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Phthalate esters in marine ecosystems: Analytical methods, occurrence and distribution

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ABSTRACT

Phthalate esters are high production volume chemicals and are widely used as additives in the plastics industry. Since they are not chemically bound to the plastics, they can easily leach into the environment. They can also be transformed into phthalate monoesters via degradation or metabolization. As numerous studies have reported the negative effects of phthalate diesters and monoesters on marine biota, these contaminants are an emerging concern.

In this article we review the most important analytical methods for determining phthalate esters in seawater, marine sediments and biota. The QuEChERS method and ultrasound-assisted extraction are the most common techniques for extracting solid samples, while solid-phase extraction is the most common technique for seawater samples. We also describe the occurrence and distribution of phthalate esters in the marine environment. Bis(2-ethylhexyl) phthalate, di-n-butyl phthalate and diisobutyl phthalate, as well as their metabolites, are the main compounds detected in the reviewed matrices.

1. Introduction

The marine environment is a delicate ecosystem that is highly sensitive to sources of chemical contamination, such as industry, cities and agriculture. One major worldwide environmental concern today is plastic pollution. According to the United Nations Environment Programme, over 300 million tonnes of plastic waste are produced each year [1], of which 1.7–4.6% are estimated to end up in the oceans [2]. Plastics can be subject to mechanical weathering and photodegradation, which fragment the products into particles called microplastics (MPs). MPs can be transported by ocean currents over vast distances and are known to have an immense impact on marine ecosystems [3]. In view of the above, it is important to determine how organic pollutants released from plastic materials affect the marine environment. Phthalate esters (PAEs), which are not chemically bound to plastic products, can leach easily into the environment and become contaminants of concern.

PAEs are High Production Volume Chemicals commonly used as plasticisers to increase the flexibility and durability of plastics such as polyvinyl chloride. They can be divided into two groups depending on the length of their carbon chain: low-molecular-weight PAEs (3–6 carbon atoms) are mainly used in medical devices, adhesives, inks and paints, while high-molecular-weight PAEs (7–13 carbon atoms) are used, for example, in flooring, wires, coated fabrics and automotive applications. PAEs with only one or two carbon atoms in their chains are used as solvents and fixatives in personal care products but not as plasticisers [4]. However, emissions from commercial products are not the only route to PAEs contamination as these compounds can also reach marine ecosystems through direct discharge, atmospheric deposition and surface runoff [5]. Moreover, their highly lipophilic nature and high octanol–water partition coefficient (log K_{ow}) mean they can be adsorbed by suspended particles that can reach the bottom of aquatic environments and accumulate in the sediments [6]. Marine sediments can also act as an uptake source by organisms in these ecosystems [7].

Several studies have shown that when PAEs enter complex living organisms, they can be metabolised to the corresponding monoesters by hydrolytic, oxidative or conjugation processes in order to be excreted [8–10]. However, some of these derivatives can also occur through the microbial degradation, photolysis and hydrolysis of PAEs in the environment [11].

PAEs are considered endocrine disruptors because of their estrogenic effects in aquatic organisms. They are also shown to cause acute developmental toxicity in zebrafish embryos, which in turn leads to developmental abnormalities such as spinal curvatures, abnormal movements and pericardial oedema, and affects bone

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Abbreviations

ACN	acetonitrile
APCI	atmospheric pressure chemical ionisation
DCM	dichloromethane
DLLME	dispersive liquid–liquid microextraction
dSPE	dispersive solid-phase extraction
EI	electron ionisation
ESI	electrospray ionisation
EtOAc	ethyl acetate
FID	flame ionisation detector
GC	gas chromatography
GCB	graphitised carbon black
GOs	graphene oxide nanosheets
HRMS	high-resolution mass spectrometry
LC	liquid chromatography
LLE	liquid–liquid extraction
LODs	limits of detection
LOQs	limits of quantification
MAE	microwave-assisted extraction
m-dSPE	magnetic dispersive solid-phase extraction
MeOH	methanol
MPEs	phthalate monoesters
MPs	microplastics
MS	mass spectrometry
MS/MS	tandem mass spectrometry
MWCNTs	multi-walled carbon nanotubes
PAEs	phthalate esters
PCPs	personal care products
PDMS	polydimethylsiloxane
PLE	pressurised liquid extraction
QqQ	triple quadrupole
QuEChERS	quick, easy, cheap, effective, rugged and safe
SBSE	stir-bar sorptive extraction
SPE	solid phase extraction
SPME	solid phase microextraction
TD	thermal desorption
USAE	ultrasound-assisted extraction

development and heart rate [12]. Di-n-butyl phthalate (DnBP) and benzyl butyl phthalate (BzBP) can also cause mortality in embryos even at low concentrations [12]. Some PAEs present chronic toxicity and are suspected of affecting thyroid hormone levels [13]. The toxic effects of PAEs are not limited to aquatic species, however, since they have demonstrated estrogenic effects also in human cells, mammals and amphibians [14]. PAEs can also impair ovarian function in women [15]. Moreover, they can pass through the placental barrier and affect the developing foetus *in utero* [16]. More specifically, exposure to bis(2-ethylhexyl) phthalate (DEHP), DnBP, BzBP and diethyl phthalate (DEP) during pregnancy is associated with worse behaviour, lower cognitive scores and psychomotor development effects in children [17].

Although information on the toxicity of phthalate metabolites, or phthalate monoesters (MPEs), is much more limited, several studies associate their presence with alterations of thyroid hormones [18]. MPEs can also affect human sperm function [19], be harmful to mitochondria functions [20], increase oxidative stress, and induce liver damage [21,22]. Some studies have suggested that the toxicity associated with PAEs may be caused solely by or in combination with their free metabolites [23,24].

In view of the endocrine-disrupting potential of PAEs and their widespread presence in the environment, several governmental and international organisations have regulated or issued statements on the use of some of these chemicals and established limits of intake [25–29].

Examining the presence of PAEs and MPEs and determining their occurrence and distribution in delicate ecosystems such as the marine environment is essential for assessing their impact on the environment. One aim of this review is therefore to describe and compare the analytical methods used to determine the presence of the compounds of interest in marine compartments such as seawater, sediments and biota. Another is to describe their occurrence and distribution in the marine environment while also highlighting the impact human activities responsible for industrial, plastic and microplastic pollution have on the environment.

2. Analytical methods

Like most emerging organic contaminants, PAEs and MPEs are found at very low concentrations in the environment (ng/g or ng/L), so suitable analytical methods are needed in order to determine them in complex samples. These methods, which we discuss at length in this review, must include efficient extraction procedures and sensitive instrumental methods. Tables 1 and 2 summarise the most important analytical methods used to determine PAEs and MPEs in marine environmental samples.

2.1. Instrumental analysis

Gas chromatography (GC) and liquid chromatography (LC) are the most common instrumental techniques for determining these compounds (Tables 1 and 2).

Due to the low solubility and polarity on account of their long side chains, GC is the usual technique for determining PAEs. The usual columns for separating these compounds are fused silica columns coated with (5%-phenyl)-methylpolysiloxane [30–37], though 100% dimethylpolysiloxane columns [38,39] (35%-phenyl)-methylpolysiloxane [40] and low-polarity polymeric columns [41,42] have also been successfully used.

To determine PAEs in marine matrices, GC is most often coupled with mass spectrometry (MS) using single quadrupole analysers [6,30,31,33–35,37,39,41] or tandem mass spectrometry (MS/MS) with triple quadrupole (QqQ) analysers [32,36,40]. Electron ionisation (EI) is the preferred ionisation source for these compounds. Flame ionisation detectors (FID) [38,42] can also be used, though their selectivity and sensitivity may not be sufficient to determine the compounds of interest at low concentrations.

Due to their high polarity and low volatility, MPEs, on the other hand, need to be derivatised to be determined by GC [43,44]. Although Baini et al. [30] proposed a GC–MS method for simultaneously determining four PAEs and three MPEs without derivatising the MPEs, they did not provide an extended discussion of the development of the GC–MS method.

MPEs are therefore almost always determined by LC on their own or in combination with PAEs. Several reversed-phase columns have been used to separate PAEs and MPEs, the most common of which are C_{18} [44–52] stationary phase columns. C_8 [32] and C_{12} [43] columns have also provided good separation results.

