



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

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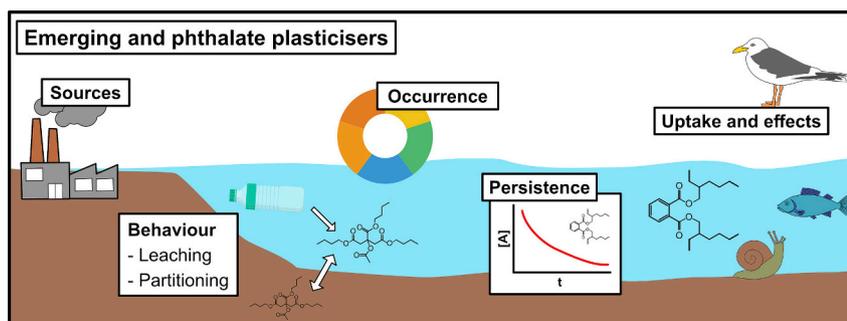
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HIGHLIGHTS

- Phthalates are being phased out of use and replaced with 'emerging' plasticisers.
- Emerging plasticisers and phthalates can enter estuarine and coastal environments.
- Emerging plasticisers may be present at comparable levels to phthalates.
- These compounds can be taken up by estuarine and marine organisms.

GRAPHICAL ABSTRACT



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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

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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.

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; ECHA, 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 (Billings et al., 2021). 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.

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.

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.

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 (Billings et al., 2021). 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 Σ phthalate concentration (16 congeners) in groundwater associated with a municipal landfill site were almost 4 times greater than in corresponding surface water, although measured concentrations were still relatively low (1.78–6.35 $\mu\text{g L}^{-1}$) compared to concentrations in leachate collected from the landfill (78 $\mu\text{g L}^{-1}$). Adjacent soils were, however, contaminated at levels higher than any water sample (681 $\mu\text{g kg}^{-1}$), 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 Σ phthalate concentrations (7 congeners) ranging from 1000 to 6000 $\mu\text{g L}^{-1}$ 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.

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; 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 (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 input of plasticisers 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).

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., 2013; 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 (Xu et al., 2022), indicating that the transfer of microplastic-associated plasticisers from soils to adjacent riverine sediments may be slow.

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., 2022a). 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 Σ phthalate (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 $\mu\text{g g}^{-1}$ 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.

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 Arfaeina et al. (2019), with Σ phthalate (16 congeners) found at greater concentrations in industrial (82 $\mu\text{g g}^{-1}$) areas than urban (13 $\mu\text{g g}^{-1}$) or natural rural (6.5 $\mu\text{g g}^{-1}$) 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 Σ phthalate concentration was an order of magnitude greater in industrial/commercial sediments (27.8 $\mu\text{g g}^{-1}$) than in agricultural ones (3.3 $\mu\text{g g}^{-1}$), and \sim 3 times greater than in residential area samples (8.8 $\mu\text{g g}^{-1}$). 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 (Arfaeina et al., 2019; Wen et al., 2018), the intensity of these inputs appears to be less than from industrial or residential sources (Arfaeina 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, Arfaeina et al. (2019) reported very high concentrations of DEHP (mean 2.0–30.3 $\mu\text{g g}^{-1}$ dw), DnBP (mean 0.9–12.0 $\mu\text{g g}^{-1}$ dw) and di-isobutyl phthalate (DiBP; mean 0.3–3.6 $\mu\text{g g}^{-1}$ 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 ($71.7 \mu\text{g L}^{-1}$), DnBP ($17.2 \mu\text{g L}^{-1}$) and DiBP ($75.4 \mu\text{g L}^{-1}$) 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.

3. Processes controlling plasticiser release and partitioning in aqueous environments

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 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.

Given the low vapour pressures (Table 1) and relatively high boiling points ($>300^\circ\text{C}$) 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 Σ phthalate was observed between pH 3–9, but concentrations of the measured phthalates at pH 11 were $<50\%$ 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 polyethylene (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-isodecyl phthalate (DiDP) and di-isononyl 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 ($\sim 0.01\text{--}4\%$ w/w), thus the effects of salinity appear complex and are likely to be compound and polymer specific.

