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Analyse, distribution, production et dégradation d'esters de phtalates (PAEs) en zone côtière méditerranéenne

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Abstract

Phthalic Acid Esters (PAEs) are a group of emerging organic contaminants that have become a serious issue because of their ubiquitous presence on the marine environment worldwide and for the endocrine disrupting effects in animals and humans. However, little is known about their distribution in the Ocean, mainly because of analytical difficulties and the high possibility of ambient sample contamination. Plastic debris in marine environment includes resin pellets, macro- and microplastic fragments, and contains additives such as PAEs that might be released in the aquatic environment in unknown proportion. In our work, we improved an analytical method for the determination of 8 PAEs, at trace levels in marine and fresh waters. In the first part of the thesis, the method was validated for different seawater salinities and wastewater treatment plant outlet. By passing 1 L of sample through glass cartridges packed with 200 mg of Oasis HLB and eluted with 6 mL of ethyl acetate, the recoveries for dimethyl phthalate (DMP), diethyl phthalate (DEP), dipropylphthalate (DPP), di-isobutyl phthalate (DiBP), di-n-butyl phthalate (DnBP), benzylbutyl phthalate (BzBP), diethylhexyl phthalate (DEHP) and d-n-octyl-phthalate (DnOP), were 101, 98, 115, 110, 99, 98, 103 and 95 %, respectively, with acceptable blank values (below 0.4-4.0 % of the masses measured in different seawater samples). In a second part, PAE distribution in the Marseille Bay has been evaluated though a one-year monitoring from December 2013 to November 2014. The results showed the occurrence of six PAEs, DMP, DEP, DiBP, DnBP, BzBP and DEHP, with total concentrations ranging from 130 to 1330 ng L⁻¹ (av. 522 ng L⁻¹). DEHP was the most abundant PAE in all of the surface samples and the summer bottom samples, followed by DiBP and DnBP. High concentrations were detected in the bottom water, suggesting that resuspension of PAE-rich sediment, in relation with the accumulation of plastic debris above the seabed plays a significant role in the PAE dynamics in coastal

water. In the last part of this thesis, two common plastic samples as trash plastic bags and insulation layer of electric cables were incubated in natural seawater in laboratory conditions and studied for the release of PAE. Release was observed for the different PAEs with kinetics varying according to the plastic type. DMP and DEP were preferentially released from the insulation layer of electric cables reaching level of release of 9.5 ± 1.4 and $68.9 \pm 10.3 \text{ ng g}^{-1}$, respectively, whereas DiBP and DnBP were released from plastic bags, reaching the highest rate after only one week, at values of 333.4 ± 50.3 and $480.5 \pm 72.1 \text{ ng g}^{-1}$, respectively.

Keywords: phthalates, DEHP, seawater, endocrine disruptors, microplastics

Résumé:

Les esters d'acide phtalique ou phtalates (PAEs) sont un groupe de contaminants organiques émergents qui sont devenus une préoccupation majeure en raison de leur omniprésence dans le milieu marin à l'échelle mondiale, et de leurs effets perturbateurs sur le système endocrinien chez les animaux et les humains. Cependant, leur répartition en Méditerranée est assez mal connue, principalement en raison des difficultés analytiques, et du risque élevé de contamination des échantillons lors du processus analytique. En outre, les débris de plastique en milieu marin (i.e., fragments de macro et microplastique) contiennent des additifs comme les PAEs, qui sont ajoutés lors de l'étape de fabrication du plastique, ou qui peuvent provenir également de la phase dissoute de l'eau de mer environnante. Dans la première partie de cette manuscrit de thèse, une méthode analytique a été optimisée et validée pour la détermination de 8 PAEs à l'état de traces en milieu marin, pour des échantillons de salinité variées à proximité notamment d'un panache fluvial et de l'exutoire de la station d'épuration des eaux usées de Marseille. Brièvement, 1 L d'échantillon filtré est passé à travers des cartouches de verre contenant 200 mg d'Oasis HLB, puis élué à l'aide de 6 mL d'acétate d'éthyle. L'extrait est ensuite concentré, et les PAEs suivants sont recherchés : phtalate de diméthyle (DMP), phtalate de diéthyle (DEP), phtalate de dipropyle (DPP), phtalate de diisobutyle (DiBP), phtalate de di-n-butyle (DnBP), le phtalate de benzylbutyle (BzBP), phtalate de diéthylhexyle (DEHP) et le phtalate de di-n-octyle (DnOP). Notre méthode donne des rendements d'extraction compris entre 95 et 115 %, et des blancs acceptables (0,4-4,0 % des masses mesurées dans les différents échantillons d'eau de mer). Dans un second temps, un suivi annuel de la contamination de la Baie de Marseille a été effectué de décembre 2013 à novembre 2014, depuis la surface jusqu'au fond ($z = 32$ m). Les résultats ont montré la présence de sept PAEs (DMP, DEP, DEP, DiBP, DnBP, BzBP et DEHP), avec des concentrations totales variant de 130 à 1330 ng L⁻¹ (av. 522 ng L⁻¹), le DEHP étant le composé le plus abondant

dans tous les échantillons de surface ainsi que les échantillons de fond estivaux, suivi du DiBP et du DnBP. Des concentrations élevées ont été détectées dans le tiers inférieur de la colonne d'eau, ce qui suggère une remise en suspension de sédiments chargés en PAEs (issus de débris plastiques au-dessus du fond marin par exemple), ou un taux de dégradation plus élevé dans la couche supérieure de la colonne d'eau, en lien avec une plus forte exposition à l'irradiation solaire. Dans la dernière partie de cette thèse, deux échantillons de plastique communs (sac de poubelle en plastique et gaine de câble électrique) ont été incubés dans de l'eau de mer naturelle dans des conditions contrôlées de laboratoire, de manière à évaluer la migration de PAEs depuis ces matériaux en fonction de différentes conditions environnementales comme la température, la présence de lumière, ou encore la présence de bactéries. Différentes cinétiques de relargage ont été mises en évidence en fonction du type de plastique, (DMP et DEP depuis la gaine électrique, 9.5 ± 1.4 and 68.9 ± 10.3 ng g⁻¹ respectivement, ainsi que DiBP et DnBP depuis les sacs en plastique, 333.4 ± 50.3 and 480.5 ± 72.1 ng g⁻¹, respectivement).

Mots-clés : phtalates, DEHP, eau de mer, perturbateurs endocriniens, microplastiques

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INTRODUCTION

Introduction

The presence of toxic substances in our ecosystem has always been a problem of great importance and social influence for nature and humans. Over the years, chemists, biologists and other researchers have highlighted several toxic substances present in the environment, derived from both natural and industrial sources. Especially from the latter, they continue to produce and release thousands of substances each year and their toxicity, health and environmental impact remains in some cases to be determined (Nazaroff et al, 2012).

Plastic has raised many concerns during the last two decades for the large diffusion in daily life and its impact on the environment. The development of modern plastics expanded with a large range of types and forms, including natural polymers, modified natural polymers, thermosetting plastics, thermoplastics and, more recently, biodegradable plastics (Andrade and Neal, 2009). Plastics can be used at a very wide range of temperatures, they are chemical and light resistant, very strong and tough, but can be easily worked as a hot melt. This versatility, together with the low cost of production, explains the reasons of the large diffusion and annual worldwide demand.

