (4.9 µg L^{-1}) or summer (2.1 µg L^{-1}) in coastal waters around the Yangtze River Delta (Z. M. Zhang et al., 2020b). The authors attributed this to the dilution effect from high rainfall outweighing the increased river flux in summer months, in addition to more rapid biodegradation in spring and summer due to increased microbial activity resulting due to higher temperatures.

In contrast to these studies that have found seasonal trends, some studies have reported minimal or insignificant changes in plasticiser concentrations in coastal waters and sediments across the year. Σphthalate (10 congeners) in sediment from the Qiantang River estuary did not change between summer and autumn, with concentrations in water only slightly higher in autumn than summer (Wang et al. 2021). Due to large spatial variability in contamination within the bay it can be concluded from this study that spatial rather than temporal trends were the main source of variation in concentration. Jebara et al. (2021) found minimal monthly difference in concentrations of 4 phthalates and DEHTP in seawater along the Tunisian coast over the course of a year. Concentrations of phthalates and emerging plasticisers (DEHA and DEHTP) in sediments were, however, significantly greater in the first two sampling months (April-May) than in the rest of year, during which concentrations were broadly similar. The authors attributed the high sediment concentrations in spring to lower rainfall during this period reducing the removal of contaminants from sediments and dilution effects. Concentrations in the following March did not, however, approach the levels seen in the previous April-May, indicating that the significantly higher levels seen in the first spring samples could have arisen from a one-off pollution event, e.g. contamination arising from a shipping incident, rather than representing an annual temporal trend. Future work looking to investigate the seasonality of plasticisers in estuaries and coastal environments should, where possible, incorporate flow and discharge data in order to calculate total flux of plasticisers, in order to estimate changes in the total plasticiser burden in these environments.

5.5 Fate of plasticisers in coastal environments

5.5.1 Persistence of plasticisers in sediments and water

Studies of the degradation of plasticisers in sediments and water have focussed on phthalates, with little to no empirical data concerning the persistence of emerging plasticisers in these environments**.** The physiochemical properties of the plasticisers themselves will play a key role in determining the relative persistence of plasticisers in the environment, e.g. plasticisers with higher logK_{OW} values may bind more strongly to sediment (Mohammadian et al., 2016) and thus may be less available for biodegradation. There are also a number of environmental factors which may determine the persistence and degradation of plasticisers in sediments and water (e.g. temperature, pH, intensity of UV light, dissolved organic matter, oxygen content). Additionally, plasticiser degradation rates may also be affected by the nature of the microbial communities present in a given environment. The factors influencing the rates of plasticiser degradation have been more fully studied in the soil environment (Chapter 2) than in the estuarine and coastal environment. Nevertheless, on the basis of bespoke knowledge from estuarine studies and relevant data from soils, there is sufficient evidence to demonstrate the primary drivers of plasticiser degradation in estuaries.

Biodegradation is the primary pathway by which plasticisers are broken down in estuarine sediments. For example, Kao et al. (2005) investigated the anaerobic degradation of DnBP and DEHP in sediments collected from estuaries in southern Taiwan. Concentrations of DnBP and DEHP in the sediment decreased by 24% and 13% over 30 days. After sterilisation of the sediment only 3% of each plasticiser was degraded over the same time period, indicating the critical role of the active microbial fauna in breakdown. The degradation of plasticisers also occurs much more rapidly under aerobic than under anaerobic conditions, e.g. the aerobic degradation rates of 8 phthalates in river sediments were up to an order of magnitude faster than anaerobic rates (Yuan et al., 2002). Thus primarily anoxic environments with little turbulence, e.g. deep bed sediments, have the potential to act as sinks for plasticisers in the environment.

Chain length and molecular weight are key determinants of relative degradation rates between plasticiser molecules. Specifically, plasticisers with longer chains are generally more resistant to degradation (Chapter 2; Kickham et al., 2012). Higher hydrophobicity of longer chain phthalates makes them less likely to be photolysed, hydrolysed or biodegraded, e.g. a lab study regarding aerobic degradation of DnBP and DEHP in mangrove sediments found half-lives ranged from 1.6-2.9 days for DnBP (C4 chains) and 5-8.3 days for DEHP (C8) (Yuan et al., 2010). Increased chain length also leads to greater persistence under aerobic conditions. Thus, the half-lives of studied phthalates increased from 2.5 days (DEP; C2) to 2.9 days (DnBP; C4) to 14.8 days (DEHP; C8), consistent with the chain lengths of these molecules

(Yuan et al., 2002). In contrast to the results reported in sediments, Paluselli et al. (2019) carried out experiments under biotic conditions in the absence of UV light and found that half-lives of shorter-chain phthalates were comparable if not greater than longer-chain phthalates, e.g. DMP (C1; 53 days), DEP (C2; 79 days), DiBP (C4; 29 days), DEHP (C8; 26 days). Additionally, the half-lives of some of these shorter-chain phthalates (e.g. DMP and DEP) were much longer than those reported in estuarine sediments by Kickham et al. (2012). Therefore, despite a theoretical basis for the assertion that plasticisers will degrade less rapidly in sediments than in water, the exact nature of this relationship remains unclear, partly due to differing test conditions and times between studies. This pattern of increasing half-life with chain length was also not observed under anaerobic conditions, as the half-lives of DEP (33.6 days) and DEHP (34.7 days) were comparable (DnBP was found to degrade more rapidly than DEP or DEHP, with a 14.4-day half-life). These results suggest that the bacteria which are primarily responsible for active phthalate degradation under aerobic conditions favour shorter molecules. In contrast, under anaerobic conditions, the degradation reactions may be controlled by anaerobic bacteria that have lower specificity for molecular weight or indeed bacterial degradation may be minimal and instead other processes may be more important.

Currently there is a lack of studies directly comparing the degradation rates of plasticisers in sediments and in the surrounding seawater under the same conditions. Thus, the relative rates of plasticiser degradation in sediments versus water must be inferred from the results of multiple single-compartment studies. Early studies suggest that the degradation of sediment-associated phthalates is slower than that of aqueous phase-associated phthalates (Turner and Rawling, 2000). This finding is consistent with the concept that phthalates are more likely to partition to sediment, and that once in this compartment they become less available for degradation. As the plasticiser burden is generally greater in sediments than in the water column, the degradation rates in sediments will be more important to the overall mass balance of these compounds in estuarine and coastal systems.

No systematic studies are currently available on the effects of temperature, organic matter, or pH on phthalate degradation in estuarine environments. The overall effect of increased temperature (across the temperature range naturally found in the environment) will likely be to increase degradation rates due to more rapid physical and biological processes, as is the case for the soil environment (Chapter 2). Elevated organic matter levels in sediments and seawater may be theoretically associated with slower degradation due to increased sorption of plasticisers to organic matter (Dong et al., 2022). There have been few systematic studies concerning the effects of pH on plasticiser degradation in soils (Chapter 2) and thus it is challenging to draw conclusions regarding the effect of pH on degradation in the sediments and water, although pH values on the extremes of the natural range have been associated with slower degradation of phthalates in soils (Chang et al., 2009).

5.5.2 Uptake by organisms

In addition to degradation processes, the uptake of plasticisers by organisms represents another fate pathway for plasticisers in the environment. The toxic and endocrine-disrupting potential of some phthalate plasticisers has been demonstrated by recent ecotoxicological studies in marine biota which have linked phthalate exposure to alterations to metabolism and reproductive capability in fish and mussels (ECHA, 2022, 2018; Forner-Piquer et al., 2019; Gu et al., 2021). Studies of the uptake and accumulation of plasticisers by marine organisms are key components of understanding the extent of exposure when assessing the risk of such chemicals in estuarine and coastal environments.

Phthalates have been detected in species of coastal and marine fish (Castro-Jiménez and Ratola, 2020; Hidalgo-Serrano et al., 2021, 2020; H. Hu et al., 2020; Hu et al., 2016; Jebara et al., 2021; Sun et al., 2021), molluscs (Castro-Jiménez and Ratola, 2020; Hu et al., 2016; Saliu et al., 2020; Sun et al., 2021; Tsochatzis et al., 2019), crustaceans (H. Hu et al., 2020; Hu et al., 2016; Lo Brutto et al., 2021), cetaceans (Baini et al., 2017; Routti et al., 2021), turtles

(Savoca et al., 2021, 2018) and plants (Castro-Jiménez and Ratola, 2020; Jebara et al., 2021). Fat and muscle tissues are often identified as the primary sites of phthalate storage (Baini et al., 2017; H. Hu et al., 2020; Routti et al., 2021; Savoca et al., 2018). Higher-molecular weight phthalates (e.g. DnBP and DEHP) are typically more frequently detected and at higher concentrations than lower molecular weight phthalates (e.g. DEP) in plants, cetaceans, molluscs, and turtles, particularly in fat and muscle tissues. However, the phthalate profiles determined from whole-body analysis of crustaceans and fish are relatively evenly distributed between low, mid and high molecular weight phthalates (Castro-Jiménez and Ratola, 2020; H. Hu et al., 2020; Jebara et al., 2021; Lo Brutto et al., 2021). Differences in the profile of phthalates present in species may result from differences in feeding behaviour (e.g. pelagic or benthic), life history, composition of tissue types within organisms, or to taxa-specific differences in metabolic capacity for different molecules.

The occurrence of emerging plasticisers in marine biota has also begun to receive attention. Lo Brutto et al. (2021) quantified the presence of DEHA and DEHTP in five species of coastal amphipod collected from the Italian Mediterranean in 2013 and 2014. DEHTP was detected in one species (albeit at a relatively high concentration of 335 ng g^{-1}), while in contrast DEHA was detected in every sample, at concentrations ranging from 9-86 ng g^{-1}. These emerging plasticisers were detected at similar levels to phthalates (e.g. DEHP ranged from 15-300 ng g^{-1}), indicating that over half a decade before phthalates were restricted in the EU (ECHA, 2022, 2018), emerging plasticisers were already present in coastal biota. DEHA and DEHTP have also been found in fish and seagrass samples collected from the Tunisian Mediterranean in 2018-2019 (Jebara et al., 2021). DEHTP was concentrated in muscle tissues of gilt-head sea bream (mean 23.2 µg g^{-1} dw), and was the most abundant plasticiser detected, above e.g. DEHA (3.04 µg g^{-1} dw) and DEHP (0.92 µg g^{-1} dw). DEHTP was also the most abundant plasticiser detected in seagrass (9.2 µg g^{-1} dw), ahead of DEHP (0.73 µg g^{-1} dw). Sediments associated with the site were also found to contain very high levels of phthalates and emerging plasticisers. Further work is required to determine whether the results of this study represent local-scale factors in a heavily polluted site, or whether the bioconcentration factors of DEHTP (and to a lesser extent, DEHA) are greater than phthalates.

A number of studies have demonstrated the impacts of phthalate contamination on marine fish species. Dietary exposure to di-iso-nonyl phthalate has been found to cause hepatic oxidative stress and negative impacts on the male reproductive system and metabolism in the gilthead sea bream (Carnevali et al., 2019; Forner-Piquer et al., 2018, 2019). DEP was also found to induce weak but measurable hepatic toxicity and oxidative damage in olive flounder (Kang et al., 2010). DEHP has been associated with cytotoxicity and genotoxicity in sea bass (Molino et al., 2019), immunotoxicity in trout (Martins et al., 2015), and endocrine disruption in marine medaka and salmon (Norman et al., 2007; Ye et al., 2014). In addition to negative impacts on fish species, phthalates have also been found to have impacts on avian, mollusc, copepod, and mammal species. For example, the occurrence of phthalates was found to be associated with oxidative stress in the eggs of the coastal European herring gull, and in a species of marine mussel (Allen et al., 2021; Gu et al., 2021). DEHP exposure resulted in negative impacts on development in a species of estuarine copepod (Forget-Leray et al., 2005), and DEHP was also able to modulate a hormone receptor in adipose tissues in marine whales sampled from an the Norwegian Arctic, an environment with a low phthalate burden, thus the effect levels were well above those found in the tissues (Routti et al., 2021). Although effects thresholds remain relatively unclear, the weight of evidence suggests that phthalates can cause negative impacts in marine organisms. Thus, as estuaries and coastal areas may exhibit some of the highest levels of plasticisers in the marine environment, it is these areas in which organisms may encounter significant risk from phthalate occurrence. Furthermore, although a critical need for risk assessment, the uptake and effects of emerging plasticisers in estuarine and coastal organisms are poorly known, despite the large body of evidence that phthalate plasticisers present in marine organisms can have toxic effects.

5.6 Knowledge gaps and future research suggestions

Knowledge on the sources, occurrence, behaviour, and fate of plasticisers in estuarine and coastal environments is generally more developed than for the terrestrial environment. There is a relatively wide body of evidence that demonstrates the sources, profiles, and fate of phthalates in sediments, seawater, and biota.

Industrial and urban areas appear to be a primary source of plasticisers in coastal systems, with areas associated with waste disposal and agricultural activity also serving as inputs. Following entry into estuaries, high molecular weight phthalates (e.g. DEHP, DiDP, DnNP) partition strongly to sediment, with low-mid molecular weight phthalates (e.g. DMP, DnBP) relatively enriched in the overlying water. Emerging plasticisers have been reported to contribute over 50% of the plasticiser burden in coastal sediments and seawater, however in the majority of studies these plasticisers only represent minor components of the plasticiser burden (<10%). Thus, emerging plasticisers likely represent an increasing proportion of the plasticiser profiles estuarine and coastal systems, in line with a shift in usage patterns. Plasticisers can be particularly persistent in sediments, with reported half-lives of higher molecular weight phthalates (e.g. DnOP) on the scale of months. Phthalates have been detected in marine biota across a range of taxa and trophic levels (e.g. seagrass, molluscs, cetaceans, and fish), with recent studies providing evidence of emerging plasticiser accumulation in biota. In particular, the emerging plasticisers DEHTP and DEHA have received recent attention, with DEHTP the most abundant plasticiser detected in biota in a number of studies.

Despite the relative wealth of knowledge of phthalates in estuaries and coastal systems, multiple questions remain relating to the sources, behaviour, occurrence, and fate of emerging plasticisers in sediments, seawater, and biota.

- What are the primary sources of emerging plasticisers in estuaries and coastal systems? Do these sources match those of phthalates?

- Are the behaviours of emerging plasticisers in estuaries and coastal environments similar to those of phthalates? Specifically, what are the kinetics and equilibrium constants of partitioning for different classes of emerging plasticiser?
- How does the occurrence of emerging plasticisers in coastal environments (seawater, sediments, and biota) compare to phthalates? Is the relative occurrence of these plasticisers changing in response to shifting production and use patterns of different types of plasticiser, driven by regional legislation?
- How persistent are emerging plasticisers in sediments and seawater? Are the key processes determining the degradation of emerging plasticisers constant among the different classes of chemical?
- How rapidly and to what extent are the different classes of emerging plasticiser taken up by marine organisms? Given the widespread occurrence of phthalates in marine biota, what are the elimination kinetics of these plasticisers?
- What are the impacts and effects thresholds of phthalates, and particularly emerging plasticisers, for organisms in estuarine and coastal environments? To what extent are there differences in these thresholds between taxa?

5.7 Acknowledgements

This work was supported by the Natural Environment Research Council NE/S007423/1, with Alex Billings's studentship through the ENVISION Doctoral Training Partnership.

6

Spatial distribution and seasonal occurrence of phthalates and emerging plasticisers in estuaries: A case study in the Firth of Forth, UK

6. Spatial distribution and seasonal occurrence of phthalates and emerging plasticisers in estuaries: A case study in the Firth of Forth, UK

Abstract

We investigated the spatial and seasonal trends of legacy phthalate and emerging plasticisers in sediments of the Firth of Forth estuary, Scotland, UK. Sediments (n=73) were collected from 50 sites in the estuary channel across winter 2020, and spring and summer 2021. We determined the concentration of 8 phthalate and 3 emerging (adipate, terephthalate, and trimellitate) plasticisers. The most frequently detected plasticisers (typical mean LOD 1.2 ng g^{-1} ww) were diethylhexyl phthalate (DEHP; 64% detection frequency), dimethyl phthalate (47% DF) and the emerging plasticiser diethylhexyl terephthalate (DEHTP; 41% DF). All other plasticisers were detected in <21% of samples. DEHP dominated the plasticiser profile in every season (mean concentration 76-290 ng g^{-1} ww; 73-97% of ∑plasticiser). DEHP (3930 ng g^{-1} ww), di-iso-decyl phthalate (312 ng g^{-1} ww) and DEHTP (94.1 ng g^{-1} ww) had the greatest maximum concentrations. ∑plasticiser was significantly greater at sites in the inner than outer estuary and was generally negatively correlated with water column depth. These patterns of distribution were attributed to proximity of pollution sources, such as wastewater treatment plant outfalls, landfill sites, and industrial areas in the inner and more urbanised parts of the estuary, and the relative proximity of sites to the urbanised shoreline. Mean ∑plasticiser sediment concentrations were greater in winter (239 ng g^{-1} ww) and spring (300 ng g^{-1} ww) than summer (103 ng g^{-1} ww), and in the outer estuary were significantly greater in winter (99.9 ng g^{-1} ww) than spring (12.8 ng g^{-1} ww). The sensitivity of estuarine biota to plasticisers currently remains uncertain, however, our results suggest that organisms in this urbanised estuary are exposed to relatively low (median 54.0 ng g^{-1} ww, mean 234 ng g^{-1} ww) sediment concentrations of plasticisers throughout the year. Thus, further work is warranted to assess the impact of plasticiser occurrence as part of a range of chemicals present in urbanised estuarine ecosystems.

6.1 Introduction

Due to their position at the boundary between the freshwater and marine environments, estuaries have the potential to act as medium-term environmental sinks for organic contaminants. The dynamics of water flows (drop in flow rate) associated with channel widening at an estuary boundary means estuaries are sites of extensive sediment deposition. Additionally, changes in salinity associated with the transition from fresh to marine water can alter the surface charge of suspended sediment particles, leading to increased agglomeration and subsequent sedimentation of particles in the water column. This increase in salinity can also result in changes in the dynamics of sorption of non-polar neutral organic contaminants to estuarine sediments. These effects can combine in a process known as ‘salting out’ (Stumm and Morgan, 1996), whereby organic chemicals transported by tributary rivers become sequestered in the estuarine sediment.

Plasticisers are organic chemicals added to plastics to increase their flexibility. The occurrence of these additives is receiving increasing research attention in the terrestrial (Chapter 2), freshwater (Baloyi et al., 2021) and marine environments (Hidalgo-Serrano et al., 2022). Plasticisers typically have high $\log K_{OW}$ (e.g. DEHP, the most widely used plasticiser globally, has a $\log K_{OW}$ value of 7.73). Thus in the freshwater and marine environment, these contaminants will partition primarily to sediments (Mohammadian et al., 2016; Zhou and Liu, 2000). For example, highly lipophilic phthalate plasticisers such as DEHP have been shown to be particularly susceptible to the effects of salting out, relative to other commonly studied environmental contaminants such as polycyclic aromatic hydrocarbons or polychlorinated biphenyls (Zhou and Liu, 2000).

Knowledge of the occurrence of phthalate plasticisers in estuarine sediments is limited (Weizhen et al., 2020; Zhang et al., 2018a). Additionally, there is very little data concerning the estuarine occurrence of the emerging plasticisers that are increasingly used as replacements for phthalates in Europe (CEFIC, 2021). Potential sources of plasticisers in estuaries include runoff from agricultural land, discharge from wastewater treatment plants and diffuse release from plastics in the environment (Chapter 5). Coastal waste sites (e.g. municipal landfills) represent a further source of contamination to estuaries (or inflowing tributaries) (Brand and Spencer, 2019; Nicholls et al., 2021). Especially where flooding and erosion increases with climate change, coastal landfill sites may represent an increasing input of contaminants, including plasticisers, into the marine environment (Neuhold and Nachtnebel, 2011).

The primary aim of this study was to investigate the spatial and season patterns of occurrence of legacy phthalate and emerging non-phthalate plasticisers in sediments of the Firth of Forth, an estuary located on the eastern coast of Scotland, northern UK. A number of potential sources of plasticisers are located along the Firth of Forth system (Figure 6.1), including coastal landfill sites, municipal and industrial wastewater treatment plant outfalls, and urban areas with diffuse sources of plasticisers, such as the city of Edinburgh. The Firth of Forth estuary has a complex topology of depths and sediment types and exhibits a large seasonal variation in flow conditions throughout the year, e.g. the annual channel flow ranges from <10 $m^3 s^{-1}$ to >300 $m^3 s^{-1}$ (Balls, 1992). Given the range in the nature and intensity of plasticiser sources, and topology and flow variations present, the First of Forth estuary provides an excellent location to study the distribution of, and seasonal trend in, phthalates and emerging plasticisers in sediments.

Sediments in the Forth estuary were sampled in winter, spring, and summer from two areas representing high- and low-proximity to potential plasticiser sources: sites in the inner estuary (in the area surrounding the island of Inchkeith) and sites in the outer estuary (in the area surrounding the Isle of May). We used GC-MS (gas chromatography-mass spectrometry) to determine the concentration of multiple phthalate and emerging plasticisers in the sediments. The analyses conducted allowed us to test four hypotheses: 1) Phthalate plasticisers will dominate the plasticiser profile due to their historic use: 2) Emerging plasticisers will be widespread due to the recent decline in the use of phthalates; 3) The concentration of plasticisers in the sediments will be related to the proximity to sources, with concentrations greater at the inner estuary than at the outer estuary; 4) Plasticiser occurrence will be greatest in the summer due to a more concentrated input of plasticisers under low flow conditions.

6.2 Materials and methods

6.2.1 Study area and sample collection

The Firth of Forth is an estuary in Scotland, northern UK. The major settlements along the course of the estuary have a total urban population of ~630,000 (National Records of Scotland, 2022). The average annual channel flow is 63 $m^3 s^{-1}$, and ranges from <10 $m^3 s^{-1}$ in summer to >300 $m^3 s^{-1}$ in winter (Balls, 1992). There are a number of legacy and operational landfill waste sites along the course of the estuary, in addition to outfalls from wastewater treatment plant (WWTPs) treating public sewerage (municipal WWTPs) and waste from manufacturing plants (industrial WWTPs) (Marine Scotland, 2020a, 2020b) (Figure 6.1).

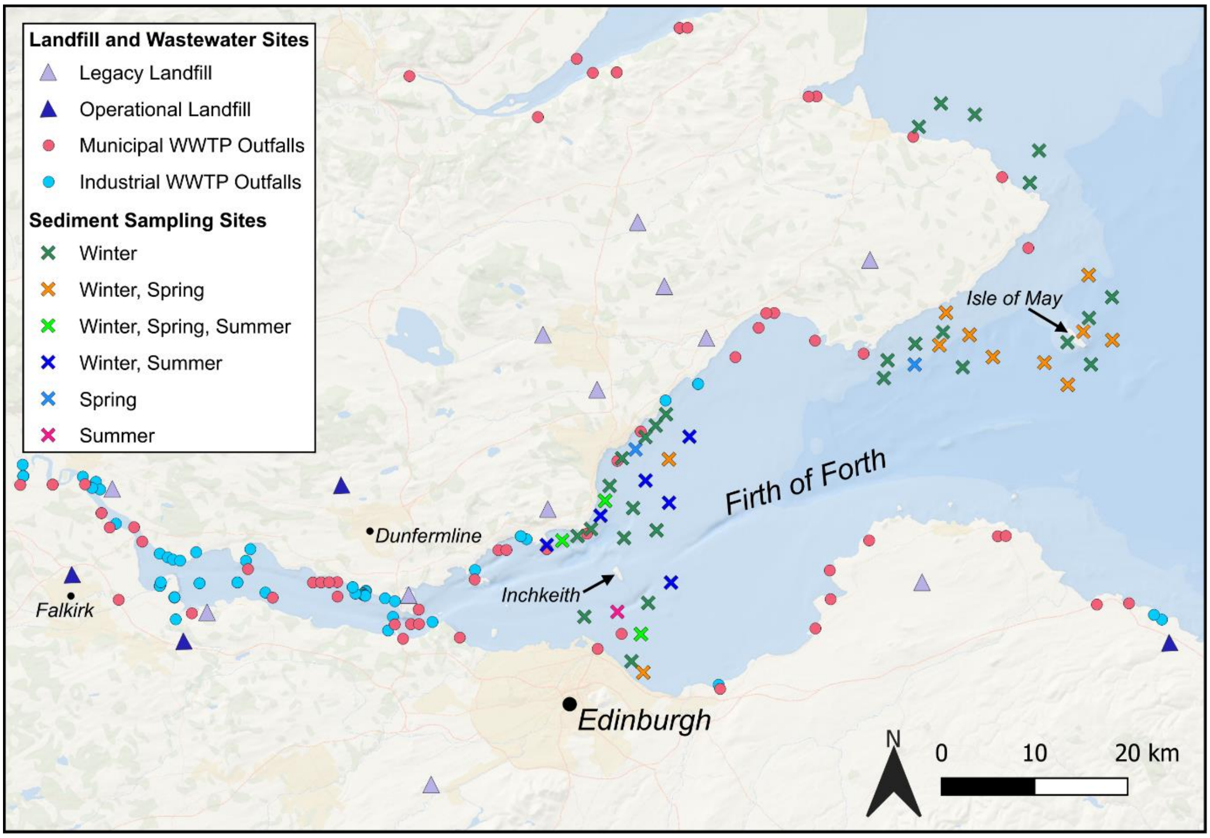


Figure 6.1: Map of coastal landfill sites, wastewater treatment plants (WWTPs), and sediment sampling sites in the Firth of Forth estuary in Scotland, UK; landfill sites within 10 km of the Firth of Forth and/or within 5 km of a tributary of the Firth of Forth are shown; Contains information from the public sector licensed under the Open Government Licence v3.0.

A total of 73 bed sediment samples were collected from November 2020 to July 2021 from sites in the inner estuary channel (near the island of Inchkeith; all sites west of longitude -2.9) and the outer estuary channel (near the Isle of May; all sites east of longitude -2.9) (Figure 6.1). A 250 cm^2 Van Veen grab sampler was used to collected sediment samples from the surface of the estuary bed at a range of depths in the water column (2-57 m). Samples were stored in glass containers at -20 °C. Samples were collected at three time periods: during winter (47 samples; 03.11.20 - 03.03.21), spring (16 samples; 07.04.21 - 09.06.21), and summer (10 samples; 14.07.21 – 23.07.21), from a total of 50 sites in the estuary and neighbouring coastal area (Figure 6.1). The on-board GPS was used to identify the sampling site coordinates, in order to minimise the potential effects of site-by-site re-sampling differences on the seasonality of plasticiser occurrence.

6.2.2 Plasticiser extraction and analysis

A suite of 8 legacy (phthalate) and 3 emerging plasticisers were measured in the collected samples (Table 6.1). The plasticisers were extracted from each sample according to a method previously used in Chapter 3. In brief, 1.5-3.0 g ww of sediment was homogenised and dried with anhydrous sodium sulfate. Samples were then spiked with deuterium-labelled recovery standards (d4-DnBP and d4-DnOP, Sigma-Aldrich, USA). Analytes were extracted for 30 minutes using an Ethos X microwave extraction system (Milestone, Italy) with 9:1 dichloromethane (DCM):acetone as the extraction solvent. Supernatants were collected and dried with anhydrous sodium sulfate. Extracts were reduced to a known volume, passed through a PTFE filter (pore size 0.45 µm), and further cleaned using size-exclusion chromatography (Agilent 1200 series HPLC, Agilent, USA). Deuterium-labelled internal standards (d4-DEP and d4-DEHP, Sigma-Aldrich, USA) were added to all samples prior to instrumental analysis.

Table 6.1: The 8 phthalate and 3 emerging plasticisers analysed in this study; solubility in water is at 25 °C unless otherwise stated.

Name and acronym		Formula	Log K_{OW}	S_{H2O} (mg L^{-1})	CAS
Dimethyl phthalate	DMP	$C_{10}H_{10}O_4$	1.61 ^{A}	4000 ^{B}	131-11-3
Diethyl phthalate	DEP	$C_{12}H_{14}O_4$	2.54 ^{A}	1080 ^{B}	84-66-2
Di-iso-butyl phthalate	DiBP	$C_{16}H_{22}O_4$	4.27 ^{A}	6.2 (24 °C) ^{B}	84-69-5
Di-n-butyl phthalate	DnBP	$C_{16}H_{22}O_4$	4.27 ^{A}	11.2 ^{B}	84-74-2
Benzyl butyl phthalate	BBP	$C_{19}H_{20}O_4$	4.7 ^{A}	2.69 ^{B}	85-68-7
Diethylhexyl phthalate	DEHP	$C_{24}H_{38}O_4$	7.73 ^{A}	0.27 ^{B}	117-81-7
Di-n-octyl phthalate	DnOP	$C_{24}H_{38}O_4$	7.73 ^{A}	0.022 ^{B}	117-84-0
Di-iso-decyl phthalate	DiDP	$C_{28}H_{46}O_4$	9.46 ^{A}	0.28 ^{B}	26761-40-0
Diethylhexyl adipate	DEHA	$C_{22}H_{42}O_4$		0.78 (22 °C) ^{B}	103-23-1
Diethylhexyl terephthalate	DEHTP	$C_{24}H_{38}O_4$		4.0 (20 °C) ^{B}	6422-86-2
Acetyl tributyl citrate	ATBC	$C_{20}H_{34}O_8$		1.7 ^{B}	77-90-7
Trioctyl trimellitate	TOTM	$C_{33}H_{54}O_6$		3.9×10^{-4} ^{B}	3319-31-1

^{A}(Net et al., 2015); ^{B}PubChem online database.

Analysis was carried out using a gas chromatograph (6890N, Agilent, USA) coupled to a single-quadrupole mass spectrometer (5975B, Agilent, USA) operating in electron ionisation mode. 1.7 µL of sample was injected in splitless mode on to an HP-5ms analytical column (30 m length, 0.25 µm film thickness, 0.25 mm internal diameter, Agilent, USA). Helium was used as the carrier gas (1.5 mL min^{-1}). The inlet and MS sources temperatures were 300 °C and 230 °C respectively. Limits of detection (LODs) were determined from the calibration curve of analytical standards (96-99.5% purity; Sigma-Aldrich, USA), the mass of sediment analysed, and the dilution factor. LODs ranged from 0.3-4.4 ng g^{-1} ww (mean 1.2 ng g^{-1} ww ± 1.4), except for DiDP, which exists as a mixture of isomers and thus had a LOD higher than other analytes of 59.5 ng g^{-1} ww (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. The method recoveries were between 60-120% (mean 88% ± 13) and 65-120% (mean 100% ± 11) for d4-DnBP and d4-DnOP. Analytes were quantified using the internal and recovery standards and calibration curves of plasticiser standards (Sigma-Aldrich, USA). Two procedural blanks were included in each batch of sample extractions. Plasticiser concentrations are reported in ng g^{-1} ww and were recovery and blank-corrected.