Table 1

Physicochemical data for selected phthalate (legacy) and the most frequently studied emerging plasticisers; adapted from Billings et al. (2021); 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_{H_2O} (mg L^{-1})
Dimethyl phthalate	DMP	Phthalate	2.63×10^{-1A}	1.61 ^A	-5.4^A	4000 ^B
Diethyl phthalate	DEP	Phthalate	6.48×10^{-2A}	2.54 ^A	-5.01^A	1080 ^B
Di-isobutyl phthalate	DiBP	Phthalate	4.73×10^{-3A}	4.27 ^A	-4.27^A	6.2 (24 °C) ^B
Di-n-butyl phthalate	DnBP	Phthalate	4.73×10^{-3A}	4.27 ^A	-4.27^A	11.2 ^B
Benzyl butyl phthalate	BBP	Phthalate	2.49×10^{-3A}	4.7 ^A	-4.08^A	2.69 ^B
Diethylhexyl phthalate	DEHP	Phthalate	2.25×10^{-5A}	7.73 ^A	-2.8^A	0.27 ^B
Di-n-octyl phthalate	DnOP	Phthalate	2.52×10^{-5A}	7.73 ^A	-2.8^A	0.022 ^B
Di-isononyl phthalate	DiNP	Phthalate	6.81×10^{-6A}	8.6 ^A	-2.43^A	0.2 (20 °C) ^B
Di-n-nonyl phthalate	DnNP	Phthalate	6.81×10^{-6A}	8.6 ^A	-2.34^A	1.73×10^{-5B}
Di-isodecyl phthalate	DiDP	Phthalate	1.84×10^{-6A}	9.46 ^A	-2.06^A	0.28 ^B
Diethylhexyl adipate	DEHA	Adipate	1.13×10^{-4B}			0.78 (22 °C) ^B
Diethylhexyl terephthalate	DEHTP	Terephthalate	2.85×10^{-3B}			4.0 (20 °C) ^B
Acetyl tributyl citrate	ATBC	Citrate	4.00×10^{-2B}			1.7 ^B
Trioctyl trimellitate	TOTM	Trimellitate	5.07×10^{-4B}			3.9×10^{-4B}

^A (Net et al., 2015);

^B PubChem online database.

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 overlying 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 h (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 (Arfaeina 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., 2022a), 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 ionisable 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 (Arfaeina et al., 2019; Sun et al., 2013).

4. Occurrence of plasticisers in coastal environments

4.1. Phthalates in estuarine and coastal environments

A diverse range of phthalates have been studied in the coastal environment (Table 2). Most of these studies have been conducted in China (e.g. Liu et al., 2020; Paluselli and Kim, 2020; Weizhen et al., 2020), in common with the situation for terrestrial environments (Billings et al., 2021), 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 (Arfaeina et al., 2019), and Europe (Huysman et al., 2019; Paluselli et al., 2018a,b).

Phthalate occurrence in coastal and estuarine sediments is broadly comparable to those found in soils (Billings et al., 2021). 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 (Arfaeina 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 (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 3.1 and 3.2).

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 physicochemical properties, phthalate profiles in coastal and estuarine waters contain a higher proportion of lower molecular weight phthalates than seen in sediments (Fig. 1). 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) (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 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. (2018a) 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 Zhang et al. (2020b). Specifically, the contributions of DEHP, DnBP and DiBP in seawater were between 31 and 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 (Billings et al., 2021).

Table 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 $n \geq 3$; see Appendix Tables S1 and S2.

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	92.9–11,965	100	17	317	4612	7.4–71,700	100
DnBP	16	253	1194	nd-6398	94	16	271	2030	20.1–17,200	100
DEP	16	61.3	314	nd-3213	94	16	40.4	860	3.7–12,600	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-75,400	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	634,000	–	–	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	–	–	–	–	–

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; Kim et al., 2020; Kim et al., 2021b; Kim et al., 2021a; 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 (Kim et al., 2020; Kim et al., 2021b; Kim et al., 2021a; 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 (Σ_{emerging}). Mean concentrations of TOTM and DEHTP were 150 ng g⁻¹ dw (46% of Σ_{emerging}) and 141 ng g⁻¹ dw (43% of Σ_{emerging}) in sediment samples ($n=35$) spanning 15 years in an artificial freshwater lake on the Korean coast (Kim et al., 2021a). The highest reported mean sediment concentration of TOTM in any study of 954 ng g⁻¹ dw (89% of Σ_{emerging}) 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 Σ_{emerging} load (Kim et al., 2021b). Mean concentrations of DEHA, ATBC and DiNCH in these 4 Korean studies range from 1.5 to 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 (Kim et al., 2020; Kim et al., 2021b; Kim

et al., 2021a; 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 later 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 to 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 and 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 than reported by Sánchez-Avila et al. (2013) at 8.9 ng mL⁻¹ (Peñalver et al., 2022). Despite concentrations in sediment exceeding 3 $\mu\text{g g}^{-1}$ dw, DEHA was not detected in coastal waters ($n=165$) from the south Mediterranean by Jebara et al. (2021).