Methanol (MeOH) and acetonitrile (ACN) are commonly used as organic modifiers for the mobile phase in LC methods. For PAEs, optimisation of the composition of the mobile phase is not described extensively in the articles. For MPEs, studies comparing separation efficiency when using MeOH/water or ACN/water as the mobile phase have reported that results are better with the latter for several types of columns [32,53,54].

Table 1
Analytical methods for determining PAEs and MPEs in seawater.

Compounds	Extraction technique	Instrumental technique	LOD (ng/L)	LOQ (ng/L)	Ref.
PAEs: DMP, DEP, DnPrP, DiBP, DnBP, BzBP, DEHP, DnOP	SPE (Oasis HLB)	GC–MS	0.11–2.73	–	[34]
MPEs: MMP, MEP, MnBP, MiHP, MBzP, MiHpP, MEHP, MnOP, MiNP, MiDP	SPE (Oasis HLB)	LC–MS/MS	0.19–3.9	–	[43]
PAEs: DMP, DEP, DnBP, DnPP, BzBP, DCHP, DnHP, DBzP, DEHP, DiNP, DiDP	SPE (Oasis HLB)	LC–HRMS	PAEs: 5–50	PAEs: 10–75	[44]
MPEs: MMP, MEP, MnBP, MnPP, MCHP, MnHP, MBzP, MEHP, MiNP			MPEs: 5–25	MPEs: 10–50	
PAEs: DMP, DEP, DnBP, BzBP, DEHP, DnOP	SPE (MWCNTs: GO)	GC-FID	36–1410	120–4700	[42]
PAEs: DnPrP, DnBP, DnPP, DiPP, BzBP, DCHP, DEHP, DiNP, DiDP	m-dSPE (Fe_3O_4@pDA)	GC–MS	–	1.8–319	[33]
PAEs: DMP, DEP, DnBP, DiBP, DnPP, BzBP, DPhP, DCHP, DnHP, DEHP, DnOP, DiNP, DMEP, DEEP, DMPP, DBEP	SPME (PDMS)	TD–GC–MS	0.05–0.32	–	[39]
PAEs: DMP, DEP, DnBP, DEHP	SBSE (PDMS)	TD–GC–MS	5–21	–	[41]
PAEs: DMP, DEP, DnBP, DiBP, DnPP, BzBP, DPhP, DCHP, DnHP, DEHP, DnOP, DMEP, DEEP, DMPP, DBEP	SBSE (PDMS)	GC–MS	0.08–489	0.27–1630	[35]
PAEs: DMP, DEP, DAP, DnBP, DiBP, DiHpP, DEHP	DLLME	GC-FID	40–4520	–	[38]

As we can see in Tables 1 and 2, LC is always coupled with mass spectrometers to determine PAEs and MPEs. The most common analysers are ion trap for MS [45], QqQ for MS/MS [32,43,46–49,51] and Orbitrap for high-resolution mass spectrometry (HRMS) [44,52,55].

Electrospray ionisation (ESI), which is the most common interface for these compounds, provides good ionisation efficiencies for PAEs in positive mode and for MPEs in negative mode [52]. However, atmospheric pressure chemical ionisation (APCI) has also been occasionally used for this purpose [56]. When a previous study by our group [52] also compared ESI and APCI for determining PAEs and MPEs, instrumental limits of detection (LODs) and limits of quantification (LOQs) were similar with both interfaces for all compounds. Mobile phase additives are usually added to enhance the ionisation efficiency obtained. In particular, concentrations of 0.01–1% of acetic acid [32,43,45,47,48,52] or formic acid [46,49,51] are usually added to the mobile phases.

2.2. Extraction techniques and clean-up strategies

The most suitable strategies for sample extraction and clean-up depend on the characteristics of the matrix and the properties of the analytes of interest.

In the next section we review the most common and most interesting methods for extracting PAEs and MPEs simultaneously or separately.

2.2.1. Seawater samples

Several techniques have been used to extract PAEs and MPEs from seawater. The most common of these is solid phase extraction (SPE) (see Table 1), though microextraction techniques have also been used.

SPE, GC and LC are currently preferred due to their low consumption of organic solvents and the simplicity of the procedures. SPE can also provide high sample preconcentration factors because they can extract large volumes of sample. Since low concentrations of some PAEs and MPEs are expected in seawater samples, it is essential to increase the enrichment factor of the extraction methods used.

Since PAEs and MPEs have a wide range of polarities, polymeric sorbents with a hydrophilic–lipophilic balance, such as Oasis HLB and Strata X, are also used to extract them. Paluselli et al. [34], for example, used Oasis HLB to extract eight PAEs from large volumes of seawater. These authors tested various elution solvents, i.e. acetone, dichloromethane (DCM), ethyl acetate (EtOAc), methanol and n-hexane, to increase extraction recoveries. N-hexane was useful only for eluting less polar PAEs such as DEHP and DnOP. In contrast, more polar solvents such as acetone and MeOH yielded low extraction recoveries for these compounds. DCM and EtOAc, with extraction recoveries above 81% and 85%, respectively, provided the best results. EtOAc was chosen as the best elution solvent. Sample volumes of 100, 200, 500 and 1000 mL and sorbent masses of 200 and 400 mg were also tested. Since the extraction recoveries were satisfactory for all combinations, the authors selected 1 L of sample to maximise the enrichment factor of the extraction step, and 200 mg of Oasis HLB to reduce the cost and time needed for the procedure. Even under optimised conditions, the extraction recoveries obtained for DEHP and DOP were 10%. The authors attributed the loss of DEHP and DOP to the absorption of the compounds onto glassware and suggested correcting it by using deuterated DEHP as a surrogate standard. With this method, relative recoveries ranged from 95% (DnOP) to 115% (DPrP), while LODs were 0.11–2.73 ng/L.

Similarly, Blair et al. [43] used 500 mg Oasis HLB cartridges to determine six single MPE isomers and four MPE isomeric mixtures in 500 mL of seawater. Ultrapure water and a 35% MeOH/water solution were used to wash the cartridges, and the compounds were eluted with EtOAc and ACN. The authors obtained recoveries between 58% (MiDP) and 122% (MBzP) and LODs of 0.19–3.9 ng/L. Huysman et al. [44] also used Oasis HLB to simultaneously extract 11 PAEs, nine MPEs and seven phenols from seawater.

Commercial sorbents are not the only option for extracting PAEs, however. Habibi et al. [42] proposed a simple SPE method combining multi-walled carbon nanotubes (MWCNTs) and graphene oxide nanosheets (GOs) as adsorbents to extract six PAEs. These authors tested several ratios of this combination and various amounts of sorbent to obtain the maximum extraction recoveries possible. They also tested several elution solvents and sample parameters. Briefly, tetrahydrofuran was more effective at eluting the compounds than other common solvents such as acetone, MeOH and *n*-hexane due to the strong, unique interactions of the compounds with the sorbents. Moreover, the volume and flow rate of the sample and the elution solvent were significant parameters for the extraction recoveries. Interestingly, adding a low percentage of

Table 2
Analytical methods for determining PAEs and MPEs in solid samples.