6.2.3 Contamination controls

Laboratory controls used during the extraction and analysis of plasticisers from the sediments were based on those used in Chapter 3. Laboratory glassware was soaked overnight in Decon 90 and heated in a muffle furnace at 450 °C for a minimum of 2 hours prior to use (non-volumetric glassware only) (Fankhauser-Noti and Grob, 2007) to reduce the contamination of phthalates. Glassware was also rinsed 2 x with DCM immediately prior to use. Operators wore cotton lab coats, and solid reagents were heated in a muffle furnace at 450 °C overnight. The use of plasticware was avoided, except for the lids of the microwave extraction vessels and gas chromatography sample vials. As discussed above, multiple procedural blanks were carried out and any contamination was accounted for in data processing.

6.2.4 Data analysis

For the calculation of ∑plasticiser concentrations, compounds <LOD were assigned a value of zero to avoid overestimation, in the calculation of mean and median values. Due to non-normality of some test groups (irrespective of log10-transformation), it was not suitable to use parametric methods to assess the significance of variation in plasticiser concentrations

between groups. Instead, the non-parametric Kruskal-Wallis ANOVA with a post-hoc Dunn's test was used. Non-normality of data (irrespective of log10-transformation) also prevented the linear modelling of the relationships between plasticiser concentrations, site distance from the shore, and water column depth. Thus, locally estimate scatterplot smoothing (LOESS) regression was used to visualise and interpret the data.

Principal component analysis (PCA) was carried out in order to investigate whether similarities in sediment plasticiser contamination across different sites were related to sample location. The PCA model used all individual plasticiser concentrations as input variables. All concentrations were mean centred and scaled to variance prior to analysis. PCAs were carried out with <LOD values substituted for both values of zero and 0.5 x LOD. However, no difference was found based on how <LOD values were treated. For consistency, the results reported in this paper are for those models with values <LOD substituted for zero.

6.3. Results and discussion

6.3.1 Concentrations and profiles of plasticisers in the Firth of Forth

Diethyl hexyl phthalate (DEHP) was the most frequently detected plasticiser in all seasons (50-70%) and also had the highest mean seasonal concentrations (76-290 ng g^{-1} ww) (Table 6.2). DEHP is one of the most widely produced plasticisers globally (CEFIC, 2021) and longer-chain phthalates also likely have a greater affinity for organic matter that may be present in sediment samples (Chapter 5). Hence, that DEHP dominated the overall plasticiser profile in the Firth of Forth, accounting for 73-97% of ∑plasticiser across the three seasons, is consistent with both its known widespread use and environmental behaviour. The dominance of DEHP in the Firth of Forth is also in accordance with previous reports of the phthalate contamination profiles of other estuary systems (L. Y. Wang et al., 2021; Zhang et al., 2018b).

The second most commonly detected plasticisers were dimethyl phthalate (DMP), which was found in 40-50% of samples across the three seasons, and the emerging plasticiser diethyl hexyl terephthalate (DEHTP), found in 10-55% of samples. DMP is the phthalate with the lowest boiling point and lowest logK_{OW}, thus has the potential to be widely transported in the environment relative to other phthalates, albeit at low concentrations. Of all of the emerging plasticisers, DEHTP had the greatest contribution to ∑plasticiser in each of winter (4.1%), spring (0.9%) and summer (2.6%). DEHTP is a structural isomer of DEHP and thus exhibits comparable organic matter binding and resistance to degradation (Chapter 4). Terephthalates, such as DEHTP, currently account for ~15% of the total European plasticiser market and are increasingly used as phthalate replacements (CEFIC, 2021). Whilst mean seasonal DEHTP concentrations (2.7-9.9 ng g^{-1} ww) in our study were low relative to DEHP, the occurrence of this plasticiser in estuaries such as the Firth of Forth indicates that their increasing use is leading to their presence in estuarine environments.

Table 6.2: Plasticiser concentrations in sediments of the Firth of Forth (ng g^{-1} ww); samples <LOD were assigned a value of zero so as to avoid overestimation, and included in the calculation of the mean and median; DF% = detection frequency.

		DMP	DEP	DiBP	DnBP	BBP	DEHP	DnOP	DiDP	Σphthalate	DEHA	DEHTP	TOTM	Σemerging	Σplasticiser
Winter 2020/21 (n=47)	Mean	1.1	0.3	4.9	2.5	1.3	195	0.2	22.4	227	0.3	9.9	1.3	11.6	239
	Median	nd	nd	nd	nd	nd	29.3	nd	nd	59.8	nd	4.3	nd	7.3	73.1
	Range	nd-5.9	nd-4.5	nd-49.8	nd-82.1	nd-26.4	nd-3120	nd-2.9	nd-312	nd-3130	nd-6.4	nd-94.1	nd-40.7	nd-101	nd-3170
	DF%	47	15	23	21	11	70	17	15	-	28	55	19	-	-
Spring 2021 (n=16)	Mean	0.4	0.02	nd	0.1	0.3	290	0.2	6.1	297	nd	2.7	0.6	3.3	300
	Median	0.2	nd	nd	nd	nd	10	Nd	nd	10.9	nd	nd	nd	nd	20.4
	Range	nd-1.8	nd-0.4	nd-0	nd-1.1	nd-5.4	nd-3930	nd-3.1	nd-97.2	nd-3930	nd-0	nd-17.6	nd-3.5	nd-17.6	nd-3930
	DF%	50	6	nd	6	6	50	6	6	-	nd	19	19	-	-
Summer 2021 (n=10)	Mean	1.8	nd	nd	nd	1.7	76	0.4	19.6	99	nd	2.7	1.6	4.3	103
	Median	nd	nd	nd	nd	nd	27.5	Nd	nd	57.9	nd	nd	nd	nd	57.9
	Range	nd-10.3	nd-0	nd-0	nd-0	nd-12.0	nd-455	nd-3.0	nd-105	nd-455	nd-0	nd-26.7	nd-6.9	nd-33.6	nd-489
	DF%	40	nd	nd	nd	20	60	20	20	-	nd	10	30	-	-

Despite a relatively low detection frequency arising from a high LOD of 59.5 ng g^{-1} ww (Al-Natsheh et al., 2015; Zou and Cai, 2013), di-iso-decyl phthalate (DiDP) had the second highest mean sediment concentration of all studied phthalates (6.1-22.4 ng ng^{-1} ww across the sampling seasons; 2.0-18.9% of ∑phthalate). The relatively high concentration can be explained by a number of factors: i) while DiDP is not as widely used as DEHP (CEFIC, 2021), it has been shown to be persistent in the environment (e.g. no significant degradation of DiDP was observed in soils over 3 months; Chapter 4), and ii) DiDP concentrations are reported as the sum of all measured branched-chain isomers (Al-Natsheh et al., 2015; Zou and Cai, 2013). Medium molecular weight phthalates (DnBP, DiBP, BBP) were detected at a wide range of concentrations, although mean concentrations of these phthalates were generally low (Table 6.2), e.g. 1.1-82.1 ng g^{-1} ww (DnBP), 2.2-49.8 ng g^{-1} ww (DiBP) and 5.0-26.4 ng g^{-1} ww (BBP). Detection frequencies of DnBP (15%), DiBP (15%) and BBP (11%) across the entire dataset (all sites and seasons combined) were also low, suggesting both low and/or localised source intensity and relatively low persistence.

The emerging plasticisers TOTM and DEHA were infrequently detected (Table 6.2) and found at low concentrations, e.g. mean TOTM and DEHA concentrations in winter were 1.3 ng g^{-1} ww (range nd-40.7 ng g^{-1} ww) and 0.3 ng g^{-1} ww (nd-6.4 ng g^{-1} ww). The low concentrations and detection frequency of TOTM in this study is in contrast to previously reports of concentrations in estuarine and coastal sediments in South Korea, were TOTM has been found to be one of the most abundant emerging plasticisers (S. Kim et al., 2021, 2020; Y. Kim et al., 2021; Lee et al., 2020). This discrepancy may represent differences in regional production and use of phthalate replacements, although there is a lack of detailed regional-scale data concerning the production and use quantities of different plasticisers both in time and across different regions. This makes assignment of relative differences in trends and patterns between studies challenging.

To date, there have been few studies of the occurrence of plasticisers in European estuarine sediments. Most research has instead focussed on sediments in China and South Korea

(Chapter 5). Plasticiser occurrence in systems in South-East Asia will be reflective of a different set of past and current sources than those that are responsible for the presence of the plasticisers in the Firth of Forth. For example, the relatively low contribution of DnBP and DiBP to ∑phthalate in our study is in contrast to studies of sediments in Chinese sediments, which typically report absolute mean concentrations of DnBP and DiBP >1 order of magnitude greater than those reported here. Correspondingly these phthalates can account for up to 50% of ∑phthalate in Chinese and South Korean estuarine sediments (L. Y. Wang et al., 2021; B. T. Zhang et al., 2020; Zhang et al., 2018a). Conversely, the mean concentrations of DiBP reported here are comparable to those in studies in South Korea, although previous studies have reported greater DnBP abundance (S. Kim et al., 2021, 2020; Y. Kim et al., 2021; Lee et al., 2020).

The least abundant phthalates in the First of Forth, based on mean or median concentration, were DMP, DEP and DnOP (Table 6.2). That DMP was the second most frequently detected phthalate indicates widespread occurrence, although at low concentrations (46.6% of all samples). The low relative abundance of DMP and DEP can be attributed to low relative production volumes (CEFIC, 2021), more rapid degradation (Chapter 4), and the fact that DMP and DEP have low logK_{OW} values relative to other phthalates, and thus partition less strongly to sediment, allowing them to be transported from the estuary in the tidal flows. The absolute concentrations of DMP, DEP and DnOP are generally an order of magnitude lower than those reported in Chinese studies (L. Y. Wang et al., 2021; B. T. Zhang et al., 2020; Zhang et al., 2018a), but are similar to results from Korea (S. Kim et al., 2021, 2020; Y. Kim et al., 2021; Lee et al., 2020). As there is currently little information about the occurrence of plasticisers in western European estuaries, further work is required to determine whether the results reported here reflect wider regional pollution patterns or represent a more localised signal, linked to specific source in the areas surrounding the Firth of Forth.

6.3.2 Spatial distribution of plasticisers in the Firth of Forth

6.3.2.1 Differences in plasticiser concentration between sampling areas - Results

The most polluted sites (based on ∑plasticiser) were typically located in the inner estuary. For example, 22 of the 28 of the sites with ∑plasticiser > 100 ng g^{-1} ww (79%) were located in the inner estuary (Figure 6.2). Consequently, in all seasons, the total plasticiser concentration was significantly greater in the inner estuary than at the outer estuary. Specifically, ∑plasticiser was significantly greater at the inner estuary sites than the outer estuary sites in winter (mean concentration of 372 vs 99.8 ng^{-1} ww; Kruskal-Wallis, $p = 0.015$) and spring (779 vs 12.8 ng^{-1} ww; Kruskal-Wallis, $p = 0.003$). Mean ∑plasticiser concentration in the inner estuary was 3.7 and 61 times greater than at outer sites during these seasons. (N.B. no samples were collected from the outer estuary during summer, so it is not possible to compare the spatial distribution of plasticisers in estuary in this season).

The spatial and seasonal patterns for ∑plasticiser were also largely reflected by those of the compound groups. Thus, ∑phthalate was also significantly greater in the inner estuary than at the outer estuary (Kruskal-Wallis; winter $p = 0.020$; spring $p = 0.005$). Mean ∑emerging plasticiser concentrations were also greater in the inner estuary than at the outer estuary (15.3 vs 7.8 ng g^{-1} ww in winter and 5.4 vs 2.0 ng g^{-1} ww in spring), although this difference was not statistically significant (Kruskal-Wallis, $p < 0.05$).

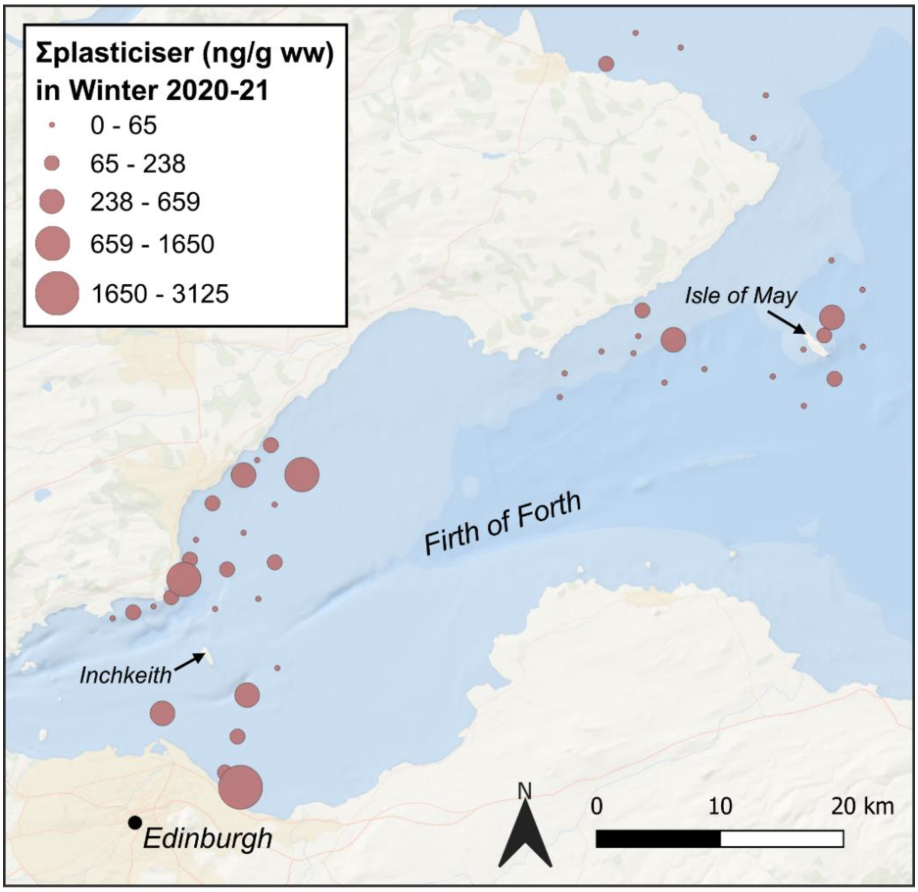


Figure 6.2: Map of ∑plasticiser concentrations (ng g^{-1} ww) in sediments sampled in the winter of 2020-2021 in the Firth of Forth estuary in Scotland, UK; non-detects were assigned a value of zero; symbol size classes were determined using Jenks natural breaks optimisation.

Within the PCA model, the first five principal components (PCs) had eigenvalues >1, indicating that they explained a greater proportion of the variance than any of the concentrations of the individual plasticisers. A total of 40% of the variation in plasticiser concentrations were explained by the first two PCs (PC1: 21.0%; PC2: 19.0%; Figure 6.3). The clustering of points of the outer estuary sites in the PC1 vs PC2 plot was denser than for the inner estuary (Figure 6.3), indicating a greater similarity in plasticiser concentrations in sediments. This is consistent with the magnitude and range of plasticiser concentrations observed between the two sampling areas. Samples with positive PC1 values were primarily influenced by the emerging plasticisers DEHA and DEHTP, and samples with positive PC2 values by the heavier molecular weight phthalates DnOP and DiDP. The inner estuary points also generally separated from the outer estuary points along the same direction of ordination as compounds found at higher concentrations in the inner estuary (e.g. DEHP, DiDP; Figure 6.3).

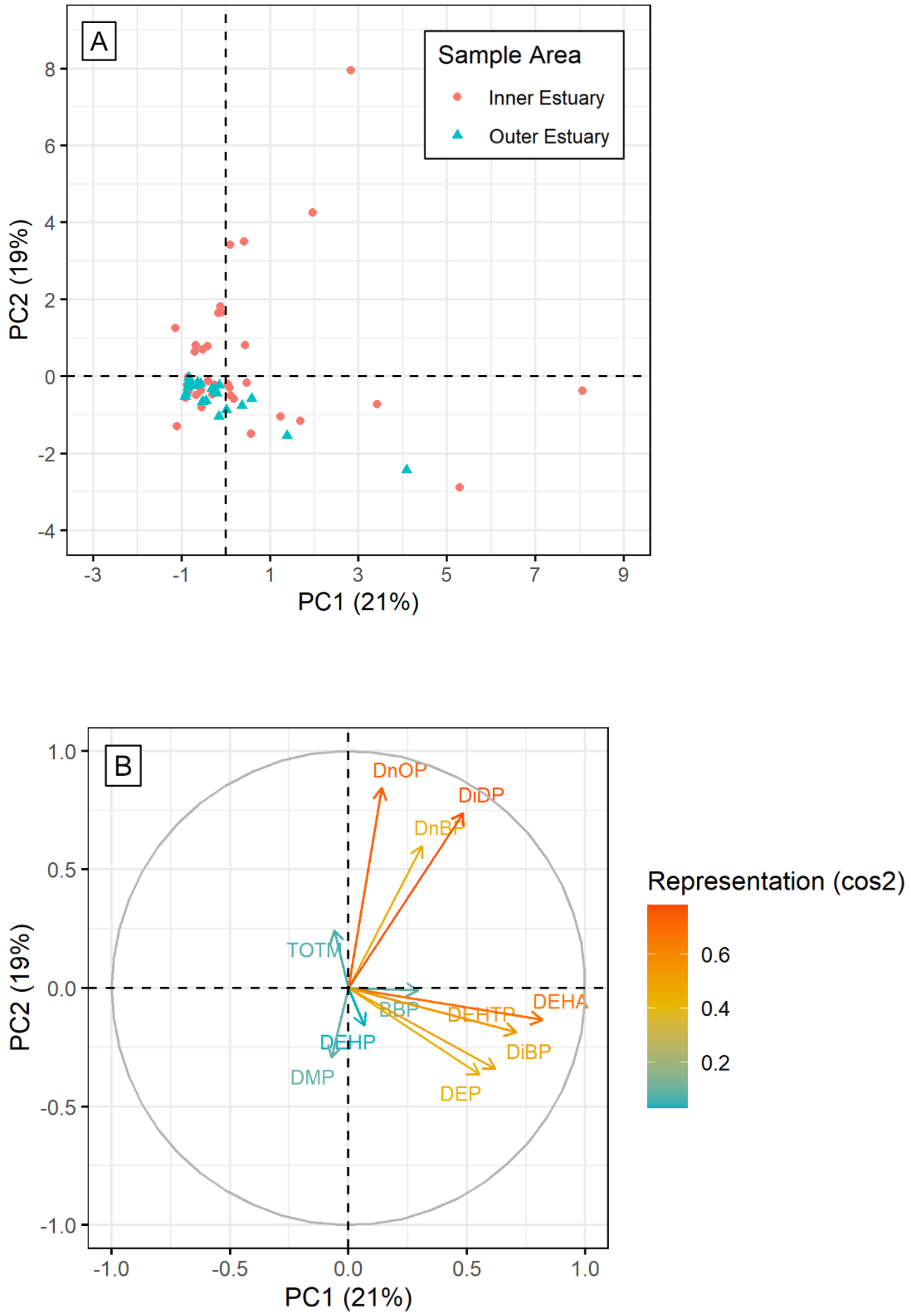


Figure 6.3: Scores (A) and contributions (B) of the first two principle components of plasticiser concentrations in the PCA model.

6.3.2.2 Differences in plasticiser concentration between sampling areas – Discussion

6.3.2.2.1 Influence of estuary properties on spatial distribution of plasticisers

It has been proposed that plasticiser concentrations will typically decrease with distance from the shore, partly due to increased dilution effects (Zhao et al., 2020). This is consistent with the observations of our study (Figure 6.4A), where the greatest plasticiser concentrations tended be located closer to the shore. LOESS regression also indicated that water column depth was negatively correlated with ∑plasticiser in the estuary (Figure 6.4B). As water column depth and distance from the shore are likely to be related, the relationship with depth may be linked more to proximity to terrestrial sources of plasticisers than to other associated factors (see section 3.2.2.2). Thus, although sediment depth in the water column appeared to account for a relatively small proportion of the measured variation in ∑plasticiser in the estuary in this analysis, this result does give some indication that channel dilution effects may have a measurable impact on plasticiser occurrence in estuarine sediments.

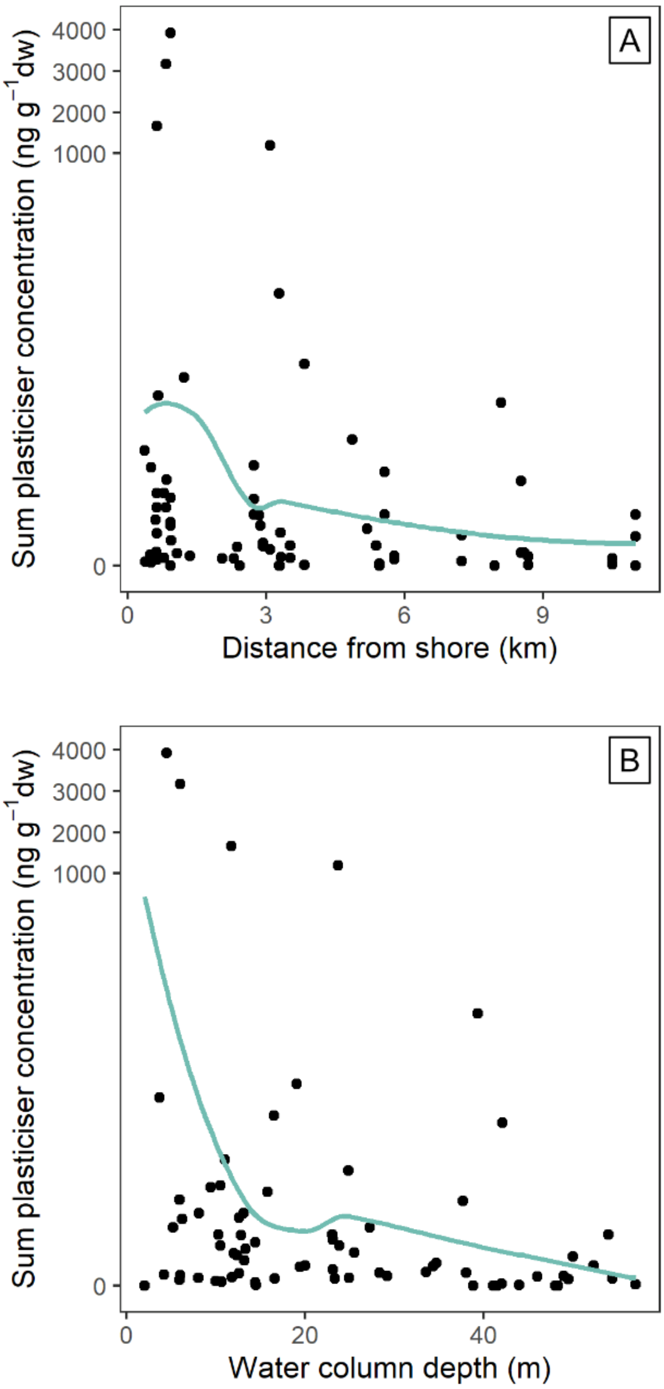


Figure 6.4: Relationships between ∑plasticiser sediment concentrations and distance from the shore (A) and water column depth (B) in the Firth of Forth between winter 2020 to summer 2021; non-parametric LOESS regression lines are shown; concentrations are plotted on a logarithmic scale.

The salinity gradient in an estuary also affects how suspended sediments and plasticisers behave. Plasticisers produced and used on land may be transported to rivers by overland or subterranean lateral flows (Chapters 2 and 5). Therefore, transport of plasticisers in rivers, likely mainly bound to suspended particulate matter, may be a major input of these contaminants into estuaries. As the river channel enters the estuary, a salinity gradient forms which results in the salting out and deposition of suspended sediments. Plasticisers bound to these particles will consequently be increasingly deposited in the bed sediments as salinity increases. Furthermore, phthalates themselves have been shown to be relatively sensitive to changes in salinity, e.g. DEHP had a significantly higher salting constant than other commonly studied environmental contaminants (Zhou and Liu, 2000). Furthermore, as the sorption of plasticisers to sediment appears to be rapid (Mohammadian et al., 2016; Zhou and Liu, 2000), this may partially confine the transport of contaminants to earlier stages of the estuary (Figure 6.2). This is in agreement with the observation that the high molecular weight phthalate DiDP ($\log K_{OW} = 9.46$) was found exclusively at inner estuary sites. These results indicate that the transition from fresh to saline water across the estuary leading to sediment deposition and compound salting out may have contributed to the elevated levels of plasticisers in the inner estuary compared to the outer estuary.

Properties of the sediments themselves may also influence the degree of plasticiser partitioning and binding, and thus concentrations. Due to the hydrophobicity of plasticisers, it is possible that sediments with greater organic matter (OM) content will see greater plasticiser binding and therefore greater plasticiser concentration relative to less OM-rich sediments in estuaries. Whilst the relationship between OM and plasticiser concentrations in estuaries has not been directly studied, a field study of river sediments reported that ∑phthalate (DMP, DEP, DnBP, BBP, DEHP, DnOP) was positively correlated with organic matter, a fact which the authors attributed to stronger phthalate binding to sediments with greater organic content (Dong et al., 2022). Conversely, organic carbon content may lead to increased plasticiser biodegradation, as organic matter will harbour a large and more diverse bacterial community that can lead to greater bacterial-associated breakdown of organic molecules, a phenomenon which has been proposed to occur in some soils (Tang et al., 2020; Tao et al., 2020). Therefore, it is possible that the differences in plasticiser concentrations between the inner and outer estuary may be partly explained by differences in OM between the two areas, although it was not possible in this study to assess the organic content of the sediments.

6.3.2.2.2. Influence of plasticiser sources on spatial distribution of plasticisers

In addition to estuary-wide effects, the proximity of sites to major sources of plasticisers may also contribute to the variation in plasticiser concentration seen between the inner and outer estuary (Figures 6.1 and 6.2). There is likely to be input of plasticisers from rivers which flow into the Firth of Forth, e.g. from wastewater treatment works and stormwater runoff from urban and agricultural land. In addition, there are a number of potential sources of plasticisers in close proximity to the estuary itself, these include multiple wastewater discharges, municipal and industrial waste sites, and urban areas used for leisure and tourism. Although establishing the extent of these contributions is challenging due to the dynamic nature of the system, the contribution of these areas to plasticiser occurrence in other estuaries has been previously postulated, with industrial and urban areas appearing to be primary sources of plasticisers (Chapter 5).

Although the majority of plasticisers removed during wastewater treatment partition to the biosolids and are thus not released directly into water courses, there is a fraction which enters the effluent (Y.S. Lee et al., 2019). Thus, particularly lower molecular weight plasticisers (e.g. DMP and DEP), may be present in the WWTP effluent which is released into water courses, with plasticisers with greater logK_{OW} (e.g. DEHP) may found generally at lower concentrations (Y.S. Lee et al., 2019). As the majority of municipal and industrial WWTP outfalls in the Firth of Forth occur upstream of the inner estuary sites (Figure 6.1), discharges of plasticisers from these outfalls, followed by salting-out and partitioning to sediment, may be contributing to the greater occurrence of plasticisers at the inner estuary relative to the outer estuary.

Of the four operational landfill sites that are within 10 km of the Firth of Forth and/or within 5 km of a tributary entering the Firth of Forth, three are to the west (upstream) of the inner estuary sites (Figure 6.1). Plasticisers have been detected in groundwater associated with landfill sites at levels ~4 times greater than that of the corresponding surface water (Liu et al., 2010), and in surface leachates from a coastal municipal landfill (Mohammadi et al., 2022). These studies suggest that lateral or vertical leaching of plasticisers from operational landfill and unlined legacy landfill sites adjacent to the Firth of Forth may have contributed to the input of these contaminants into the estuary. However, further evidence is required to assess the extent of this potential groundwater input, such as groundwater flow patterns and targeted analysis of plasticisers in groundwater suspected to be contaminated. Furthermore, monitoring studies to establish the temporal nature of any relationships (e.g. pollution events, storm events contributing to sewage overflows) could provide further evidence of the role that these locations play in the occurrence of plasticisers in the Firth of Forth.

6.3.3 Seasonality of plasticisers in the Firth of Forth

∑plasticiser concentrations in the Firth of Forth (all sites combined) were generally greatest in the winter (Figure 6.5; median concentration 73.1 ng g^{-1} ww), with lower median summer (57.9 ng g^{-1} ww) and spring (10.9 ng g^{-1} ww) values. Due to the wide range of concentrations measured in the estuary, no significant seasonal differences were found in the estuary-wide ∑plasticiser (Kruskal-Wallis, $p < 0.05$). However, concentrations at the outer estuary sites were significantly greater in winter than spring (Kruskal-Wallis, $p = 0.0095$), with mean and median concentrations of 99.9 and 44.8 ng g^{-1} ww in winter and 12.8 and 1.7 ng g^{-1} ww in spring. No statistically significant seasonal changes in ∑plasticiser were found at the inner estuary sites ($p < 0.05$; Figure 6.5), despite median concentrations increasing from winter to spring (116 to 170 ng g^{-1} ww; Kruskal-Wallis p = 0.39), before falling from spring to summer (57.9 ng g^{-1} ww; Kruskal-Wallis p = 0.066).

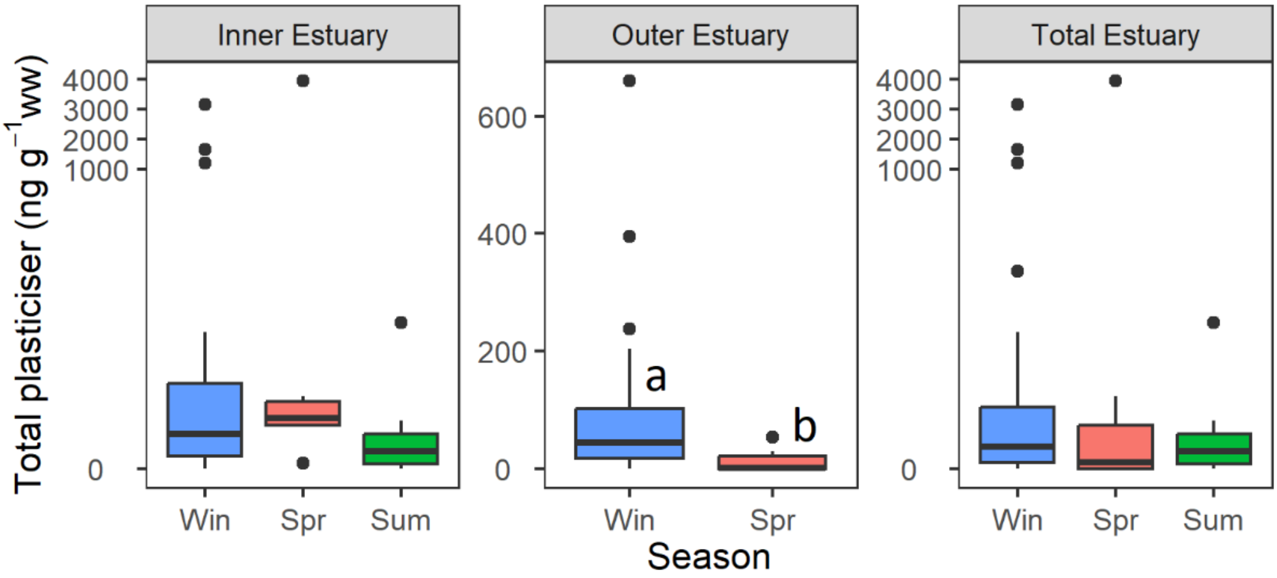


Figure 6.5: Seasonality of ∑plasticiser concentrations in sediments of the Firth of Forth (ng g^{-1} ww); Win = winter; Spr = spring; Sum = summer; samples <LOD (n=7/73) were assigned a value of zero so as to avoid overestimation; statistically significant differences are indicated by letters (a, b; Kruskal-Wallis, $p < 0.05$).