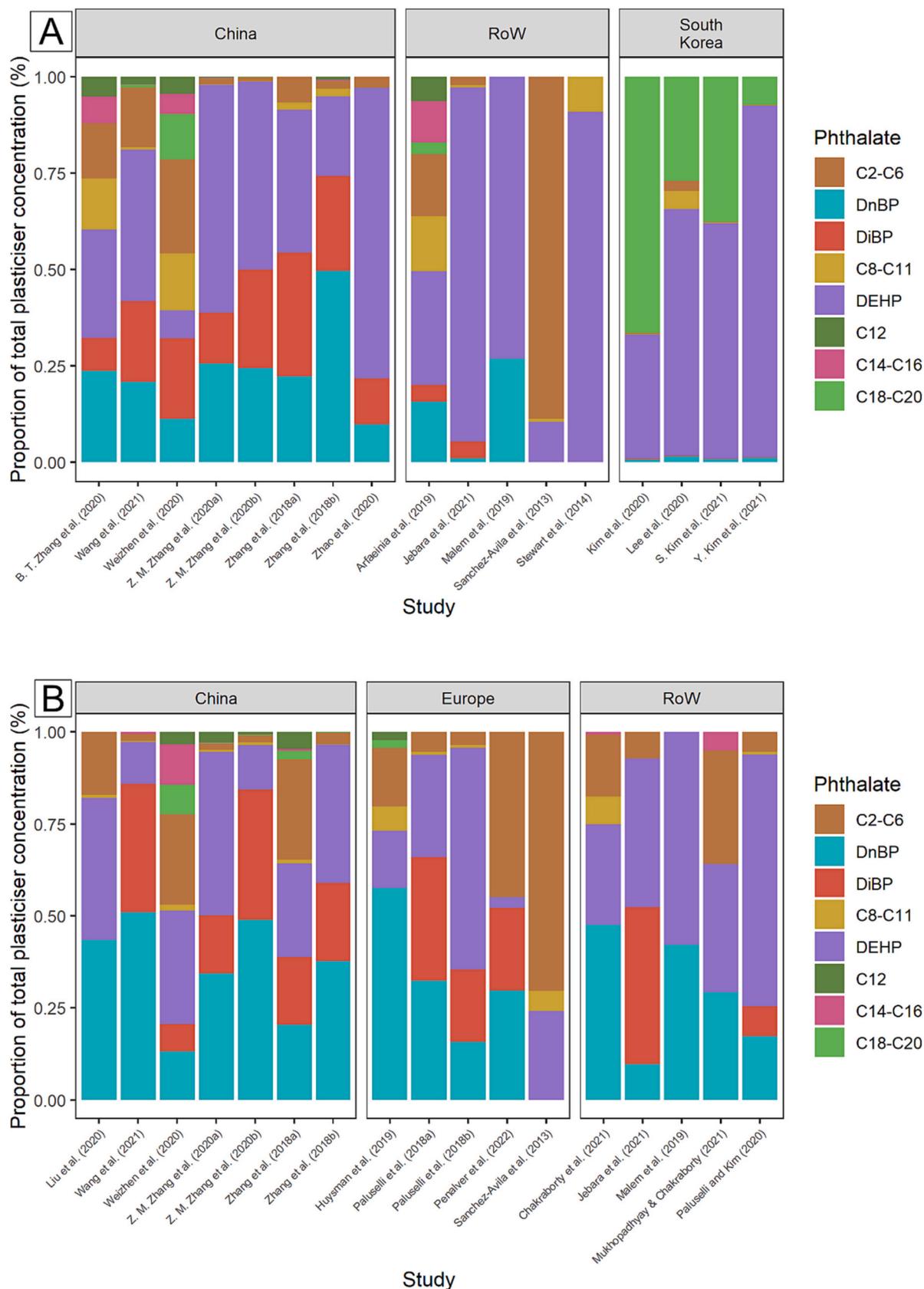


Fig. 1. Phthalate profiles in estuarine and coastal sediments (A) and water (B) from studies discussed in this review; profiles were calculated using the mean value for each phthalate reported in the study; data has been grouped by region and country where sensible to do so; RoW = rest of world; phthalates <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.

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 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 5.1), 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.