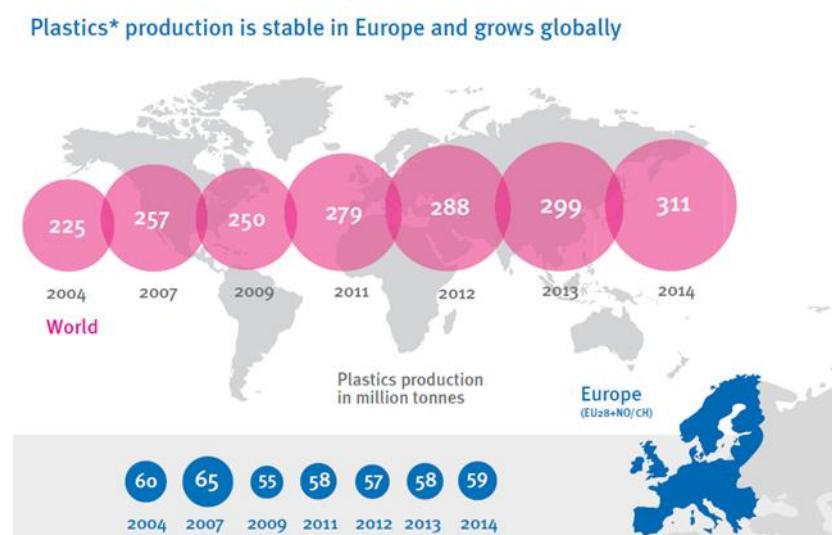


Figure 1. Worldwide production of plastic (in pink) and in Europe (blue) from 2004 to 2014. (Plastics Europe, 2015)

Indeed in 2014, 311 million tons of plastic were produced worldwide and 48 million tons were consumed in Europe (Fig. 1), with around 40% for packaging and 20% for building and construction (Plastics Europe, 2015). Moreover, the European plastic demand is dominated by polypropylene (PP) for 19%, low-density polyethylene (LDPE) for 17%, high-density polyethylene (HDPE) for 12%, polyvinyl chloride (PVC) for 10% and polyethylene terephthalate (PET) and polystyrene (PS) for 7% each (Plastics Europe, 2015). Because a large amount of plastic (31% in Europe in 2014) is not recycled and end up to landfill and part of this fraction find their way into rivers and then into the oceans (Fig. 2), plastic pollution is ubiquitous throughout the environment and in the ocean (Eriksen et al., 2014). In addition, these plastic resins are mixed with other materials called additives to enhance performance. These may include inorganic fillers to reinforce the plastic material, thermal stabilizers to allow the plastics to be processed at high temperatures, plasticizers to render the material pliable and flexible, UV stabilizers to prevent degradation when exposed to sunlight and fire retardants to discourage ignition and burning (Fischer et al., 2014). Plasticizers are a particular group of additives that has raised concerns for their health and environmental effects, especially as endocrine disruptors, and phthalates, among them, are commonly used in a large amount of plastic products. Phthalates can easily be released into the environment directly and/or indirectly, during manufacture, use and disposal and their distribution is ubiquitous in the environment.

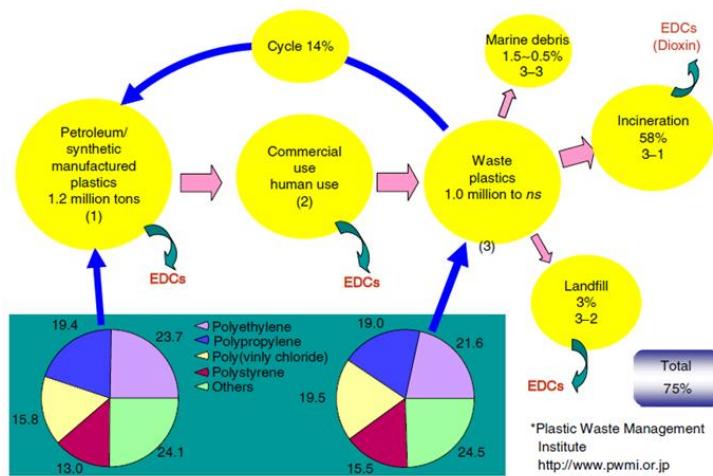


Figure 2. Plastic products, plastic waste and resource recovery in Japan in 2009. Endocrine disrupting chemicals (EDCs). From Saito, 2014.

Phthalic acid ester or phthalates (PAEs) are widely used in the manufacture and processing of products as plasticizers. Production of PAEs began in the 1920s and has intensified since 1960, when these compounds were used as important additives, which impart flexibility to polyvinyl chloride (PVC) resins (Kimber and Dearman, 2010; Peng et al., 2013). They are also mixed in other resins such as polyvinyl acetates, cellulosic and polyurethanes. The stability, fluidity and low volatility of higher molecular weight phthalate esters make them highly suitable as plasticizers. Since the annual production of plastics has reached a level of 311 million tons in 2014 (Plastics Europe, 2015), plasticizers are used in a very broad range of industrial applications on the worldwide scale (Huang et al., 2013; Pei et al., 2013; Li et al., 2016). The production of PAEs increased from 1.8 million tons in 1975 (Peijnenburg and Struijs, 2006) to more than 8 million tons in 2011 (Schreiber et al., 2011; Meng et al., 2014). PAEs are present in many plastic materials including PVC products, building materials (paint, adhesive, wall covering, insulation layer of electric cables), personal-care products (perfume, eye shadow, deodorizer, liquid soap and hair spray), medical devices, detergents and surfactants, packaging, children's toys, printing

inks and coatings, pharmaceuticals and food products, household applications such as shower curtains, floor tiles, food containers and wrappers, cleaning materials (Li et al., 2016; Pei et al., 2013).

The chemical structure of phthalates is shown in Figure 3 and consists of a dialkyl ester of o-benzeneddicarboxylic acid (o-phthalic acid). They possess different characteristics dependent on the length and isomeric structure of the alcohol chain. Table 1 gives an overview of all available phthalates and includes the molecular formulas, abbreviations, molar masses and CAS numbers. Seven of them are commercially significant and these are the target analytes in this thesis: di-methylphthalate (DMP), di-ethylphthalate (DEP), di-isobutylphthalate (DiBP), di-n-butylphthalate (DnBP), benzylbutylphthalate (BzBP), di-(2-ethylhexyl)phthalate (DEHP), di-n-octylphthalate (DnOP). With the exception of DEHP, which is a pure isomer, higher molecular weight phthalates (alkyl chain > 6 C) are mixture based on the alcohols used for synthesis (Staples et al., 1997).

Low molecular weights phthalates as DMP, DEP, DiBP, DnBP and BzBP are used for their emulsifying properties and they are components of industrial solvents, solvents in perfumes, adhesives, waxes, inks, pharmaceutical products, insecticide materials and cosmetics (Koniecki et al., 2011). DMP and DEP allow perfume fragrances to evaporate more slowly, lengthening the duration of the scent and a small amount of DnBP gives nail polish a chip-resistant property. Higher molecular weight PAEs, as DEHP, are principally incorporated in polymers as plasticizers, especially PVC, to improve flexibility, workability and general handling properties and 80% of PAEs are used for this purpose (IARC, 2000; Meng et al., 2014). Phthalates are not chemically bound to the end plastic products to which they are added and this led to their ubiquitous spread in the environment. The dispersion of PAEs in the environment can occur at all stages of their use, from their synthesis to their transformation or degradation.