The average annual channel flow in the Firth of Forth is 63 m^3 s^{-1}, although there is marked seasonal variation, with flows reaching <10 m^3 s^{-1} in summer and >300 m^3 s^{-1} in winter (Balls, 1992). Such a range of flows is likely to act as one of the primary regulators of seasonal contaminant input and transport into and from the estuary. That ∑plasticiser was greater at the outer estuary in winter than in spring, but was greatest at the inner estuary in spring, indicates that distance from estuary mouth may play a role in determining the overall effect of changes in channel flow. That total estuary concentrations were generally greater in winter and spring than in summer may be partly due to a greater number of storm events that result in urban runoff inputs and uncontrolled release of untreated sewage from storm overflows during winter and spring. Furthermore, as the outer estuary sites were situated on the eastern extent at the boundary with the North Sea (Figure 6.1), the reduction in flow rate associated with the increased channel width in this region may further cause the deposition of any contaminated sediments transport from upstream (e.g. at the inner estuary) during these high-flow periods, potentially explaining why concentrations at the outer estuary were higher in winter.

Consistent with the results found in our study, Zhang et al. (2020a) found that increased plasticiser flux from terrestrial sources due to runoff and leaching during the wet season contributed to greater plasticiser concentrations in water and sediment. In contrast to the results here and those of Zhang et al. (2020a), other studies have reported greater plasticiser concentrations in the dry season, attributed primarily to greater dilution effects in the wet season (Paluselli et al., 2018b; Z. M. Zhang et al., 2020b), or little seasonal impact (Wang et al. 2021). Local-scale factors such as the degree and nature of source intensity, in addition to regional climate factors, may account for the differences in the results between these studies.

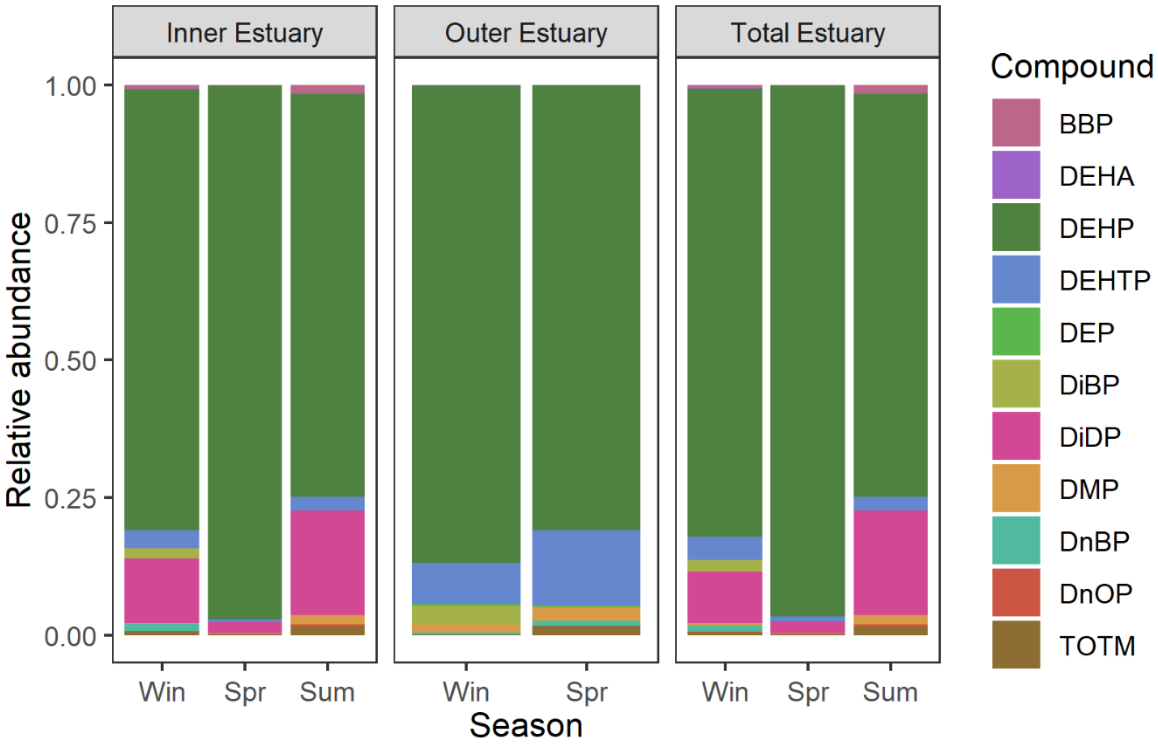


Figure 6.6: Plasticiser profiles in sediments in the Firth of Forth; Win = winter; Spr = spring; Sum = summer.

The plasticiser profiles at the inner estuary and the outer estuary were dominated by DEHP in every season (73-97% of ∑plasticiser). Two primary differences were found between the plasticiser profiles between the two sampling areas. Firstly, DiDP was not detected at any outer estuary sampling sites, but accounted for up to 19% of ∑plasticiser at the inner estuary (Figure 6.6). Secondly, the emerging plasticiser DEHTP contributed 7.4% and 14% to the total plasticiser load at the outer estuary sites in winter and spring, but only 3.3% and 0.5% at the inner estuary in those seasons. The differences in these profiles may partly reflect differences in plasticiser transport. For example, DiDP is highly hydrophobic (logK_{OW} = 9.46) and therefore may partition rapidly to sediment and be retained closer to sources, resulting in the higher relative abundance at the inner estuary. Furthermore, the high LOD of DiDP (59.5 ng g^{-1} ww) may be masking low-level DiDP contamination at outer estuary sites, particularly as the concentrations of all plasticisers were generally lower at the outer than at the inner estuary sites. That DEHTP was present at higher relative abundance in the outer estuary than inner estuary may partly arise from the lack of detection of DiDP at the outer estuary, in addition to greater transport of DEHTP than e.g. DiDP or TOTM, which have greater $\log K_{OW}$ values and thus may partition more strongly to sediment closer to the inner estuary.

6.3.4 Implications of plasticisers in the Firth of Forth

The uptake of phthalates and emerging plasticisers has been shown to occur in a range of coastal and marine species, e.g. fish (Castro-Jiménez and Ratola, 2020; H. Hu et al., 2020; Hu et al., 2016), molluscs (Castro-Jiménez and Ratola, 2020; Hu et al., 2016; Tsochatzis et al., 2019), and crustaceans (H. Hu et al., 2020; Hu et al., 2016). The Firth of Forth is home to a number of benthic fish species which may be particularly exposed to plasticiser contamination of bed sediments due to their feeding patterns which can lead to direct exposure through the ingestion of contaminated sediment (Greenwood and Hill, 2003). The phthalate DEHP has been associated with endocrine disruption in medaka and salmon (Norman et al., 2007; Ye et al., 2014), immunotoxicity in trout (Martins et al., 2015), and cytotoxicity and genotoxicity in sea bass (Molino et al., 2019). DEHP may also harm development in marine copepods (Forget-leray et al., 2005). Therefore, the occurrence of some phthalates with known toxicity (e.g. DEHP) in estuary sediments of almost 4000 ng g^{-1} ww indicates that plasticisers may be presenting an exposure of uncertain risk to some species in the Firth of Forth. The effects levels seen in the majority of toxicity studies are based on experiments that typically administer the chemical through diet conducted via in vitro tests. This makes it difficult to link such results to sediment concentrations that lead to exposure over highly extended timescales. Further work is therefore required to understand the implications of plasticiser contamination on the benthic species in this estuary, such as studies of how plasticisers are taken up in common species and whether there is any potential for these compounds to transfer through tropic networks.

The First of Forth is recognised as one of the most important estuaries in the UK for its wildlife and conservation value. The island of Inchkeith (in the inner estuary) and the Isle of May (in the outer estuary) host nationally important colonies of numerous seabirds, such as shags, common guillemots, Atlantic puffins, and razorbills (Wanless et al., 2018). Furthermore, Bass Rock (another island in the outer estuary, to the south west of the Isle of May) is an internationally important breeding ground for the northern gannet, representing approximately 11% of the total global northern gannet population during the breeding season (Mitchell et al., 2004). Sandeels and benthic fish have been identified as primary constituents of the diets of these seabirds (Wanless et al., 2018). Thus, due to feeding behaviours and the occurrence of plasticisers in the estuary sediments, there is potential for the bioaccumulation of plasticisers in seabird species in the Firth of Forth. There is no data available on the bioaccumulation and concentrations of plasticisers in seabirds, and the toxicity and effects levels of plasticisers in seabirds have also not been assessed. However, the concentrations of plasticisers in the sediments measured here indicate a small, but likely year-round exposure potential.

Although we found that emerging plasticisers represent only a small proportion of the total measured plasticiser concentration relative to phthalates, market trends indicate that the use of emerging plasticisers will increase in the future as phthalates are increasingly phased out (CEFIC, 2021). To date, there are only a handful of studies of the occurrence of emerging plasticisers in marine species. Despite their relatively low abundance, some emerging plasticisers have been detected at similar levels to phthalates such as DEHP in the tissues of amphipods (Lo Brutto et al., 2021), fish and seagrass (Jebara et al., 2021). Despite this, very little is known about the ecotoxicological state of these compounds in coastal and marine biota (Chapter 5).

6.4 Conclusions

This study investigated the occurrence of legacy phthalate plasticisers and emerging plasticisers in sediments from the Firth of Forth estuary in Scotland, UK. The plasticiser profile remains dominated by the phthalate DEHP. The emerging plasticiser DEHTP was the third most frequently detected plasticiser in the study and had the third greatest maximum concentration, indicating that the growing use of this substance as a replacement for phthalates may be leading to increased environmental occurrence. Aside from DEHP, DMP and DEHTP, other phthalates (e.g. DiBP, DnBP) and emerging plasticisers (DEHA and TOTM) were rarely detected although were present in comparable quantities. Thus, it appears that emerging plasticisers are as widespread as the phthalate compounds which they have been designed to replace, albeit at low concentrations.

∑plasticiser concentrations in the estuary were significantly greater in the inner than outer estuary, likely due to increased dilution of contaminants towards the estuary mouth, and the proximity of the inner estuary sites to sources of plasticisers such as wastewater treatment plant outfalls (both municipal and industrial), current-use and legacy landfill sites, and other discharges from industrial and urban areas. ∑plasticiser concentrations were also generally greatest in winter and spring than in summer, and differences were observed in the seasonal patterns of ∑plasticiser between the inner and outer estuary. These differences were possibly driven by contrasts in the degree and timing of sediment resuspension caused by distance from the estuary mouth and variations in flow conditions between winter and summer. ∑plasticiser concentrations were negatively correlated with water column depth and distance from the shore, indicating that the magnitude of plasticiser contamination declines with distance from source areas.

The occurrence of plasticisers may be posing an exposure risk to biota in the estuary, with DEHP exhibiting particularly high sediment concentrations of ~4 $\mu g\ g^{-1}$ ww. This is similar to soil concentrations which have been shown to bioaccumulate in terrestrial invertebrates (Hu et al., 2005). Phthalates have also been shown to be taken up by marine biota, and the occurrence of plasticisers in sediments in the Firth of Forth may result in the uptake of these contaminants by sediment-dwelling biota such as sandeels, and benthic fish, both of which form a significant portion of the diet of a number of seabird species. Better understanding of the ecotoxicology and effects thresholds of legacy and emerging plasticisers is needed in order to assess the existing and future risks that these contaminants may pose to estuarine and near-shore ecosystems.

6.5 Acknowledgements

This work was supported by the Natural Environment Research Council NE/S007423/1, with Alex Billings' studentship through the ENVISION Doctoral Training Partnership. This work was also supported by The Natural Environment Research Council NE/T003596/1.

7

Final conclusions and future perspectives

7.1 Conclusions

Based on the field studies and laboratory experimental work conducted during the course of this PhD project, we can draw a number of conclusions:

- **Multiple classes of plasticiser are widely present in UK soils and sediments**. Prior to the work described in Chapters 3 and 6, there had been few studies of the occurrence of plasticisers in the UK terrestrial or estuarine environments. As far as the author is aware, the only monitoring of plasticisers in UK soils to have been conducted prior to the publication of this thesis was a survey of single phthalate in Scottish soils, as part of a larger analytical monitoring suite (Rhind et al., 2013a). Studies of the occurrence of plasticisers in UK estuaries date from over 25 years ago, and also focussed on a limited number of key phthalates (Law et al., 1991; Long et al., 1998; Preston and Al-Omran, 1989). The results from Chapters 3 and 6 represent the first multi-class survey of legacy and emerging plasticisers in the UK environment. Work of this nature is increasingly important as the current shifts in use from phthalates to emerging plasticisers continue.

- ***In situ* plastic waste is only partially responsible for the occurrence of plasticisers in soils**. The field study (Chapter 3) showed that whilst plasticiser concentrations in soils were significantly correlated with surface plastic waste, this correlation could only explain ~25% of the variance in plasticiser concentrations. Furthermore, no significant correlation was found between plasticiser and microplastic concentrations in the soils. Even after limitations in analytical methods and sample sizes are taken into account, these results suggest that a proportion of the plasticiser contamination in UK soils is derived from external sources, such as airborne transport or runoff from adjacent land.

- **Phthalates remain the dominant class of plasticiser in UK soils and sediments**. Plasticiser profiles in soils (Chapter 3) as well as estuarine and coastal sediments (Chapter 6) were found to be typically dominated by phthalates. Emerging plasticisers such as trimellitates, adipates, terephthalates and citrates were found to be widespread and in comparable concentrations to some restricted phthalates, although the absolute concentrations of these emerging plasticisers were generally low and below those of the major detected phthalates.

- **Plasticisers can be released rapidly from microplastics in soils**. The results from the plasticiser release experiment (Chapter 4) indicated that a proportion of the plasticiser load associated with microplastics is rapidly released into soils following microplastic addition. Whilst the proportion of total plasticiser release from the pellets was estimated to be low (<0.02 w/w), this raises questions around the longer-term ‘chronic’ input of the remainder of the plasticiser present in the microplastic particles into soils. The differences seen in plasticiser release rate between different soil types suggests that soil properties can play a significant role in the release of plasticisers from plastics. Therefore, spatial differences in plasticiser leaching rates may be expected, based on differences in soil properties in addition to climate and seasonal variations.

- **Some emerging plasticisers are among the most persistent plasticisers in soils, and therefore may accumulate in the terrestrial environment**. The degradation experiment discussed in Chapter 4 demonstrated that the three most persistent plasticisers that we studied were either non-phthalate emerging plasticisers (DEHPT, TOTM) or phthalate plasticisers that are being used as replacements for restricted phthalates (DiDP). Therefore, this persistence, in addition to the increasing use and production of emerging plasticisers as phthalate-replacements, may cause the accumulation of such compounds in the terrestrial environment.

- **Plasticisers are significantly retained close to source areas in UK estuaries**. Chapter 6 demonstrated that plasticisers in sediments in the Firth of Forth estuary were significantly more abundant in the inner estuary than at the outer estuary. This is likely related to degree of local source intensity in addition to the salting-out and partitioning behaviour of riverine-associated plasticisers as they enter the estuary channel. The retention of plasticisers within the Forth estuary may have implications for the organisms present in the estuary channel itself.

- **Plasticiser contamination of UK soils and sediments may present a risk to organisms, although effects thresholds are not well understood.** The highest levels of ∑plasticiser detected in UK soils and estuarine/coastal sediments were ~3 µg g^{-1} dw and 4 µg g^{-1} ww respectively (Chapters 3 and 6). These concentrations are comparable to soil plasticiser concentrations which have been show to bioaccumulate in terrestrial invertebrates (Hu et al., 2005; Chapter 2). However, as discussed in Chapters 2 and 5, whilst plasticisers have been shown to be taken up by terrestrial and marine organisms, the effects levels of plasticisers, and in particular emerging plasticisers, are poorly understood. Therefore, assessment of the risks posed by these contaminants in the UK warrants further study.

7.2 Suggestions for future work

The work carried out in Chapter 4 regarding the release of plasticisers from microplastic particles could be built upon by expanding the types of polymeric material that are tested for plasticiser release. This should include both pristine plastic materials, and environmentally degraded plastics, in order to test the effects that aging of different polymer matrices has on the release of plasticisers. Furthermore, the mass and type of plasticiser present in plastic materials may depend not only on the intended use of the material, but the polymer used. These properties may directly impact the mass balance of plasticiser between the particles and the surrounding medium (e.g. soil, sediment). Thus in order to better capture the diverse range of plastic waste detected in the environment (Chapter 3), an expanded range of materials should be tested.

The persistence of some of the higher molecular weight plasticisers in soils (Chapter 4) raises concerns around the potential for accumulation of these compounds in the terrestrial environment. Better understanding of the fate of these chemicals could be gained by ‘real-field’ experiments of the degradation rates of emerging plasticisers relative to legacy phthalates, as the observed half-lives of phthalates in soils appear to vary between studies conducted in the laboratory and in the field (Chapter 2).

Plasticisers are an important part of the wider plastics debate. Due to their association with plastic waste, the ongoing research into the impacts of microplastic on biota must therefore take in to account the effects of plasticisers themselves on these organisms. Given the evidence of widespread plasticiser contamination of both the terrestrial and estuarine environments (Chapters 2 and 5), including in the UK (Chapters 3 and 6), a key future research need is the determination of effects levels of plasticisers in soil and estuarine sediment dwelling organisms. In particular, whilst there is evidence of the effects of phthalates on these organisms, there are very few published studies concerning the ecotoxicological impacts and potential for trophic transfer of emerging plasticisers in biota. Furthermore, the uptake and elimination kinetics of plasticisers in terrestrial and estuarine organisms are virtually unknown. Due to the occurrence in, and release of, plasticisers in microplastics, there is a possibility that these particulates may act as vectors for plasticiser entry into organisms. Given the trends in the increasing use of emerging non-phthalate plasticisers (and plastics as a whole), a re-assessment of the risks posed by plasticisers in the environment is warranted. Future work to investigate the fate of microplastics and plasticisers in terrestrial and estuarine organisms can inform these assessments.

7.3 Personal reflections on working with microplastics and plasticisers - challenges and opportunities

Any efforts to understand the true extent of the impact of plastic and plasticiser contamination in the environment require the development and application of sound methods for the analysis of these contaminants. Methods for the analysis of microplastics and emerging plasticisers are constantly being refined and developed, and therefore if the results obtained from contemporary studies are to be analysed and reinterpreted in the context of future work that may use increasingly optimised and refined methods, it is vital to clearly report the specifics of the analytical methodologies used to measure these contaminants. This advice is particularly applicable in the field of microplastics, e.g. detailed reporting of the size ranges and limits of detection in microplastic studies will improve the relevance of contemporary microplastic studies to researchers working in these fields in the future.

Given the current trends in the use of plasticisers (and plastics), it would be pertinent to increase the scale to which these plastic additives are monitored in the environment, in addition to broadening the analytical horizons of such monitoring. The results of the work carried out during this project indicate that current and future environmental plasticiser burdens are much more diverse than a small set of phthalates. Therefore, for researchers moving into the field or for those revisiting existing methods and analytical suites, it will be necessary to include not just phthalates in these analyses, but also emerging plasticisers such as terephthalates, citrates, adipates, and trimellitates. This will enable us to ensure the relevance and usefulness of such research moving forward, and increase the ability of the data to answer the questions posed by future challenges of plasticisers, in order to more accurately understand the behaviour and impact of these contaminants in the environment. Additionally, acknowledging the limitations and challenges posed by such methods is essential, as plasticisers and microplastics are often surprising in the number of ways in which they can contaminate samples in the laboratory. For example, we would recommend sonicating all analytical standards before use in order to eliminate, or at least minimise, the changes in concentration of the plasticisers in solution caused by the sorption of the compounds to the walls of the glassware. Furthermore, it is worth keeping in mind that the development of methods for the extraction and analysis of plasticisers and microplastics is a fine balance between sample clean-up (e.g. to ensure the best analytical sensitivity) whilst also minimising the number of processing steps in order to reduce potential contamination or loss of the sample during the extraction process.

The fields of plastic and plasticiser pollution are growing increasingly relevant. Despite this, there remains a relative dearth of studies of these contaminants in the terrestrial environment. In particular, given the almost total lack of knowledge of the occurrence and impacts of emerging plasticisers in the soil environment, studies to fill these knowledge gaps should be prioritised (see Section 7.2). The use and production of emerging plasticisers will likely only increase in the coming decade, and the relative persistence of some of these compounds in soils indicates that ecotoxicological studies of the impacts of emerging plasticisers on terrestrial, and in particular soil-dwelling organisms, are warranted. These investigations will not only allow us to assess the impacts that these emerging contaminants pose at acute levels, but they will also allow the chronic, sublethal effects of phthalates and emerging plasticisers to be more clearly understood. Given the intrinsic link between plastics and plasticisers, these contaminants cannot be viewed in isolation. Thus a holistic view of plastic pollution is required if we are to properly assess the risk posed by plastic waste and plasticisers in the environment.

8

Bibliography

Al-Jaibachi, R., Cuthbert, R.N., Callaghan, A., 2018. Up and away: Ontogenic transference as a pathway for aerial dispersal of microplastics. Biol. Lett. 14, 20180479. https://doi.org/10.1098/rsbl.2018.0479

Al-Natsheh, M., Alawi, M., Fayyad, M., Tarawneh, I., 2015. Simultaneous GC-MS determination of eight phthalates in total and migrated portions of plasticized polymeric toys and childcare articles. J. Chromatogr. B Anal. Technol. Biomed. Life Sci. 985, 103–109. https://doi.org/10.1016/j.jchromb.2015.01.010

Allen, S.F., Ellis, F., Mitchell, C., Wang, X., Boogert, N.J., Lin, C.Y., Clokey, J., Thomas, K. V., Blount, J.D., 2021. Phthalate diversity in eggs and associations with oxidative stress in the European herring gull (Larus argentatus). Mar. Pollut. Bull. 169, 112564. https://doi.org/10.1016/j.marpolbul.2021.112564

Arfaeinia, H., Fazlzadeh, M., Taghizadeh, F., Saeedi, R., Spitz, J., Dobaradaran, S., 2019. Phthalate acid esters (PAEs) accumulation in coastal sediments from regions with different land use configuration along the Persian Gulf. Ecotoxicol. Environ. Saf. 169, 496–506. https://doi.org/10.1016/j.ecoenv.2018.11.033

Arthur, C., Baker, J., Bamford, H., 2009. Proceedings of the International Research Workshop on the Occurrence , Effects , and Fate of Microplastic Marine Debris, Group.

Baini, M., Martellini, T., Cincinelli, A., Campani, T., Minutoli, R., Panti, C., Finoia, M.G., Fossi, M.C., 2017. First detection of seven phthalate esters (PAEs) as plastic tracers in superficial neustonic/planktonic samples and cetacean blubber. Anal. Methods 9, 1512–1520. https://doi.org/10.1039/c6ay02674e

Ball, H., Cross, R., Grove, E., Horton, A., Johnson, A., Jürgens, M., Read, D., Svendsen, C., 2019. Sink to River - River to Tap: A Review of Potential Risks from Nanoparticles and Microplastics.

Balls, P.W., 1992. Nutrient behaviour in two contrasting Scottish estuaries, the Forth and

Tay. Oceanol. Acta 15, 261–277.

Baloyi, N.D., Tekere, M., Maphangwa, K.W., Masindi, V., 2021. Insights Into the Prevalence and Impacts of Phthalate Esters in Aquatic Ecosystems. Front. Environ. Sci. 9. https://doi.org/10.3389/fenvs.2021.684190

Bergmann, M., Wirzberger, V., Krumpen, T., Lorenz, C., Primpke, S., Tekman, M.B., Gerdts, G., 2017. High Quantities of Microplastic in Arctic Deep-Sea Sediments from the HAUSGARTEN Observatory. Environ. Sci. Technol. 51, 11000–11010. https://doi.org/10.1021/acs.est.7b03331

Bernard, L., Cueff, R., Breysse, C., Décaudin, B., Sautou, V., 2015. Migrability of PVC plasticizers from medical devices into a simulant of infused solutions. Int. J. Pharm. 485, 341–347. https://doi.org/10.1016/j.ijpharm.2015.03.030

Boots, B., Russell, C.W., Green, D.S., 2019. Effects of Microplastics in Soil Ecosystems: Above and Below Ground. Environ. Sci. Technol. 53, 11496–11506. https://doi.org/10.1021/acs.est.9b03304

Brand, J.H., Spencer, K.L., 2019. Potential contamination of the coastal zone by eroding historic landfills. Mar. Pollut. Bull. 146, 282–291. https://doi.org/10.1016/j.marpolbul.2019.06.017

Bueno-Ferrer, C., Jiménez, A., Garrigós, M.C., 2010. Migration analysis of epoxidized soybean oil and other plasticizers in commercial lids for food packaging by gas chromatography-mass spectrometry. Food Addit. Contam. - Part A Chem. Anal. Control. Expo. Risk Assess. 27, 1469–1477. https://doi.org/10.1080/19440049.2010.502129

Büks, F., Kaupenjohann, M., 2020. Global concentrations of microplastic in soils, a review. SOIL Discuss. 6, 649–662. https://doi.org/10.5194/soil-2020-50

Cai, Q.Y., Xiao, P.Y., Chen, T., Lü, H., Zhao, H.M., Zeng, Q.Y., Li, Y.W., Li, H., Xiang, L., Mo, C.H., 2015. Genotypic variation in the uptake, accumulation, and translocation of di-(2-ethylhexyl) phthalate by twenty cultivars of rice (Oryza sativa L.). Ecotoxicol. Environ. Saf. 116, 50–58. https://doi.org/10.1016/j.ecoenv.2015.02.038

Cao, D., Wang, X., Luo, X., Liu, G., Zheng, H., 2017. Effects of polystyrene microplastics on the fitness of earthworms in an agricultural soil. IOP Conf. Ser. Earth Environ. Sci. 61, 0012148. https://doi.org/10.1088/1755-1315/61/1/012148

Cao, Y., Lin, H., Zhang, K., Xu, S., Yan, M., Leung, K.M.Y., Lam, P.K.S., 2022. Microplastics: A major source of phthalate esters in aquatic environments. J. Hazard. Mater. 432, 128731. https://doi.org/10.1016/j.jhazmat.2022.128731

Carnevali, O., Santobuono, M., Forner, I., Basilio, P., Constantinos, R., Ancillai, D., Giorgini, E., Maradonna, F., 2019. Dietary diisononylphthalate contamination induces hepatic stress : a multidisciplinary investigation in gilthead seabream (Sparus aurata) liver. Arch. Toxicol. 93, 2361–2373. https://doi.org/10.1007/s00204-019-02494-7

Cartwright, C.D., Thompson, I.P., Burns, R.G., 2000. Degradation and impact of phthalate plasticizers on soil microbial communities. Environ. Toxicol. Chem. 19, 1253–1261. https://doi.org/10.1002/etc.5620190506

Castro-Jiménez, J., Ratola, N., 2020. An innovative approach for the simultaneous quantitative screening of organic plastic additives in complex matrices in marine coastal areas. Environ. Sci. Pollut. Res. 27, 11450–11457. https://doi.org/10.1007/s11356-020-08069-9

CEFIC, 2018. Plasticisers fact sheet [WWW Document]. URL https://www.plasticisers.org/wp-content/uploads/2019/08/Plasticisers_Factsheet_EN_MAY2020.pdf

CEFIC, 2021. Plasticisers facts sheet [WWW Document] URL https://www.plasticisers.org/wp-content/uploads/2019/08/Plasticisers_Factsheet_EN_MAY2021.pdf

Chai, C., Cheng, H., Ge, W., Ma, D., Shi, Y., 2014. Phthalic acid esters in soils from vegetable greenhouses in Shandong Peninsula, East China. PLoS One 9, e95701. https://doi.org/10.1371/journal.pone.0095701

Chakraborty, P., Sampath, S., Mukhopadhyay, M., Selvaraj, S., Bharat, G.K., Nizzetto, L., 2019. Baseline investigation on plasticizers, bisphenol A, polycyclic aromatic hydrocarbons and heavy metals in the surface soil of the informal electronic waste recycling workshops and nearby open dumpsites in Indian metropolitan cities. Environ. Pollut. 248, 1036–1045. https://doi.org/10.1016/j.envpol.2018.11.010

Chakraborty, P., Shappell, N.W., Mukhopadhyay, M., Onanong, S., Rex, K.R., Snow, D., 2021. Surveillance of plasticizers, bisphenol A, steroids and caffeine in surface water of River Ganga and Sundarban wetland along the Bay of Bengal: occurrence, sources, estrogenicity screening and ecotoxicological risk assessment. Water Res. 190, 116668. https://doi.org/10.1016/j.watres.2020.116668

Chang, B. V., Lu, Y.S., Yuan, S.Y., Tsao, T.M., Wang, M.K., 2009. Biodegradation of phthalate esters in compost-amended soil. Chemosphere 74, 873–877. https://doi.org/10.1016/j.chemosphere.2008.10.003

Chapman, P.M., Wang, F., 2001. Assessing sediment contamination in estuaries. Environ. Toxicol. Chem. https://doi.org/10.1002/etc.5620200102

Chen, C.F., Ju, Y.R., Lim, Y.C., Chang, J.H., Chen, C.W., Dong, C. Di, 2018. Spatial and temporal distribution of Di-(2-ethylhexyl) phthalate in urban river sediments. Int. J. Environ. Res. Public Health 15, 1–12. https://doi.org/10.3390/ijerph15102228

Chen, N., Shuai, W., Hao, X., Zhang, H., Zhou, D., Gao, J., 2017. Contamination of Phthalate Esters in Vegetable Agriculture and Human Cumulative Risk Assessment.