Compounds	Matrices	Extraction technique and clean-up	Instrumental technique	LOD (ng/g)	LOQ (ng/g)	Ref.
PAEs: DMP, DEP, DnBP, DiBP, DnPP, BzBP, DCHP, DnHP, DEHP, DnOP, DnNP, DMEP, DEEP, DMPP, DBEP	Sediments	USAE (Acetone/Hexane 1:1)	GC–MS	7–27	23–74	[6]
PAEs: DEHP **MPEs:** MEHP	Krill, basking shark (muscle), stranded fin whale (blubber and muscle)	USAE (Acetone)	LC–MS	1–5	2–10	[45]
PAEs: DMP, DEP, DnBP, BzBP, DEHP, DnOP	Marine turtles (muscle, liver, gonad and fat tissues)	USAE (ACN)	LC–HRMS	–	0.1–10	[50]
PAEs: BzBP, DnHP, DEHP, DiOP, DnDP **MPEs:** MnBP, MBzP, MEHP	Neuston–plankton, cetaceans (Blubber)	USAE (DCM/Hexane) and lipid digestion with sulphuric acid	GC–MS	1–10	–	[30]
PAEs: DMP, DEP, DnBP, BzBP, DEHP **MPEs:** MEHP	Neuston–plankton, scleractinian coral	USAE (acetone) and LLE (water and hexane)	LC–MS/MS	0.7–21	–	[49]
PAEs: DMP, DEP, DnBP, DiBP, DnPP, BzBP, DPhP, DCHP, DnHP, DEHP, DnOP, DiNP, DMEP, DEEP, DMPP, DBEP	Sediments	USAE (DCM) and SPE (CNW-BOND Si)	GC–MS	0.12–1.60	–	[39]
PAEs: DnPrP, DnBP, DnPP, DiPP, BzBP, DCHP, DEHP, DiNP, DiDP	Sea sand	USAE (ACN) and m-dSPE (Fe_3O_4@pDA)	GC–MS	–	0.020–4.0	[33]
PAEs: DMP, DEP, DnBP, BzBP, DEHP, DnOP	Sediments	USAE (MeOH) and HS-SPME	GC–MS	1–79	1–142	[64]
PAEs: DMP, DEP, DnBP, BzBP, DEHP **MPEs:** MEHP	Scleractinian coral, sponge, clam, colonial hydrozoan	USAE (Acetone) and BioSPME (C_{18})	LC–MS/MS	0.2–2.1	1–5	[48]
PAEs: DMP, DEP, DAP, DnPrP, DiPrP, DnBP, DiBP, DnPP, BzBP, DPhP, DCHP, DnHP, DEHP, DnOP, DnNP, DMEP, DEEP, DMPP, DBEP	Fish	QuEChERS and dSPE (PSA, $MgSO_4$)	GC–MS/MS	0.01–10	0.05–20	[36]
PAEs: DMP, DnBP, BzBP, DEHP, DnOP **MPEs:** MnBP	Mussels	QuEChERS and dSPE (PSA, $MgSO_4$)	LC–MS/MS	3–15	9–45	[51]
PAEs: DMP, DEP, DnBP, BzBP, DEHP, DnOP **MPEs:** MMP, MEP, MnBP, MBzP, MEHP, MnOP	Seafood	QuEChERS and dSPE (PAEs: Lipifiltr®; MPEs: C_{18})	LC–HRMS	1–100	5–250	[55]
PAEs: DMP, DEP, DnBP, DEHP, DnOP **MPEs:** MMP, MEP, MnBP, MEHP, MnOP	Seafood	QuEChERS and SPE (PSA)	LC–MS/MS (MPEs) GC–MS/MS (PAEs)	PAEs: 0.034–2.2 MPEs: 0.019–1.0	–	[32]
PAEs: DMP, DEP, DnBP, DiBP, DnPP, BzBP, DPhP, DCHP, DnHP, DEHP, DnOP, DiNP, DMEP, DEEP, DMPP, DBEP	Seafood	QuEChERS and SPE (Cleanert® PAE)	GC–MS/MS	0.15–0.78	–	[40]
PAEs: DMP, DEP, DnBP, DiBP, BzBP, DEHP, DnOP	Posidonia oceanica (a), seafood (b), sediments (c)	QuEChERS	GC–MS	–	(a, b): 0.002–0.020 (c): 0.0003–0.0017	[31]
MPEs: MMP, MEP, MnBP, MiHP, MBzP, MiHpP, MEHP, MnOP, MiNP, MiDP	Sediments (a), seafood (b)	PLE (Water) and SPE (Oasis MAX)	LC–MS/MS	(a): 0.01–0.20 (b): 0.05–0.99	–	[43]
PAEs: DMP, DEP, DnBP, BzBP, DEHP **MPEs:** MMP, MEP, MnBP, MBzP, MEHP, MnOP	Seafood	PLE (MeOH), SPE (Bond Elut Plexa)	LC–HRMS	1–100	2.5–250	[52]
PAEs: DMP, DEP, DnPrP, DnBP, DiBP, DnPP, BzBP, DCHP, DnHP, DEHP, DnOP, DMEP, DEEP, DMPP, DBEP	Sediments	MAE (MeOH/EtOAc 1:1)	GC–MS	24–392[a]	–	[37]
MPEs: MMP, MEP, MnBP, MiBP, MBzP, MEHP, MnOP, MEOHP, MEHHP	Fish	Deconjugation and SPE (Oasis HLB)	LC–MS/MS	0.10–25.8	0.21–65.5	[46]
MPEs: MMP, MEP, MnBP, MiBP, MnPP, MiPP, MCHP, MnHP, MBzP, MnHpP, MEHP, MnOP, MnNP, MnDP, MEOHP, MEHHP	Harbour porpoises	Deconjugation and SPE (ABS Elut-NEXUS cartridges)	LC–MS/MS	0.17–0.84	0.50–2.50	[47]

[a] LOD expressed as ng/L instead of ng/g.

organic modifier (MeOH) to the samples before loading greatly increased the extraction recoveries of the less polar compounds due to the greater solubility of the long-chain PAEs in water, which hindered their adsorption onto glassware. However, the extraction recoveries obtained with this method ranged from 83 to 98%, which are similar to those obtained by methods using Oasis HLB. Also, the LODs were 36–1410 ng/L, which are between two and three orders of magnitude higher than those obtained by GC–MS (see Table 1) due to the low sample volume (100 mL) and the use of GC-FID.

Despite the good results, SPE has an important handicap when used to extract PAEs from any kind of sample. Most commercial sorbents are available only in the form of plastic cartridges, which can leach PAEs into the extract and alter the results of the analyses [57]. If glass SPE cartridges are unavailable, procedural blanks must be regularly performed to correct contamination from the plastic cartridges.

Dispersive solid-phase extraction (dSPE), a variant of SPE, has also been used to extract PAEs from seawater samples (Table 1). The main advantage of dSPE is that it is less time-consuming than SPE. It can also prevent some of the most common difficulties of sample-loading in SPE, such as cartridge blocking or the need for a controlled constant sample flow rate [58]. The fact that no plastic cartridges are needed for this procedure also minimises plastic-derived interferences. Jiménez-Skrzypek et al. [33] developed a magnetic-dispersive solid-phase extraction (m-dSPE) method using polymer-coated magnetic nanoparticles as the sorbent to extract 10 PAEs from 50 mL of seawater. Recoveries ranged from 79 to 116%. LOQs (using GC–MS) were 1.8–319 ng/L, which are slightly higher than those obtained with conventional SPE, probably because of a low enrichment factor.

Microextraction techniques such as solid-phase microextraction (SPME) followed by thermal desorption (TD) can also be used to extract PAEs from seawater samples. The main advantages of this technique are that it is both fast and simple because the sampling, extraction and preconcentration are conducted in a single step [59,60]. Also, desorbing the analytes from the probe does not require organic solvents, which makes it a promising extraction technique for green sample treatment methods [61]. It should also be borne in mind, however, that, due to their low volatility, this technique is not suitable for subsequently determining MPEs.

Zhang et al. [39] used a SPME fibre (coated with polydimethylsiloxane (PDMS)) to extract 16 PAEs from 10 mL of sample by direct immersion. These authors optimised extraction time and temperature, which affect the efficiency of the extraction, and evaluated the effects of salinity on extraction efficiency. Their results suggested that since salinity had little effect on recoveries, the method can be applied to samples with different salinities without affecting the results. Good relative recoveries ranging from 77 to 114% were obtained for all compounds except DMP and DEEP. The low recoveries (55%) for DMP can be explained by its log K_{ow}, which is much smaller than that of the others. The LODs were 0.05–0.32 ng/L, which are similar to those obtained by GC–MS with conventional SPE methods (Table 1).