Table 1. Overview of all available phthalates.

Compound	Formula	Acronym	Molar Mass	Cas n°
Di-methylphthalate	C ₁₀ H ₁₀ O ₄	DMP	194.2	131-11-3
Di-ethyl phthalate	C ₁₂ H ₁₄ O ₄	DEP	222.4	84-66-2
Di-allylphthalate	C ₁₄ H ₁₄ O ₄	DalP	246.3	131-17-9
Di-(1-methylethyl)phthalate	C ₁₄ H ₁₈ O ₄	DiPP	250.3	605-45-8
Di-propylphthalate	C ₁₄ H ₁₈ O ₄	DPP	250.3	131-16-8
Butyl-2-methylpropylphthalate	C ₁₆ H ₂₂ O ₄	BMPP	278.4	17851-53-5
Di-n-butylphthalate	C ₁₆ H ₂₂ O ₄	DnBP	278.4	84-74-2
Di-i-butylphthalate	C ₁₆ H ₂₂ O ₄	DiBP	278.4	84-69-5
Di-cyclopentylphthalate	C ₁₈ H ₂₂ O ₄	DCPeP	302.4	18699-38-2
Butylcyclohexylphthalate	C ₁₈ H ₂₄ O ₄	BCHP	304.4	84-64-0
Di-(3-methylbutyl)phthalate	C ₁₈ H ₂₆ O ₄	DMBP	306.4	605-50-5
Di-pentylphthalate	C ₁₈ H ₂₆ O ₄	DPeP	306.4	131-18-0
Benzylbutylphthalate	C ₁₉ H ₂₀ O ₄	BzBP	312.4	85-68-7
Di-phenylphthalate	C ₂₀ H ₁₄ O ₄	DPhP	318.3	84-62-8
Di-cyclohexylphthalate	C ₂₀ H ₂₆ O ₄	DCHP	330.4	84-61-7
Butyl 2-ethylhexylphthalate	C ₂₀ H ₃₀ O ₄	BEHP	334.5	85-69-8
Butyloctylphthalate	C ₂₀ H ₃₀ O ₄	BOP	334.5	84-78-6
Di-(2-ethylbutyl)phthalate	C ₂₀ H ₃₀ O ₄	DEBP	334.5	7299-89-0
Di-hexylphthalate	C ₂₀ H ₃₀ O ₄	DHP	334.5	84-75-3
Di-benzylphthalate	C ₂₂ H ₁₈ O ₄	DBzP	346.3	523-31-9
Butyldecylphthalate	C ₂₂ H ₃₄ O ₄	BDcP	362.6	89-19-0
Di-heptylphthalate	C ₂₂ H ₃₄ O ₄	DHpP	362.5	3648-21-3
Benzyl 2-ethylhexylphthalate	C ₂₃ H ₂₈ O ₄	BzEHP	368.6	18750-05-5
Di-(2-ethylhexyl)phthalate	C ₂₄ H ₃₈ O ₄	DEHP	390.6	117-81-7
Di-n-octylphthalate	C ₂₄ H ₃₈ O ₄	DnOP	390.6	117-84-0
Hexyldecylphthalate	C ₂₄ H ₃₈ O ₄	HDcP	390.6	25724-58-7
Octyldecylphthalate	C ₂₆ H ₂₆ O ₄	ODcP	418.6	119-07-3
Di-nonylphthalate	C ₂₆ H ₄₂ O ₄	DNP	418.6	84-76-4
Di-decylphthalate	C ₂₈ H ₄₆ O ₄	DDcP	446.7	84-77-5
Di-undecylphthalate	C ₃₀ H ₅₀ O ₄	DUP	474.7	3648-20-2
Di-dodecylphthalate	C ₃₂ H ₅₄ O ₄	DDDP	502.8	2438-90-8
Di-i-heptylphthalate	C ₂₂ H ₃₄ O ₄	DiHpP	362.5	
Di-i-nonylphthalate	C ₂₆ H ₄₂ O ₄	DiNP	418.6	
Di-i-decylphthalate	C ₂₈ H ₄₆ O ₄	DiDP	446.7	

During the last 20 years, there has been a growing concern about their acute and chronic toxic impact as endocrine disruptors (ECDs) and environmental distribution. Consequently, six of them have been placed on the priority pollutant list of the United States Environmental Protection Agency (U.S. EPA, 2014), the European Union (EU) (CEC, 2007) and on the list of priority pollutants in Chinese waters (National Standard of the People's Republic of China, Standard for drinking water quality GB 5749-2006) and the concentrations of PAEs have been regulated for water consumption. The use of PAEs is now subject to stricter control and some have been prohibited or their reduction in numerous products has been recommended.

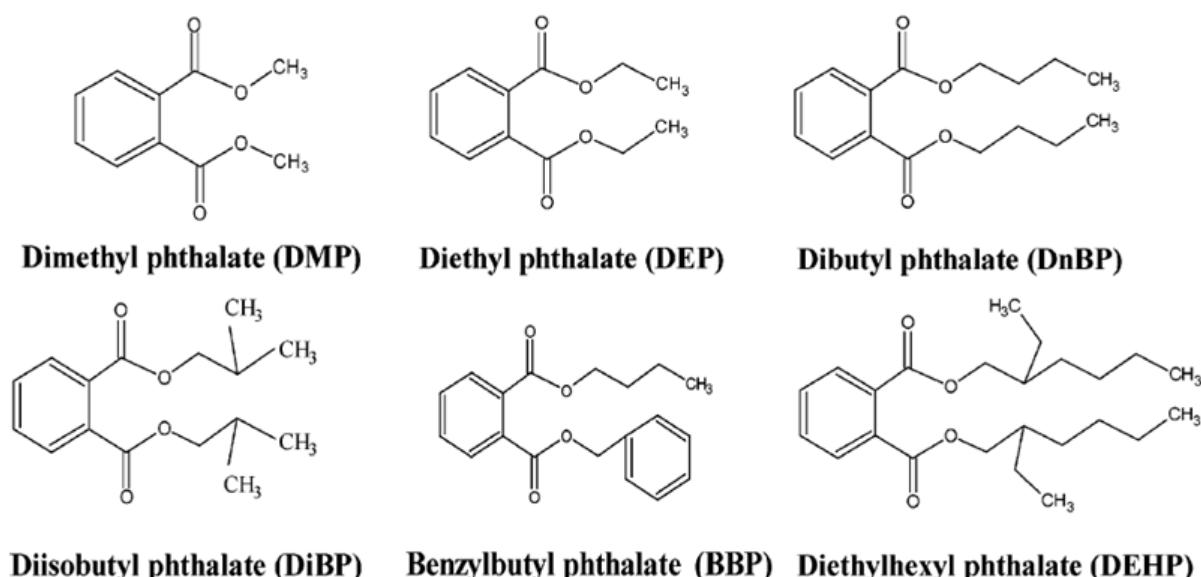


Figure 3. Chemical structure of 6 of the most abundant phthalates in the environment (adapted from Xie et al., 2007)

1 Physiochemical properties

Phthalate esters in environmental and biological systems show large varieties of behavior depending on the physical-chemical characteristics of the individual solutes. Because of their environmental and possible toxicological impact as endocrine disruptors (ECDs), many efforts have been made in the last decade to accurately measure key physicochemical properties including water solubility (WS), vapor pressure (Vp), Henry's constant (H), air/water partitioning (K_{AW}), octanol/air partition (K_{OA}), and octanol/water partitioning (K_{ow}), organic carbon partitioning (K_{OC}) (Cousin et al., 2003; Staples et al., 1997). Such parameters determine the behavior, transport and fate in the environment and also the exchanges between the different reservoirs such as atmosphere, lithosphere, hydrosphere, and biosphere (Staples et al., 1997; Cousins and Mackay, 2000). In Table 2, a selection of physical-chemical parameters was made for seven most abundant dialkyl phthalates. Since mono-alkyl phthalates are considered to be the primary metabolites of phthalate di-esters, these values are also discussed for the mono-esters.