Pedosphere 27, 439–451. https://doi.org/10.1016/S1002-0160(17)60340-0

Chen, Y., Leng, Y., Liu, X., Wang, J., 2020. Microplastic pollution in vegetable farmlands of suburb Wuhan, central China. Environ. Pollut. 257, 113449. https://doi.org/10.1016/j.envpol.2019.113449

Cheng, H.F., Kumar, M., Lin, J.G., 2008. Degradation kinetics of di-(2-ethylhexyl) phthalate (DEHP) and organic matter of sewage sludge during composting. J. Hazard. Mater. 154, 55–62. https://doi.org/10.1016/j.jhazmat.2007.09.105

Cheng, H.F., Kumar, M., Lin, J.G., 2010. Assessment of di-(2-ethylhexyl)phthalate (DEHP) removal in a rotating biological contactor and activated sludge process treating domestic wastewater. Sep. Sci. Technol. 45, 221–227. https://doi.org/10.1080/01496390903409385

Cheng, J., Liu, Y., Wan, Q., Yuan, L., Yu, X., 2018. Degradation of dibutyl phthalate in two contrasting agricultural soils and its long-term effects on soil microbial community. Sci. Total Environ. 640–641, 821–829. https://doi.org/10.1016/j.scitotenv.2018.05.336

Cheng, J., Wan, Q., Ge, J., Feng, F., Yu, X., 2019. Major factors dominating the fate of dibutyl phthalate in agricultural soils. Ecotoxicol. Environ. Saf. 183, 109569. https://doi.org/10.1016/j.ecoenv.2019.109569

Cheng, X., Ma, L., Xu, D., Cheng, H., Yang, G., Luo, M., 2015. Mapping of phthalate esters in suburban surface and deep soils around a metropolis-Beijing, China. J. Geochemical Explor. 155, 56–61. https://doi.org/10.1016/j.gexplo.2015.04.007

Cho, Y., Shim, W.J., Jang, M., Han, G.M., Hong, S.H., 2019. Abundance and characteristics of microplastics in market bivalves from South Korea. Environ. Pollut. 245, 1107–1116. https://doi.org/10.1016/j.envpol.2018.11.091

Choi, M.S., Rehman, S.U., Kim, H., Han, S.B., Lee, J., Hong, J., Yoo, H.H., 2018. Migration of epoxidized soybean oil from polyvinyl chloride/polyvinylidene chloride food packaging wraps into food simulants. Environ. Sci. Pollut. Res. 25, 5033–5039. https://doi.org/10.1007/s11356-017-0951-9

Christensen, J.R., MacDuffee, M., MacDonald, R.W., Whiticar, M., Ross, P.S., 2005. Persistent organic pollutants in British Columbia grizzly bears: Consequence of divergent diets. Environ. Sci. Technol. 39, 6952–6960. https://doi.org/10.1021/es050749f

Coltro, L., Pitta, J.B., da Costa, P.A., Fávaro Perez, M.Â., de Araújo, V.A., Rodrigues, R., 2014. Migration of conventional and new plasticizers from PVC films into food simulants: A comparative study. Food Control 44, 118–129. https://doi.org/10.1016/j.foodcont.2014.03.058

Crossman, J., Hurley, R.R., Futter, M., Nizzetto, L., 2020. Transfer and transport of microplastics from biosolids to agricultural soils and the wider environment. Sci. Total Environ. 724, 138334. https://doi.org/10.1016/j.scitotenv.2020.138334

da Costa, J.P., Santos, P.S.M., Duarte, A.C., Rocha-Santos, T., 2016. (Nano)plastics in the environment - Sources, fates and effects. Sci. Total Environ. 566–567, 15–26. https://doi.org/10.1016/j.scitotenv.2016.05.041

DEFRA, 2012. Waste water treatment in the United Kingdom – 2012.

Dhavamani, J., Beck, A.J., Gledhill, M., El-Shahawi, M.S., Kadi, M.W., Ismail, I.M.I., Achterberg, E.P., 2022. The effects of salinity, temperature, and UV irradiation on leaching and adsorption of phthalate esters from polyethylene in seawater. Sci. Total Environ. 838, 155461. https://doi.org/10.1016/j.scitotenv.2022.155461

Ding, L., Zhang, S., Wang, X., Yang, X., Zhang, C., Qi, Y., Guo, X., 2020. The occurrence and distribution characteristics of microplastics in the agricultural soils of Shaanxi Province, in north-western China. Sci. Total Environ. 720, 137525.

https://doi.org/10.1016/j.scitotenv.2020.137525

Domínguez-Romero, E., Scheringer, M., 2019. A review of phthalate pharmacokinetics in human and rat: what factors drive phthalate distribution and partitioning? Drug Metab. Rev. 51, 314–329. https://doi.org/10.1080/03602532.2019.1620762

Dong, L., Lin, L., Pan, X., Zhang, S., Lv, Z., Mi, C., 2022. Distribution Dynamics of Phthalate Esters in Surface Water and Sediment of the Middle-Lower Hanjiang River, China. Int. J. Environ. Res. Public Health 19. https://doi.org/10.3390/ijerph19052702

Du, L., Li, G., Liu, M., Li, Y., Yin, S., Zhao, J., 2015. Biomarker responses in earthworms (Eisenia fetida) to soils contaminated with di-n-butyl phthalates. Environ. Sci. Pollut. Res. 22, 4660–4669. https://doi.org/10.1007/s11356-014-3716-8

ECHA, 2013. Evaluation of new scientific evidence concerning DINP and DIDP [WWW Document].URL https://echa.europa.eu/documents/10162/31b4067e-de40-4044-93e8-9c9ff1960715

ECHA, 2018. ANNEX XVII TO REACH – Conditions of restriction [WWW Document]. Off. J. Eur. Union. URL https://echa.europa.eu/documents/10162/aaa92146-a005-1dc2-debe-93c80b57c5ee

ECHA, 2022. Bis(2-ethylhexyl) phthalate substance infocard [WWW Document]. URL https://echa.europa.eu/substance-information/-/substanceinfo/100.003.829

Eckert, E., Münch, F., Göen, T., Purbojo, A., Müller, J., Cesnjevar, R., 2016. Comparative study on the migration of di-2-ethylhexyl phthalate (DEHP) and tri-2-ethylhexyl trimellitate (TOTM) into blood from PVC tubing material of a heart-lung machine. Chemosphere 145, 10–16. https://doi.org/10.1016/j.chemosphere.2015.11.067

Endo, S., Yuyama, M., Takada, H., 2013. Desorption kinetics of hydrophobic organic contaminants from marine plastic pellets. Mar. Pollut. Bull. 74, 125–131.

https://doi.org/10.1016/j.marpolbul.2013.07.018

Erythropel, H.C., Brown, T., Maric, M., Nicell, J.A., Cooper, D.G., Leask, R.L., 2015. Designing greener plasticizers: Effects of alkyl chain length and branching on the biodegradation of maleate based plasticizers. Chemosphere 134, 106–112. https://doi.org/10.1016/j.chemosphere.2015.04.014

Espí, E., Salmerón, A., Fontecha, A., García, Y., Real, A.I., 2006. Plastic films for agricultural applications. J. Plast. Film Sheeting 22, 85–102. https://doi.org/10.1177/8756087906064220

European Union, 2011. Commission Regulation (EU) No 10/2011 of 14 January 2011. Off. J. Eur. Union 1–89 [WWW Document]. URL https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011:012:0001:0089:en:PDF

Fankhauser-Noti, A., Biedermann-Brem, S., Grob, K., 2006. PVC plasticizers/additives migrating from the gaskets of metal closures into oily food: Swiss market survey June 2005. Eur. Food Res. Technol. 223, 447–453. https://doi.org/10.1007/s00217-005-0223-7

Fankhauser-Noti, A., Grob, K., 2007. Blank problems in trace analysis of diethylhexyl and dibutyl phthalate: Investigation of the sources, tips and tricks. Anal. Chim. Acta 582, 353–360. https://doi.org/10.1016/j.aca.2006.09.012

Feng, Q., Zhong, L., Xu, S., Qiu, L., Wu, S., 2016. Biomarker Response of the Earthworm (Eisenia fetida) Exposed to Three Phthalic Acid Esters. Environ. Eng. Sci. 33, 105–111. https://doi.org/10.1089/ees.2015.0121

Feng, S., Lu, H., Tian, P., Xue, Y., Lu, J., Tang, M., Feng, W., 2020. Analysis of microplastics in a remote region of the Tibetan Plateau: Implications for natural environmental response to human activities. Sci. Total Environ. 739, 140087. https://doi.org/10.1016/j.scitotenv.2020.140087

Ferrara, G., Bertoldo, M., Scoponi, M., Ciardelli, F., 2001. Diffusion coefficient and activation energy of Irganox 1010 in poly(propylene-co-ethylene) copolymers. Polym. Degrad. Stab. 73, 411–416. https://doi.org/10.1016/S0141-3910(01)00121-5

Forget-leray, Ã., Landriau, I., Minier, C., 2005. Impact of endocrine toxicants on survival , development , and reproduction of the estuarine copepod Eurytemora affinis (Poppe). Ecotoxicol. Environ. Saf. 60, 288–294. https://doi.org/10.1016/j.ecoenv.2004.06.008

Forner-Piquer, I., Mylonas, C.C., Calduch-Giner, J., Maradonna, F., Gioacchini, G., Allarà, M., Piscitelli, F., Di, V., 2018. Endocrine disruptors in the diet of male Sparus aurata : Modulation of the endocannabinoid system at the hepatic and central level by Di-isononyl phthalate and Bisphenol A. Environ. Int. 119, 54–65. https://doi.org/10.1016/j.envint.2018.06.011

Forner-Piquer, I., Mylonas, C.C., Fakriadis, I., Papadaki, M., Piscitelli, F., Di Marzo, V., Calduch-Giner, J., Pérez-Sánchez, J., Carnevali, O., 2019. Effects of diisononyl phthalate (DiNP) on the endocannabinoid and reproductive systems of male gilthead sea bream (Sparus aurata) during the spawning season. Arch. Toxicol. 93, 727–741. https://doi.org/10.1007/s00204-018-2378-6

Frederiksen, H., Skakkebæk, N.E., Andersson, A.M., 2007. Metabolism of phthalates in humans. Mol. Nutr. Food Res. 51, 899–911. https://doi.org/10.1002/mnfr.200600243

Fromme, H., Küchler, T., Otto, T., Pilz, K., Müller, J., Wenzel, A., 2002. Occurrence of phthalates and bisphenol A and F in the environment. Water Res. 36, 1429–1438. https://doi.org/10.1016/S0043-1354(01)00367-0

Fromme, H., Schütze, A., Lahrz, T., Kraft, M., Fembacher, L., Siewering, S., Burkardt, R., Dietrich, S., Koch, H.M., Völkel, W., 2016. Non-phthalate plasticizers in German daycare centers and human biomonitoring of DINCH metabolites in children attending the centers (LUPE 3). Int. J. Hyg. Environ. Health 219, 33–39.

https://doi.org/10.1016/j.ijheh.2015.08.002

Fuller, S., Gautam, A., 2016. A Procedure for Measuring Microplastics using Pressurized Fluid Extraction. Environ. Sci. Technol. 50, 5774–5780. https://doi.org/10.1021/acs.est.6b00816

Gao, D.W., Wen, Z.D., 2016. Phthalate esters in the environment: A critical review of their occurrence, biodegradation, and removal during wastewater treatment processes. Sci. Total Environ. 541, 986–1001. https://doi.org/10.1016/j.scitotenv.2015.09.148

García Ibarra, V., Rodríguez Bernaldo de Quirós, A., Paseiro Losada, P., Sendón, R., 2018. Identification of intentionally and non-intentionally added substances in plastic packaging materials and their migration into food products. Anal. Bioanal. Chem. 410, 3789–3803. https://doi.org/10.1007/s00216-018-1058-y

Gibson, R., Wang, M.J., Padgett, E., Beck, A.J., 2005. Analysis of 4-nonylphenols, phthalates, and polychlorinated biphenyls in soils and biosolids. Chemosphere 61, 1336–1344. https://doi.org/10.1016/j.chemosphere.2005.03.072

Goulas, A.E., Anifantaki, K.I., Kolioulis, D.G., Kontominas, M.G., 2000. Migration of di-(2-ethylhexylexyl)adipate plasticizer from food-grade polyvinyl chloride film into hard and soft cheeses. J. Dairy Sci. 83, 1712–1718. https://doi.org/10.3168/jds.S0022-0302(00)75040-5

Goulas, A.E., Zygoura, P., Karatapanis, A., Georgantelis, D., Kontominas, M.G., 2007. Migration of di(2-ethylhexyl) adipate and acetyltributyl citrate plasticizers from food-grade PVC film into sweetened sesame paste (halawa tehineh): Kinetic and penetration study. Food Chem. Toxicol. 45, 585–591. https://doi.org/10.1016/j.fct.2006.10.003

Greenwood, M.F.D., Hill, A.S., 2003. Temporal, spatial and tidal influences on benthic and demersal fish abundance in the Forth estuary. Estuar. Coast. Shelf Sci. 58, 211–225. https://doi.org/10.1016/S0272-7714(03)00071-4

Griffiths, R.I., Thomson, B.C., James, P., Bell, T., Bailey, M., Whiteley, A.S., 2011. The bacterial biogeography of British soils. Environ. Microbiol. 13, 1642–1654. https://doi.org/10.1111/j.1462-2920.2011.02480.x

Gu, Y.Y., Wei, Q., Wang, L.Y., Zhang, Z.M., Zhang, X.Q., Sun, A.L., Chen, J., Shi, X.Z., 2021. A comprehensive study of the effects of phthalates on marine mussels: Bioconcentration, enzymatic activities and metabolomics. Mar. Pollut. Bull. 168, 112393. https://doi.org/10.1016/j.marpolbul.2021.112393

Hahladakis, J.N., Velis, C.A., Weber, R., Iacovidou, E., Purnell, P., 2018. An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling. J. Hazard. Mater. 344, 179–199. https://doi.org/10.1016/j.jhazmat.2017.10.014

Hansen, E., Nilsson, N.H., Lithner, D., Lassen, C., 2013. Hazardous substances in plastic materials, Hazardous substances in plastic materials.

Hanušová, K., Rajchl, A., Votavová, L., Dobiáš, J., Steiner, I., 2013. Testing the influence of various conditions on the migration of epoxidised soybean oil from polyvinylchloride gaskets. Food Addit. Contam. - Part A Chem. Anal. Control. Expo. Risk Assess. 30, 1963–1975. https://doi.org/10.1080/19440049.2013.825818

Hartmann, N.B., Hüffer, T., Thompson, R.C., Hassellöv, M., Verschoor, A., Daugaard, A.E., Rist, S., Karlsson, T., Brennholt, N., Cole, M., Herrling, M.P., Hess, M.C., Ivleva, N.P., Lusher, A.L., Wagner, M., 2019. Are We Speaking the Same Language? Recommendations for a Definition and Categorization Framework for Plastic Debris. Environ. Sci. Technol. 53, 1039–1047. https://doi.org/10.1021/acs.est.8b05297

He, M.J., Yang, T., Yang, Z.H., Zhou, H., Wei, S.Q., 2018. Current State, Distribution, and Sources of Phthalate Esters and Organophosphate Esters in Soils of the Three Gorges Reservoir Region, China. Arch. Environ. Contam. Toxicol. 74, 502–513.

https://doi.org/10.1007/s00244-017-0469-7

Hendrickson, E., Minor, E.C., Schreiner, K., 2018. Microplastic Abundance and Composition in Western Lake Superior As Determined via Microscopy, Pyr-GC/MS, and FTIR. Environ. Sci. Technol. 52, 1787–1796. https://doi.org/10.1021/acs.est.7b05829

Henkel, C., Hüffer, T., Hofmann, T., 2019. The leaching of phthalates from PVC can be determined with an infinite sink approach. MethodsX 6, 2729–2734. https://doi.org/10.1016/j.mex.2019.10.026

Heo, H., Choi, M.J., Park, J., Nam, T., Cho, J., 2020. Anthropogenic occurrence of phthalate esters in beach seawater in the southeast coast region, South Korea. Water (Switzerland) 12. https://doi.org/10.3390/w12010122

Hermabessiere, L., Dehaut, A., Paul-Pont, I., Lacroix, C., Jezequel, R., Soudant, P., Duflos, G., 2017. Occurrence and effects of plastic additives on marine environments and organisms: A review. Chemosphere 182, 781–793. https://doi.org/10.1016/j.chemosphere.2017.05.096

Hidalgo-Serrano, M., Borrull, F., Pocurull, E., Marcé, R.M., 2020. Pressurised Liquid Extraction and Liquid Chromatography–High Resolution Mass Spectrometry for the Simultaneous Determination of Phthalate Diesters and Their Metabolites in Seafood Species. Food Anal. Methods 13, 1442–1453. https://doi.org/10.1007/s12161-020-01759-7

Hidalgo-Serrano, M., Borrull, F., Marcé, R.M., Pocurull, E., 2021. Simple method for determining phthalate diesters and their metabolites in seafood species using QuEChERS extraction and liquid chromatography-high resolution mass spectrometry. Food Chem. 336, 127722. https://doi.org/10.1016/j.foodchem.2020.127722

Hidalgo-Serrano, M., Borrull, F., Marcé, R.M., Pocurull, E., 2022. Phthalate esters in marine ecosystems: Analytical methods, occurrence and distribution. TrAC - Trends Anal.

Chem. 151. https://doi.org/10.1016/j.trac.2022.116598

Hongjun, Y., Wenjun, X., Qing, L., Jingtao, L., Hongwen, Y., Zhaohua, L., 2013. Distribution of phthalate esters in topsoil: A case study in the Yellow River Delta, China. Environ. Monit. Assess. 185, 8489–8500. https://doi.org/10.1007/s10661-013-3190-7

Horton, A.A., Svendsen, C., Williams, R.J., Spurgeon, D.J., Lahive, E., 2017a. Large microplastic particles in sediments of tributaries of the River Thames, UK – Abundance, sources and methods for effective quantification. Mar. Pollut. Bull. 114, 218–226. https://doi.org/10.1016/j.marpolbul.2016.09.004

Horton, A.A., Walton, A., Spurgeon, D.J., Lahive, E., Svendsen, C., 2017b. Microplastics in freshwater and terrestrial environments: Evaluating the current understanding to identify the knowledge gaps and future research priorities. Sci. Total Environ. 586, 127–141. https://doi.org/10.1016/j.scitotenv.2017.01.190

Horton, A.A., Dixon, S.J., 2018. Microplastics: An introduction to environmental transport processes. Wiley Interdiscip. Rev. Water 5, e1268. https://doi.org/10.1002/wat2.1268

Horton, A.A., Cross, R.K., Read, D.S., Jürgens, M.D., Ball, H.L., Svendsen, C., Vollertsen, J., Johnson, A.C., 2021. Semi-automated analysis of microplastics in complex wastewater samples. Environ. Pollut. 268, 115841. https://doi.org/10.1016/j.envpol.2020.115841

Howell, E.A., Bograd, S.J., Morishige, C., Seki, M.P., Polovina, J.J., 2012. On North Pacific circulation and associated marine debris concentration. Mar. Pollut. Bull. 65, 16–22. https://doi.org/10.1016/j.marpolbul.2011.04.034

Hu, A., Qiu, M., Liu, H., Xu, Y., Tao, Y., Yang, G., He, Y., Xu, J., Lu, Z., 2020. Simultaneous determination of phthalate diesters and monoesters in soil using accelerated solvent extraction and ultra-performance liquid chromatography coupled with tandem mass spectrometry. J. Chromatogr. A 1626, 461347.

https://doi.org/10.1016/j.chroma.2020.461347

Hu, H., Mao, L., Fang, S., Xie, J., Zhao, M., Jin, H., 2020. Occurrence of phthalic acid esters in marine organisms from Hangzhou Bay, China: Implications for human exposure. Sci. Total Environ. 721, 137605. https://doi.org/10.1016/j.scitotenv.2020.137605

Hu, X., Gu, Y., Huang, W., Yin, D., 2016. Phthalate monoesters as markers of phthalate contamination in wild marine organisms. Environ. Pollut. 218, 410–418. https://doi.org/10.1016/j.envpol.2016.07.020

Hu, X.Y., Wen, B., Shan, X.Q., 2003. Survey of phthalate pollution in arable soils in China. J. Environ. Monit. 5, 649–653. https://doi.org/10.1039/b304669a

Hu, X.Y., Wen, B., Zhang, S., Shan, X.Q., 2005. Bioavailability of phthalate congeners to earthworms (Eisenia fetida) in artificially contaminated soils. Ecotoxicol. Environ. Saf. 62, 26–34. https://doi.org/10.1016/j.ecoenv.2005.02.012

Huang, B., Sun, L., Liu, M., Huang, H., He, H., Han, F., Wang, X., Xu, Z., Li, B., Pan, X., 2021. Abundance and distribution characteristics of microplastic in plateau cultivated land of Yunnan Province, China. Environ. Sci. Pollut. Res. 28, 1675–1688. https://doi.org/10.1007/s11356-020-10527-3

Huang, P.C., Tien, C.J., Sun, Y.M., Hsieh, C.Y., Lee, C.C., 2008. Occurrence of phthalates in sediment and biota: Relationship to aquatic factors and the biota-sediment accumulation factor. Chemosphere 73, 539–544. https://doi.org/10.1016/j.chemosphere.2008.06.019

Huang, Y., Liu, Q., Jia, W., Yan, C., Wang, J., 2020. Agricultural plastic mulching as a source of microplastics in the terrestrial environment. Environ. Pollut. 260, 114096. https://doi.org/10.1016/j.envpol.2020.114096

Huerta Lwanga, E., Gertsen, H., Gooren, H., Peters, P., Salánki, T., Van Der Ploeg, M., Besseling, E., Koelmans, A.A., Geissen, V., 2016. Microplastics in the Terrestrial Ecosystem: Implications for Lumbricus terrestris (Oligochaeta, Lumbricidae). Environ. Sci. Technol. 50, 2685–2691. https://doi.org/10.1021/acs.est.5b05478

Huerta Lwanga, E., Mendoza Vega, J., Ku Quej, V., Chi, J. de los A., Sanchez del Cid, L., Chi, C., Escalona Segura, G., Gertsen, H., Salánki, T., van der Ploeg, M., Koelmans, A.A., Geissen, V., 2017. Field evidence for transfer of plastic debris along a terrestrial food chain. Sci. Rep. 7, 14071. https://doi.org/10.1038/s41598-017-14588-2

Hurley, R.R., Lusher, A.L., Olsen, M., Nizzetto, L., 2018. Validation of a Method for Extracting Microplastics from Complex, Organic-Rich, Environmental Matrices. Environ. Sci. Technol. 52, 7409–7417. https://doi.org/10.1021/acs.est.8b01517

Hurtado, C., Montano-Chávez, Y.N., Domínguez, C., Bayona, J.M., 2017. Degradation of Emerging Organic Contaminants in an Agricultural Soil: Decoupling Biotic and Abiotic Processes. Water. Air. Soil Pollut. 228, 243. https://doi.org/10.1007/s11270-017-3402-9

Huysman, S., Van Meulebroek, L., Janssens, O., Vanryckeghem, F., Van Langenhove, H., Demeestere, K., Vanhaecke, L., 2019. Targeted quantification and untargeted screening of alkylphenols, bisphenol A and phthalates in aquatic matrices using ultra-high-performance liquid chromatography coupled to hybrid Q-Orbitrap mass spectrometry. Anal. Chim. Acta 1049, 141–151. https://doi.org/10.1016/j.aca.2018.10.045

Jaffé, R., Rushdi, A.I., Medeiros, P.M., Simoneit, B.R.T., 2006. Natural product biomarkers as indicators of sources and transport of sedimentary organic matter in a subtropical river. Chemosphere 64, 1870–1884. https://doi.org/10.1016/j.chemosphere.2006.01.048

Jebara, A., Albergamo, A., Rando, R., Potortì, A.G., Lo Turco, V., Mansour, H. Ben, Di Bella, G., 2021. Phthalates and non-phthalate plasticizers in Tunisian marine samples:

Occurrence, spatial distribution and seasonal variation. Mar. Pollut. Bull. 163, 111967. https://doi.org/10.1016/j.marpolbul.2021.111967

Jianlong, W., Xuan, Z., Weizhong, W., 2004. Biodegradation of phthalic acid esters (PAEs) in soil bioaugmented with acclimated activated sludge. Process Biochem. 39, 1837–1841. https://doi.org/10.1016/j.procbio.2003.08.005

Johnson, A.C., Ball, H., Cross, R., Horton, A.A., Jürgens, M.D., Read, D.S., Vollertsen, J., Svendsen, C., 2020. Identification and Quantification of Microplastics in Potable Water and Their Sources within Water Treatment Works in England and Wales. Environ. Sci. Technol. 54, 12326–12334. https://doi.org/10.1021/acs.est.0c03211

Jonsson, S., Ejlertsson, J., Ledin, A., Mersiowsky, I., Svensson, B.H., 2003. Mono- and diesters from o-phthalic acid in leachates from different European landfills. Water Res. 37, 609–617. https://doi.org/10.1016/S0043-1354(02)00304-4

Jung, M.R., Horgen, F.D., Orski, S. V., Rodriguez C., V., Beers, K.L., Balazs, G.H., Jones, T.T., Work, T.M., Brignac, K.C., Royer, S.J., Hyrenbach, K.D., Jensen, B.A., Lynch, J.M., 2018. Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms. Mar. Pollut. Bull. 127, 704–716. https://doi.org/10.1016/j.marpolbul.2017.12.061

Kaewlaoyoong, A., Vu, C.T., Lin, C., Liao, C. Sen, Chen, J.R., 2018. Occurrence of phthalate esters around the major plastic industrial area in southern Taiwan. Environ. Earth Sci. 77, 457. https://doi.org/10.1007/s12665-018-7655-4

Kanaly, R.A., Harayama, S., 2000. Biodegradation of High-Molecular-Weight Polycyclic Aromatic Hydrocarbons by Bacteria. J. Bacteriol. 182, 2059–2067. https://doi.org/10.1128/JB.182.8.2059-2067.2000

Kang, J., Jee, J., Koo, J., Keum, Y., Jo, S., Ha, K., 2010. Ecotoxicology and Environmental Safety Anti-oxidative status and hepatic enzymes following acute administration of diethyl phthalate in olive flounder Paralichthys olivaceus , a marine culture fish. Ecotoxicol. Environ. Saf. 73, 1449–1455. https://doi.org/10.1016/j.ecoenv.2010.07.025

Kao, P.H., Lee, F.Y., Hseu, Z.Y., 2005. Sorption and biodegradation of phthalic acid esters in freshwater sediments. J. Environ. Sci. Heal. - Part A Toxic/Hazardous Subst. Environ. Eng. 40, 103–115. https://doi.org/10.1081/ESE-200033605

Kastner, J., Cooper, D.G., Marić, M., Dodd, P., Yargeau, V., 2012. Aqueous leaching of di-2-ethylhexyl phthalate and “green” plasticizers from poly(vinyl chloride). Sci. Total Environ. 432, 357–364. https://doi.org/10.1016/j.scitotenv.2012.06.014

Katsumi, N., Kusube, T., Nagao, S., Okochi, H., 2021. Accumulation of microcapsules derived from coated fertilizer in paddy fields. Chemosphere 267, 129185. https://doi.org/10.1016/j.chemosphere.2020.129185

Kickham, P., Otton, S.V., Moore, M.M., Ikonomou, M.G., Gobas, F.A.P.C., 2012. Relationship between biodegradation and sorption of phthalate esters and their metabolites in natural sediments. Environ. Toxicol. Chem. 31, 1730–1737. https://doi.org/10.1002/etc.1903

Kim, D., Cui, R., Moon, J., Kwak, J. Il, An, Y.J., 2019. Soil ecotoxicity study of DEHP with respect to multiple soil species. Chemosphere 216, 387–395. https://doi.org/10.1016/j.chemosphere.2018.10.163

Kim, S., Lee, Y.S., Moon, H.B., 2020. Occurrence, distribution, and sources of phthalates and non-phthalate plasticizers in sediment from semi-enclosed bays of Korea. Mar. Pollut. Bull. 151, 110824. https://doi.org/10.1016/j.marpolbul.2019.110824

Kim, S., Kim, Y., Moon, H.B., 2021. Contamination and historical trends of legacy and emerging plasticizers in sediment from highly industrialized bays of Korea. Sci. Total Environ. 765, 142751. https://doi.org/10.1016/j.scitotenv.2020.142751

Kim, S.W., Waldman, W.R., Kim, T.Y., Rillig, M.C., 2020. Effects of Different Microplastics on Nematodes in the Soil Environment: Tracking the Extractable Additives Using an Ecotoxicological Approach. Environ. Sci. Technol. 54, 13868–13878. https://doi.org/10.1021/acs.est.0c04641

Kim, Y., Kim, S., Liao, C., Moon, H.B., 2021. Severe contamination and time trend of legacy and alternative plasticizers in a highly industrialized lake associated with regulations and coastal development. Mar. Pollut. Bull. 171, 112787. https://doi.org/10.1016/j.marpolbul.2021.112787

Knight, L.J., Parker-Jurd, F.N.F., Al-Sid-Cheikh, M., Thompson, R.C., 2020. Tyre wear particles: an abundant yet widely unreported microplastic? Environ. Sci. Pollut. Res. 27, 18345–18354. https://doi.org/10.1007/s11356-020-08187-4

Koelmans, A.A., Besseling, E., Shim, W.J., 2015. Nanoplastics in the Aquatic Environment. Critical Review, in: Bergmann, M., Gutow, L., Klages, M. (Eds.), Marine Anthropogenic Litter. Springer International Publishing, Cham, pp. 325–340. https://doi.org/10.1007/978-3-319-16510-3_12

Kong, S., Ji, Y., Liu, L., Chen, L., Zhao, X., Wang, J., Bai, Z., Sun, Z., 2012. Diversities of phthalate esters in suburban agricultural soils and wasteland soil appeared with urbanization in China. Environ. Pollut. 170, 161–168. https://doi.org/10.1016/j.envpol.2012.06.017

Kraaij, R., Ciarelli, S., Tolls, J., Kater, B.J., Belfroid, A., 2001. Bioavailability of lab-contaminated and native polycyclic aromatic hydrocarbons to the amphipod Corophium volutator relates to chemical desorption. Environ. Toxicol. Chem. 20, 1716–1724. https://doi.org/10.1002/etc.5620200814

Kumari, A., Kaur, R., 2020. A review on morpho-physiological traits of plants under phthalates stress and insights into their uptake and translocation. Plant Growth Regul.