Another useful microextraction technique is stir-bar sorptive extraction (SBSE). Like SPME, SBSE can be followed by TD to extract the analytes from the sorbent. PDMS-coated magnetic stir bars have been used to extract DMP, DEP, DnBP and DEHP, with recoveries of 14%, 47%, 136% and 102%, respectively [41]. These large differences in recoveries are again caused by the log K_{ow} of the analytes. SBSE methods usually have more sensitivity than SPME methods due to the greater coating and, therefore, the greater surface contact area [35,59]. However, in this case the LODs ranged from 5 to 21 ng/L, which is slightly higher than the values obtained by SPME and GC–MS. However, the authors provided no information about the instrumental limits or the optimisation of the SBSE parameters, which makes it difficult to explain the results. SBSE can also be combined with liquid desorption, which makes the extraction technique also compatible with LC. Si et al. [35] developed a method to extract 14 PAEs from seawater by optimising both SBSE and desorption efficiency. Though they provided no information about extraction recoveries (comparing only peak areas for the optimisation), the LODs ranged from 0.08 to 489.13 ng/L. The authors pointed out that the LODs for high-molecular-weight PAEs were higher than those for the most hydrophilic compounds (such as DMP) since compounds such as DOP and DEHP interact strongly with PDMS and cannot be desorbed efficiently from the adsorbent. Although SBSE can present the same advantages as SPME in comparison with SPE, it should be borne in mind that SBSE often requires longer extraction times.

Dispersive liquid–liquid microextraction (DLLME) has also been used successfully to determine PAEs in seawater samples. The main advantages of this technique are its speed and simplicity. The dispersion of the extraction solvent in the liquid sample also leads to large enrichment factors, high recoveries, and low extraction times [62]. Although the solvent volumes are very small, the solvents themselves are non-environmentally friendly, which makes this technique incompatible with green-analytical-chemistry approaches [63]. When 20 μL of carbon tetrachloride dispersed in 0.5 mL of MeOH was used to successfully extract seven PAEs from seawater [38], the LODs were 40–4520 ng/L, which are similar to those obtained by Habibi et al. [42] (Table 1).

Although several microextraction techniques appear promising for extracting PAEs from seawater samples, SPE is the most common technique thanks to its high recoveries and high enrichment factors (see Table 1). It should also be borne in mind that SPE carried out with a suitable sorbent/solvent combination enables the PAEs and their metabolites to be extracted simultaneously, thus making this procedure extremely useful for monitoring these contaminants in the environment. However, since SPE plastic cartridges are also a source of PAE and MPE contamination, procedural blanks should be taken regularly for adjustment purposes.

2.2.2. *Solid samples*

Sediments and biota are the most analysed solid samples from aquatic environments. Such samples are usually freeze-dried, homogenised and sieved before extraction, though there are also reports of extraction from wet samples. Moreover, the complexity of these samples means that a clean-up step is usually later required to remove any co-extracted matrix components that may interfere with analyses of the compounds of interest. The same clean-up procedures can be used for both sediment and biota samples. However, activated copper is sometimes added to sediment samples during extraction to remove sulphur interferents [6,31]. Note also, however, that as most authors do not report any clean-up optimisation or matrix effect values, it is difficult to evaluate the effectiveness of these procedures.

Several extraction techniques have been used to extract solid samples. These include ultrasound-assisted extraction (USAE), quick, easy, cheap, effective, rugged and safe (QuEChERS) extraction, pressurised liquid extraction (PLE), and microwave-assisted extraction (MAE) (Table 2). The most common of these techniques is USAE [6,30,33,39,45,48–50,64]. USAE is simple and versatile and allows the use of lower quantities of solvent and shorter working times than other extraction techniques [65]. Also, it can be performed with organic solvents of different polarities to extract the compounds of interest. Studies in the literature on the extraction of PAEs and MPEs, for example, used acetone [45,48,49], ACN [33,50], MeOH [64], DCM [39] and solvent mixtures such as acetone/hexane (1:1) [6] and DCM/hexane (1:1) [30]. Major drawbacks with this technique, however, are the low power of ultrasound baths and the need for repeated extractions [61,66].

USAE has occasionally been used to extract a wide range of PAEs from sediments and biota without any clean-up step [6,45], yielding relative recoveries ranging from 67 to 111% and LODs ranging, respectively, from 7 to 27 ng/g (GC–MS) and from 1 to 5 ng/g (LC–MS). Similar recoveries and LOQs were obtained by Savoca et al. [50] with LC–HRMS by diluting the extract before injection. Lipid digestion with sulphuric acid [30] and liquid–liquid extraction (LLE) with water and hexane [49] have been used as simple clean-up procedures to remove interferents from coral and neustonic/planktonic samples and from cetacean blubber. SPE and variants of the technique can also be used to remove matrix interferents from extracts and increase the selectivity of the methods. When, for example, Zhang et al. [39], conducted the clean-up step with a silica-based SPE cartridge, they obtained comparable recoveries and better LODs for the determination of PAEs in sediments than those obtained with no clean-up step by GC–MS. Similarly, Jiménez-Skrzypek et al. [33] successfully used a m-dSPE method developed for extracting PAEs from seawater as a clean-up step for sea sand extracts. SPME with PDMS–DVB [64] and biocompatible [48] fibre coatings have also been used with satisfactory results to clean up sediment and biota extracts.

QuEChERS has also widely been used to extract PAEs and MPEs from solid samples (Table 2). This technique involves initially extracting a wet sample with an organic solvent followed by a salting-out step to separate the two liquid phases (aqueous and organic). ACN is the usual organic solvent for most QuEChERS methods, though solvent mixtures such as hexane/DCM (1:1) [40] and DCM/EtOAc (1:1) [31] have also been reported. This first extraction step can also be complemented with USAE after adding the salts to the mixture [32,36,40]. NaCl and $MgSO_4$ are widely used in most QuEChERS methods for the salting-out step [67]. In a previous paper [55], we compared the extraction efficiency of PAEs and MPEs from fish with salt mixtures from three official QuEChERS methods: the original QuEChERS method (1 g NaCl, 4 g $MgSO_4$), the European standard method EN 15662:2019 (1 g NaCl, 4 g $MgSO_4$, 1 g sodium citrate tribasic dihydrate, 0.5 g sodium citrate dibasic sesquihydrate), and the AOAC official method (1.5 g sodium acetate, 6 g $MgSO_4$). We found no significant differences between the original method and the AOAC method. The EN method, however, yielded the best results, obtaining extraction recoveries ranging from 79 to 120% for most compounds.

After extraction by QuEChERS, a clean-up step with dSPE is usually added to remove interferents. For PAEs, 50–150 mg of PSA is reported to yield the best extraction efficiencies in biota samples [36,51], though other sorbents such as C_{18}, Florisil, alumina and combinations with graphitised carbon black (GCB) have also yielded good results. However, neither of the above studies evaluated the improvement or otherwise of the matrix effect after dSPE, which makes it difficult to evaluate the usefulness of the clean-up steps. However, in a previous study [55] we compared the matrix effect in seafood extracts after dSPE using three sorbents: PSA, Florisil and a novel sorbent named Lipifiltr®, which is indicated for removing lipids from samples following QuEChERS extraction. The lowest values of the matrix effect were obtained with Lipifiltr®. Little information is available about dSPE as a clean-up step for MPEs following QuEChERS extraction. Only C_{18} and GCB are reported to yield good extraction efficiencies for a wide range of MPEs, with the best matrix effects being achieved with 200 mg of C_{18} [55]. SPE has also been used to clean up QuEChERS extracts from biota samples, with PSA cartridges [32] and specific SPE cartridges being used to extract PAEs [40]. These methods yielded similar LODs and LOQs to those obtained with USAE followed by LC–MS/MS and GC–MS, which shows that QuEChERS is a good alternative.

Castro-Jiménez et al. [31] proposed a different approach based on QuEChERS to extract PAEs and other compounds from sediments and biota: the extraction of lyophilised samples by sonication followed by two clean-up steps. First, they evaluated the extraction solvent mixture by comparing the background noise and blank levels of five organic solvent mixtures. They then compared a traditional QuEChERS first step (i.e. $MgSO_4$ and sodium acetate) with dSPE without extraction salts (i.e. $MgSO_4$, PSA and C_{18}) followed by sonication. The latter technique yielded slightly better results for most compounds and acted as an extra clean-up step. The authors proposed a second dSPE step with Florisil and alumina. As mentioned earlier, classic QuEChERS procedures involve extraction with an organic solvent of a sample with water content. Salts must then be added to promote the separation of phases and the partitioning of the analytes into the organic phase. Although the authors view this method as an innovative QuEChERS sequence, it could also be defined as a USAE followed by two dSPE clean-up steps since the water content of the sample and the salting-out step are completely disregarded in the extraction procedure. However, as Table 2 shows, the LOQs with this method are much lower than those achieved with traditional QuEChERS procedures and USAE methods (using GC–MS in all cases).