1.1 Physical state

Common commercial phthalate esters are liquids at ambient temperature and nearly all have melting point below -25 °C and boiling points ranging from about 230 to 486 °C. Higher molecular weight phthalate esters, as DEHP, decompose when exposed at elevated temperatures for longer times. The low melting point and the high boiling point of these PAEs contribute to their usefulness as plasticizer, heat transfer fluids and carriers. Phthalate monoesters boil higher than their parent compounds because of hydrogen bridging of the polar groups.

1.2 Water solubility

Water solubility (WS) is an extremely important property that influences the biodegradation and bioaccumulation potential of a chemical. Water solubility is also determining factor controlling the environmental distribution between water, soil/sediment, and atmosphere. PAEs are characterized by low solubility in water and by a declining trend in water solubility with increased carbon number of the alcohol moiety or molecular weight (Tab. 2), ranging from 2.4×10^{-3} mg/L for DEHP to 5220 mg/L for DMP (Cousins and Mackay, 2000). Phthalate monoesters are more polar than their parent diesters and show higher water solubility.

1.3 Octanol/Water partitioning

The octanol/water partition coefficient (K_{ow}) represents the equilibrium distribution of a solute between water and octanol and therefore is a physical constant that is linked to its hydrophobicity. Generally, the K_{ow} or the hydrophobicity increases proportionately to the molecular weight of alkyl phthalates or the chain length of the alcohol moiety. High molecular weight plasticizers (DEHP, DiNP, DiDP) show therefore very high affinity for apolar matrix substances like fat, biomatrices or suspended solids in surface or wastewater, while monoalkyl phthalates are much more polar because of their free carboxylic acid group. Indeed, K_{ow} reflects the affinity of an organic compound with the lipid molecules in living organisms and it has been used to predict the tendency of a contaminant to concentrate in aquatic organisms (Lyman et al., 1990), indicating greater bioconcentration with increasing of Log K_{ow} (Table 2). The median log K_{ow} values for DMP, DEP, DnBP, BzBP and DEHP are 1.61, 2.54, 4.27, 4.7 and 7.73.

Table 2. Physiochemical properties of the main phthalates in the environment. Vp, H, log K_{ow}, log K_{OA} and Log K_{AW} values were estimated by Cousins and Mackay (2000) and Staples et al. (1997).

Comp	Bp (°C)	Mp (°C)	SW (mg L ⁻¹)	Vp (Pa)	H (Pa m ³ mol ⁻¹)	log K _{ow}	log K _{OA}	log K _{AW}
DMP	249	5.5	5220	0.263	9.78 x 10 ⁻³	1.61	7.01	-5.40
DEP	282	-40	591	6.48 x 10 ⁻²	2.44 x 10 ⁻²	2.54	7.55	-5.01
DiBP	323	-58	9.9	4.73 x 10 ⁻³	0.133	4.27	8.54	-4.27
DnBP	338	-35	9.9	4.73 x 10 ⁻³	0.133	4.27	8.54	-4.27
BzBP	387	-35	3.8	2.49 x 10 ⁻³	0.205	4.7	8.78	-4.08
DEHP	417	-47	2.49 x 10 ⁻³	2.52 x 10 ⁻⁵	3.95	7.73	10.53	-2.80
DnOP			2.49 x 10 ⁻³	2.52 x 10 ⁻⁵	3.95	7.73	10.53	-2.80

1.4 Vapor pressure and Air/Water partitioning

Vapor pressure (Vp) plays an important role in the fate of fugitive emissions and other releases of phthalate esters to the atmosphere. The vapor pressure of phthalate esters declines more than 7 orders of magnitude with increasing alkyl chain length (Staples et al., 1997). Despite the relative low vapor pressures, phthalate esters can be considered as semi-volatile compounds and are present in the vapor phase at environmental temperatures. Henry's constant (H) indicates the tendency of a substance to escape from water into air. H can be calculated from Vp and WS. Compounds with H values $\sim 1.01 \times 10^{-2}$ Pa·m³/mol are generally considered to have negligible volatility. PAEs with higher alkyl chains, ranging from 4 to 13 carbon atoms, are characterized by H values range from 0.133 to 275 Pa·m³/mol which indicates that transfer from the aqueous phase to the gas phase is important. The main 6 PAEs detected in the environment are characterized by Vp ranging from 2.52×10^{-5} Pa for DnOP to 0.26 Pa for DMP and by H ranging from 9.78×10^{-3} Pa m³/mol for DMP to 3.95 Pa m³/mol for DnOP and DEHP (Table 2). However, the distributions of the low molecular weight phthalates as DMP, DEP, DiBP, DnBP and BzBP from water into air are less favorable compared to these of DEHP, DiNP and DiDP,

despite their high volatilities. This is largely due to the limited solubility of these larger phthalate molecules in water. K_{AW} and K_{OA} partition coefficients are key factors controlling the distribution of PAEs in different matrices in the environment. Log K_{AW} and log K_{OA} increase with the increasing of PAEs alkyl chain length. Indeed, Log K_{AW} values range from -5.4 for DMP to -2.8 for DnOP and DEHP and Log K_{OA} range from 7 for DMP to 10.5 for DnOP and DEHP (Table 2). High values of log K_{OA} suggest that PAEs present in the atmosphere will be appreciably sorbed on particles, whereas high values of log K_{AW} suggest that PAEs potentially evaporate more rapidly from water. However, in environmental surface waters large quantities of suspended solids or colloidal particles are present and high molecular weight phthalates, as DEHP and DnOP, tend to adsorb onto this fraction. This restricts their migration into the air drastically. The lower molecular weight PAEs, as DMP and DEP, are quite volatile and have very low log K_{AW} values, then they will volatilize rapidly from the pure state but only very slowly from aqueous solution (Cousins and Mackay, 2000). Phthalate monoesters are more polar and remain for the most part in the aqueous phase.

1.5 Water/organic solid partitioning

Phthalates containing longer alkyl chains tend to adsorb onto particulate matter or colloids rather than being in the dissolved state. The propensity of the phthalates to associate with particulates or colloids is strongly dependent on the hydrophobicity. Log K_{OC} values of phthalates ranging from 1.57 of DMP to 6.20 of DiDP.