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 (Σ plasticiser) in estuarine and coastal media varies greatly between these studies (see Fig. 2). Generally, emerging plasticisers represent a relatively minor (<4%) proportion of Σ plasticiser in sediments (Kim et al., 2020; Kim et al., 2021a; Lee et al., 2020), however there are some exceptions to this

general trend. For example, DEHA represented 9.2% of Σ plasticiser (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 Σ plasticiser (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 Σ plasticiser (2 emerging, 6 phthalates), with DEHP again the dominant plasticiser (44% of Σ plasticiser). 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.

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 Σ plasticiser (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 Σ plasticiser), with the phthalates DiBP and DEHP accounting for only 9.3% and 8.8% of Σ plasticiser.

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

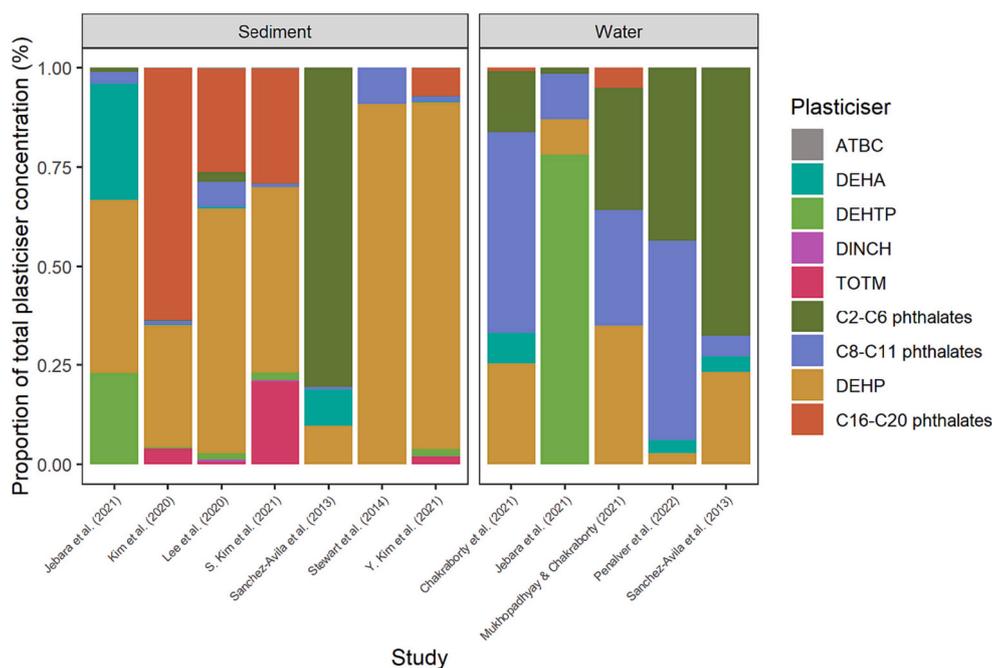


Fig. 2. Emerging and phthalate plasticiser profiles in estuarine and coastal systems in studies discussed in this review; only studies of co-occurrence of >1 class of plasticiser are shown; profiles were calculated using the mean value for each plasticiser reported in the study; plasticisers <LOD were 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.

plasticiser burden in estuarine and coastal environments.

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. Zhang et al. (2020a) found greater Σ phthalate 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. Σ phthalate (16 congeners) concentrations were significantly higher ($p < 0.05$) in the winter ($10.2 \mu\text{g L}^{-1}$) than in spring ($4.9 \mu\text{g L}^{-1}$) or summer ($2.1 \mu\text{g L}^{-1}$) 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. Σ phthalate (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 DEHP in seawater along the Tunisian coast over the course of a year. Concentrations of phthalates and emerging plasticisers (DEHA and DEHP) 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. Fate of plasticisers in coastal environments

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 $\log K_{OW}$ 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 (Billings et al., 2021) 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 (Billings et al., 2021; 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 to 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 (Billings et al., 2021). 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., 2022b). There have been few systematic studies concerning the effects of pH on plasticiser degradation in soils (Billings et al., 2021) 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).

5.2. 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; ECHA, 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; Hidalgo-Serrano et al., 2020; 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 (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; Savoca et al., 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; 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; 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 to 86 ng g⁻¹. These emerging plasticisers were detected at similar levels to phthalates (e.g. DEHP ranged from 15 to 300 ng g⁻¹), indicating that over half a decade before phthalates were restricted in the EU (ECHA, 2022; ECHA, 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. 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-isonyl 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; Forner-Piquer et al., 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.

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?

CRedit authorship contribution statement

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

Declaration of competing interest

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

Data availability

No new data was generated for this review article thus data sharing does not apply.

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Appendix A. Supplementary data

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