Blair et al. [43] developed a PLE method to analyse MPEs in sediments and seafood tissues. The extraction was performed with an accelerated solvent extractor, using water as the extraction solvent, at 70°C for 5 min through three cycles. SPE with Oasis MAX cartridges was used to clean up the extracts. This method yielded high recoveries for most MPEs. The LODs ranged from 0.01 to 0.99 ng/g, which are similar to those obtained by USAE and QuEChERS followed by LC–MS/MS [32,48,51] (Table 2). In contrast, in a previous study [52] we proposed a PLE method to simultaneously analyse PAEs and MPEs in seafood in which, for the extraction, we used MeOH at 80°C for 10 min. We then purified the extracts with a freezing lipid filtration to promote the precipitation of lipids and interfering compounds followed by SPE with Bond Elut Plexa cartridges. Since this method enables the simultaneous determination of PAEs and MPEs, it is a useful tool for monitorisation.

MAE [37] has also been used to extract PAEs from sediments. The main advantages of MAE are lower extraction times and less solvent consumption thanks to the use of microwaves to heat the solvent [68]. The extraction was performed with a microwave digestion system using a mixture of MeOH/EtOAc 1:1 (v/v) as the extraction solvent at 150°C for 20 min and a microwave power of 750 W. This method yielded recoveries ranging from 84 to 105% for all compounds.

As we mentioned earlier, when PAEs enter complex living organisms, they are rapidly transformed into MPEs and conjugated in order to be excreted. Most studies therefore only analyse what are called free-MPEs. To analyse all MPEs present, a deconjugation step is needed, which is performed by adding ammonium acetate (1 M) and β-glucuronidase to the sample before digestion at 37°C [46,47]. SPE can then be used to further extract and clean up the samples.

Although similar results are obtained with all the extraction techniques discussed (see Table 2), QuEChERS is the only one that can be performed without the need for special equipment such as an ultrasonic bath, a PLE or a microwave digestion system. This probably makes QuEChERS the fastest and simplest technique for analysing PAEs and MPEs in solid marine samples. However, since it also requires more manipulation than the other techniques, it can more easily lead to environmental contamination.

3. Occurrence and distribution

Although the occurrence of PAEs in environmental marine samples has been a focus of study in recent years, much less attention has been devoted to the occurrence of MPEs. In the next section we detail the occurrence of these compounds in marine ecosystems, discuss potential sources of PAE contamination, and analyse their spatial and temporal variations (see Fig. 1).

3.1. Seawater

Numerous PAEs and several MPEs have been determined in seawater samples collected from water masses around the world [33–35,38,39,41–44]. Detailed information about the occurrence of these compounds in seawater is shown in Table 3.

According to the studies in our review, 23 PAEs have been detected, mainly on the coast of China (the Yellow Sea, the Bohai Sea and the East China Sea). DEHP, DnBP and DiBP, with the highest concentrations and detection frequencies in most studies, are the main PAEs detected in the aquatic environment.

As Table 3 shows, the highest DEHP concentration (168 μg/L) was recorded in Tunisia along the coastline of the Mahdia

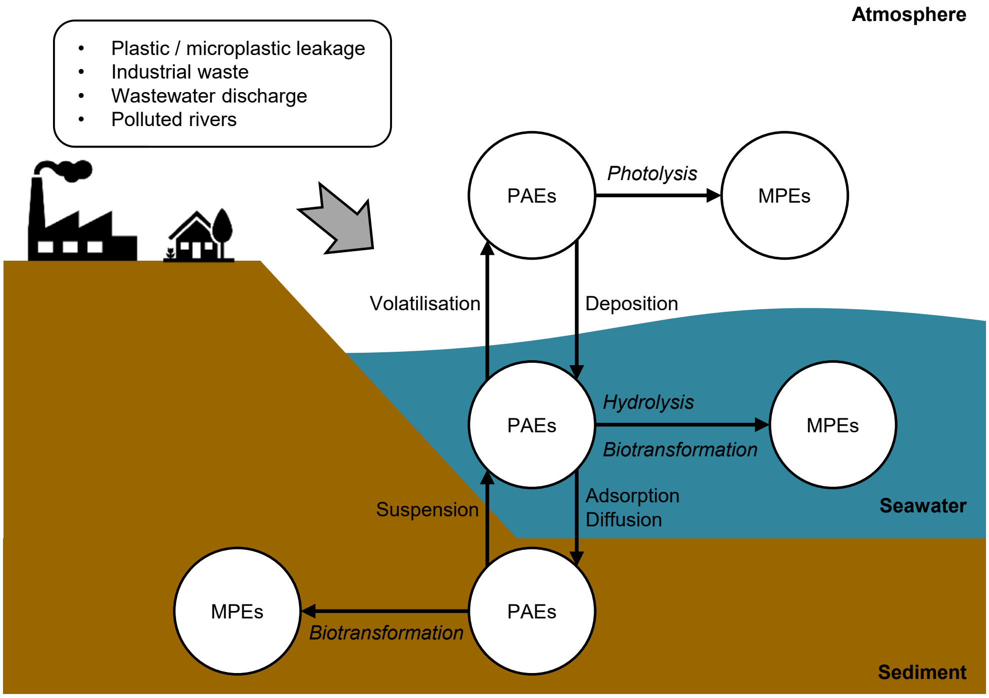

Fig. 1. Sources, spatial distribution and degradation of phthalate esters in the environment.

Governorate. In that study [69], the detection frequency of DEHP was 93%. Surface water samples were collected at sampling stations close to pollution sources such as factories, towns and tourist areas [69]. The second highest concentration of DEHP (9738 ng/L) was found at Hangzhou Bay in China (East China Sea). In this case the detection frequency was 100% with samples collected near Shanghai, the largest and most populated city in China [70]. Lower but still significant concentrations of DEHP were reported in the Gulf of Thailand (1160 ng/L) [71] and in the North Sea along the Belgian coastline (766 ng/L) [44]. In both cases, the samples were taken from coastal zones near populated areas. The lowest maximum concentrations (9.2 ng/L), on the other hand, were detected in the seamount area of the Tropical Western Pacific Ocean, far from any human activity [72]. Similar associations can be made with regard to DnBP and DiBP. The highest concentrations (30.5 μg/L for DnBP and 106 μg/L for DiBP) were also found in Tunisia, with detection frequencies of 89 and 93%, respectively [69]. The second highest concentrations (17.952 μg/L for DnBP and 17.256 μg/L for DiBP) were also reported at Hangzhou Bay in China [70].

The sources of these compounds are diverse and include plastic leakage, industry and household waste. The high log K_{ow} and, therefore, the high hydrophobicity of DEHP, DnBP and DiBP also make their degradation by photolysis, hydrolysis or biological processes more difficult, which can facilitate their accumulation [73].

Since PAEs are not homogenous in seawater, their spatial (horizontal and vertical) distribution has been studied on various occasions. With regard to their horizontal distribution, most studies agree that the total concentration of PAEs is significantly lower in offshore areas than in inshore regions, which are strongly influenced by large rivers, ports and cities, all of which are affected by human activities that cause heavy pollution [5,41,70,72,73]. Coastal current transportation also seems to increase PAE concentrations in certain areas, probably due to the large amounts of plastic waste that are accumulated due to surrounding currents [74,75]. A significant positive correlation has been found between MP abundance and PAE concentration in surface water, since MPs tend to adsorb waterborne contaminants while simultaneously leaching their own plasticisers. The degradation and decomposition of the MPs and plastic debris then release a multitude of chemicals (such as PAEs) into the seawater [5,73]. By taking into account this correlation, the migration of organic contaminants such as PAEs can be used as an indirect method for tracing MPs in the environment. In addition to MPs, atmospheric deposition is also a potential source of PAEs [72,74].