2 Plastics in the ocean

Plastics debris find their way into the marine environment from various land-based sources and human activities conducted on water and the proportion of plastic contributing to municipal waste constitutes ~ 5-10 % of waste generated worldwide (Jambeck et al., 2015; Suhrhoff and Scholz-Botter, 2016; Barnes et al., 2009). Products generally contributing to plastics debris include containers and packaging materials, plastic bags, fishing gear, disposable dishware and toys and as well as solid-waste disposal, sewage treatment overflow, storm water runoff, beach litter and plastic from manufacturing activities including resin pellets (Saido, 2014; Barnes et al., 2002; Hirai et al., 2011). Most of these materials contain a considerable amount of phthalates.

Degradation processes of plastics are extremely slow and they are subjected to a series of physical, chemical and biological interactions, varying with respect to the quality, shape and size of the plastic fragment (Barnes et al., 2009; Browne et al., 2013). Wave action stimulates physical degradation and breakdown of macro to microplastics ($\leq 5\text{mm}$) (Andrady and Neal, 2009; Cózar et al., 2014), which is intensified in coastal environments due to increased wave action, abrasion and sand/coastline induced mechanical weathering and UV contact (Suhrhoff and Scholz-Botter, 2016) and thus microplastics potentially persist for very long time in seawater (Rios et al., 2011). In addition, because of its small size, microplastics can easily be ingested by biota (Neves et al., 2015). Most of the plastic material are positively buoyant and are dispersed by wind and currents, but a significant amounts become neutrally buoyant and sink below the surface into the water column (Moore, 2008) or sink further to become incorporated into the sediments (Cooper and Corcoran, 2010). Approximately $270\ 10^3$ tons of plastic are suspected to float in the ocean (Eriksen et al., 2014).

The Mediterranean Sea is greatly affected by marine litter (Collignon et al., 2012; Cozar et al., 2014, 2015; Faure et al., 2015; Collignon et al., 2014; Fossi et al., 2016, 2017) and it is considered by few groups as the sixth accumulation area for marine litter together with the main five oceanic gyre (Eriksen et al., 2014). The surface load of plastic particles in the Mediterranean Sea has been estimated to be around 1,455 tons (Ruiz-Orejon et al., 2016). Other estimates range from 756 to 2,969 tons (Cozar et al., 2015) and from 874 to 2,576 tons (Suaria et al., 2016). The most abundant polymer detected in the north-western Mediterranean Sea was polyethylene (76 %), suggesting that the fragmentation of larger packaging items represent the main origin of microplastics in this area (Fossi et al., 2017).

Knowledge of plastics distribution remain still limited in Mediterranean Sea (Ruiz-Orejon et al., 2016; Suaria et al., 2016) and as well of plastics contribution to phthalates occurrence in marine environment. Little is known about the interaction between plastics and phthalates in seawater and many efforts have to be done to completely understand the complexity of this phenomena.

3 Phthalates occurrence and fate in the environment

3.1 Water

Among the large variety of PAEs, DMP, DEP, DiBP, DnBP, BBP, DEHP and DnOP are among the most frequently detected in surface water (Brossa et al., 2005; Xie et al., 2005; Sanchez-Avila et al., 2012). Generally, studies focused on the six PAEs listed as priority substances, which are the most toxic and also the predominant PAEs in the environment (Xie et al., 2005; Zheng et al., 2014). Indeed, Zheng et al. (2014) measured the concentration of 15 PAEs in water both in dissolved phase and associated with suspended solids matter (SSM). The Σ 6PAEs (DMP, DEP, DnBP, BBzP, DEHP, and DnOP) represents 64.8 and 66.9 % of the Σ 15PAEs respectively in dissolved phase and associated with SSM. DEHP and DnBP were predominant PAEs following by DiBP and BBzP (Zheng et al., 2014). Marine and coastal environment present low level of PAEs compared to freshwater, but very limited data are available for the occurrence and fate of PAEs in marine water, especially in the Mediterranean Sea. DEHP concentrations were reported by Sanchez-Avila et al. (2012) for Catalan coastal water (Spain, NW Mediterranean Sea) and by Turner and Rowling (2000) for the south coast of the UK, respectively, with range of 31-617 ng/L and 99-2200 ng/L. Higher DEHP concentration was reported by Brossa et al. (2005) for the Spanish coast and riverine water ranging from 0.07 to 12 μ g/L. Similarly, DnBP and BzBP concentration were reported as 0.3-4.6 μ g/L and 0.1-0.5 μ g/L, respectively. Lower concentrations have been only reported for North Sea with concentration ranges of 0.5-5.3 ng/L for DEHP and 0.02-4.0 ng/L for DMP and DEP (Xie et al., 2005).

Numerous processes such as wastewater treatment plant (WWTP) output, leaching, drainage and atmospheric deposition are the main sources of PAEs in aquatic environment

(Fig. 4) (Wang et al., 2012; Zeng et al., 2009; Xu et al., 2008). Hydrolysis, photodegradation and biodegradation are the major PAEs removal processes in water (Wolfe et al., 1980). i) Light irradiation induces photolysis of PAEs either directly by absorption of radiation or indirectly by the oxidation reactions of reactive chemical species and chromophoric dissolved organic matter (CDOM) triplet states produced in surface waters by sunlight illumination of photoactive molecules such as nitrate, nitrite and CDOM (Vione et al., 2014; Tedetti et al., 2007). Under these conditions, aqueous half-lives of PAEs decrease considerably ranging from 2.4 to 12 years and from 0.12 to 1.5 years for DEP and DEHP, respectively (Peng et al., 2013; Okamoto et al., 2006). ii) Biodegradation can be the most important process for the removal of PAEs from water (Liang et al., 2008). Indeed, PAEs can be accumulated and degraded rapidly by microorganism under both aerobic and anaerobic conditions (Hashizume et al., 2002). In surface waters (seawater or freshwater) under aerobic conditions the half-lives of primary degradation vary from less than 1 day to 2 weeks and the half-lives for complete mineralization are approximately 10 times longer (Staples et al., 1997). iii) Hydrolysis of PAEs is negligible at neutral pH with aqueous hydrolysis half-lives in order of several years and up to more than 100 years for DnOP, DiOP and DEHP (Wolfe et al., 1980).

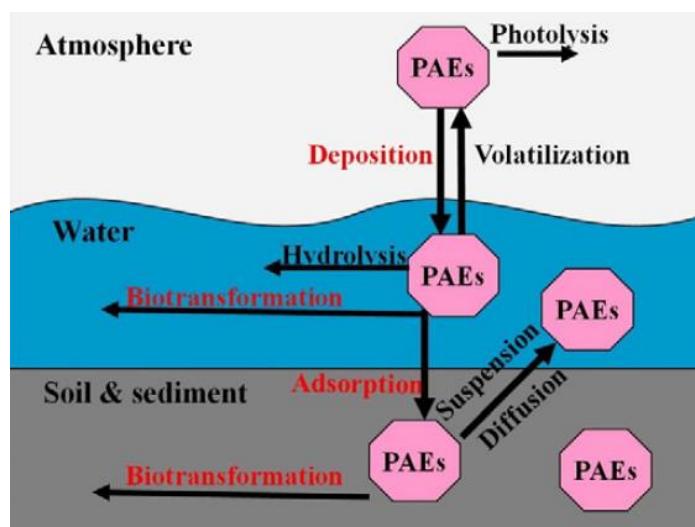


Figure 4. Occurrence and biodegradation of PAEs in the environment (From Gao and Wen, 2016)

The contamination level of PAEs in fresh and marine water, measured on worldwide scale, frequently exceeded the guidelines or recommend values. It is difficult to evaluate the effects of PAEs on the aquatic environment because several parameters should be taken into consideration, but some values have been proposed by many research groups. Based on NQE, values fixed by EU, DEHP should be below the limit of 1.3 µg/L or according to the predicted effect concentration (PEC), which identifies the concentration above which harmful effects on organisms were expected to occur frequently, the limit value has been proposed at 3.2 µg/L (Naito et al., 2006). It is clear that the majority of concentrations reported in literature are considerably higher than all the limit values previously reported. Thus, PAEs may affect not only aquatic organisms but also the groundwater resources.