91, 327–347. https://doi.org/10.1007/s10725-020-00625-0

Kundu, M.N., Komakech, H.C., Lugomela, G., 2022. Analysis of Macro- and Microplastics in Riverine, Riverbanks, and Irrigated Farms in Arusha, Tanzania. Arch. Environ. Contam. Toxicol. 82, 142–157. https://doi.org/10.1007/s00244-021-00897-1

Lahive, E., Walton, A., Horton, A.A., Spurgeon, D.J., Svendsen, C., 2019. Microplastic particles reduce reproduction in the terrestrial worm Enchytraeus crypticus in a soil exposure. Environ. Pollut. 255, 113174. https://doi.org/10.1016/j.envpol.2019.113174

Langová, R., Jarošová, A., Poláková, Š., Kos, I., 2020. Analysis of phthalic acid esters in agricultural soils. Environ. Monit. Assess. 192, 92. https://doi.org/10.1007/s10661-019-8052-5

Larsson, K., Lindh, C.H., Jönsson, B.A., Giovanoulis, G., Bibi, M., Bottai, M., Bergström, A., Berglund, M., 2017. Phthalates, non-phthalate plasticizers and bisphenols in Swedish preschool dust in relation to children’s exposure. Environ. Int. 102, 114–124. https://doi.org/10.1016/j.envint.2017.02.006

Law, R.J., Fileman, T.W., Matthiessen, P., 1991. Phthalate esters and other industrial organic chemicals in the North and Irish Seas. Water Sci. Technol. 24, 127–134. https://doi.org/10.2166/wst.1991.0283

Lee, Y.M., Lee, J.E., Choe, W., Kim, T., Lee, J.Y., Kho, Y., Choi, K., Zoh, K.D., 2019. Distribution of phthalate esters in air, water, sediments, and fish in the Asan Lake of Korea. Environ. Int. 126, 635–643. https://doi.org/10.1016/j.envint.2019.02.059

Lee, Y.S., Lee, S., Lim, J.E., Moon, H.B., 2019. Occurrence and emission of phthalates and non-phthalate plasticizers in sludge from wastewater treatment plants in Korea. Sci. Total Environ. 692, 354–360. https://doi.org/10.1016/j.scitotenv.2019.07.301

Lee, Y.S., Lim, J.E., Lee, S., Moon, H.B., 2020. Phthalates and non-phthalate plasticizers in sediment from Korean coastal waters: Occurrence, spatial distribution, and ecological risks. Mar. Pollut. Bull. 154, 111119. https://doi.org/10.1016/j.marpolbul.2020.111119

Li, C., Chen, J., Wang, J., Han, P., Luan, Y., Ma, X., Lu, A., 2016. Phthalate esters in soil, plastic film, and vegetable from greenhouse vegetable production bases in Beijing, China: Concentrations, sources, and risk assessment. Sci. Total Environ. 568, 1037–1043. https://doi.org/10.1016/j.scitotenv.2016.06.077

Li, K., Ma, D., Wu, J., Chai, C., Shi, Y., 2016. Distribution of phthalate esters in agricultural soil with plastic film mulching in Shandong Peninsula, East China. Chemosphere 164, 314–321. https://doi.org/10.1016/j.chemosphere.2016.08.068

Li, S, Ding, F., Flury, M., Wang, Z., Xu, L., Li, Shuangyi, Jones, D.L., Wang, J., 2022. Macro- and microplastic accumulation in soil after 32 years of plastic film mulching. Environ. Pollut. 300. https://doi.org/10.1016/j.envpol.2022.118945

Li, Q., Zeng, A., Jiang, X., Gu, X., 2021. Are microplastics correlated to phthalates in facility agriculture soil? J. Hazard. Mater. 412, 125164. https://doi.org/10.1016/j.jhazmat.2021.125164

Li, X., Liu, W., Zhang, C., Song, P., Wang, J., 2020. Fate of Phthalic Acid Esters (PAEs) in Typical Greenhouse Soils of Different Cultivation Ages. Bull. Environ. Contam. Toxicol. 104, 301–306. https://doi.org/10.1007/s00128-019-02756-1

Li, X.H., Ma, L.L., Liu, X.F., Fu, S., Cheng, H.X., Xu, X.B., 2006. Phthalate ester pollution in urban soil of Beijing, People’s Republic of China. Bull. Environ. Contam. Toxicol. 77, 252–259. https://doi.org/10.1007/s00128-006-1057-0

Liao, C. Sen, 2010. Biodegradation of di-n-butyl phthalate in a soil microcosm. J. Environ. Sci. Heal. - Part B Pestic. Food Contam. Agric. Wastes 45, 366–371. https://doi.org/10.1080/03601231003799838

Liechty, W.B., 2010. NIH Public Access Polymer for Drug Delivery. Annu. Rev. Chem. Biomol. Eng. 1, 149–173. https://doi.org/10.1146/annurev-chembioeng-073009-100847.Polymers

Lin, C., Lee, C.J., Mao, W.M., Nadim, F., 2009. Identifying the potential sources of di-(2-ethylhexyl) phthalate contamination in the sediment of the Houjing River in southern Taiwan. J. Hazard. Mater. 161, 270–275. https://doi.org/10.1016/j.jhazmat.2008.03.082

Liu, H., Liang, H., Liang, Y., Zhang, D., Wang, C., Cai, H., Shvartsev, S.L., 2010a. Distribution of phthalate esters in alluvial sediment: A case study at JiangHan Plain, Central China. Chemosphere 78, 382–388. https://doi.org/10.1016/j.chemosphere.2009.11.009

Liu, H., Liang, Y., Zhang, D., Wang, C., Liang, H., Cai, H., 2010b. Impact of MSW landfill on the environmental contamination of phthalate esters. Waste Manag. 30, 1569–1576. https://doi.org/10.1016/j.wasman.2010.01.040

Liu, M., Lu, S., Song, Y., Lei, L., Hu, J., Lv, W., Zhou, W., Cao, C., Shi, H., Yang, X., He, D., 2018. Microplastic and mesoplastic pollution in farmland soils in suburbs of Shanghai, China. Environ. Pollut. 242, 855–862. https://doi.org/10.1016/j.envpol.2018.07.051

Liu, W.L., Shen, C.F., Zhang, Z., Zhang, C.B., 2009. Distribution of phthalate esters in soil of E-waste recycling sites from taizhou city in China. Bull. Environ. Contam. Toxicol. 82, 665–667. https://doi.org/10.1007/s00128-009-9699-3

Liu, X., Yuan, W., Di, M., Li, Z., Wang, J., 2019. Transfer and fate of microplastics during the conventional activated sludge process in one wastewater treatment plant of China. Chem. Eng. J. 362, 176–182. https://doi.org/10.1016/j.cej.2019.01.033

Liu, Y., Li, Z., Jalón-Rojas, I., Wang, X.H., Fredj, E., Zhang, D., Feng, L., Li, X., 2020. Assessing the potential risk and relationship between microplastics and phthalates in surface seawater of a heavily human-impacted metropolitan bay in northern China.

Ecotoxicol. Environ. Saf. 204. https://doi.org/10.1016/j.ecoenv.2020.111067

Liu, Y.E., Luo, X.J., Huang, C.C., Zeng, Y.H., Lu, Q., Wang, S., Mai, B.X., 2021. Legacy and alternative plasticizers in surface sediment of black-odorous urban rivers across China: Occurrence, spatial distribution, and ecological risk assessment. Chemosphere 283, 131206. https://doi.org/10.1016/j.chemosphere.2021.131206

Ljung, E., Borg-Olesen, K., Andersson, P.-G., Fältström, E., Vollertsen, J., Wittgren, H.B., Hagman, M., 2018. Microplastics in the water and nutrient-cycle, Svenskt Vatten.

Lo Brutto, S., Iaciofano, D., Lo Turco, V., Potortì, A.G., Rando, R., Arizza, V., Di Stefano, V., 2021. First assessment of plasticizers in marine coastal litter-feeder fauna in the mediterranean sea. Toxics 9, 1–9. https://doi.org/10.3390/toxics9020031

Lohmann, R., Breivik, K., Dachs, J., Muir, D., 2007. Global fate of POPs: Current and future research directions. Environ. Pollut. 150, 150–165. https://doi.org/10.1016/j.envpol.2007.06.051

Long, J.L.A., House, W.A., Parker, A., Rae, J.E., 1998. Micro-organic compounds associated with sediments in the Humber rivers. Sci. Total Environ. 229–253.

Lv, Weiwei, Zhou, W., Lu, S., Huang, W., Yuan, Q., Tian, M., Lv, Weiguang, He, D., 2019. Microplastic pollution in rice-fish co-culture system: A report of three farmland stations in Shanghai, China. Sci. Total Environ. 652, 1209–1218. https://doi.org/10.1016/j.scitotenv.2018.10.321

Ma, T., Christie, P., Luo, Y.M., Teng, Y., 2013. Phthalate esters contamination in soil and plants on agricultural land near an electronic waste recycling site. Environ. Geochem. Health 35, 465–476. https://doi.org/10.1007/s10653-012-9508-5

Ma, T., Chen, L., Wu, L., Zhang, H., Luo, Y., 2016. Oxidative Stress, Cytotoxicity and Genotoxicity in Earthworm Eisenia fetida at Different Di-n-Butyl Phthalate Exposure

Levels. PLoS One 11, e0151128. https://doi.org/10.1371/journal.pone.0151128

Ma, T., Zhou, W., Chen, L., Wu, L., Christie, P., Zhang, H., Luo, Y., 2017. Toxicity effects of di-(2-ethylhexyl) phthalate to Eisenia fetida at enzyme, cellular and genetic levels. PLoS One 12, e0173957. https://doi.org/10.1371/journal.pone.0173957

Ma, T., Zhou, W., Chen, L., Christie, P., Luo, Y., Wu, P., 2019. Phthalate ester contamination in intensively managed greenhouse facilities and the assessment of carcinogenic and non-carcinogenic risk: A regional study. Int. J. Environ. Res. Public Health 16, 2818. https://doi.org/10.3390/ijerph16162818

Ma, T., Zhou, W., Chen, L., Li, Y., Luo, Y., Wu, P., 2020. Phthalate esters contamination in vegetable–soil system of facility greenhouses in Jingmen, central China and the assessment of health risk. Environ. Geochem. Health 42, 2703–2721. https://doi.org/10.1007/s10653-019-00504-2

Mackintosh, C.E., Maldonado, J., Hongwu, J., Hoover, N., Chong, A., Ikonomou, M.G., Gobas, F.A.P.C., 2004. Distribution of Phthalate Esters in a Marine Aquatic Food Web: Comparison to Polychlorinated Biphenyls. Environ. Sci. Technol. 38, 2011–2020. https://doi.org/10.1021/es034745r

Madsen, P.L., Thyme, J.B., Henriksen, K., MØldrup, P., Roslev, P., 1999. Kinetics of di-(2-ethylhexyl)phthalate mineralization in sludge-amended soil. Environ. Sci. Technol. 33, 2601–2606. https://doi.org/10.1021/es981015o

Malem, F., Soonthondecha, P., Khawmodjod, P., Chunhakorn, V., Whitlow, H.J., Chienthavorn, O., 2019. Occurrence of phthalate esters in the eastern coast of Thailand. Environ. Monit. Assess. 191, 4–6. https://doi.org/10.1007/s10661-019-7785-5

Marine Scotland, 2020a. Location and type of waste water treatment plants (2018) [WWW Document]. URL https://marine.gov.scot/maps/1880.

Marine Scotland, 2020b. Scottish Pollutant Release Inventory (SPRI) - Industrial marine discharges (2018) [WWW Document]. URL https://marine.gov.scot/maps/1879.

Martins, K., Applegate, B., Hagedorn, B., Kennish, J., Zwollo, P., 2015. Di (2-ethylhexyl) phthalate inhibits B cell proliferation and reduces the abundance of IgM-secreting cells in cultured immune tissues of the rainbow trout. Fish Shellfish Immunol. 44, 332–341. https://doi.org/10.1016/j.fsi.2015.02.037

Meng, X.Z., Wang, Y., Xiang, N., Chen, L., Liu, Z., Wu, B., Dai, X., Zhang, Y.H., Xie, Z., Ebinghaus, R., 2014. Flow of sewage sludge-borne phthalate esters (PAEs) from human release to human intake: Implication for risk assessment of sludge applied to soil. Sci. Total Environ. 476–477, 242–249. https://doi.org/10.1016/j.scitotenv.2014.01.007

Mitchell, P., Newton, S., Norman, R., Dunn, T., 2004. Seabird Populations of Britain and Ireland. T. & A.D. Poyser Publishers, London.

Mo, C.H., Cai, Q.Y., Li, Y.H., Zeng, Q.Y., 2008. Occurrence of priority organic pollutants in the fertilizers, China. J. Hazard. Mater. 152, 1208–1213. https://doi.org/10.1016/j.jhazmat.2007.07.105

Mohammadian, S., Ghanemi, K., Nikpour, Y., 2016. Competitive adsorption of phthalate esters on marine surface sediments: kinetic, thermodynamic, and environmental considerations. Environ. Sci. Pollut. Res. 23, 24991–25002. https://doi.org/10.1007/s11356-016-7723-9

Mohammadi, A., Malakootian, M., Dobaradaran, S., Hashemi, M., Jaafarzadeh, N., 2022. Occurrence, seasonal distribution, and ecological risk assessment of microplastics and phthalate esters in leachates of a landfill site located near the marine environment: Bushehr port, Iran as a case. Sci. Total Environ. 842, 156838. https://doi.org/10.1016/j.scitotenv.2022.156838

Molino, C., Filippi, S., Antonio, G., Meschini, R., Angeletti, D., 2019. Toxicology in Vitro In vitro evaluation of cytotoxic and genotoxic e ff ects of Di (2-ethylhexyl) - phthalate (DEHP) on European sea bass (Dicentrarchus labrax) embryonic cell line. Toxicol. Vitr. 56, 118–125. https://doi.org/10.1016/j.tiv.2019.01.017

Möller, J.N., Löder, M.G.J., Laforsch, C., 2020. Finding Microplastics in Soils: A Review of Analytical Methods. Environ. Sci. Technol. 54, 2078–2090. https://doi.org/10.1021/acs.est.9b04618

Mukhopadhyay, M., Chakraborty, P., 2021. Plasticizers and bisphenol A: Emerging organic pollutants along the lower stretch of River Ganga, north-east coast of the Bay of Bengal. Environ. Pollut. 276, 116697. https://doi.org/10.1016/j.envpol.2021.116697

Murillo-Torres, R., Durán-Alvarez, J.C., Prado-Pano, B., Jiménez-Cisneros, B., 2012. Mobility of 4-nonylphenol and di(2-ethylhexyl) phthalate in three agricultural soils irrigated with untreated wastewater. Water Sci. Technol. 66, 292–298. https://doi.org/10.2166/wst.2012.174

Nara, K., Nishiyama, K., Natsugari, H., Takeshita, A., Takahashi, H., 2009. Leaching of the Plasticizer, Acetyl Tributyl Citrate: (ATBC) from Plastic Kitchen Wrap. J. Heal. Sci. 55, 281–284. https://doi.org/10.1248/jhs.55.281

National Records of Scotland, 2022. Population Estimates for Settlements and Localities in Scotland, Mid-2020. Natl. Stat. [WWW Document]. URL https://www.nrscotland.gov.uk/files/statistics/settlements-localities/set-loc-20/set-loc-2020-report.pdf

Natural England, 2021. Ancient Woodland (England) [WWW Document]. URL https://data.gov.uk/dataset/9461f463-c363-4309-ae77-fdcd7e9df7d3/ancient-woodland-england

Neina, D., 2019. The Role of Soil pH in Plant Nutrition and Soil Remediation. Appl. Environ.

Soil Sci. 2019. https://doi.org/10.1155/2019/5794869

Net, S., Sempéré, R., Delmont, A., Paluselli, A., Ouddane, B., 2015. Occurrence, fate, behavior and ecotoxicological state of phthalates in different environmental matrices. Environ. Sci. Technol. 49, 4019–4035. https://doi.org/10.1021/es505233b

Neuhold, C., Nachtnebel, H.P., 2011. Assessing flood risk associated with waste disposals: Methodology, application and uncertainties. Nat. Hazards 56, 359–370. https://doi.org/10.1007/s11069-010-9575-9

Nicholls, R.J., Beaven, R.P., Stringfellow, A., Monfort, D., Le Cozannet, G., Wahl, T., Gebert, J., Wadey, M., Arns, A., Spencer, K.L., Reinhart, D., Heimovaara, T., Santos, V.M., Enríquez, A.R., Cope, S., 2021. Coastal Landfills and Rising Sea Levels: A Challenge for the 21st Century. Front. Mar. Sci. 8. https://doi.org/10.3389/fmars.2021.710342

Norman, A., Bçrjeson, H., David, F., Tienpont, B., Norrgren, L., 2007. Studies of Uptake , Elimination , and Late Effects in Atlantic Salmon (Salmo salar) Dietary Exposed to Di-2-Ethylhexyl Phthalate (DEHP) During Early Life. Arch. Environ. Contam. Toxicol. 242, 235–242. https://doi.org/10.1007/s00244-005-5089-y

Oakdene Hollins, 2010. A Study to Facilitate the Implementation of the Waste Related Provisions of Regulation (EC) No 850/2004 on Persistent Organic Pollutants.

OECD, 2009. OECD guidelines for the testing of chemicals - bioaccumulation in terrestrial oligochaetes. https://doi.org/10.1787/9789264090934-en

Paluselli, A., Aminot, Y., Galgani, F., Net, S., Sempéré, R., 2018a. Occurrence of phthalate acid esters (PAEs) in the northwestern Mediterranean Sea and the Rhone River. Prog. Oceanogr. 163, 221–231. https://doi.org/10.1016/j.pocean.2017.06.002

Paluselli, A., Fauvelle, V., Schmidt, N., Galgani, F., Net, S., Sempéré, R., 2018b. Distribution of phthalates in Marseille Bay (NW Mediterranean Sea). Sci. Total Environ. 621, 578–

587. https://doi.org/10.1016/j.scitotenv.2017.11.306

Paluselli, A., Fauvelle, V., Galgani, F., Sempéré, R., 2019. Phthalate Release from Plastic Fragments and Degradation in Seawater. Environ. Sci. Technol. 53, 166–175. https://doi.org/10.1021/acs.est.8b05083

Paluselli, A., Kim, S.K., 2020. Horizontal and vertical distribution of phthalates acid ester (PAEs) in seawater and sediment of East China Sea and Korean South Sea: Traces of plastic debris? Mar. Pollut. Bull. 151, 110831. https://doi.org/10.1016/j.marpolbul.2019.110831

Patureau, D., Laforie, M., Lichtfouse, E., Caria, G., Denaix, L., Schmidt, J.E., 2007. Fate of organic pollutants after sewage sludge spreading on agricultural soils: a 30-years field-scale recording. Water Pract. Technol. 2. https://doi.org/10.2166/wpt.2007.008

Pedersen, G.A., Jensen, L.K., Fankhauser, A., Biedermann, S., Petersen, J.H., Fabech, B., 2008. Migration of epoxidized soybean oil (ESBO) and phthalates from twist closures into food and enforcement of the overall migration limit. Food Addit. Contam. - Part A Chem. Anal. Control. Expo. Risk Assess. 25, 503–510. https://doi.org/10.1080/02652030701519088

Peijnenburg, W.J.G.M., Struijs, J., 2006. Occurrence of phthalate esters in the environment of the Netherlands. Ecotoxicol. Environ. Saf. 63, 204–215. https://doi.org/10.1016/j.ecoenv.2005.07.023

Peñalver, R., Ortiz, A., Arroyo-Manzanares, N., Campillo, N., López-García, I., Viñas, P., 2022. Non-targeted analysis by DLLME-GC-MS for the monitoring of pollutants in the Mar Menor lagoon. Chemosphere 286. https://doi.org/10.1016/j.chemosphere.2021.131588

Pereira, M.G., Lacorte, S., Walker, L.A., Shore, R.F., 2021. Contrasting long term temporal trends in perfluoroalkyl substances (PFAS) in eggs of the northern gannet (Morus bassanus) from two UK colonies. Sci. Total Environ. 754, 141900. https://doi.org/10.1016/j.scitotenv.2020.141900

Piehl, S., Leibner, A., Löder, M.G.J., Dris, R., Bogner, C., Laforsch, C., 2018. Identification and quantification of macro- and microplastics on an agricultural farmland. Sci. Rep. 8, 1–9. https://doi.org/10.1038/s41598-018-36172-y

Plastics Europe, 2021. Plastics - the Facts 2021 [WWW Document]. URL https://plasticseurope.org/knowledge-hub/plastics-the-facts-2021/

Potočnik, J., 2011. Commission recommendation of 18 October 2011 on the definition of nanomaterial (2011/696/EU). Off. J. Eur. Union L275, 38–40. https://doi.org/10.2777/13162

Prendergast-Miller, M.T., Katsiamides, A., Abbass, M., Sturzenbaum, S.R., Thorpe, K.L., Hodson, M.E., 2019. Polyester-derived microfibre impacts on the soil-dwelling earthworm Lumbricus terrestris. Environ. Pollut. 251, 453–459. https://doi.org/10.1016/j.envpol.2019.05.037

Preston, M.R., Al-Omran, L.A., 1989. Phthalate ester speciation in estuarine water, suspended particulates and sediments. Environ. Pollut. 62, 183–193. https://doi.org/10.1016/0269-7491(89)90186-3

Previšić, A., Vilenica, M., Vučković, N., Petrović, M., Rožman, M., 2021. Aquatic Insects Transfer Pharmaceuticals and Endocrine Disruptors from Aquatic to Terrestrial Ecosystems. Environ. Sci. Technol. 55, 3736–3746. https://doi.org/10.1021/acs.est.0c07609

Primpke, S., Wirth, M., Lorenz, C., Gerdts, G., 2018. Reference database design for the automated analysis of microplastic samples based on Fourier transform infrared (FTIR) spectroscopy. Anal. Bioanal. Chem. 410, 5131–5141. https://doi.org/10.1007/s00216-018-1156-x

Primpke, S., Christiansen, S.H., Cowger, W., De Frond, H., Deshpande, A., Fischer, M., Holland, E.B., Meyns, M., O'Donnell, B.A., Ossmann, B.E., Pittroff, M., Sarau, G., Scholz-Böttcher, B.M., Wiggin, K.J., 2020a. Critical Assessment of Analytical Methods for the Harmonized and Cost-Efficient Analysis of Microplastics, Applied Spectroscopy. https://doi.org/10.1177/0003702820921465

Primpke, S., Cross, R.K., Mintenig, S.M., Simon, M., Vianello, A., Gerdts, G., Vollertsen, J., 2020b. Toward the Systematic Identification of Microplastics in the Environment: Evaluation of a New Independent Software Tool (siMPle) for Spectroscopic Analysis. Appl. Spectrosc. 74, 1127–1138. https://doi.org/10.1177/0003702820917760

Rhind, S.M., Smith, A., Kyle, C.E., Telfer, G., Martin, G., Duff, E., Mayes, R.W., 2002. Phthalate and alkyl phenol concentrations in soil following applications of inorganic fertiliser or sewage sludge to pasture and potential rates of ingestion by grazing ruminants. J. Environ. Monit. 4, 142–148. https://doi.org/10.1039/b107539j

Rhind, S.M., Kyle, C.E., Kerr, C., Osprey, M., Zhang, Z.L., Duff, E.I., Lilly, A., Nolan, A., Hudson, G., Towers, W., Bell, J., Coull, M., McKenzie, C., 2013a. Concentrations and geographic distribution of selected organic pollutants in Scottish surface soils. Environ. Pollut. 182, 15–27. https://doi.org/10.1016/j.envpol.2013.06.041

Rhind, S.M., Kyle, C.E., Ruffie, H., Calmettes, E., Osprey, M., Zhang, Z.L., Hamilton, D., McKenzie, C., 2013b. Short- and long-term temporal changes in soil concentrations of selected endocrine disrupting compounds (EDCs) following single or multiple applications of sewage sludge to pastures. Environ. Pollut. 181, 262–270. https://doi.org/10.1016/j.envpol.2013.06.011

Rochman, C.M., Brookson, C., Bikker, J., Djuric, N., Earn, A., Bucci, K., Athey, S., Huntington, A., McIlwraith, H., Munno, K., Frond, H. De, Kolomijeca, A., Erdle, L., Grbic, J., Bayoumi, M., Borrelle, S.B., Wu, T., Santoro, S., Werbowski, L.M., Zhu, X., Giles, R.K., Hamilton, B.M., Thaysen, C., Kaura, A., Klasios, N., Ead, L., Kim, J., Sherlock, C., Ho, A., Hung, C., 2019. Rethinking microplastics as a diverse contaminant suite. Environ. Toxicol. Chem. 38, 703–711. https://doi.org/10.1002/etc.4371

Roscher, L., Halbach, M., Nguyen, M.T., Hebeler, M., Luschtinetz, F., Scholz-Böttcher, B.M., Primpke, S., Gerdts, G., 2022. Microplastics in two German wastewater treatment plants: Year-long effluent analysis with FTIR and Py-GC/MS. Sci. Total Environ. 817. https://doi.org/10.1016/j.scitotenv.2021.152619

Routti, H., Harju, M., Lühmann, K., Aars, J., Ask, A., Goksøyr, A., Kovacs, K.M., Lydersen, C., 2021. Concentrations and endocrine disruptive potential of phthalates in marine mammals from the Norwegian Arctic. Environ. Int. 152. https://doi.org/10.1016/j.envint.2021.106458

Rüdel, H., Schmidt, S., Kördel, W., Klein, W., 1993. Degradation of pesticides in soil: comparison of laboratory experiments in a biometer system and outdoor lysimeter experiments. Sci. Total Environ. 132, 181–200. https://doi.org/10.1016/0048-9697(93)90131-O

Saliu, F., Montano, S., Lasagni, M., Galli, P., 2020. Biocompatible solid-phase microextraction coupled to liquid chromatography triple quadrupole mass spectrometry analysis for the determination of phthalates in marine invertebrate. J. Chromatogr. A 1618. https://doi.org/10.1016/j.chroma.2020.460852

Sánchez-Avila, J., Vicente, J., Echavarri-Erasun, B., Porte, C., Tauler, R., Lacorte, S., 2013. Sources, fluxes and risk of organic micropollutants to the Cantabrian Sea (Spain). Mar. Pollut. Bull. 72, 119–132. https://doi.org/10.1016/j.marpolbul.2013.04.010

Savoca, D., Arculeo, M., Barreca, S., Buscemi, S., Caracappa, S., Gentile, A., Persichetti, M.F., Pace, A., 2018. Chasing phthalates in tissues of marine turtles from the Mediterranean sea. Mar. Pollut. Bull. 127, 165–169. https://doi.org/10.1016/j.marpolbul.2017.11.069

Savoca, D., Arculeo, M., Vecchioni, L., Cambera, I., Visconti, G., Melfi, R., Arizza, V., Palumbo Piccionello, A., Buscemi, S., Pace, A., 2021. Can phthalates move into the eggs of the loggerhead sea turtle Caretta caretta? The case of the nests on the Linosa Island in the Mediterranean Sea. Mar. Pollut. Bull. 168, 112395. https://doi.org/10.1016/j.marpolbul.2021.112395

Scheurer, M., Bigalke, M., 2018. Microplastics in Swiss Floodplain Soils. Environ. Sci. Technol. 52, 3591–3598. https://doi.org/10.1021/acs.est.7b06003

Shanker, R., Ramakrishma, C., Seth, P.K., 1985. Degradation of some phthalic acid esters in soil. Environ. Pollution. Ser. A, Ecol. Biol. 39, 1–7. https://doi.org/10.1016/0143-1471(85)90057-1

Sijm, D., Kraaij, R., Belfroid, A., 2000. Bioavailability in soil or sediment: Exposure of different organisms and approaches to study it. Environ. Pollut. 108, 113–119. https://doi.org/10.1016/S0269-7491(99)00207-9

Simon, M., van Alst, N., Vollertsen, J., 2018. Quantification of microplastic mass and removal rates at wastewater treatment plants applying Focal Plane Array (FPA)-based Fourier Transform Infrared (FT-IR) imaging. Water Res. 142, 1–9. https://doi.org/10.1016/j.watres.2018.05.019

Škrbić, B.D., Ji, Y., Đurišić-Mladenović, N., Zhao, J., 2016. Occurence of the phthalate esters in soil and street dust samples from the Novi Sad city area, Serbia, and the influence on the children’s and adults’ exposure. J. Hazard. Mater. 312, 272–279. https://doi.org/10.1016/j.jhazmat.2016.03.045

Smith, A.J., McGowan, T., Devlin, M.J., Massoud, M.S., Al-Enezi, M., Al-Zaidan, A.S., Al-Sarawi, H.A., Lyons, B.P., 2015. Screening for contaminant hotspots in the marine environment of Kuwait using ecotoxicological and chemical screening techniques. Mar. Pollut. Bull. 100, 681–688. https://doi.org/10.1016/j.marpolbul.2015.08.043

Song, D., Sun, H., Yang, Y., Wang, X., Sun, Y., Liu, X., Huang, M., Feng, C., Zhuang, Y., Zhang, J., Kong, F., 2021. Status of phthalate esters in tobacco cultivation soils and its health risk to Chinese people. J. Soils Sediments 21, 307–318. https://doi.org/10.1007/s11368-020-02773-2

Song, P., Gao, J., Li, X., Zhang, C., Zhu, L., Wang, Jinhua, Wang, Jun, 2019. Phthalate induced oxidative stress and DNA damage in earthworms (Eisenia fetida). Environ. Int. 129, 10–17. https://doi.org/10.1016/j.envint.2019.04.074

Spurgeon, D.J., Hopkin, S.P., 1995. Extrapolation of the laboratory-based OECD earthworm toxicity test to metal-contaminated field sites. Ecotoxicology 4, 190–205. https://doi.org/10.1007/BF00116481

Stalling, D.L., Hogan, J.W., Johnson, J.L., 1973. Phthalate ester residues--their metabolism and analysis in fish. Environ. Health Perspect. 3, 159–173. https://doi.org/10.1289/ehp.7303159

Steinmetz, Z., Wollmann, C., Schaefer, M., Buchmann, C., David, J., Tröger, J., Muñoz, K., Frör, O., Schaumann, G.E., 2016. Plastic mulching in agriculture. Trading short-term agronomic benefits for long-term soil degradation? Sci. Total Environ. 550, 690–705. https://doi.org/10.1016/j.scitotenv.2016.01.153

Stewart, M., Olsen, G., Hickey, C.W., Ferreira, B., Jelić, A., Petrović, M., Barcelo, D., 2014. A survey of emerging contaminants in the estuarine receiving environment around Auckland, New Zealand. Sci. Total Environ. 468–469, 202–210. https://doi.org/10.1016/j.scitotenv.2013.08.039

Stumm, W., Morgan, J., 1996. Aquatic chemistry: chemical equilibria and rates in natural waters, 3rd ed, Choice Reviews Online. Wiley. https://doi.org/10.5860/choice.33-6312

Subedi, B., Sullivan, K.D., Dhungana, B., 2017. Phthalate and non-phthalate plasticizers in indoor dust from childcare facilities, salons, and homes across the USA. Environ. Pollut.