With regard to the vertical distribution of PAEs, the concentration range seems to be more homogenous at offshore sites than at coastal sites due to the lack of heavily polluted inputs [74]. Most studies report high concentrations at the surface, followed by a slight decrease at greater depths before a final increase near the bottom. The decrease in concentration with depth is probably due to microbial degradation, while the increase near the bottom appears to be caused by the remobilisation of sediments. Due to their log K_{ow}, PAEs tend to be adsorbed onto particulate matter which then settles on the seabed. Combined with the degradation of MPs and plastic debris accumulated on the seafloor, this means that the resuspension of sediments can easily cause PAEs to migrate from the sediments into the seawater [34,75,76].

Significant differences in the concentrations of PAEs have also been observed depending on the season and the weather. The total concentration of PAEs is generally higher in dry seasons than in wet seasons because seawater is somewhat diluted in wet seasons by increased river flows [41,70,76]. Moreover, as microbial bioreactivity and biomass levels drop in winter, there is less PAEs degradation, which could explain the higher PAE concentrations in areas where the dry season corresponds to winter [76]. Another factor that could influence PAE concentration is tide. In seasons when tides are stronger, they can enhance the resuspension of sediment, thus increasing the concentration of contaminants [70]. Heo et al. [41] also studied the influence of rainfall on PAE concentration by sampling the same areas before and after rainfall

Table 3
Occurrence of PAEs and MPEs in seawater (ng/L) and sediment samples (ng/g).

Compounds	Seawater	Sediment	Sampling zone	Ref.
Phthalate acid estersrowhead				
DMP	0.08–830	4–4180	China	[5,37,70,73–78]
	1.4–6.4	<0.002–0.2	Mediterranean Sea	[31,34]
	–	70–6670	Persian Gulf	[6]
	20–100	–	South Korea	[41]
	n.d.–7	–	Tropical western Pacific Ocean	[72]
DEP	0.25–2404	2.5–1778	China	[5,37,70,73–78]
	6.9–50	<0.001–2.1	Mediterranean Sea	[31,34]
	<25–753	–	North Sea (Belgium)	[44]
	–	290–6360	Persian Gulf	[6]
	20–150	–	South Korea	[41]
	n.d.–2.1	–	Tropical western Pacific Ocean	[72]
	<10–17,000	64–142	Tunisia	[69]
DAP	0.67–52	0.78–28	China	[70]
DnPrP	–	1.12–492	China	[37,70]
	1.30–1.31	–	Tropical western Pacific Ocean	[72]
	–	10.3–20.2	Tunisia	[69]
DiPrP	–	0.11–7.39	China	[70]
	n.d.–0.89	–	Tropical western Pacific Ocean	[72]
DnBP	11–17,952	0.17–15,103	China	[5,37,70,73–78]
	63.4–466	0.3–3.1	Mediterranean Sea	[31,34]
	<5–2645	–	North Sea (Belgium)	[44]
	–	720–12,650	Persian Gulf	[6]
	40–360	–	South Korea	[41]
	230–770	n.d.–800	Thailand	[71]
	2.2–13	–	Tropical western Pacific Ocean	[72]
	<29–30,500	42–82	Tunisia	[69]
DiBP	5–17,256	1.78–7980	China	[5,37,70,73–78]
	1.9–14	–	Tropical western Pacific Ocean	[72]
	–	110–4238	Persian Gulf	[6]
	56.5–383.4	1.9–5.7	Mediterranean Sea	[31,34]
	<5–106,000	152–394	Tunisia	[69]
DnPP	0.04–146	0.13–2170	China	[5,37,70,75,77]
	–	80–1100	Persian Gulf	[6]
	n.d.–1.6	–	Tropical western Pacific Ocean	[72]
BzBP	0.09–344	0.29–1283	China	[5,37,70,73–75,77]
	3.2–4.8	0.8–1.9	Mediterranean Sea	[31,34]
	<10–343	–	North Sea (Belgium)	[44]
	–	450–10,110	Persian Gulf	[6]
	n.d.–5.5	–	Tropical western Pacific Ocean	[72]
	–	<0.37–43	Tunisia	[69]
DPhP	0.27–1996	0.14–710	China	[5,70,75]
	0.84–5.3	–	Tropical western Pacific Ocean	[72]
DCHP	0.05–705	0.2–37	China	[5,70,75,77]
	–	100–2340	Persian Gulf	[6]
	1.1–7	–	Tropical western Pacific Ocean	[72]
DnHP	0.05–443	8.4–395	China	[5,37,75,77]
	<10–37	–	North Sea (Belgium)	[44]
	–	80–1530	Persian Gulf	[6]
DiHP	n.d.–2.3	–	Tropical western Pacific Ocean	[72]
DEHP	9–9738	0.31–22,160	China	[5,37,70,73–75,77,78]
	102.9–296.5	4.2–319.5	Mediterranean Sea	[31,34]
	66–766	–	North Sea (Belgium)	[44]
	–	1080–35,000	Persian Gulf	[6]
	30–300	–	South Korea	[41]
	310–1160	n.d.–1650	Thailand	[71]
	2.0–9.2	–	Tropical western Pacific Ocean	[72]
	<26–168,000	4150–5240	Tunisia	[69]
DnOP	0.09–1386	0.12–970	China	[5,37,70,75,77]
	–	<0.003–0.1	Mediterranean Sea	[31]
	–	680–8589	Persian Gulf	[6]
	n.d.–1.7	–	Tropical western Pacific Ocean	[72]
DnNP	0.22–3.32	1–30	China	[70]
	–	120–3350	Persian Gulf	[6]
DiNP	0.13–126	10–70	China	[5,75,77]
DiDP	<25–108	–	North Sea (Belgium)	[44]
	n.d.–4.4	–	Tropical western Pacific Ocean	[72]
DMEP	0.2–811	0.3–585	China	[5,37,70,75–77]
	–	30–1620	Persian Gulf	[6]
DEEP	1.07–95	2–1670	China	[5,37,75]
		60–620	Persian Gulf	[6]

Table 3 (*continued*)

Compounds	Seawater	Sediment	Sampling zone	Ref.
	–			
DMPP	1.57–579	8–280	China	[5,75,77]
	–	40–240	Persian Gulf	[6]
DBEP	0.64–234	0.40–879	China	[5,37,70,75,77]
	–	90–1020	Persian Gulf	[6]
HEHP	–	40–510	Persian Gulf	[6]
Phthalate acid ester metabolitesrowhead				
MMP	0.42–20	1.28–4.16	Canada	[43]
	<20–2542	–	North Sea (Belgium)	[44]
MEP	4.41–39	0.45–3.63	Canada	[43]
MnBP	51–108	5.3–20	Canada	[43]
	<5–292	–	North Sea (Belgium)	[44]
MnPP	<20–138	–	North Sea (Belgium)	[44]
MBzP	<0.22–6.05	0.19–3.02	Canada	[43]
	<5–58	–	North Sea (Belgium)	[44]
MiHP	<1.3–0.52	<0.07–0.53	Canada	[43]
MiHpP	2.71–6.61	0.05–0.07	Canada	[43]
MEHP	45–57	0.33–0.84	Canada	[43]
	<25–740	–	North Sea (Belgium)	[44]
MnOP	<0.5–1.06	0.04–0.2	Canada	[43]
MiNP	<0.48–29	0.01–1.83	Canada	[43]
MiDP	2.23–8.25	<0.13–0.14	Canada	[43]

events. These authors found that the total concentration of PAEs and the individual concentrations of DnBP and DEHP fell by over 80% after rainfall whereas the concentrations of DMP and DEP remained stable. This can be explained by the fact that these compounds, which are typically present in personal care products (PCPs) [74], are more associated with proximity to large cities and wastewater discharges than with atmospheric deposition, sediment resuspension, plastic degradation or river influence. Since PAE concentrations seem to be sensitive to weather changes, in order to observe trends over time passive sampling should perhaps be included when monitoring these compounds.

Little information is available about the occurrence and distribution of MPEs in seawater. From the articles reviewed, we found that 11 MPEs have been determined in water masses from Canada and Belgium. MEHP and MnBP, which are the metabolites of the predominant PAEs in seawater, are the main MPEs detected in the samples. Table 3 shows that the highest MPE concentrations were reported in the North Sea along the Belgian coast. Specifically, the highest concentrations were 740 ng/L for MEHP and 292 ng/L for MnBP. This study also reported high concentrations of MMP, which may be linked to the use of PCPs [74].