3.2 Air

PAEs are ubiquitous in the atmosphere, including air indoors where people spend 65-90 % of their time (Hwang et al., 2008; Brasche and Bischof, 2005). Worldwide, Σ 6PAEs were detected at higher levels in indoor air than outdoor air, ranging from 1014 to 1828 ng/m³ in China (Zhang et al., 2014), and from 545 to 2160 ng/m³ in the U.S (Rudel et al., 2010). Indoor environments increase the lifetime of pollutants adsorbed to particles and dust by minimizing or eliminating the natural decomposition processes catalyzed by sunlight and rain (Cizdziel and Hodge, 2000). Indeed, direct photolysis and photodegradation are major reaction pathways of PAEs responsible for PAE decay in the atmosphere, where the half-lives of individual PAEs were estimated to be several days (Behnke et al., 1987). Half-life of photo-oxidation of PAEs increases with the increasing alkyl chain length and OH• concentration. DnBP and DEHP have been used as softeners in synthetic paintings (Orecchio et al., 2014), so these compounds can be released into the

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atmosphere from painted surfaces (Pei et al., 2013) or photodegraded on mural painting surfaces under UV light irradiation in a dozen of hours (CEC, 2007). PAEs can also be removed from the atmosphere by wet and dry deposition (Wang et al., 2014; Zeng et al., 2010; Teil et al., 2006). PAEs with short carbon chains (<6), as DMP, DEP, DiBP and DnBP, are present mainly in the gas phase, while PAEs with longer chains (>6), as DEHP and DnOP, are mainly adsorbed on the particles (Wang et al., 2014). Wet deposition is an important source of removal of short alkyl chains, while dry deposition is an important source of removal of PAEs with long alkyl chains (Zeng et al., 2010). Depositional fluxes of $\Sigma 16$ PAEs were estimated from 3.41 to 190 $\mu\text{g}\cdot\text{m}^2/\text{day}$ for strong anthropogenic activity zones (Zeng et al., 2010). The association of PAEs with atmospheric particles initiates this deposition process preliminarily.

DnBP and DEHP were detected as the predominant PAEs in air (Sampath et al., 2017; Wang et al., 2014; Wang et al., 2008; Wang et al., 2006) and a recommend limiting value of concentration for these compounds in ambient air have not been established. As PAEs are released from anthropogenic activities, their concentrations are present at higher levels in a urban center than in suburban areas. $\Sigma 6$ PAEs were detected at 97 ng/m^3 in the urban center *versus* 27.8 ng/m^3 in the suburban areas (Wang et al., 2006). The total atmospheric levels of $\Sigma 6$ PAEs was 57.4 ng/m^3 in Paris (Teil et al., 2006). Otherwise, in the remote Arctic, the total concentration of atmospheric $\Sigma 6$ PAEs was detected at 2.14 ng/m^3 (Fig. 5) (Xie et al., 2007). A possible source of PAEs in the Arctic troposphere may be associated with long-range transport from midlatitudes and the subsequent deposition on the snow/ice sheet. The deposited PAEs onto snow and ice can also be released into the atmosphere with the increase of the ambient temperature during the spring and summer months (Fu et al., 2013).

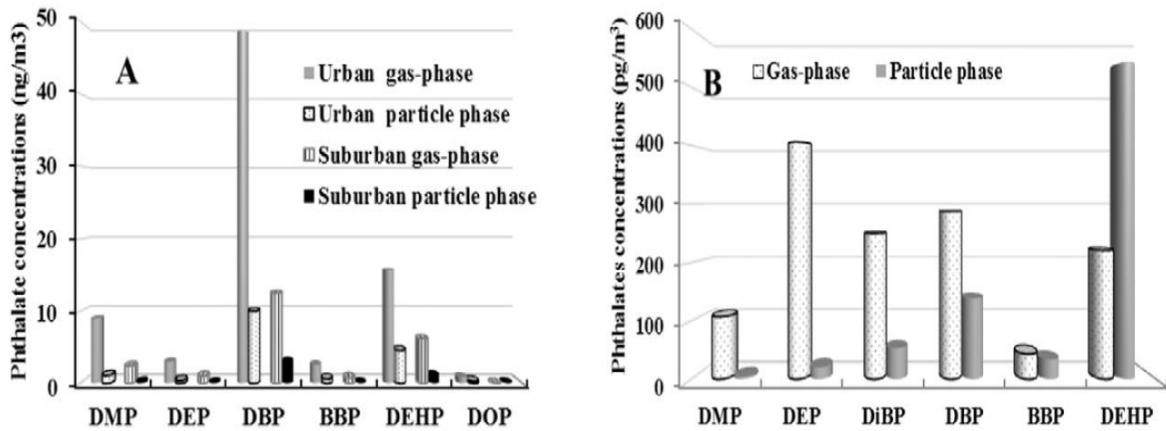


Figure 5. Comparison between atmospheric PAEs concentration detected in (a) East China (Wang et al., 2008) and (b) in the Arctic (Xie et al., 2007).

DMP, DEP, DiBP, DnBP, and DEHP were detected in marine aerosols. Their total concentrations were 0.79-12.4 ng/ m³, with an average of 2.6 ng/m³, which were higher than those reported in the North Sea to the high Arctic atmosphere (0.38-1.02 ng/m³) during the summer of 2004 (Xie et al., 2005; Fu et al., 2013). In the gas phase, DiBP and DnBP were present in the highest frequency, which led to these compounds possessing the highest concentrations of the PAEs investigated. DEHP was also frequently detected in the gas phase air, but its concentration was much lower than the concentrations detected for DiBP and DnBP. In the dust phase, DEHP was the predominant PAE identified, followed by DnBP and DiBP.

The average of the air-sea exchange fluxes was estimated at -338 ng/m²/day for DnBP and -13 ng/m²/day for BBzP, suggesting a net deposition (Xie et al., 2005). However, the air-sea exchange fluxes of DEHP ranged from -95 to 686 ng/m²/day with average of 53 ng/m²/day, indicating that DEHP can be both deposited and volatilized from the surface water but volatilization is dominant. Volatilization and deposition process of PAEs in air-sea interface depend on the H value. PAEs with low H values such as DnBP and BBzP were preferentially deposited on sea surface, whereas DEHP with high H was

dominated by volatilization. Air-sea exchanges of PAEs have also been estimated for the Norwegian, the Greenland and the Arctic seas (Xie et al., 2007), where DEHP deposition dominated the air-sea gas exchange, while volatilization from seawater took place in the near-coast environment. The estimated net gas deposition of DEHP was 5, 30 and 190 tons per year for the Norwegian, the Greenland and the Arctic Seas (Xie et al., 2007), respectively, suggesting that atmospheric transport and deposition of PAEs is a significant process for their occurrence in the remote Atlantic and Arctic Oceans.