230, 701–708. https://doi.org/10.1016/j.envpol.2017.07.028

Suhrhoff, T.J., Scholz-Böttcher, B.M., 2016. Qualitative impact of salinity, UV radiation and turbulence on leaching of organic plastic additives from four common plastics - A lab experiment. Mar. Pollut. Bull. 102, 84–94. https://doi.org/10.1016/j.marpolbul.2015.11.054

Sun, C., Chen, L., Zhao, S., Guo, W., Luo, Y., Wang, L., Tang, L., Li, F., Zhang, J., 2021. Seasonal distribution and ecological risk of phthalate esters in surface water and marine organisms of the Bohai Sea. Mar. Pollut. Bull. 169, 112449. https://doi.org/10.1016/j.marpolbul.2021.112449

Sun, J., Huang, J., Zhang, A., Liu, W., Cheng, W., 2013. Occurrence of phthalate esters in sediments in Qiantang River, China and inference with urbanization and river flow regime. J. Hazard. Mater. 248–249, 142–149. https://doi.org/10.1016/j.jhazmat.2012.12.057

Sun, J., Pan, L., Zhan, Y., Lu, H., Tsang, D.C.W., Liu, W., Wang, X., Li, X., Zhu, L., 2016. Contamination of phthalate esters , organochlorine pesticides and polybrominated diphenyl ethers in agricultural soils from the Yangtze River Delta of China. Sci. Total Environ. 544, 670–676. https://doi.org/10.1016/j.scitotenv.2015.12.012

Svendsen, C., Walker, L.A., Matzke, M., Lahive, E., Harrison, S., Crossley, A., Park, B., Lofts, S., Lynch, I., Vázquez-Campos, S., Kaegi, R., Gogos, A., Asbach, C., Cornelis, G., von der Kammer, F., van den Brink, N.W., Mays, C., Spurgeon, D.J., 2020. Key principles and operational practices for improved nanotechnology environmental exposure assessment. Nat. Nanotechnol. 15, 731–742. https://doi.org/10.1038/s41565-020-0742-1

Takeuchi, S., Kojima, H., Saito, I., Jin, K., Kobayashi, S., Tanaka-Kagawa, T., Jinno, H., 2014. Detection of 34 plasticizers and 25 flame retardants in indoor air from houses in

Sapporo, Japan. Sci. Total Environ. 491–492, 28–33. https://doi.org/10.1016/j.scitotenv.2014.04.011

Talvitie, J., Mikola, A., Setälä, O., Heinonen, M., Koistinen, A., 2017. How well is microlitter purified from wastewater? – A detailed study on the stepwise removal of microlitter in a tertiary level wastewater treatment plant. Water Res. 109, 164–172. https://doi.org/10.1016/j.watres.2016.11.046

Tang, J., Rong, X., Jin, D., Gu, C., Chen, A., Luo, S., 2020. Biodegradation of phthalate esters in four agricultural soils: Main influencing factors and mechanisms. Int. Biodeterior. Biodegrad. 147, 104867. https://doi.org/10.1016/j.ibiod.2019.104867

Tao, H., Wang, Y., Liang, H., Zhang, X., Liu, X., Li, J., 2020. Pollution characteristics of phthalate acid esters in agricultural soil of Yinchuan, northwest China, and health risk assessment. Environ. Geochem. Health 42, 4313–4326. https://doi.org/10.1007/s10653-019-00502-4

Tao, Y., Shi, H., Jiao, Y., Han, S., Akindolie, M.S., Yang, Y., Chen, Z., Zhang, Y., 2020. Effects of humic acid on the biodegradation of di-n-butyl phthalate in mollisol. J. Clean. Prod. 249, 119404. https://doi.org/10.1016/j.jclepro.2019.119404

Teng, Y., Li, J., Wu, J., Lu, S., Wang, Y., Chen, H., 2015. Environmental distribution and associated human health risk due to trace elements and organic compounds in soil in Jiangxi province, China. Ecotoxicol. Environ. Saf. 122, 406–416. https://doi.org/10.1016/j.ecoenv.2015.09.005

Thompson, R.C., Olson, Y., Mitchell, R.P., Davis, A., Rowland, S.J., John, A.W.G., McGonigle, D., Russell, A.E., 2004. Lost at Sea: Where Is All the Plastic? Science (80-.). 304, 838. https://doi.org/10.1126/science.1094559

Tran, B.C., Teil, M.J., Blanchard, M., Alliot, F., Chevreuil, M., 2015. Fate of phthalates and BPA in agricultural and non-agricultural soils of the Paris area (France). Environ. Sci.

Pollut. Res. 22, 11118–11126. https://doi.org/10.1007/s11356-015-4178-3

Tsochatzis, E., Karayannakidis, P., Kalogiannis, S., 2019. Determination of selected dichloroanilines and phthalates in lyophilised mussels samples with ultra-high performance liquid chromatography-tandem mass spectrometry after QuEChERS clean-up. Food Addit. Contam. - Part A Chem. Anal. Control. Expo. Risk Assess. 36, 1253–1260. https://doi.org/10.1080/19440049.2019.1615642

Turner, A., Rawling, M.C., 2000. The behaviour of di-(2-ethylhexyl) phthalate in estuaries. Mar. Chem. 68, 203–217. https://doi.org/10.1016/S0304-4203(99)00078-X

Tüzüm Demir, A.P., Ulutan, S., 2013. Migration of phthalate and non-phthalate plasticizers out of plasticized PVC films into air. J. Appl. Polym. Sci. 128, 1948–1961. https://doi.org/10.1002/app.38291

US EPA, 2006. Voluntary Estuary Monitoring Manual. Volunt. Estuary Monit. Manual, A Methods Man. 1–13 [WWW Document]. URL https://www.epa.gov/sites/default/files/2015-09/documents/2007_04_09_estuaries_monitoruments_manual.pdf

Vikelsoe, J., Thomsen, M., Carlsen, L., 2002. Phthalates and nonylphenols in profiles of differently dressed soils. Sci. Total Environ. 296, 105–116. https://doi.org/10.1016/S0048-9697(02)00063-3

Viljoen, S.J., Brailsford, F.L., Murphy, D. V., Hoyle, F.C., Chadwick, D.R., Jones, D.L., 2023. Leaching of phthalate acid esters from plastic mulch films and their degradation in response to UV irradiation and contrasting soil conditions. J. Hazard. Mater. 443, 130256. https://doi.org/10.1016/j.jhazmat.2022.130256

Vollertsen, J., Hansen, A.A., 2017. Microplastic in Danish wastewater: Sources, occurrences and fate.

Wagner, S., Hüffer, T., Klöckner, P., Wehrhahn, M., Hofmann, T., Reemtsma, T., 2018. Tire wear particles in the aquatic environment - A review on generation, analysis, occurrence, fate and effects. Water Res. 139, 83–100. https://doi.org/10.1016/j.watres.2018.03.051

Wang, C., Zhao, J., Xing, B., 2021. Environmental source, fate, and toxicity of microplastics. J. Hazard. Mater. 407, 124357. https://doi.org/10.1016/j.jhazmat.2020.124357

Wang, D., Xi, Y., Shi, X.Y., Zhong, Y.J., Guo, C.L., Han, Y.N., Li, F.M., 2021. Effect of plastic film mulching and film residues on phthalate esters concentrations in soil and plants, and its risk assessment. Environ. Pollut. 286, 117546. https://doi.org/10.1016/j.envpol.2021.117546

Wang, F., Xia, X., Sha, Y., 2008. Distribution of Phthalic Acid Esters in Wuhan section of the Yangtze River, China. J. Hazard. Mater. 154, 317–324. https://doi.org/10.1016/j.jhazmat.2007.10.028

Wang, G., Wang, Jun, Zhu, L., Wang, Jinhua, Li, H., Zhang, Y., Liu, W., Gao, J., 2018. Oxidative Damage and Genetic Toxicity Induced by DBP in Earthworms (Eisenia fetida). Arch. Environ. Contam. Toxicol. 74, 527–538. https://doi.org/10.1007/s00244-017-0451-4

Wang, H., Liang, H., Gao, D.W., 2017. Occurrence and risk assessment of phthalate esters (PAEs) in agricultural soils of the Sanjiang Plain, northeast China. Environ. Sci. Pollut. Res. 24, 19723–19732. https://doi.org/10.1007/s11356-017-9646-5

Wang, J., Liu, P., Shi, H., Qian, Y., 1997. Kinetics of phthalic acid ester degradation by acclimated activated sludge. Process Biochem. 32, 567–571. https://doi.org/10.1016/S0032-9592(97)00015-0

Wang, J., Luo, Y., Teng, Y., Ma, W., Christie, P., Li, Z., 2013. Soil contamination by phthalate esters in Chinese intensive vegetable production systems with different modes of use of plastic film. Environ. Pollut. 180, 265–273. https://doi.org/10.1016/j.envpol.2013.05.036

Wang, J., Bo, L., Li, L., Wang, D., Chen, G., Christie, P., Teng, Y., 2014. Occurrence of phthalate esters in river sediments in areas with different land use patterns. Sci. Total Environ. 500–501, 113–119. https://doi.org/10.1016/j.scitotenv.2014.08.092

Wang, J., Chen, G., Christie, P., Zhang, M., Luo, Y., Teng, Y., 2015. Occurrence and risk assessment of phthalate esters (PAEs) in vegetables and soils of suburban plastic film greenhouses. Sci. Total Environ. 523, 129–137. https://doi.org/10.1016/j.scitotenv.2015.02.101

Wang, L., Xu, X., Lu, X., 2015. Phthalic acid esters (PAEs) in vegetable soil from the suburbs of Xianyang city, Northwest China. Environ. Earth Sci. 74, 1487–1496. https://doi.org/10.1007/s12665-015-4141-0

Wang, L., Liu, M., Tao, W., Zhang, W., Wang, Li, Shi, X., Lu, X., Li, X., 2018. Pollution characteristics and health risk assessment of phthalate esters in urban soil in the typical semi-arid city of Xi’an, Northwest China. Chemosphere 191, 467–476. https://doi.org/10.1016/j.chemosphere.2017.10.066

Wang, L.Y., Gu, Y.Y., Zhang, Z.M., Sun, A.L., Shi, X.Z., Chen, J., Lu, Y., 2021. Contaminant occurrence, mobility and ecological risk assessment of phthalate esters in the sediment-water system of the Hangzhou Bay. Sci. Total Environ. 770, 144705. https://doi.org/10.1016/j.scitotenv.2020.144705

Wang, X., Lin, Q., Wang, J., Lu, X., Wang, G., 2013. Effect of wetland reclamation and tillage conversion on accumulation and distribution of phthalate esters residues in soils. Ecol. Eng. 51, 10–15. https://doi.org/10.1016/j.ecoleng.2012.12.079

Wania, F., 2003. Assessing the potential of persistent organic chemicals for long-range transport and accumulation in polar regions. Environ. Sci. Technol. 37, 1344–1351.

https://doi.org/10.1021/es026019e

Wanless, S., Harris, M.P., Newell, M.A., Speakman, J.R., Daunt, F., 2018. Community-wide decline in the occurrence of lesser sandeels Ammodytes marinus in seabird chick diets at a North Sea colony. Mar. Ecol. Prog. Ser. 600, 193–206. https://doi.org/10.3354/meps12679

Wei, L., Li, Z., Sun, J., Zhu, L., 2020. Pollution characteristics and health risk assessment of phthalate esters in agricultural soil and vegetables in the Yangtze River Delta of China. Sci. Total Environ. 726, 137978. https://doi.org/10.1016/j.scitotenv.2020.137978

Weizhen, Z., Xiaowei, Z., Peng, G., Ning, W., Zini, L., Jian, H., Zheng, Z., 2020. Distribution and risk assessment of phthalates in water and sediment of the Pearl River Delta. Environ. Sci. Pollut. Res. 27, 12550–12565. https://doi.org/10.1007/s11356-019-06819-y

Welle, F., Wolz, G., Franz, R., 2005. Migration of plasticizers from PVC tubes into enteral feeding solutions. Pharma Int. 3, 17–21.

Wen, Z., Huang, X., Gao, D., Liu, G., Fang, C., Shang, Y., Du, J., Zhao, Y., Lv, L., Song, K., 2018. Phthalate esters in surface water of Songhua River watershed associated with land use types, Northeast China. Environ. Sci. Pollut. Res. 25, 7688–7698. https://doi.org/10.1007/s11356-017-1119-3

World Bank, 2017. No Title [WWW Document]. URL https://data.worldbank.org/indicator/AG.LND.TOTL.K2?locations=EU.

Wu, R.T., Cai, Y.F., Chen, Y.X., Yang, Y.W., Xing, S.C., Liao, X. Di, 2021. Occurrence of microplastic in livestock and poultry manure in South China. Environ. Pollut. 277, 116790. https://doi.org/10.1016/j.envpol.2021.116790

Wu, W., Hu, J., Wang, J., Chen, X., Yao, N., Tao, J., Zhou, Y.K., 2015. Analysis of phthalate esters in soils near an electronics manufacturing facility and from a non-industrialized area by gas purge microsyringe extraction and gas chromatography. Sci. Total Environ. 508, 445–451. https://doi.org/10.1016/j.scitotenv.2014.11.081

Xia, X., Yang, L., Bu, Q., Liu, R., 2011. Levels, Distribution, and Health Risk of Phthalate Esters in Urban Soils of Beijing, China. J. Environ. Qual. 40, 1643–1651. https://doi.org/10.2134/jeq2011.0032

Xie, H.J., Shi, Y.J., Zhang, J., Cui, Y., Teng, S.X., Wang, S.G., Zhao, R., 2010. Degradation of phthalate esters (PAEs) in soil and the effects of PAEs on soilmicrocosm activity. J. Chem. Technol. Biotechnol. 85, 1108–1116. https://doi.org/10.1002/jctb.2406

Xu, G., Li, F., Wang, Q., 2008. Occurrence and degradation characteristics of dibutyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DEHP) in typical agricultural soils of China. Sci. Total Environ. 393, 333–340. https://doi.org/10.1016/j.scitotenv.2008.01.001

Xu, L., Han, L., Li, J., Zhang, H., Jones, K., Xu, E.G., 2022. Missing relationship between meso- and microplastics in adjacent soils and sediments. J. Hazard. Mater. 424. https://doi.org/10.1016/j.jhazmat.2021.127234

Xu, Y., Jia, W., Hu, A., Wang, J., Huang, Y., Xu, J., He, Y., Lu, Z., 2022. Co-occurrence of light microplastics and phthalate esters in soils of China. Sci. Total Environ. 852, 158384. https://doi.org/10.1016/j.scitotenv.2022.158384

Yang, F., Wang, M., Wang, Z., 2013. Sorption behavior of 17 phthalic acid esters on three soils: Effects of pH and dissolved organic matter, sorption coefficient measurement and QSPR study. Chemosphere 93, 82–89. https://doi.org/10.1016/j.chemosphere.2013.04.081

Yao, S., Li, X., Wang, T., Jiang, X., Song, Y., Arp, H.P.H., 2023. Soil Metabolome Impacts the Formation of the Eco-corona and Adsorption Processes on Microplastic Surfaces. Environ. Sci. Technol. 57, 8139–8148. https://doi.org/10.1021/acs.est.3c01877

Ye, T., Kang, M., Huang, Q., Fang, C., Chen, Y., Shen, H., Dong, S., 2014. Exposure to DEHP and MEHP from hatching to adulthood causes reproductive dysfunction and endocrine disruption in marine medaka (Oryzias melastigma). Aquat. Toxicol. 146, 115–126. https://doi.org/10.1016/j.aquatox.2013.10.025

Yu, L., Zhang, J. Di, Liu, Y., Chen, L.Y., Tao, S., Liu, W.X., 2021. Distribution characteristics of microplastics in agricultural soils from the largest vegetable production base in China. Sci. Total Environ. 756, 143860. https://doi.org/10.1016/j.scitotenv.2020.143860

Yuan, L., Cheng, J., Wang, Y., Liu, Y., Wang, W., Gao, R., Yu, X., 2020. Uptake and toxicity of di-(2-ethylhexyl) phthalate in Brassica chinensis L. Chemosphere 252, 126640. https://doi.org/10.1016/j.chemosphere.2020.126640

Yuan, S.Y., Liu, C., Liao, C.S., Chang, B. V., 2002. Occurrence and microbial degradation of phthalate esters in Taiwan river sediments. Chemosphere 49, 1295–1299. https://doi.org/10.1016/S0045-6535(02)00495-2

Yuan, S.Y., Huang, I.C., Chang, B.V., 2010. Biodegradation of dibutyl phthalate and di-(2-ethylhexyl) phthalate and microbial community changes in mangrove sediment. J. Hazard. Mater. 184, 826–831. https://doi.org/10.1016/j.jhazmat.2010.08.116

Yuan, S.Y., Lin, Y.Y., Chang, B. V., 2011. Biodegradation of phthalate esters in polluted soil by using organic amendment. J. Environ. Sci. Heal. - Part B Pestic. Food Contam. Agric. Wastes 46, 419–425. https://doi.org/10.1080/03601234.2011.572512

Zeng, F., Cui, K., Xie, Z., Wu, L., Liu, M., Sun, G., Lin, Y., Luo, D., Zeng, Z., 2008. Phthalate esters (PAEs): Emerging organic contaminants in agricultural soils in peri-urban areas around Guangzhou, China. Environ. Pollut. 156, 425–434. https://doi.org/10.1016/j.envpol.2008.01.045

Zeng, F., Cui, K., Xie, Z., Wu, L., Luo, D., Chen, L., Lin, Y., Liu, M., Sun, G., 2009. Distribution of phthalate esters in urban soils of subtropical city, Guangzhou, China. J.

Hazard. Mater. 164, 1171–1178. https://doi.org/10.1016/j.jhazmat.2008.09.029

Zeng, L.J., Huang, Y.H., Chen, X.T., Chen, X.H., Mo, C.H., Feng, Y.X., Lü, H., Xiang, L., Li, Y.W., Li, H., Cai, Q.Y., Wong, M.H., 2020. Prevalent phthalates in air-soil-vegetable systems of plastic greenhouses in a subtropical city and health risk assessments. Sci. Total Environ. 743, 140755. https://doi.org/10.1016/j.scitotenv.2020.140755

Zhang, B.T., Gao, Y., Lin, C., Yang, W., Liu, T., Liu, X., Wang, Y., 2020. Spatial distribution of phthalate acid esters in sediments of the Laizhou Bay and its relationship with anthropogenic activities and geochemical variables. Sci. Total Environ. 722, 137912. https://doi.org/10.1016/j.scitotenv.2020.137912

Zhang, G.S., Liu, Y.F., 2018. The distribution of microplastics in soil aggregate fractions in southwestern China. Sci. Total Environ. 642, 12–20. https://doi.org/10.1016/j.scitotenv.2018.06.004

Zhang, S. hui, Guo, A. jing, Fan, T. tong, Zhang, R., Niu, Y. jie, 2019. Phthalates in residential and agricultural soils from an electronic waste-polluted region in South China: distribution, compositional profile and sources. Environ. Sci. Pollut. Res. 26, 12227–12236. https://doi.org/10.1007/s11356-019-04669-2

Zhang, Y., Liang, Q., Gao, R., Hou, H., Tan, W., He, X., Zhang, H., Yu, M., Ma, L., Xi, B., Wang, X., 2015a. Contamination of phthalate esters (PAEs) in typical wastewater-irrigated agricultural soils in Hebei, North China. PLoS One 10, e0137998. https://doi.org/10.1371/journal.pone.0137998

Zhang, Y., Wang, P., Wang, L., Sun, G., Zhao, J., Zhang, H., Du, N., 2015b. The influence of facility agriculture production on phthalate esters distribution in black soils of northeast China. Sci. Total Environ. 506–507, 118–125. https://doi.org/10.1016/j.scitotenv.2014.10.075

Zhang, Z., He, G., Peng, X., Lu, L., 2014. Distribution and sources of phthalate esters in the topsoils of Beijing, China. Environ. Geochem. Health 36, 505–515. https://doi.org/10.1007/s10653-013-9577-0

Zhang, Z.M., Zhang, H.H., Zhang, J., Wang, Q.W., Yang, G.P., 2018a. Occurrence, distribution, and ecological risks of phthalate esters in the seawater and sediment of Changjiang River Estuary and its adjacent area. Sci. Total Environ. 619–620, 93–102. https://doi.org/10.1016/j.scitotenv.2017.11.070

Zhang, Z.M., Zhang, H.H., Zou, Y.W., Yang, G.P., 2018b. Distribution and ecotoxicological state of phthalate esters in the sea-surface microlayer, seawater and sediment of the Bohai Sea and the Yellow Sea. Environ. Pollut. 240, 235–247. https://doi.org/10.1016/j.envpol.2018.04.056

Zhang, Z.M., Yang, G.P., Zhang, H.H., Shi, X.Z., Zou, Y.W., Zhang, J., 2020a. Phthalic acid esters in the sea-surface microlayer, seawater and sediments of the East China Sea: Spatiotemporal variation and ecological risk assessment. Environ. Pollut. 259, 113802. https://doi.org/10.1016/j.envpol.2019.113802

Zhang, Z.M., Zhang, J., Zhang, H.H., Shi, X.Z., Zou, Y.W., Yang, G.P., 2020b. Pollution characteristics, spatial variation, and potential risks of phthalate esters in the water–sediment system of the Yangtze River estuary and its adjacent East China Sea. Environ. Pollut. 265, 114913. https://doi.org/10.1016/j.envpol.2020.114913

Zhao, X., Jin, H., Ji, Z., Li, D., Kaw, H.Y., Chen, J., Xie, Z., Zhang, T., 2020. PAES and PAHs in the surface sediments of the East China Sea: Occurrence, distribution and influence factors. Sci. Total Environ. 703, 134763. https://doi.org/10.1016/j.scitotenv.2019.134763

Zhou, B., Zhao, L., Wang, Y., Sun, Y., Li, X., Xu, H., Weng, L., Pan, Z., Yang, S., Chang, X., Li, Y., 2020a. Spatial distribution of phthalate esters and the associated response of enzyme activities and microbial community composition in typical plastic-shed vegetable soils in China. Ecotoxicol. Environ. Saf. 195, 110495. https://doi.org/10.1016/j.ecoenv.2020.110495

Zhou, B., Wang, J., Zhang, H., Shi, H., Fei, Y., Huang, S., Tong, Y., Wen, D., Luo, Y., Barceló, D., 2020b. Microplastics in agricultural soils on the coastal plain of Hangzhou Bay, east China: Multiple sources other than plastic mulching film. J. Hazard. Mater. 388, 121814. https://doi.org/10.1016/j.jhazmat.2019.121814

Zhou, Q.H., Wu, Z.B., Cheng, S.P., He, F., Fu, G.P., 2005. Enzymatic activities in constructed wetlands and di-n-butyl phthalate (DBP) biodegradation. Soil Biol. Biochem. 37, 1454–1459. https://doi.org/10.1016/j.soilbio.2005.01.003

Zhu, D., Chen, Q.L., An, X.L., Yang, X.R., Christie, P., Ke, X., Wu, L.H., Zhu, Y.G., 2018. Exposure of soil collembolans to microplastics perturbs their gut microbiota and alters their isotopic composition. Soil Biol. Biochem. 116, 302–310. https://doi.org/10.1016/j.soilbio.2017.10.027

Zhu, F., Zhu, C., Chen, N., Zhou, D., Gao, J., 2018a. Will spent mushroom substrate application affect the dissipation and plant uptake of phthalate esters? J. Soils Sediments 18, 1579–1589. https://doi.org/10.1007/s11368-017-1876-0

Zhu, F., Zhu, C., Doyle, E., Liu, H., Zhou, D., Gao, J., 2018b. Fate of di (2-ethylhexyl) phthalate in different soils and associated bacterial community changes. Sci. Total Environ. 637–638, 460–469. https://doi.org/10.1016/j.scitotenv.2018.05.055

Zhou, J.L., Liu, Y.P., 2000. Kinetics and equilibria of the interactions between diethylhexyl phthalate and sediment particles in simulated estuarine systems. Mar. Chem. 71, 165–176. https://doi.org/10.1016/S0304-4203(00)00047-5

Zolfaghari, M., Drogui, P., Seyhi, B., Brar, S.K., Buelna, G., Dubé, R., 2014. Occurrence, fate and effects of di (2-ethylhexyl) phthalate in wastewater treatment plants: A review. Environ. Pollut. 194, 281–293. https://doi.org/10.1016/j.envpol.2014.07.014

Zou, Y., Cai, M., 2013. Determination of Phthalate Concentration in Toys and Children's Products. Agil. Rep. 9 [WWW Document]. URL https://www.agilent.com/cs/library/applications/5990-4863EN.pdf

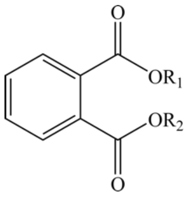
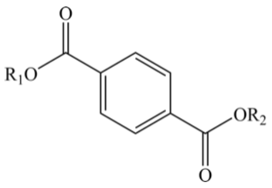
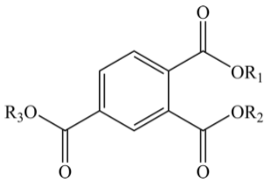
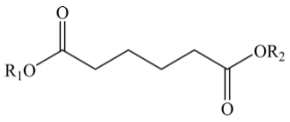
Zorníková, G., Jarošová, A., Hřivna, L., 2011. Distribution of phthalic acid esters in agricultural plants and soil. Acta Univ. Agric. Silvic. Mendelianae Brun. LIX, 233–238.

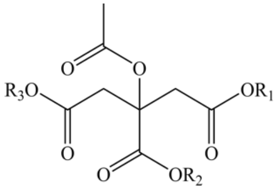
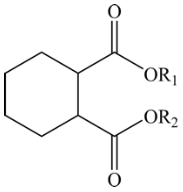
Zubris, K.A. V., Richards, B.K., 2005. Synthetic fibers as an indicator of land application of sludge. Environ. Pollut. 138, 201–211. https://doi.org/10.1016/j.envpol.2005.04.013

9

Appendices

Appendix Table S2.1: Chemical structures of the common classes of plasticiser.

Class	Structure	Example	R_1	R_2	R_3
Phthalate		DEP	CH_2CH_3	R_1	
		BBP	$(CH_2)_3CH_3$	CH_2Ar	
		DEHP	$CH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_3$	R_1	
		DnOP	$(CH_2)_7CH_3$	R_1	
Terephthalate		DEHTP	$CH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_3$	R_1	
Trimellitate		TOTM	$(CH_2)_7CH_3$	R_1	R_1
Adipate		DEHA	$CH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_3$	R_1	

Citrate		ATBC	$(CH_2)_3CH_3$	R_1	R_1
DiNCH		DiNCH	C_9H_{19} (mixture of isomers)	R_1	

Appendix Table S2.2: Mean phthalate concentrations (µg g^{-1}) extracted from all studies of plasticiser soil occurrence. Instances where phthalates were present below the detection limit were assigned null values. Data was calculated manually for sampling groups 35-37 and 98-101. Any non-detects were assigned concentrations of half of the detection limit during manual mean concentration calculations. Data for sampling groups 98-101 were calculated as the mean value for the year from the 3 different sampling points. For the sake of consistency, the total sum phthalate concentration for each sampling group was calculated from the individual mean concentrations reported in each study.

Study sample group	Region	Description	Land use	Target analytes	DMP	DEP	DiBP	DnBP	BBP	DEHP	DnOP	DnNP	DiNP	DiDP	DPrP	DMEP	DMPP	DEEP	DnPP	DnHxP	DnHpP	HEHP	DBEP	DCHxP	DPhP	Sum phthalates	Study
1	China	Soil from vegetable greenhouses (n=111)	Agriculture	16	0.364	0.108	1.118	1.471	0.194	1.465	1.239	0.026				0.015	0.246	0.041	0.088	0.084			0.015	0.035	0.240	6.749	(Chai et al. 2014)
2	China	Agricultural soil from greenhouses and open fields from Shenyang (n=16)	Agriculture	5	0.032	0.114	0.325	0.961		0.407																1.839	(Chen et al. 2017)
3	China	Agricultural soil from greenhouses and open fields from Beijing (n=12)	Agriculture	5	0.047	0.116	0.315	0.597		0.448																1.523	
4	China	Agricultural soil from greenhouses and open fields from Xianyang (n=6)	Agriculture	5	0.038	0.147	0.298	0.362		0.382																1.227	
5	China	Agricultural soil from greenhouses and open fields from Shouguang (n=12)	Agriculture	5	0.046	0.149	0.341	0.659		0.491																1.686	

6	China	Agricultural soil from greenhouses and open fields from Siyang (n=11)	Agriculture	5	0.023	0.095	0.241	0.65		0.336																1.345	
7	China	Agricultural soil from greenhouses and open fields from Haimen (n=12)	Agriculture	5	0.026	0.09	0.243	0.55		0.344																1.253	
8	China	Agricultural soil from greenhouses and open fields from Nanjing (n=13)	Agriculture	5	0.031	0.108	0.221	0.491		0.39																1.241	
9	China	Agricultural soil from greenhouses and open fields from Changshu (n=5)	Agriculture	5	0.022	0.108	0.223	0.157		0.365																0.875	
10	China	Agricultural soil from greenhouses and open fields from Fuzhou (n=12)	Agriculture	5	0.04	0.128	0.363	0.463		0.446																1.440	
11	China	Agricultural soil from greenhouses and open fields from Kunming (n=12)	Agriculture	5	0.032	0.088	0.311	0.263		0.314																1.008	
12	China	Urban surface soils (n=?)	Urban	13	0.01	0.01	0.1	0.09	0.05	0.11	0.05	0.06					0.04		0.03	0.01		0.01		0.06		0.630	(Cheng et al. 2015)
13	China	Urban deep soils (n=?)	Urban	13	0.01	0.02	0.04	0.04	0.05	0.08	0.01	0.04					0.03		0.04	0.01		0.01		0.03		0.410	
14	China	Agricultural soil (n=32)	Agriculture	7	0.0131	0.00874	0.217	0.254	0.00013	0.118	0.00681															0.618	(He et al. 2018)
15	China	Riparian soil (n=26)	Mixed	7	0.0144	0.0113	0.194	0.225	0.00037	0.108	0.00667															0.560	
16	China	Urban soils of the YRD (n=17)	Urban	11	0.030	0.001	0.049	1.392	0	3.399	0.011	0			0				0	0.018						4.900	(Hongjun et al. 2013)
17	China	Suburban soils of the	Urban	11	0.027	0.251	0.104	0.657	0	2.701	0.025	0.005			0.053				0	0.061						3.884	

		YRD (n=28)																									
18	China	Rural soils of the YRD (n=37)	Rural	11	0.032	0	0.089	0.413	0	1.224	0.005	0			0				0	0.019						1.782	
19	China	Agricultural soil from Chongquing (n=1)	Agriculture	8	0.0035	0.0015	0.0094	0.0092		0.0798										0		0		0		0.103	(Hu et al. 2020)
20	China	Agricultural soil from Shanxi (n=1)	Agriculture	8	0.0029	0.001	0.0113	0.0095		0.0369										0		0		0		0.062	
21	China	Forest soil from Zheijang (n=1)	Rural	8	0.0037	0.0021	0.0177	0.0161		0.0824										0		0		0		0.122	
22	China	Urban soil from Jilin (n=1)	Urban	8	0.0167	0.0072	0.1232	0.1007		1.1422										0.0015		0.0087		0.0069		1.407	
23	China	Agricultural soil from Zheijang (n=1)	Agriculture	8	0.0047	0.002	0.0289	0.1005		0.1462										0		0		0		0.282	
24	China	Agricultural soil (n=8)	Agriculture	6	0.001	0		0.01	0	0.44	0.20															0.651	(Kaewlaoyoong et al. 2018)
25	China	Garden soil (n=10)	Urban	6	0	0		0.04	0	0.16	0.003															0.203	
26	China	Roadside soils (n=6)	Urban	6	0	0		0.07	0	0.15	0.03															0.250	
27	China	Suburban agricultural and wasteland soil - farmland, vegetable and orchard (n=85)	Mixed	6	0.018	0.022		0.070	0.064	0.295	0.189															0.658	(Kong et al. 2012)
28	China	Urban soils (n=30)	Urban	7	0.010	0.016	0.311	0.790	0.029	1.875	0.031															3.062	(Li et al. 2006)
29	China	Soil from vegetable greenhouses (n=60)	Agriculture	15	0.008	0.02	0.13	0.44	0.004	0.38	0.002					0.0003	0	0.0005	0.001	0.002			0	0	0.002	0.990	(Li et al. 2016a)
30	China	Agricultural soils from 36 fields (n=108)	Agriculture	16	0.14	0.34	1.118	1.987	0.49	0.292	0.364	0				0.131	0.102	0.196	0	0.019			1.071	0.125	0	6.375	(Li et al. 2016b)
31	China	Agricultural soil from suburban greenhouses (n=32)	Agriculture	6	0	0.01775		0.09888	0.01906	0.19237	0.02368															0.352	(Li et al. 2020)