More studies are needed, however, to better determine the occurrence of MPEs in seawater, ascertain whether these concentrations are correlated, and examine the sources of MPE pollution in seawaters.

3.2. Sediments

In addition to seawater samples, several PAEs and MPEs have been determined in marine sediment samples all over the world. For example, 21 PAEs have been determined in various sampling zones, with DEHP, DnBP and DiBP the main species in all studies. Other compounds, including DMP and DEP, were mainly determined in coastal areas on account of their relationship with PCPs [74].

Table 3 shows that the highest DEHP concentration (35 μg/g) was recorded in Asalouyeh, a town in the Persian Gulf where sediment samples were collected from sampling stations close to an industrial region. The detection frequency of DEHP in that study was 100% [6]. The second highest concentration (22 μg/g) was observed near Hangzhou Bay in the East China Sea. In this case, the detection frequency was also 100%, while DEHP concentrations were 59% of total PAE concentrations [5]. Lower concentrations of DEHP were also reported in Tunisia (5240 ng/g) [69] and the Gulf of Thailand (1650 ng/g) [71]. The highest concentrations for both DnBP and DiBP (15.1 μg/g and 7980 ng/g, respectively) were reported in the same sampling zones in the East China Sea [5]. The second-highest concentrations of DnBP and DiBP (12.7 μg/g and 4238 ng/g, respectively) were found in the Persian Gulf [6].

In general, most studies report that concentrations in the sediments are significantly higher than those in the surrounding seawater [5,69,70,75–77]. This can be explained by the lipophilic properties of PAEs, especially those with high molecular weights, which enable them to adsorb into carbon-rich particles and surfaces [6,69,75]. Wang et al. [70] concluded that the partitioning of PAEs between sediments and seawater depends on the properties of the compounds. More specifically, they found that while PAEs with low molecular weights tend to migrate from sediments to seawater and those with high molecular weights tend to diffuse from seawater to sediments, PAEs with medium molecular weights fall into a dynamic equilibrium distribution between both phases. This partitioning mechanism can explain why in some studies DEHP has the highest concentrations observed in sediments while the main species detected in the overlying water is DnBP [76].

The spatial distribution of PAEs has also been studied in sediments. All these studies agree that PAE concentrations are higher in coastal or inshore areas than in offshore areas owing to the large input of wastewater, sediments and contaminants from land carried mainly by rivers and water discharges [5,31,37,70,77,78]. For this reason, Arfaeinia et al. [6] evaluated how land use affects PAE concentration in marine sediment samples. These authors found that total PAE concentration was significantly higher in areas affected by industries or located near agricultural fields than in urban and natural areas. They also associated the concentrations in industrial regions with industrial wastewater discharges and those close to agricultural fields with the consumption of plastic films in agriculture (e.g. for greenhouses, plastic mulching, fertilisers and packaging) and the fact that the water used for irrigation usually comes from heavily polluted rivers located nearby.

Only Blair et al. [43] studied the occurrence of MPEs at significantly lower concentrations than those of PAEs. Unlike what is observed with seawater, MEHP was detected at very low concentrations in all sediment samples (Table 3), whereas low-molecular-weight MPEs such as MMP, MEP and MnBP were the predominant

Table 4
Occurrence of PAEs and MPEs in biota samples (ng/g).

Compounds	Fish and cetacean	Crustacean	Mollusc	Invertebrates	Neuston/plankton	Seagrass/Posidonia	Sampling zone	Ref.
Phthalate acid estersrowhead								
DMP	–	–	19.6–27.3	–	–	–	Aegean Sea	[51]
	0.03–220	0.18–282	0.14–6.1	–	–	–	China	[8,40]
	<0.01–0.3	–	<0.01–0.3	–	–	<0.01–1.2	Mediterranean Sea	[31]
	<2.5–10	–	–	–	–	–	Spain	[55]
DEP	0.11–28	0.16–114	0.02–27	–	–	–	China	[8,40]
	–	–	2.3	0.4–2.2	1.4–18.3	–	Maldives	[48,49]
	1.6–7.0	29–230	2.4–3.1	–	–	2.7–8.9	Mediterranean Sea	[31,83]
	<50–492	<50–3393	53–401	–	–	–	Spain	[52,55]
	561–2700	–	–	–	–	32.3–80.9	Tunisia	[69]
DnPrP	<0.274–322	–	–	–	–	<0.133–38.6	Tunisia	[69]
DnBP	–	–	103–109	–	–	–	Aegean Sea	[51]
	0.22–491	0.47–437	1.51–138	–	–	–	China	[8,40]
	–	–	8.4	0.5–7.1	4.2–22	–	Maldives	[48,49]
	2.6–36.9	9–46	<0.002–17.6	–	–	12.1–166.7	Mediterranean Sea	[31,83]
	<50–373	–	<10–135	–	–	–	Spain	[52,55]
	<0.318–2990	–	–	–	–	307–491	Tunisia	[69]
DiBP	22–777	33–5313	46–78	–	–	–	China	[40]
	3.4–22.9	27–240	4.8–22.8	–	–	15.4–15.8	Mediterranean Sea	[31,83]
	434–1480	–	–	–	–	<0.094–120	Tunisia	[69]
BzBP	–	–	13.4–15.5	–	–	–	Aegean Sea	[51]
	–	–	1.9	0.5–1.6	3.2–25.1	–	Maldives	[48,49]
	<0.01–3.6	–	<0.01–17.5	–	54–475	<0.01–5.6	Mediterranean Sea	[30,31]
	<7.5–161	–	–	–	–	–	Spain	[52,55]
	<0.763–739	–	–	–	–	<0.510–171	Tunisia	[69]
DCHP	<0.19–127	<0.19–83	–	–	–	–	China	[40]
DnHP	–	–	–	–	17.47–889	–	Mediterranean Sea	[30]
DEHP	–	–	261–280	–	–	–	Aegean Sea	[51]
	3.9–1941	1.58–717	47.4–828	–	–	–	China	[8,40]
	–	–	28.4	2.1–20.2	18–228	–	Maldives	[48,49]
	11.4–12.3	15–300	53.5–638	–	34.95–2699	149.5–699.6	Mediterranean Sea	[30,31,83]
	<100–1562	<100–482	<100–656	–	–	–	Spain	[52,55]
	<12–398	–	–	–	–	–	Svalbard	[82]
	772–1460	–	–	–	–	465–845	Tunisia	[69]
DnOP	–	–	42.8–73.0	–	–	–	Aegean Sea	[51]
	1.54–28.1	0.51–0.91	1.65–4.96	–	–	–	China	[8]
	–	–	15.3–18.8	–	–	<0.02–23.6	Mediterranean Sea	[31]
DiOP	–	–	–	–	13.21–513	–	Mediterranean Sea	[30]
DnNP	<0.67–208	<0.67–109	–	–	–	–	China	[40]
DBEP	<0.3–291	<0.3–23	–	–	–	–	China	[40]
Phthalate acid ester metabolites								
MMP	–	–	4.43–21.82	–	–	–	Canada	[43]
	0.06–3.12	0.07–5.07	0.02–1.71	–	–	–	China	[8]
	5.67–5.73	–	–	–	–	–	Mediterranean Sea	[46]
	0.34–8.72	–	–	–	–	–	Norwegian Sea	[47]
MEP	–	0.29–2.61	5.63–25.54	–	–	–	Canada	[43]
	0.06–4.98	0.30–7.13	0.30–3.31	–	–	–	China	[8]
	–	–	4.5	1.1–3.2	1.9–27.1	–	Maldives	[48,49]
	32–34	–	–	–	–	–	Mediterranean Sea	[46]
	2.62–17.4	–	–	–	–	–	Norwegian Sea	[47]
	<5–178	<5–260	12–39	–	–	–	Spain	[52,55]
MnBP	6.63–60.9	8.66–38.2	75.0–585	–	–	–	Canada	[43]
	0.81–49.0	2.41–59.1	2.81–34.5	–	–	–	China	[8]
	141–207	–	–	–	8.5–590	–	Mediterranean Sea	[30,46]
	1.73–299	–	–	–	–	–	Norwegian Sea	[47]
	<5–10	<5	<5–72	–	–	–	Spain	[52,55]
MiBP	159–253	–	–	–	–	–	Mediterranean Sea	[46]
	3.78–419	–	–	–	–	–	Norwegian Sea	[47]
MnHP	0.17–4.64	–	–	–	–	–	Norwegian Sea	[47]
MiHP	–	–	0.61–1.55	–	–	–	Canada	[43]
MBzP	–	–	<0.06–1.74	–	–	–	Canada	[43]
	1.99–2.01	–	–	–	6.0–93.7	–	Mediterranean Sea	[30,46]
	0.69–7.29	–	–	–	–	–	Norwegian Sea	[47]
MnHpP	0.21–1.87	–	–	–	–	–	Norwegian Sea	[47]
MiHpP	–	0.017–0.31	1.83–2.97	–	–	–	Canada	[43]
MEHP	0.24–1.1	0.39–1.13	3.30–6.72	–	–	–	Canada	[43]
	1.34–56.3	2.9–72.9	6.72–11.6	–	–	–	China	[8]
	–	–	1.8	1.5	3.5–12.1	–	Maldives	[48,49]
	1.48–377.82	–	–	–	98.41–2709	–	Mediterranean Sea	[30,45,46,84]
	<25–162	7–40	35–117	–	–	–	Spain	[52,55]
MnOP	–	–	0.34–0.43	–	–	–	Canada	[43]
	0.05–8.56	0.04–1.74	0.20–2.15	–	–	–	China	[8]