3.3 Sediment

Levels of phthalates in sediment are affected by many water quality factors, such as oxygen supply in the water, water temperature and pH. It has been reported that half-lives of phthalates in sediment with an anaerobic condition were 3-10 times higher than those with aerobic condition (Clara et al., 2010; Chang et al., 2004; 2005). PAEs in sediment are dominated by DEHP, in few studies > 95%, ranging from 0.2 to 8.4 $\mu\text{g/g}$ dw (average: 0.7 $\mu\text{g g dw}$) (Cuvillier-Hot et al., 2018; Chen et al., 2017, 2016; Blair et el., 2009).

3.4 Biota

PAEs and their metabolites were detected from the top of food chain (plankton, algae) to predator organisms (fish, marine mammals) (Ye et al., 2014; Cheng et al., 2013; Guven et al., 2013; Fossi et al., 2012; Huang et al., 2008). DnBP, DnOP, and DEHP were the three PAEs that can be bioconcentrated at high level in fish, shellfish and green algae (Huang et al., 2008; Jonsson and Baun, 2003; Munshi et al., 2013). Plankton and shellfish can accumulate individual PAE up to few hundreds ng/g (Han and Liu, 2017; Xiang et al., 2017; Huang et al., 2015; Morin, 2003). For freshwater ecosystem, the concentrations of

individual PAE detected in fish species were in the range of not detected levels (nd) to few hundreds µg/g (Cheng et al., 2013; Huang et al., 2008, 2015) and two order of magnitude lower were reported for marine fish (Guven et al., 2013; Cheng et al., 2013). In marine mammal, individual PAE was detected in the range of <LOQ to few µg/g (Fossi et al., 2012). The highest concentration was detected in liver of Beluga whale *Delphinapterus leucas*, which the concentration can be up to 4.15 µg/g of DEHP in wet weight animal (Morin, 2003). Bioaccumulation and bioconcentration factors (BAF or BCF) have been calculated for PAEs. A BCF or BAF >1000 indicates a high capacity for the species to accumulate or concentrate the pollutant (Porter and Hayden, 2002). Few study was focused on BAF of PAEs in biota. Fishes have been reported to concentrate PAEs at significant level with total BCF of 57, 117, 45–663, 11–900, 207, and 2668–2125 mL/g/wet, respectively for DMP, DEP, BBzP, DEHP, DiOP, and DnDP. BCF for aquatic organisms were reported by Staples et al. (1997). Crustaceans and insects can accumulate DnBP with total BCF of 185–1485 and 458–714 mL/g/wet, respectively. DnBP accumulation in Antarctic krill was reported in a recent study, reaching value of 104.3 ± 0.05 mg/kg (Han and Liu, 2017). Total BCF of 100 mL/g/wet has been reported for BBzP for Mollusca. DnOP can bioconcentrate various aquatic species including in algae, mollusca, crustacean and insecta with total BCF of 8412, 699, 1429, and 1338 mL/g/wet, respectively. Similarly, DEHP were measured at high level of total BCF at 987, 264-2627, 83-3916, and 315-1892 mL/g/wet respectively for algae, mollusca, crustaceans and insects. Low molecular weight PAEs (DMP and DEP) were detected to accumulate at low level in aquatic species. The low values of BAF and BCF for some PAEs may be due to the fact that PAEs can be degraded or metabolized. Indeed, microbes from diverse habitats have been showed to degrade PAEs (Staples et al., 1997). High metabolite product of DEHP (MEHP) has been detected in plankton (Morin, 2003) which indicates that plankton can biodegrade DEHP by converting to MEHP.

4 PAEs biodegradation

Numerous studies have demonstrated that microorganisms play the major roles in the phthalates degradation in the environment under various conditions (Staples et al., 1997). PAEs with shorter ester chains like DMP, DEP, DiBP, DnBP and BzBP can be readily biodegraded and mineralized. Otherwise, phthalates with longer ester chains, such as DHP, DEHP and DnOP, are less susceptible to biodegradation (Chang et al. ,2004). Most phthalate-degrading isolates are either aerobes or facultative anaerobes, mainly from four divisions in Bacteria, i.e. Proteobacteria, Actinobacteria, Firmicutes and Bacteroids/Chlorobi. Among them, the commonly found genera are Sphingomonas (α -Proteobacteria), Comamonas (β -Proteobacteria), Pseudomonas (γ -Proteobacteria), as well as Arthrobacter and Rhodococcus (Liang et al., 2008). In addition, few fungi species (Lee et al., 2007; Kim and Lee, 2005) as well as green microalga (Gao and Chi, 2015; Yan and Pan 2004; Yan et al., 2002) can also degrade phthalates. In natural environments, complete degradation of phthalates is always carried out syntrophically by several members of microorganisms (Gu et al. 2005). The biodegradation of phthalates primarily involves the sequential hydrolysis of ester linkage, which results in monoesters, and then phthalic acid (PA), while forming alcohols simultaneously. Thus, the microbial assimilation of phthalates requires diverse metabolic genes and enzymes, indicating a single organism is unlikely able to completely mineralize phthalates (Staples et al., 1997).

PAEs biodegradation is normally characterized by four common elements in different environmental matrix: i) decrease in biodegradability with the increase in phthalates side chain length; ii) anaerobic degradation of phthalates is generally much slower than aerobic degradation (Staples et al., 1997; Clara et al., 2010); iii) the primary biodegradation of phthalates is always expressed in the first-order kinetics (Wang et al.,

1997; Gavala et al., 2003); iii) high concentration of phthalates and their metabolites inhibit their biodegradation (Liang et al., 2008). Generally, PAEs are not readily mineralized in the wastewater treatment processes since high hydrophobicity and low solubility allow phthalates to be adsorbed to suspended organic matter and subsequently transferred to settled sludges (Gavala et al., 2003). Although adsorption is found to be dominant, biodegradation also contributes to the removal of phthalates (Marttinen et al., 2003; Oliver et al., 2005). In the river sediment, the 6PAEs could be biodegraded with average half-lives of 2.5-14.8 in aerobic conditions and 14.4-34.7 days in anaerobic conditions (Amir et al., 2005) and the biodegradation of DEHP is reported almost complete in 2 days in water (Yuwatini et al., 2006). Aerobic microorganisms, such as *Acinetobacter lwoffii* (Hashizume et al., 2002) and *Sphingomonas* sp. (Kim et al. 2008) and anaerobes, such as *Clostrium* sp. and *Bacillus* sp. (Chang et al., 2005), that can degrade phthalates have been isolated from river sediment. Additionally, few PAE-degrading bacteria have been isolated from marine environments (Chen et al., 2017; Wang et al., 2016; Gu et al., 2009) and a recent study suggests that the ability to degrade phthalate and its monoesters is widespread in Japanese seawater from bacteria related to 11 different genera (Iwaki et al., 2012) and in seawater sediment in Taiwan from 1784 potentially species of bacteria (Chen et al., 2017). Phytoplankton in the aquatic environment can also efficiently degrade phthalates under proper nitrogen and phosphorous nutrient and illumination conditions (Gao and Chi, 2015; Ozkan and Berberoglu, 2013; Li et al. 2007). However, little is known on the marine bacterial degradation of PAEs in seawater and more investigations are needed to fully understand the impact of bacterial community on PAEs distribution in the ocean.