32	China	Soil in the vicinity of landfill (n=4)	Landfill	16	0.0272	0.0124	0.2327	0.0603	0.0197	0.3021	0		0.1473			0	0.0267	0.0630	0	0.0055		0.0212	0	0.0044		0.923	(Liu et al. 2010b)
33	China	Soil used to cover landfill (n=2)	Landfill	16	0.0648	0	0.2528	0.1706	0.0905	3.3102	0		0			0	0.0518	0	0	0		0.0528	0	0.2257		4.219	
34	China	Alluvial soils (n=26)	Mixed	16	0.0209	0.2045	0.1442	0.0815	0.0159	0.3292	0		0.0274			0.0173	0.0049	0.0099	0	0.0111		0.0214	0.0071	0.0315		0.927	
35	China	Agricultural soils from industrial greenhouses (n=40)	Agriculture	6	0.017925	0.020525		1.7325	0	0.843675	0.0119															2.627	(Ma et al. 2019)
36	China	Agricultural soils from industrial greenhouses (n=40)	Agriculture	6	0.0192	0.0316		0.81665	0.0005	1.187275	0.407325															2.463	(Ma et al. 2020)
37	China	Agricultural soils (n=15)	Agriculture	6	0.02831	0.044667		0.306927	0.00019	0.227027	0.00415667															0.611	(Song et al. 2021)
38	China	Agricultural soils (n=241)	Agriculture	15	0.023	0.0038	0.086	0.0949	0.001	0.546	0.0069	0.0083				0.002	0.0014	0.0033	0.0022	0.0005			0.0183	0.0353		0.833	(Sun et al. 2016)
39	China	Agricultural soils (n=89)	Agriculture	16	1.836	0.25	0.252	0.919	0.023	0.96	0.685	0.005				0.246	0.006	0.053	0.005	0.006			0.072	0.007	0	5.325	(Tao et al. 2020a)
40	China	Mixed land uses (n=1757)	Mixed	6	0.00497	0.0104		0.1718	0.00893	0.342	0.011															0.549	(Teng et al. 2015)
41	China	Agricultural soil - CK (no polytunnel or mulch film) (n=8)	Agriculture	6	0.003	0.003		0.023	0.001	0.411	0.013															0.454	(Wang et al. 2013a)
42	China	Agricultural soil - HS (n=31)	Agriculture	6	0.002	0.003		0.115	0.001	0.622	0.064															0.807	
43	China	Agricultural soil - GL (double polytunnel, single layer mulch film) (n=39)	Agriculture	6	0.008	0.006		0.262	0.006	2.445	0.458															3.185	
44	China	Agricultural soil - SS (single layer polytunnel, single layer mulch film) (n=27)	Agriculture	6	0.001	0.007		0.201	0.001	1.419	0.240															1.869	
45	China	Agricultural soil - PK (single layer polytunnels , mulch	Agriculture	6	0.003	0.006		0.236	0.007	2.877	0.026															3.155	

		film, alternating every 2-3 years) (n=22)																									
46	China	Agricultural soils - paddy field	Agriculture	6	0.0278	0.0603		0.1596	0.020	0.2215	0.0434															0.533	(Wang et al. 2017)
47	China	Agricultural soils - vegetable field	Agriculture	6	0.0252	0.0364		0.0704	0.0124	0.1365	0.0274															0.308	
48	China	Agricultural soils - bean field	Agriculture	6	0.0212	0.0361		0.0299	0.0102	0.1454	0.0255															0.268	
49	China	Suburban agricultural soil in greenhouses (n=44)	Agriculture	6	0.004	0.005		0.17	0.006	1.84	0.2															2.225	(Wang et al. 2015a)
50	China	Urban soils (n=62)	Urban	6	0.0235	0.0234		0.5217	0.0117	0.7653	0.0235															1.346	(Wang et al. 2018)
51	China	Agricultural soils from 4 fields (n=59)	Agriculture	6	0.05431	0.01946		0.31659	0.03948	0.16617	0.0423															0.638	(Wang et al. 2015b)
52	China	Cultivated agricultural surface soils (n=23)	Agriculture	4	0.0266	0.0349		0.0285		0.0279																0.118	(Wang et al. 2013b)
53	China	Agricultural soils (n=228)	Agriculture	6	0	0		0.00612	0.000861	0.183	0.00697															0.197	(Wei et al. 2020)
54	China	Residential soils from a non-industrialised area (n=44)	Urban	6	0.67	1.08		1.66	1.25	11.12	0.65															16.430	(Wu et al. 2015)
55	China	Roadside soils from a non-industrialised area (n=36)	Urban	6	0.83	1.37		1.77	1.48	14.5	0.76															20.710	
56	China	Farmland soils from a non-industrialised area (n=32)	Agriculture	6	1.1	1.76		2.22	1.86	16.59	0.67															24.200	
57	China	Non-cultivated soils from a non-industrialised area (n=33)	Rural	6	0.53	0.91		1.23	1.3	11.4	0.56															15.930	

58	China	Residential soils from an industrialised area (n=44)	Urban	6	1.53	3.91		5.63	1.6	26	1.16															39.830	
59	China	Roadside soils from an industrialised area (n=36)	Urban	6	2.17	4.41		8.79	1.75	31	1.49															49.610	
60	China	Farmland soils from an industrialised area (n=32)	Agriculture	6	2.1	4.01		4.88	2.36	16.61	1.49															31.450	
61	China	Non-cultivated soils from an industrialised area (n=33)	Rural	6	1.24	2.62		3.51	1.3	11.5	1.25															21.420	
62	China	Urban soils (n=127)	Urban	5	0.006184	0.001274		0.99003		0.1397	0.002374															1.140	(Xia et al. 2011)
63	China	Rural soils (n=40)	Rural	2				0.3551		0.02214																0.377	
64	China	Agricultural soils	Agriculture	2				14.06		4.858																18.918	(Xu et al. 2008)
65	China	Agricultural soils	Agriculture	2				7.60		2.35																9.950	
66	China	Agricultural soils, Panyu district (n=10)	Agriculture	16	0.005	0.008	0.056	0.095	0	0.729	0	0.001				0.001	0.015	0.001	0.005	0.003		0.002	0	0.007		0.928	(Zeng et al. 2008)
67	China	Agricultural soils, Haizhou district (n=4)	Agriculture	16	0.026	0.052	0.585	1.08	0.454	2.75	0	0				0	0.077	0.024	0.052	0.008		0.016	0.008	0.044		5.176	
68	China	Agricultural soils, Tianhe district (n=12)	Agriculture	16	0.006	0.006	0.071	0.121	0.004	0.597	0.007	0.001				0.001	0.035	0.003	0.015	0		0	0.003	0.007		0.877	
69	China	Agricultural soils, Liwan district (n=8)	Agriculture	16	0.025	0.039	0.273	0.323	0.035	4.09	0.009	0				0.009	0.034	0.004	0.007	0.002		0.010	0.015	0.014		4.889	
70	China	Agricultural soils, Baiyun district (n=6)	Agriculture	16	0.009	0.012	0.068	0.089	0.025	0.610	0	0				0.006	0.025	0.005	0.037	0.092		0	0.001	0.027		1.006	

71	China	Roadside soils (n=17)	Urban	16	0.152	0.092	7.15	8.13	0.402	63.2	0.561	0.001				0.003	0.093	0.038	0.064	0.002		0.073	0.026	0.036		80.053	(Zeng et al. 2009)
72	China	Soil from residental areas (n=13)	Urban	16	0.074	0.034	1.59	2.06	0.032	16.1	0.017	0.007				0.025	0.118	0.043	0.004	0.026		0.033	0.008	0.025		20.196	
73	China	Parkland soils (n=7)	Urban	16	0.067	0.036	1.69	2.01	0.047	29.4	0.004	0.008				0.025	0.062	0.018	0.007	0.003		0.009	0	0.014		33.400	
74	China	Agricultural soils from both open and greenhoused-fields (n=78)	Agriculture	16	0.019	0.039	0.637	0.249	0.016	0.669	0.004	0.004				0.028	0.009	0.013	0.097	0.007			0	0.046	0.016	1.853	(Zeng et al. 2020)
75	China	Residential soil (n=11)	Urban	16	0.11759	0.01946	0.94001	2.13107	0.07116	2.95386	0.30139	0.95283	0.03331				3.71906	0	0	0.01395			12.54289	3.9576	0.03093	27.785	(Zhang et al. 2019)
76	China	Residential soil (n=7)	Urban	16	0.13671	0.01083	0.55048	1.66546	0.03208	0.70835	0.02596	0.50638	0.04541				2.72003	0	0	0.0049			2.20679	1.84014	0.00391	10.457	
77	China	Agricultural soil (n=28)	Agriculture	16	0.0964	0.01332	0.44304	1.90148	0.03483	0.3838	0.06273	0.14471	0.01917				2.58417	0	0	0.00689			1.89301	0.70356	0.00673	8.294	
78	China	Agricultural soils (n=13)	Agriculture	6	0.024	0.026		0.045	0.022	0.143	0.036															0.296	(Zhang et al. 2015a)
79	China	Soils from agricultural greenhouse facilities sampled in Spring (n=9)	Agriculture	15	0.219	0.248	0.071	0.462	0.053	0.898	0.05		0.05			0.049	0.042	0.058			0.048		0.096	0.043	0.054	2.441	(Zhang et al. 2015b)
80	China	Soils from agricultural greenhouse facilities sampled in Summer (n=9)	Agriculture	15	0.156	0.556	0.076	0.655	0.059	1.471	0.047		0.05			0.072	0.060	0.038			0.053		0.067	0.090	0.049	3.499	
81	China	Soils from agricultural greenhouse facilities sampled in Autumn (n=9)	Agriculture	15	0.013	0.286	0.046	0.263	0.033	0.995	0.064		0.059			0.056	0.037	0.028			0.048		0.077	0.048	0.093	2.146	
82	China	Soil (n=93) from 'plastic-sheds' (n=31) used to grow vegetables	Agriculture	16	0.0352	0.0187	0.197	0.144	0.0697	0.181	0.091	0				0	0.0303	0.0669	0	0.0608			0.143	0	0	1.038	(Zhou et al. 2020a)
83	Europe	Agricultural soils collected from across the Czech Republic (n=40), collected in 2011, 2013 and 2017. I	Agriculture	2				0.47		0.48																0.950	(Langová et al. 2020)

		have noted her the 2011 concentrations.																									
84	Europe	Agricultural soils collected from across the Czech Republic (n=40), collected in 2011, 2013 and 2017. I have noted her the 2013 concentrations.	Agriculture	2				0.47		0.27																0.740	
85	Europe	Agricultural soils collected from across the Czech Republic (n=40), collected in 2011, 2013 and 2017.. I have noted her the 2017 concentrations.	Agriculture	2				0.39		0.38																0.770	
86	Europe	Soils of various vegetations and soil types collected from all over Scotland over three years - Arable (n=17)	Agriculture	1						0.153																0.153	(Rhind et al. 2013)
87	Europe	Soils of various vegetations and soil types collected from all over Scotland over three years - Dry and moist heath (n=38).	Rural	1						0.234																0.234	
88	Europe	Soils of various vegetations and soil types collected from all over Scotland over three years - Improved	Rural	1						0.0949																0.095	

		grassland (n=28)																									
89	Europe	Soils of various vegetations and soil types collected from all over Scotland over three years - Mire and wet heath (n=59).	Rural	1						0.302																0.302	
90	Europe	Soils of various vegetations and soil types collected from all over Scotland over three years - Non-native conifer (n=21).	Rural	1						0.210																0.210	
91	Europe	Soils of various vegetations and soil types collected from all over Scotland over three years - Unimproved grassland (n=20).	Rural	1						0.167																0.167	
92	Europe	Urban soils (n=30)	Urban	6	0.014	0.007		0.072	0.003	0.729	0.005															0.830	(Škrbić et al. 2016)
93	Europe	Forest soil (n=1)	Rural	9	0.00002	0.00144	0.0173	0.0052	0	0.0274	0		0.0082	0												0.060	(Tran et al. 2015)
94	Europe	Rural soil (n=1)	Rural	9	0.001	0.0047	0.0026	0.004	0.00039	0.121	0.0035		0.0033	0.0135												0.154	
95	Europe	Agricultural soil (n=1)	Agriculture	9	0	0.0075	0.0389	0.0096	0.0013	0.242	0		0.0674	0.0402												0.407	
96	Europe	Urban soil (n=2)	Urban	9	0.00125	0.093	0.0215	0.0925	0.0026	0.31	0.0034		0.5	0.065												1.089	
97	Europe	Soil samples from 4 different locations used to grow crops, sampled at three times throughout the year.	Agriculture	2				0.4		0.185																0.585	(Zorníková et al. 2011)

98	Europe	Soil samples from 4 different locations used to grow crops, sampled at three times throughout the year	Agriculture	2				0.61		0.06833333																0.678	
99	Europe	Soil samples from 4 different locations used to grow crops, sampled at three times throughout the year	Agriculture	2				1.13		0.62																1.750	
100	Europe	Soil samples from 4 different locations used to grow crops, sampled at three times throughout the year	Agriculture	2				0.54		0.075																0.615	
101	India	Soil in vicnity of E-waste dismantling sites (n=5)	Urban	6	0.023	0.028		0.039	0.140	0.614	0.034															0.878	(Chakraborty et al. 2019)
102	India	Soil in vicinity of E-waste shredding sites (n=4)	Urban	6	0.007	0.013		0.029	0.029	0.029	0.011															0.118	
103	India	Soil in vicinity of E-waste precious metal recovery sites (n=5)	Urban	6	0.006	0.010		0.021	0.054	0.044	0.004															0.139	
104	India	Soil near open municial landfill sites (n=11)	Landfill	6	0.005	0.010		0.021	0.023	0.021	0.013															0.093	

Appendix Table S2.3: Limits of detection (LODs) for phthalates from all studies (n=43) of soil occurrence. If method LODs were not available, instrumental LODs were noted instead, if possible to do so. Values are in mg L^{-1} or µg g^{-1}. nr = not reported, M = method, I = instrumental

Study	LOD Range	Unit	Type	DMP	DEP	DiBP	DnBP	BBP	DEHP	DnOP	DnNP	DiNP	DiDP	DPrP	DMEP	DMPP	DEEP	DnPP	DnHxP	DnHpP	HEHP	DBEP	DCHxP	DPhP
(Chai et al. 2014)	0.002-0.024	mg kg^{-1}	M	nr	0.002	nr	nr	nr	0.024	nr	nr				nr	nr	nr	nr	nr			nr	nr	nr
(Chakraborty et al. 2019)	0.00009-0.00024	mg kg^{-1}	M	0.00016	0.00009		0.00015	0.00024	0.00018	0.00015														
(Chen et al. 2017)	<0.00212	mg kg^{-1}	M	nr	nr	nr	nr		nr															
(Cheng et al. 2015)	0.002-0.022	mg kg^{-1}	nr	0.002	nr	nr	nr	nr	0.022	nr	nr					nr		nr	nr		nr		nr	
(He et al. 2018)	0.00003-0.00014	mg kg^{-1}	nr	nr	nr	nr	nr	nr	nr	nr														
(Hongjun et al. 2013)	0.0002-0.0025	mg kg^{-1}	I	nr	nr	nr	nr	nr	nr	nr	nr			nr				nr	nr					
(Hu et al. 2020)	0.00059-0.0108	mg kg^{-1}	M	0.00141	0.0025	0.00311	0.0047	0.0011	0.0108	0.00074					0.00059	0.00144	0.00119		0.00108		0.00102	0.00084	0.00096	
(Kaewlaoyoong et al. 2018)	0.11-0.13	mg kg^{-1}	M	nr	0.11		nr	nr	0.13	nr														
(Kong et al. 2012)	nr																							
(Langová et al. 2020)	0.00005-0.00011	mg L^{-1}	nr				0.00011		0.00005															
(Li et al. 2006)	0.002-0.0197	mg kg^{-1}	nr	nr	0.002	nr	nr	nr	0.0197	nr														
(Li et al. 2016a)	0.00023–0.0008	mg L^{-1}	I	nr	nr	nr	nr	nr	nr	nr					nr	nr	nr	nr	nr			nr	nr	nr
(Li et al. 2016b)	0.002-0.024	mg kg^{-1}	M	nr	0.002	nr	nr	nr	0.024	nr	nr				nr	nr	nr	nr	nr			nr	nr	nr
(Li et al. 2020)	0.0001-0.0001	mg kg^{-1}	M	0.0001	0.0001		0.0001	0.0001	0.0001	0.0001														
(Liu et al. 2010b)	0.000022-0.000341	mg L^{-1}	nr	nr	nr	nr	nr	nr	nr	nr		nr			nr	nr	nr	nr	nr		nr	nr	nr	
(Liu et al. 2010a)	0.000022-0.000341	mg L^{-1}	nr	nr	nr	nr	nr	nr	nr	nr		nr			nr	nr	nr	nr	nr		nr	nr	nr	
(Ma et al. 2019)	0.00010-0.00035	mg L^{-1}	nr	nr	nr		nr	nr	nr	nr														

(Ma et al. 2020)	0.00010-0.00035	mg L^{-1}	nr	nr	nr		nr	nr	nr	nr														
(Rhind et al. 2013)	0.05	mg kg^{-1}	nr						0.05															
(Škrbić et al. 2016)	nr																							
(Song et al. 2021)	0.0001-0.0006	mg kg^{-1}	I	nr	nr		nr	nr	nr	nr														
(Sun et al. 2016)	0.00005–0.00028	mg kg^{-1}	nr	nr	nr	nr	nr	nr	nr	nr	nr				nr	nr	nr	nr	nr			nr	nr	
(Tao et al. 2020a)	nr																							
(Teng et al. 2015)	0.00001-0.000025	mg kg^{-1}	nr	nr	nr		nr	nr	nr	nr														
(Tran et al. 2015)	0.0000012-0.0000071	mg kg^{-1}	nr	0.0000022	0.0000012	0.0000015	0.0000013	0.0000035	0.0000015	0.0000018		0.0000071	0.0000031											
(Wang et al. 2013a)	0.00010-0.00031	mg L^{-1}	I	nr	nr		nr	nr	nr	nr														
(Wang et al. 2017)	0.00276-0.00684	mg kg^{-1}	M	0.00375	0.00421		0.00276	0.00353	0.00684	0.00411														
(Wang et al. 2015a)	0.02-0.11	mg kg^{-1}	M	0.03	0.04		0.05	0.02	0.08	0.11														
(Wang et al. 2018)	0.0008-0.0089	mg kg^{-1}	M	0.0016	0.0035		0.0008	0.0089	0.0019	0.0014														
(Wang et al. 2015b)	0.006-0.071	mg L^{-1}	I	0.013	0.028		0.071	0.006	0.015	0.011														
(Wang et al. 2013b)	0.0001-0.001	mg kg^{-1}	nr	nr	nr		nr		nr															
(Wei et al. 2020)	0.0001-0.0005	mg kg^{-1}	nr	nr	nr		nr	nr	nr	nr														
(Wu et al. 2015)	0.02-0.04	mg kg^{-1}	nr	0.02	0.03		0.03	0.02	0.04	0.04														
(Xia et al. 2011)	0.000143-0.002857	mg kg^{-1}	M	0.000143	0.000143		0.000286		0.000286	0.002857														
(Xu et al. 2008)	0.01-0.01	mg kg^{-1}	nr				0.01		0.01															
(Zeng et al. 2008)	nr																							
(Zeng et al. 2009)	nr																							
(Zeng et al. 2020)	0.000459-0.00305	mg kg^{-1}	nr	0.000695	0.000499	0.000505	0.000948	0.000736	0.00127	0.00255	0.00305				0.000635	0.000826	0.000668	0.000459	0.00059			0.000832	0.000885	0.00125

(Zhang et al. 2019)	0.00016-0.00165	mg L^{-1}	nr	nr	nr	nr	nr	nr	nr	nr	nr	nr				nr	nr	nr	nr			nr	nr	nr
(Zhang et al. 2015a)	0.00013–0.0021	mg kg^{-1}	M	nr	nr		nr	nr	nr	nr														
(Zhang et al. 2015b)	0.0005-0.00779	mg kg^{-1}	M	0.00251	0.0038	0.00469	0.00187	0.00313	0.00079	0.00137		0.0005			0.00331	0.00434	0.00113			0.00779		0.0022	0.0019	0.00143
(Zhou et al. 2020a)	0.0018-0.0078	mg kg^{-1}	nr	0.0045	0.0035	0.002	0.0018	0.0025	0.0078	0.0068	0.0066				0.0022	0.002	0.0038	0.0027	0.0023			0.0032	0.0058	0.0052
(Zorníková et al. 2011)	0.03-0.03	mg kg^{-1}	nr				0.03		0.03															

Appendix Table S2.4: Half-lives of phthalates in soils and amended soils.

Phthalate	**Half-life (days)**	**Media**	**Initial concentration (µg g^{-1})**	**Temperature (ºC)**	**Soil pH**	**Study**
DEP	0.75	Soil	0.1	20	6.25	(Cartwright et al. 2000)
DEHP	14	Soil	50	30	4	(Chang et al. 2009)
DEHP	6.3	Soil	50	30	7	
DEHP	8.7	Soil	50	30	9	
DnBP	2.8	Amended soil	50	30	7	
DnBP	1.7	Amended soil	50	30	7	
DnBP	2.2	Amended soil	50	30	7	
DnBP	1.9	Amended soil	50	30	7	
DnBP	1.5	Amended soil	50	30	7	
DnBP	2.6	Amended soil	50	30	7	
DnBP	2.8	Amended soil	50	30	7	
DnBP	2.4	Amended soil	50	30	7	
DnBP	3.2	Amended soil	50	30	7	
DnBP	2.8	Amended soil	50	30	7	
DnBP	2.2	Amended soil	50	30	7	
DnBP	3	Amended soil	50	30	7	
DnBP	35	Soil	50	5	7	
DnBP	6.9	Soil	50	15	7	
DnBP	2.8	Soil	50	30	7	
DnBP	5	Soil	50	40	7	
DnBP	5.8	Soil	50	30	4	
DnBP	2.8	Soil	50	30	7	

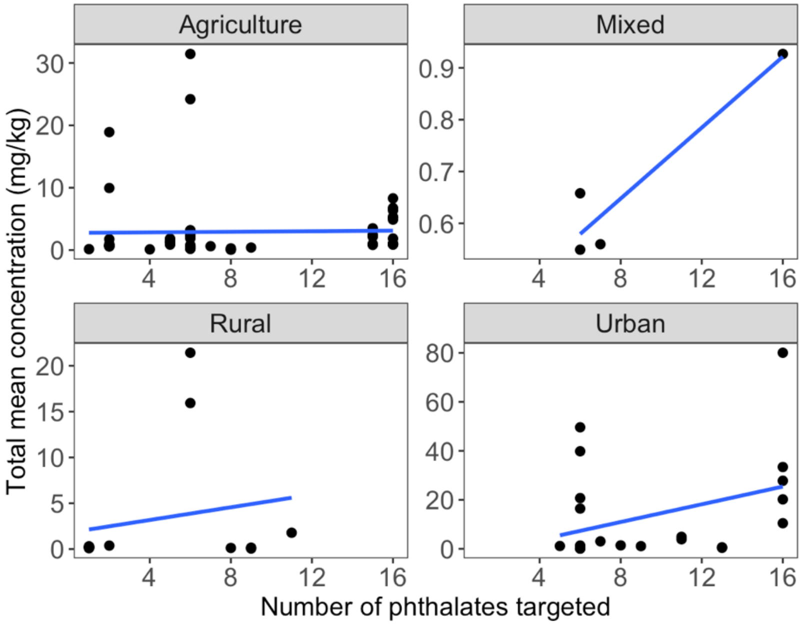
DnBP	4.6	Soil	50	30	9	
DEHP	6.3	Amended soil	50	30	7	
DEHP	5.3	Amended soil	50	30	7	
DEHP	5.8	Amended soil	50	30	7	
DEHP	5	Amended soil	50	30	7	
DEHP	4.6	Amended soil	50	30	7	
DEHP	6.3	Amended soil	50	30	7	
DEHP	6.3	Amended soil	50	30	7	
DEHP	5.8	Amended soil	50	30	7	
DEHP	6.9	Amended soil	50	30	7	
DEHP	5.8	Amended soil	50	30	7	
DEHP	5	Amended soil	50	30	7	
DEHP	6.3	Amended soil	50	30	7	
DEHP	69	Soil	50	5	7	
DEHP	23	Soil	50	15	7	
DEHP	6.3	Soil	50	30	7	
DEHP	8.7	Soil	50	40	7	
DnBP	0.653	Soil	20	25	8.33	(Cheng et al. 2018)
DnBP	0.338	Soil	20	25	8.33	
DnBP	0.315	Soil	20	25	8.33	
DnBP	0.872	Soil	2	25	8.33	
DnBP	0.459	Soil	10	25	8.33	
DnBP	0.338	Soil	20	25	8.33	
DnBP	0.946	Soil	2	25	5.15	
DnBP	0.983	Soil	10	25	5.15	

DnBP	1.2	Soil	20	25	5.15	
DnBP	1.41	Soil	20	5	8.33	
DnBP	0.754	Soil	20	15	8.33	
DnBP	0.338	Soil	20	25	8.33	
DnBP	0.286	Soil	20	35	8.33	
DnBP	20.4	Soil	20	25	5.15	
DnBP	1.2	Soil	20	25	5.15	
DnBP	0.918	Soil	20	25	5.15	
DnBP	4.6	Soil	20	5	5.15	
DnBP	2.79	Soil	20	15	5.15	
DnBP	1.2	Soil	20	25	5.15	
DnBP	0.87	Soil	20	35	5.15	
DnBP	1.37	Soil	20	25	5.22	(Cheng et al. 2019)
DnBP	1.23	Soil	20	25	5.15	
DnBP	4.99	Soil	20	25	4.38	
DnBP	0.82	Soil	20	25	7.24	
DnBP	0.721	Soil	20	25	8.44	
DnBP	0.768	Soil	20	25	8.48	
DnBP	0.513	Soil	20	25	8.33	
DnBP	0.594	Soil	20	25	8.58	
DnBP	0.503	Soil	20	25	8.33	
DnBP	2.2	Soil	20	25	5.5	
DnBP	1.67	Soil	20	25	5.29	
DnBP	1.04	Soil	20	25	5.23	
DnBP	0.43	Soil	20	25	7.6	

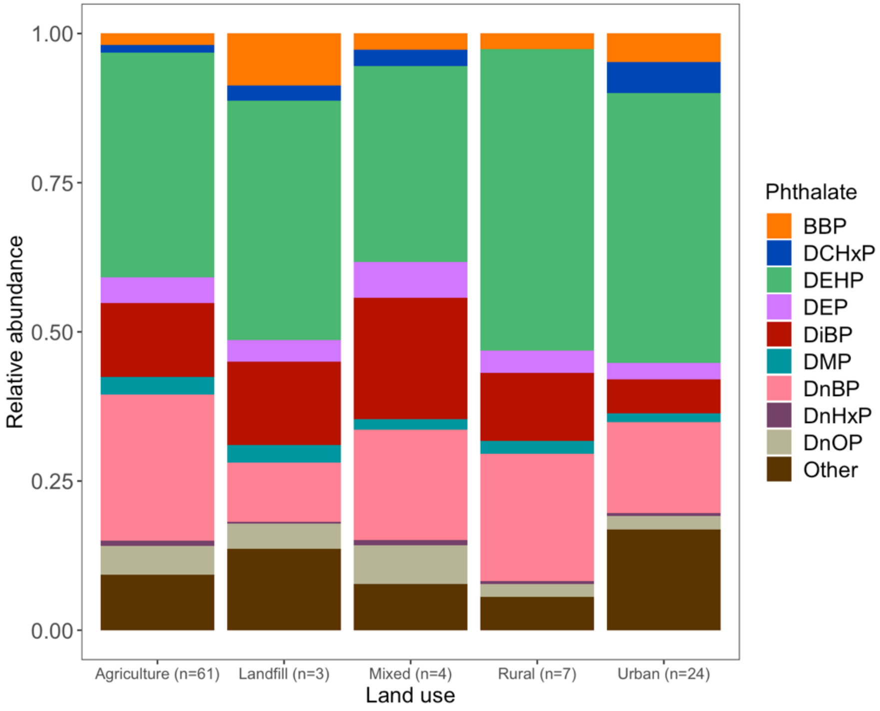
DnBP	0.725	Soil	20	25	7.06	
DnBP	1.3	Soil	20	25	4.68	
DnBP	0.941	Soil	20	25	6.33	
DnBP	0.985	Soil	20	25	8.35	
DnBP	0.739	Soil	20	25	6.98	
DnBP	2.2	Soil	20	25	5.5	
DnBP	0.514	Soil	20	25	7.9	
DEP	3.3	Soil	0.5	23	8.1	(Hurtado et al. 2017)
DEP	9.7	Sterile soil	0.5	23	8.1	
DMP	2.29	Amended soil	100	25	7.2	(Jianlong et al. 2004)
DEP	3.7	Amended soil	100	25	7.2	
DnBP	8.53	Amended soil	100	25	7.2	
DEHP	28.4	Amended soil	100	25	7.2	
DnBP	8.5	Soil	5	30	6.5	(Liao 2010)
DnBP	7.87	Soil	5	30	7	
DnBP	8.31	Soil	5	30	7.5	
DnBP	8.74	Soil	5	30	8	
DnBP	8.82	Soil	5	25	6.8	
DnBP	7.87	Soil	5	30	6.8	
DnBP	11.01	Soil	5	35	6.8	
DnBP	7.95	Soil	5	40	6.8	
DEHP	158	Soil	1.6	5	5.9	(Madsen et al. 1999)
DEHP	86	Soil	1.6	10	5.9	
DEHP	52	Soil	1.6	20	5.9	
DEHP	301	Amended soil	1.6	5	5.9	

DEHP	125	Amended soil	1.6	10	5.9	
DEHP	55	Amended soil	1.6	20	5.9	
DEHP	79	Amended soil	1.6	20	5.9	
DEHP	86	Amended soil	3.2	20	5.9	
DEHP	89	Amended soil	9.9	20	5.9	
DEHP	77	Amended soil	35.1	20	5.9	
DEHP	20	Soil	1	13.3	7.6	(Rüdel et al. 1993)
DEHP	31	Soil	1	14.1	7.6	
DEHP	68	Soil	1	13.3	6.9	
DEHP	170	Soil	1	12.8	6.9	
DnBP	3.36	Amended soil	20	nr	7.785	(Tao et al. 2020b)
DnBP	11.65	Soil	20	nr	7.785	
DEHP	64	Soil	nr	nr	nr	(Tran et al. 2015)
DnBP	14.68	Soil	0	28	8	(Xie et al. 2010)
DnBP	30.88	Soil	1	28	8	
DnBP	19.58	Soil	10	28	8	
DnBP	31.31	Soil	30	28	8	
DEP	3.47	Soil	0	28	8	
DEP	10.19	Soil	1	28	8	
DEP	9.39	Soil	10	28	8	
DEP	19.33	Soil	30	28	8	
DMP	3.79	Soil	0	28	8	
DMP	7.02	Soil	1	28	8	
DMP	9.13	Soil	10	28	8	
DMP	15.68	Soil	30	28	8	

DnOP	78.84	Soil	0	28	8	
DnOP	61.14	Soil	1	28	8	
DnOP	51.65	Soil	10	28	8	
DnOP	115.22	Soil	30	28	8	
DnBP	7.8	Soil	20	25	7.12	(Xu et al. 2008)
DnBP	8.3	Soil	20	25	7.3	
DEHP	26.3	Soil	20	25	7.12	
DEHP	30.8	Soil	20	25	7.3	
DnBP	1.6	Amended soil	100	30	7	(Yuan et al. 2011)
DnBP	1.2	Amended soil	100	30	7	
DnBP	1.4	Amended soil	100	30	7	
DnBP	1	Amended soil	100	30	7	
DnBP	1.8	Amended soil	100	30	7	
DnBP	2.6	Amended soil	100	30	7	
DEHP	8.7	Amended soil	100	30	7	
DEHP	6.3	Amended soil	100	30	7	
DEHP	6.9	Amended soil	100	30	7	
DEHP	5.8	Amended soil	100	30	7	
DEHP	6.9	Amended soil	100	30	7	
DEHP	9.9	Amended soil	100	30	7	
DnBP	1.4	Soil	nr	nr	nr	(Zhou et al. 2005)
DnBP	4	Soil	nr	nr	nr	



Appendix Figure S2.1: Relationship between analytical breadth (number of phthalates target) and total measured phthalate concentration (data for landfill studies not shown due to insufficient data points). Each data point represents the total mean phthalate concentration reported for a distinct sampling group within a study.