Table 4 (*continued*)

Compounds	Fish and cetacean	Crustacean	Mollusc	Invertebrates	Neuston/plankton	Seagrass/Posidonia	Sampling zone	Ref.
	75–89	–	–	–	–	–	Mediterranean Sea	[46]
	0.19–5.53	–	–	–	–	–	Norwegian Sea	[47]
MnNP	24.0–98.9	–	–	–	–	–	Norwegian Sea	[47]
MnDP	0.25–17.6	–	–	–	–	–	Norwegian Sea	[47]
MEOHP	33–35	–	–	–	–	–	Mediterranean Sea	[46]
	0.20–2.12	–	–	–	–	–	Norwegian Sea	[47]
MEHHP	85–103	–	–	–	–	–	Mediterranean Sea	[46]
	0.17–5.93	–	–	–	–	–	Norwegian Sea	[47]

species in those samples. The fact that low-molecular-weight PAEs (such as DMP, DEP and DnBP) have higher degradation rates than high-molecular-weight PAEs (such as DEHP) may explain this change in distribution [79–81]. However, no definitive conclusions can be drawn from only one sampling zone. More studies are needed to confirm whether this trend can be extended to sediment samples from other areas.

3.3. Biota

A wide range of marine-inhabiting species, from simple living forms such as seagrass and invertebrates to extremely complex organisms like cetaceans and sharks, have been subject to the determination of PAEs and MPEs.

Table 4 shows that, like in seawater and sediment samples, the most frequently determined PAEs in biota are DEHP, DnBP and DiBP, followed closely by DEP. The highest concentrations were determined in muscle tissue samples from edible fish, crustaceans and molluscs. The highest concentration of PAEs, for example, was reported for DiBP in species of crab captured in Hangzhou Bay in China (5313 ng/g) [40], while the highest concentration of DEP was found in shrimp samples bought in Spanish markets (3393 ng/g) [52]. The highest DnBP concentration (2990 ng/g) was reported in gilt-head bream caught near the Tunisian coastline. This last study also reported that the highest concentrations of DiBP (1480 ng/g) and DEP (2700 ng/g) were in fish [69]. On the other hand, the highest concentration of DEHP was found in neuston/plankton samples collected from the Mediterranean Sea near the coastline of Genoa [30].

Much more information is available about the occurrence of MPEs in marine biota than about their occurrence in seawater or sediment samples. MEHP, MnBP and MiBP, followed by MEP (Table 4), are the predominant MPEs in most species. Unlike with PAEs, the highest MPE concentrations were detected in neuston/plankton samples. Baini et al. [30] reported 2709 ng/g of MEHP and 590 ng/g of MnBP in neuston/plankton samples collected near the coastline of Genoa. Lower but significant concentrations of some MPEs were also found in samples of edible crustaceans and molluscs. Blair et al. [43] reported 585 ng/g of MnBP in blue mussels from Vancouver, while Hidalgo-Serrano et al. [52] found 260 ng/g of MEP in shrimp samples bought from Spanish markets.

Although all species have similar PAE and MPE detection frequencies, differences in PAE concentration levels have been observed. While some authors report a decrease in PAE concentrations as trophic levels increase, others report the opposite effect. Hu et al. [8], for instance, observed a slight trophic dilution in the food web between fish, molluscs and crustaceans that may be caused by a more efficient metabolic transformation at higher trophic levels. Routti et al. [82] also observed lower PAE detection rates in large mammals, which they attributed either to a lower presence of these contaminants in their food web or to a more rapid metabolization and excretion of the pollutants. Lo Brutto et al. [83], on the other hand, reported higher concentrations of PAEs in fish than in crustaceans.

These changes in the distribution of contaminants across trophic levels result from the interaction of many factors. On one hand, they may be associated with the feeding and living habits of each species. Several studies report greater contamination in molluscs than in fish or crustaceans, which suggests that the exposure of molluscs to PAEs is higher due to the pollution of marine sediments [8,43]. Higher PAE accumulation has also been observed in fish species that consume benthic organisms or in demersal fish species, which have higher bioconcentration factors [8]. Moreover, Rian et al. [47] found that PAE and MPE concentrations were lower in porpoises that inhabit less populated coastal areas than in those that inhabit more populated areas. However, these variations may also be associated with the bioavailability of PAEs and MPEs in the environment. Fourgous et al. [46] observed a temporal variation for DEHP metabolites in *Anguilla anguilla* between March, June and October which they attributed to a seasonal change in the exposure of eels to PAEs. These authors observed the highest concentrations of pollutants during the months when recreational activity in the area is most intense, when the release of plasticisers into the environment is potentially boosted. Interestingly, regardless of these variations, no significant differences due to age, sex or body dimension have been observed in individuals of the same species [46,47].

MPs also seem to be a source of PAE contamination in marine biota. Saliu et al. [49], for example, found higher PAE concentrations in corals located in areas most affected by MP contamination. Baini et al. [30] also reported a positive correlation between PAE and MPE concentrations in neuston/plankton samples and MPs. However, more studies are needed to evaluate whether PAEs and MPEs can be used as markers of marine biota exposure to MPs.

4. Conclusions

PAEs and MPEs are present in marine matrices at detectable concentration levels in samples collected worldwide. The most common separation and detection techniques are GC for determining PAEs and LC for determining MPEs, both of which are usually coupled to MS, MS/MS or HRMS.

The optimal performance of the extraction techniques depends on the characteristics of the matrix and the properties of the analytes. SPE is the most common technique for seawater samples thanks to its simplicity, high recoveries and enrichment factors. Extraction from solid matrices is more challenging due to the high matrix effects usually present in such samples, which require clean-up steps to remove interfering matrix components. For these samples, USAE is the most common extraction technique, though QuEChERS has increasingly been used in recent years.

Numerous studies have determined the occurrence of PAEs in seawater, marine sediments and biota but less information is available about the occurrence of MPEs in those samples. Generally speaking, DEHP, DnBP and DiBP, as well as their main metabolites (MEHP, MnBP and MiBP), are the most frequently detected compounds in all samples regardless of their origin.

Polluted rivers and wastewater discharges from large cities and industrial zones appear to be the main sources of pollution in most areas, though coastal currents and atmospheric depositions are also potential sources of PAEs. Several studies have found a significant positive correlation between the abundance of MPs and plastic debris and PAE contamination in seawater, sediments and biota. This highlights the grave impact human activities and plastic pollution have on the marine environment.

More information is needed on MPE concentrations in the environment since these are also contaminants with concerning effects on biota. Further investigation is also needed to evaluate whether PAEs and MPEs can be used as markers of marine plastic contamination worldwide.

Declaration of competing interest

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

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Appendix A. Supplementary data

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