Appendix Figure S2.2: Average phthalate profiles in soils of different land uses. n refers to number of sampling groups of that land use. The 6 sampling groups extracted for one study (Rhind et al. 2013) only targeted 1 phthalate so could not provide any relative abundance information, so were removed from the dataset before calculation All other sampling groups targeted at least 2 phthalates. The data was produced by calculating the relative abundance value for each phthalate targeted within a sampling group (nd=0). These were then used to calculate the mean relative abundance for each phthalate for each land use, which were used give a mean relative abundance profile for each land use.

Appendix Table S3.1: Site characteristics data for this field study.

Land use	**Site code**	**Site name**	**Ordnance Survey grid reference**	**Date sampled (dd/mm/yyyy)**	**Time sampled**	**Altitude (m)**	**Weather**	**Grid dimensions (m x m)**	**Further notes**
Woodland	BG1	West Woods	SU 161 665	20/01/2020	13:30	191	Sunny, dry, settled	5 x 5	No macroplastic found. Leaf litter covering forest floor.
Woodland	BG2	Whytham Woods	SP 452 078	23/01/2020	11:40	114	Dry, overcast, settled	5 x 5	No macroplastic found. Leaf litter covering forest floor.
Woodland	BG3	Bernwood Forest	SP 616 118	23/01/2020	13:50	85	Dry, overcast, settled	5 x 5	No macroplastic found. Leaf litter covering forest floor.
Woodland	BG4	Bush Wood	SU 688 843	23/01/2020	15:30	117	Dry, overcast, settled	5 x 5	Stony ground - shallow topsoil. No macroplastic found. Leaf litter covering forest floor. Forest contains PVC sapling covers. Sampled as far away as possible.
Woodland	BG5	Nettlebed Woods	SU 705 858	31/01/2020	08:20	152	Dry, overcast, settled	5 x 5	No macroplastic found. Leaf litter covering forest floor.
Woodland	BG6	Greenfield Wood	SU 709 920	31/01/2020	09:35	229	Dry, overcast, settled	5 x 5	1 item of MaP found. Leaf litter covering forest floor.
Woodland	BG7	Giles Wood	SP 825 039	31/01/2020	11:00	171	Dry, overcast, settled	5 x 5	No macroplastic found. Leaf litter covering forest floor.
Landfill	LF1	Lower Compton	SU 021 720	20/01/2020	12:00	87	Sunny, dry, settled	3 x 8.33	
Landfill	LF2	Ling Hall	SP 450 740	04/02/2020	10:45	112	Windy, dry, overcast	2 x 12.5	
Landfill	LF3	Cotesbach	SP 542 816	04/02/2020	11:35	128	Windy, dry, overcast	5 x 5	

Landfill	LF4	Parkgate Farm	SU 081 889	06/02/2020	10:10	86	Foggy, settled	2 x 12.5	
Landfill	LF5	Slape Hill	SP 420 197	06/02/2020	13:00	109	Sunny, dry, settled	1 x 25	Roadside verge downwind of suspected landfill.
Landfill	LF6	Sutton Courtenay	SU 523 925	06/02/2020	14:30	51	Sunny, dry, settled	2 x 12.5	Found a broken item that had lots of plastic in - could not collect all in 10 minutes so after the 10 minutes was up, collected the rest of the 'item' in a separate bag.
Urban parkland	UP1	Florence Park	SP 536 043	21/01/2020	11:00	57	Dry, sunny, settled	5 x 5	
Urban parkland	UP2	South Park	SP 530 060	21/01/2020	12:10	69	Sunny, dry, settled	5 x 5	
Urban parkland	UP3	Christ Church Meadow	SP 515 056	21/01/2020	15:30	55	Sunny, dry, settled	5 x 5	
Urban roadside	UR1	Eastern Bypass	SP 535 031	21/01/2020	09:40	81	Dry, sunny, settled	2 x 12.5	
Urban roadside	UR2	Parks Road	SP 512 071	21/01/2020	13:40	63	Sunny, dry, settled	3 x 8.33	
Urban roadside	UR3	Botley Road	SP 502 062	21/01/2020	14:35	56	Sunny, dry, settled	5 x 5	

Appendix Table S3.2: Items used to create the in-house polymer spectra library.

Polymer	**Name in library**	**Description**
HDPE	HDPE	Milk bottle
HDPE	HDPE	Milk bottle lid
HPDE	HDPE	Lid for drinks bottle
LDPE	LDPE	Lid for bouillon stock
LDPE	LDPE	Ice cube bag
LDPE	LDPE	Wash bottle
PVC	PVC	Soft tubing
PVC	PVC	PVC Pellets
PVC	PVC	PVC cling film
Polypropene	Polypropene	Peanut butter tub
Polypropene	Polypropene	Clotted cream tub
Polypropene	Polypropene	Film holding invoice documents
PET (polyester)	Polyester	Tray for biscuits
PET (polyester)	Polyester	Pastry tray
PET (polyester)	Polyester	Football shorts
Polystyrene	Polystyrene	Centrifuge tube tray
Polystyrene	Polystyrene	Sample vial tray
Polystyrene	Polystyrene	Coffee cup lid
ABS (acrylonitrile butadiene styrene)	ABS	Children's toy brick piece - green
ABS (acrylonitrile butadiene styrene)	ABS	Children's toy brick piece - white
ABS (acrylonitrile butadiene styrene)	ABS	Sheet
Polyamide/nylon	Polyamide	Black cable tie (Brand A)
Polyamide/nylon	Polyamide	White cable tie
Polyamide/nylon	Polyamide	Black cable tie (Brand B)

Nitrile (acrylonitrile butadiene rubber)	Nitrile	Nitrile glove (Brand A)
Nitrile (acrylonitrile butadiene rubber)	Nitrile	Nitrile glove (Brand B)
Nitrile (acrylonitrile butadiene rubber)	Nitrile	Nitrile glove (Brand C)
Polycarbonate	Polycarbonate	Water dispenser
PMMA/acrylic	PMMA	Perspex sheet (white)
PMMA/acrylic	PMMA	Perspex sheet (clear)
Polyurethane	Polyurethane	Wash bag
PTFE	PTFE	Stopcock for separating funnel
PTFE	PTFE	Tubing
PTFE	PTFE	Stirrer bar
Ethene vinyl acetate (EVA)	EVA	Vial septa
Tire wear particle (fresh)	TWP_fresh	Tire shaving (Brand A)
Tire wear particles (fresh)	TWP_fresh	Tire shaving (Brand B)
Tire wear particles (worn)	TWP_worn	Tire shaving (Brand A)
Tire wear particles (worn)	TWP_worn	Tire shaving (Brand B)
Polylactic acid	PLA	Coffee cup lid
Polylactic acid	PLA	Soup cup lid

Appendix S3.3: Criteria used to visually identify potential microplastic particles using light microscopy in this study.

Particles must match at least one of the criteria and at least one of the physical tests, and not have a clearly cellulitic structure.

Criteria:

- Unnatural shape
- Unnatural texture e.g. shiny, glassy, foamy
- Featureless fibre with a consistent width and texture
- Films of a homogeneous texture
- Unnatural colour compared to other particles in the sample, and is a homogeneous material/texture

Physical tests:

- Holds its shape when stretched or poked
- Resistance to easy breakage

Appendix Table S3.4:

Limits of detection (particles g^{-1} dw soil) for fine (25-178 µm) and medium (178-567 µm) microplastics in field soils collected in this study; determined from procedural blanks (n=8); LOD = mean of blanks + 3.3 x standard deviation; if a polymer was never detected in any blank samples, the LOD was set to 1 particle on the filter area; LF = landfill; UR = urban roadside; UP = urban parkland; WL = woodland.

NB: For coarse samples (>5678 µm), the entire 10 g extract was analysed under the light microscope and all suspected microplastic particles analysed with ATR-FTIR. No microplastics were detected in blank samples (n=8) for the coarse fraction. Taking 1 particle in the sample as the LOD (as was done for fine and medium fractions in this instance), the LOD for each polymer in each sample in the coarse fraction was 0.1 particles g^{-1} dw soil.

			Limit of detection (particles g^{-1} dw soil)																									
Site	Landuse	Fraction	Cellulose artfical modified	ethylene-vinyl-acetate	nitrile rubber	polyamide	Polybutadiene	polycaprolactone	polycarbonate	polychloroprene	polyester	polyetheretherketone	polyethylene	polyethylene, chlorinated	polyetyhlene oxidized	polyimide	polyisoprene-chlorinated	polylactic acid	polyoxymethlyene	polypropylene	polystyrene	polysulfone	polyvinylchloride	rubber type 1	rubber type 2	rubber type 3	acrylonitrile-butadiene	polyoxymethylene
LF1	LF	Fine	0.8	1.5	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	1.4	3.5	0.8	0.8	0.8	0.8	0.8	31.1	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
LF2	LF	Fine	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.4	3.3	3.3	3.3	3.3	3.3	29.9	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3
LF3	LF	Fine	0.8	1.4	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	1.4	3.4	0.8	0.8	0.8	0.8	0.8	29.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
LF4	LF	Fine	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	3.4	2.8	2.8	2.8	2.8	2.8	30.4	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8
LF5	LF	Fine	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	3.4	1.5	1.5	1.5	1.5	1.5	30.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
LF6	LF	Fine	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	3.5	2.7	2.7	2.7	2.7	2.7	30.9	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7

UR1	UR	Fine	1.1	1.4	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.4	3.3	1.1	1.1	1.1	1.1	1.1	29.6	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
UR2	UR	Fine	1.1	1.4	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.3	3.3	1.1	1.1	1.1	1.1	1.1	29.3	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
UR3	UR	Fine	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	3.4	1.7	1.7	1.7	1.7	1.7	29.8	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
UP1	UP	Fine	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	3.5	2.8	2.8	2.8	2.8	2.8	31.0	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8
UP2	UP	Fine	1.2	1.5	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.4	3.4	1.2	1.2	1.2	1.2	1.2	30.4	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
UP3	UP	Fine	1.3	1.4	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.4	3.3	1.3	1.3	1.3	1.3	1.3	29.6	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
BG1	WL	Fine	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	3.5	2.3	2.3	2.3	2.3	2.3	31.2	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
BG2	WL	Fine	1.0	1.5	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.4	3.4	1.0	1.0	1.0	1.0	1.0	30.2	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
BG3	WL	Fine	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	3.5	1.7	1.7	1.7	1.7	1.7	30.8	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
BG4	WL	Fine	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.4	3.1	3.1	3.1	3.1	3.1	30.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1
BG5	WL	Fine	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4	30.7	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4
BG6	WL	Fine	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.5	3.3	3.3	3.3	3.3	3.3	30.9	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3
BG7	WL	Fine	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	31.1	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
LF1	LF	Medium	1.7	4.3	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	3.1	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
LF2	LF	Medium	2.0	4.1	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	3.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
LF3	LF	Medium	0.7	4.1	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	1.4	0.7	0.7	0.7	0.7	0.7	3.0	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
LF4	LF	Medium	2.2	4.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	3.1	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
LF5	LF	Medium	2.1	4.2	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	3.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
LF6	LF	Medium	1.3	4.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.5	1.3	1.3	1.3	1.3	1.3	3.1	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
UR1	UR	Medium	0.6	4.1	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	1.4	0.6	0.6	0.6	0.6	0.6	3.0	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
UR2	UR	Medium	0.9	4.0	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	1.4	0.9	0.9	0.9	0.9	0.9	2.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9

UR3	UR	Medium	0.9	4.1	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	1.4	0.9	0.9	0.9	0.9	0.9	3.0	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
UP1	UP	Medium	0.6	4.3	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	1.5	0.6	0.6	0.6	0.6	0.6	3.1	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
UP2	UP	Medium	0.7	4.2	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	1.5	0.7	0.7	0.7	0.7	0.7	3.1	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
UP3	UP	Medium	0.6	4.1	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	1.4	0.6	0.6	0.6	0.6	0.6	3.0	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
BG1	WL	Medium	3.5	4.3	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
BG2	WL	Medium	1.6	4.2	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	3.0	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
BG3	WL	Medium	0.7	4.2	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	1.5	0.7	0.7	0.7	0.7	0.7	3.1	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
BG4	WL	Medium	1.7	4.1	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	3.0	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
BG5	WL	Medium	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
BG6	WL	Medium	1.6	4.2	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	3.1	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
BG7	WL	Medium	3.2	4.3	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2

Appendix Table S3.5:

Microplastic concentrations (number of particles g^{-1} dw soil) detected in field soils; only sites where microplastics were >LOD are shown; assignments of 'polyethene', 'polyethene (chlorinated)' and 'polyethene (oxidised)' from the siMPle reference library were combined to give a total particle number for polyethene.

Polymer	Fraction	Microplastic concentration (particles g^{-1} dw soil)							
		LF1	**LF4**	**LF6**	**UR1**	**UR2**	**UR3**	**UP1**	**UP3**
EVA	Fine (25-178 µm)							5.2	
	Medium (178-567 µm)								
	Coarse (>567 µm)	0.1							
Polyamide	Fine (25-178 µm)			2.7					
	Medium (178-567 µm)								
	Coarse (>567 µm)								
Polyethene	Fine (25-178 µm)			7.7			5.9	4.5	4.3
	Medium (178-567 µm)								
	Coarse (>567 µm)			0.2					
Polypropene	Fine (25-178 µm)			57.7	40.7				32.1
	Medium (178-567 µm)				3.2				
	Coarse (>567 µm)				0.1				
Polystyrene	Fine (25-178 µm)	2.4	2.8		1.1	1.1			
	Medium (178-567 µm)								
	Coarse (>567 µm)								
Polyester	Fine (25-178 µm)								
	Medium (178-567 µm)								1.2
	Coarse (>567 µm)								

Appendix S4.1: Protocols for the determination of pH, water holding capacity and organic matter content of soils used in this study.

pH: 3 x replicates of minimum 5.0 g dw of each soil was sampled for pH analysis. For this measurement, the sampled soil was shaken thoroughly for 5 minutes in 25 mL 0.01 M $CaCl_{2(aq)}$, left for a minimum of 2.5 hours, and measured using a pH probe (Sartorius PP-25; Sartorius Lab Instruments, Germany). The pH probe was calibrated daily at pH 4, 7 and 10.

Water holding capacity: For each soil, 100 g of soil of was added to a glass funnel, which was placed in a measuring cylinder. Glass wool was placed in the neck of the funnel to prevent soil from entering the measuring cylinder, whilst still retaining the ability for water to pass through. 100 mL of water was added to each soil. After no water was seen to pass into the measuring cylinder for 15 minutes, the volume in the measuring cylinder was recorded. The determination was performed in triplicate and a mean value for water holding capacity for each soil was calculated.

Organic matter content: Organic matter was measured by a loss on ignition (LOI) method. Aluminium trays were ashed in a preheated muffle furnace at 500 °C for 30 minutes. 5 g of soil was added to each tray. The trays were then dried in a preheated oven at 105 °C for 2 hours. Trays were then removed from the oven, cooled to 30 °C, and the mass was recorded. Trays were then placed in a preheated muffle furnace at 500 °C for exactly 120 minutes. Samples were removed from the furnace, cooled, and the mass was recorded. Samples were heated for a further 120 minutes at 500 °C to ensure complete loss of organic matter. 3 replicates were carried out for each soil, in addition to 3 blank trays.

Appendix S4.2: Oven temperature ramps in GC-MS analysis of plasticisers from the leaching and degradation experiments.

For leaching samples, 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.

For degradation samples, 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 278 °C, 1.5 °C min^{-1} to 282 °C, 120 °C min^{-1} to 300 °C, and held at 300 °C for 7.5 min.

Appendix Table S4.3: Model fit parameters for plasticiser degradation in Chiltern soil.

Plasticiser	0 order				1st order				2nd order			
	Adjusted R2	p value	k	t1/2 (days)	Adjusted R2	p value	k	t1/2 (days)	Adjusted R2	p value	k	t1/2 (days)
ATBC	0.5	0.00066	5.77	6.5	0.95	3E-12	0.281	2.5	0.64	0.000037	0.0869	-1.5
BBP	0.73	4.1E-06	6.64	9.7	0.71	6.5E-06	0.158	4.4	0.51	0.0005	0.00843	-1.3
DEHA	0.4	0.00057	0.4	35.0	0.64	1.6E-06	0.0344	20.1	0.81	1.6E-09	0.00571	7.6
DEHP	0.17	0.026	0.64	115.6	0.23	0.0098	0.00526	131.8	0.26	0.006	4.53E-05	157.2
DEHTP	0.63	2.1E-06	1.05	62.4	0.72	8.5E-08	0.0125	55.5	0.75	3.2E-08	0.000167	44.3
DEP	0.89	2.2E-06	17	2.6	0.87	5.6E-06	0.429	1.6	0.81	0.000041	0.0135	0.2
DiBP	0.87	1.1E-08	8.84	8.1	0.78	7.1E-07	0.263	2.6	0.27	0.015	0.0673	-2.3
DiDP	0.03	0.2	0.264	244.3	0.03	0.21	0.00216	320.9	0.04	0.18	0.000018	447.8
DMP	0.76	1.3E-06	4.24	6.6	0.99	2.5E-16	0.354	2.0	0.82	1.2E-07	0.197	-2.1
DnBP	0.84	6.4E-08	7.18	8.1	0.78	6.1E-07	0.247	2.8	0.32	0.0089	0.056	-2.2
DnOP	0.32	0.0022	0.927	85.8	0.45	0.00022	0.00778	89.1	0.54	0.000028	6.92E-05	93.6
TOTM	0.21	0.014	0.687	104.1	0.26	0.0063	0.0059	117.5	0.35	0.0013	5.39E-05	135.3

Appendix Table S4.4: Model fit parameters for plasticiser degradation in Dorset soil.

Plasticiser	0 order				1st order				2nd order			
	Adjusted R2	p value	k	t1/2 (days)	Adjusted R2	p value	k	t1/2 (days)	Adjusted R2	p value	k	t1/2 (days)
ATBC	0.9	0.000000036	2.78	42.6	0.84	0.00000084	0.0358	19.4	0.59	0.00051	0.00102	-8.8
BBP	0.68	0.00059	1.88	45.5	0.38	0.019	0.0237	29.2	0.21	0.074	0.00063	1.3
DEHA	0.47	0.0027	1.03	37.4	0.77	0.00001	0.0839	8.3	0.68	0.000088	0.00253	0.7
DEHP	0.36	0.011	0.902	116.4	0.14	0.091	0.00498	139.2	0.37	0.0092	0.0000293	168.9
DEHTP	0.44	0.0043	0.996	108.9	0.15	0.082	0.00526	131.8	0.53	0.0012	0.000029	165.2
DEP	0.93	0.00000027	2.79	33.2	0.77	0.0001	0.0519	13.4	0.31	0.034	0.00337	-7.7
DiBP	0.81	0.0000025	2.88	49.5	0.4	0.0064	0.0824	8.4	0.12	0.11	0.00297	-12.8
DiDP	<0.01	0.41	0.151	546.4	<0.01	0.68	0.00081	855.7	<0.01	0.56	0.00000432	1444.4
DMP	0.9	0.000000042	1.92	36.7	0.95	3.7E-10	0.0737	9.4	0.72	0.000036	0.0232	-11.8
DnBP	0.83	0.0000014	2.09	44.5	0.49	0.0023	0.0381	18.2	0.13	0.1	0.00589	-13.2
DnOP	0.33	0.015	0.679	130.3	0.1	0.14	0.00431	160.8	0.41	0.0061	0.0000288	202.8
TOTM	0.3	0.021	0.412	184.5	0.15	0.083	0.00284	244.1	0.27	0.028	0.0000199	339.2

Appendix Table S4.5: Model fit parameters for plasticiser degradation in Lufa soil.

Plasticiser	0 order				1st order				2nd order			
	Adjusted R2	p value	k	t1/2 (days)	Adjusted R2	p value	k	t1/2 (days)	Adjusted R2	p value	k	t1/2 (days)
ATBC	0.72	0.0000055	1.49	34.6	0.9	1.2E-09	0.0761	9.1	0.6	0.00011	0.0478	-12.9
BBP	0.91	0.00000078	5.5	18.8	0.7	0.00042	0.079	8.8	0.33	0.03	0.00267	-4.0
DEHA	0.75	0.000002	0.771	37.9	0.92	1.7E-10	0.0368	18.8	0.79	0.00000057	0.00339	-3.3
DEHP	0.38	0.0036	0.657	142.3	0.44	0.0015	0.00462	150.0	0.4	0.0031	0.0000334	156.3
DEHTP	0.25	0.02	0.582	167.5	0.32	0.0089	0.00378	183.4	0.38	0.0041	0.000025	202.4
DEP	0.59	0.0005	1.83	25.0	0.79	0.0000058	0.111	6.2	0.76	0.000014	0.0871	-3.5
DiBP	0.87	0.0000069	5.81	19.6	0.45	0.0097	0.105	6.6	0.14	0.12	0.028	-6.0
DiDP	0.01	0.28	0.185	462.2	0.05	0.19	0.00128	541.5	0.07	0.16	0.00000888	662.2
DMP	0.95	0.0000043	4.97	8.2	0.79	0.0008	0.348	2.0	0.68	0.004	0.208	-2.6
DnBP	0.82	0.00046	6.38	11.0	0.86	0.00022	0.0716	9.7	0.79	0.00081	0.00092	7.6
DnOP	0.52	0.00047	0.611	121.9	0.53	0.0004	0.00566	122.5	0.48	0.00081	0.0000549	116.6
TOTM	<0.01	0.66	0.113	885.0	<0.01	0.64	0.000607	1141.9	<0.01	0.58	0.00000345	1478.3

Appendix Table S4.6: Estimated pseudo-first order $t_{1/2}$ (days) of plasticisers in this study; * indicates insignificant degradation over the course of the experiment according to pseudo-first order model fit ($p < 0.05$); mean values for $t_{1/2}$ of individual plasticisers were only calculated when ≥2 soils produced significant model fits; see Appendix S3-S5 for full details of model fit parameters.

Soil	**DMP**	**DiBP**	**DEP**	**DnBP**	**ATBC**	**BBP**	**DEHA**	**DnOP**	**DEHTP**	**DEHP**	**TOTM**	**DiDP**
Agricultural	2.0	6.6	6.2	9.7	9.1	8.8	18.8	122.5	183.4	150.0	1141.9*	541.5*
Alkaline grassland	2.0	2.6	1.6	2.8	2.5	4.4	20.1	89.1	55.5	131.8	117.5	320.9*
Acidic heathland	9.4	8.4	13.4	18.2	19.4	29.2	8.3	160.8*	131.8	139.2	244.1	855.7*
Mean (± SD)	4.5 ± 4.3	5.9 ± 3.0	7.1 ± 5.9	10.2 ± 7.7	10.3 ± 8.5	14.1 ± 13.3	15.7 ± 6.5	105.8 ± 23.6	123.5 ± 64.4	140.3 ± 9.2	180.8 ± 89.5	-
LogK_{OW}	1.61	4.27	2.54	4.27	-	4.7	-	7.73	-	7.73	-	9.46
RMM	194	278	222	278	403	312	371	391	391	391	547	447

Appendix Table S5.1: Collated literature data concerning plasticiser occurrence in estuarine and coastal sediments; values refer to mean concentration (ng g^{-1}).

Study	DMP	DEP	DiBP	DnBP	BBP	DEHP	DnOP	DiNP	DiDP	DnNP	DPrP	DMEP	DMPP	DnHP	HEHP	DBEP	DCHP	DnPP	DPhP	DiPrP	DEEP	DEHA	DEHTP	ATBC	DINCH	TOTM
(Arfaeinia et al., 2019)	2547.5	3212.5	1747.5	6397.5	5280	11965	4125	nd	nd	1257.5	nd	770	70	672.5	190	742.5	1100	520								
(Jebara et al., 2021)		95	219	55	28.1	4590					13.7											3080	2420			
(S. Kim et al., 2020)	2.92	0.82	2.92	10.6	1.99	460		842	109													1.47	4.29	0.46	0.88	58.9
(S. Kim et al., 2021)	3.09	0.21	1.22	31.3	7.84	2140		826	493													3.48	84.6	9.84	15.9	954
(Y. Kim et al., 2021)	13	0.77	6.75	93	3.86	6960		483	69.1													16	141	8.12	12.8	150
(Lee et al., 2020)	14.7	0.52	1.36	9.1	28.3	380		116	44.6													2.57	9.66	0.83	3.77	3.6
(Malem et al., 2019)				250	nd	680	nd																			
(Sánchez-Avila et al., 2013)	nd	931			8	111																106.8				
(Stewart et al., 2014)	nd	nd		nd	166.2	1658	nd															nd				
(L. Y. Wang et al., 2021)	85.92375	99.22646	254.1833	255.0148	0.980833	478.8567	1.350833			7.266042	3.437708	0.953958				24.19146	0.163125	6.168542	0.248542	0.514167						
(Weizhen et al., 2020)	106.0557	72.15929	264.8414	144.0979	7.404286	92.92286	65.30786			149.1921	51.82357	80.28143		2.379286		55.585		97.57143			81.915					
(Zhang et al., 2018a)	622.3529	233.5294	4146.471	2866.471		4782.353												241.7647								
(Zhang et al., 2018b)	38.94737	42.63158	1466.053	2947.895	52.36842	1221.053	21.84211			2.894737		34.21053	21.84211				0.263158	0.526316	20.78947		67.10526					
(B. T. Zhang et al., 2020)	118.6	169.9	368.3	1021.6	458.8	1209.1	296.3				169.3	156.6	nd	101.3		123	nd	41.5			66.7					
(Z. M. Zhang et al., 2020a)	34.3	29.64737	977.2632	1886.053	6.226316	4345.842	6.225789	9.421053				44.37368	1.837895	7.236842		nd	3.521053	0.991053	9.157895		1.414211					
(Z. M. Zhang et al., 2020b)	16.71732	50.47679	2890.054	2760.607	20.72732	5506.321	nd	11.17375				42.24375	nd	1.73		nd	5.164107	0.994464	0.139643							
(Zhao et al., 2020)	29.09655	81.68966	466.2276	380.0931		2916.79																				

Appendix Table S5.2: Collated literature data concerning plasticiser occurrence in estuarine and coastal waters; values refer to mean concentrations (ng L^{-1}).

Reference	DMP	DEP	DiBP	DnBP	BBP	DEHP	DnOP	DiNP	DiDP	DnNP	DPrP	DMEP	DMPP	DnHP	DBEP	DCHP	DnPP	DPhP	DiPrP	DEEP	DEHA	DEHTP
(Chakraborty et al., 2021)	50	150		570	90	330	10														100	
(Huysman et al., 2019)		184.8438		669.75	76.71875	179.4063			23.625					11.25		14.65625	0					
(Jebara et al., 2021)		12600	75400	17200	0	71700					0										0	634000
(Liu et al., 2020)	33.31	28.45	0	158.09	3.09	140.31	0															
(Malem et al., 2019)				350	0	480	0															
(Mukhopadhyay and Chakraborty, 2021)	0	52.3		49.6	0	59.1	8.4														0	
(Paluselli et al., 2018a)	3.72	22.04	162.86	156.82	4.12	134.44	0				0											
(Paluselli et al., 2018b)	3.2	15.7	102.7	83.2	3.8	317.2																
(Paluselli and Kim, 2020)	1.487805	4.75122	9.331707	20.12927	0.792683	79.30976	0															
(Peñalver et al., 2022)		116	57.8	76.5		7.4															8.9	
(Sánchez-Avila et al., 2013)	2.1	189.3			14.7	65.7															11.5	
(L. Y. Wang et al., 2021)	17.43933	302.5567	5854.883	8526.467	39.00583	1887.52	87.55167			0.3005	0	0			0	0	8.824333	0	0			
(Weizhen et al., 2020)	238.7279	9.61	92.95857	167.5743	6.288571	390.9743	139.3993			101.6236	2.455	61.71714		5.947857	36.52857		0.838571			14.09571		
(Zhang et al., 2018a)	110.8105	59.85671	173.1048	192.8085	2.531519	241.3871	5.367089	20.92684				86.12342	15.35633	5.107089	3.406329	16.02177	4.559873	3.443671		2.82519		
(Zhang et al., 2018b)	3.69587	3.909348	423.0609	744.6957	0.738043	742.0087	0.210652			1.580652		55.29522	0.113261	0.135	0.766957	0.206957	0.287609	0				
(Z. M. Zhang et al., 2020a)	1.515519	3.729481	345.9838	750.7195	6.835649	972.3449	2.792857	5.269481				32.73805	5.112792	12.80526	0.479091	15.84468	2.490974	27.38143		1.341364		
(Z. M. Zhang et al., 2020b)	4.253795	9.389337	2000.557	2762.151	35.42018	682.8373	2.823072	8.761084				95.8609	2.229337	2.291084	3.249398	31.75711	4.537108	0.222289				