4.1 Biodegradation pathways

Generally, PAEs biodegradation consists of two processes: primary biodegradation from diesters to monoesters and then to PA and ultimate biodegradation from PA to CO₂ and/or CH₄ (Wang et al., 2016; Wu et al., 2011; Staples et al., 1997). Primary degradation consists of different type of pathways, including de-esterification or dealkylation, β-oxidation and trans-esterification (Fig. 6). i) De-esterification: the most common one is the de-esterification of PDEs serially to form PMEs and PA (Wu et al., 2011). ii) β-oxidation: Phthalates with longer side chains than DEP are occasionally converted to those with shorter chains by β-oxidation, which removes one ethyl group each time (Amir et al., 2005). Then, DEP is further converted to PA by de-esterification or an alternative trans-esterification. iii) Transesterification (or demethylation): DEP can be degraded by replacing a ethyl group with a methyl group in each step, producing ethyl-methyl phthalate and then DMP (Cartwright et al., 2000).

The final step of degradation consist in the ring cleavage of PA and two different paths are identified under aerobic and anaerobic conditions (Cartwright et al., 2000). Under the aerobic condition, PA is degraded by two dioxygenase catalized pathways, forming the common intermediate protocatechuate (3, 4-dihydroxy benzoate; Nomura et al., 1992). Protocatechuate is then metabolized further through either ortho- or meta-cleavage by ring cleavage enzymes (Eaton and Ribbons, 1982) to pyruvate and oxaloacetate. Anaerobic degradation of PA was reported through decarboxylation to benzoate (Liu and Chi, 2003). Benzoate is then cleaved and degraded via β-oxidation to hydrogen, carbon dioxide, and acetate (Elder and Kelly, 1994).

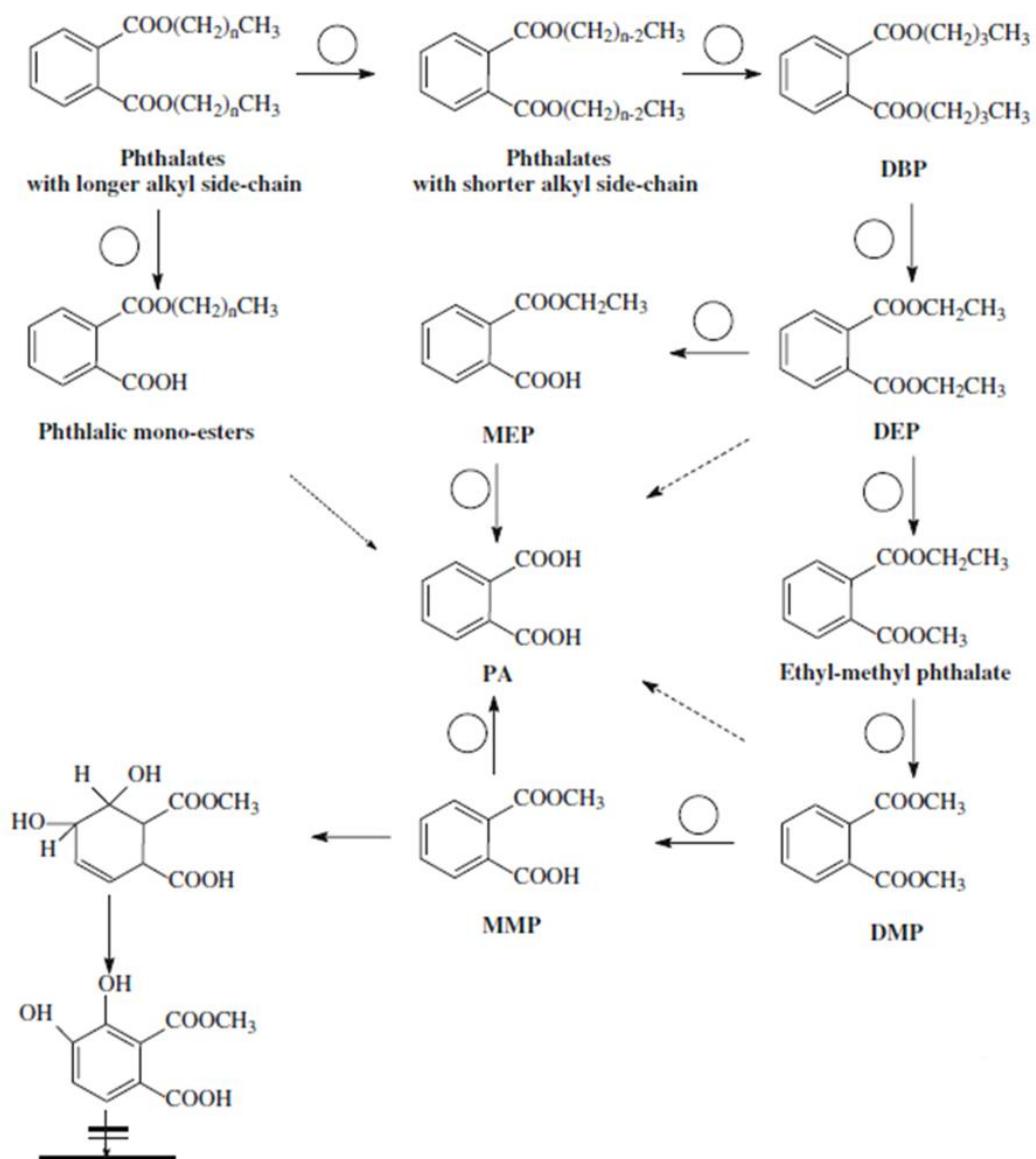


Figure 6. PAEs primary biodegradation pathways

5 Exposure, toxicity and regulation

The potential of PAEs to produce adverse effects in humans has been the subject of considerable discussion. Many toxicity studies have been conducted in laboratory animals, especially in rats (Corton and Lapinskas, 2005; Foster, 2006) and some PAEs and their metabolites produce reproductive and developmental toxicities in laboratory animals. Despite studies in human populations have not been adequate to assess the toxic potential on human health, some recent studies have suggested possible associations between environmental exposure to PAEs and adverse effects on human reproductive health (Wang et al., 2016; Wang et al., 2014; Han et al., 2014). Humans are mainly exposed to PAEs from food contaminated during growth, processing and packaging or from storage, drinking water, indoor air or dermal contact with cosmetics containing PAEs (Koniecki et al., 2011; Guo and Kannan, 2011; Guo et al., 2014). DEHP, DnBP and BzBP were particularly found in fatty foods including dairy products (Kavlock et al., 2002). Blood, serum and urine are the general choice of biological matrixes to assess the level of PAEs and their metabolites exposure in human and daily intake of DMP, DEP, DnBP, DiBP, BBzP, and DEHP has been estimated in the range of 0.08–69.58 µg/kg/day (Das et al., 2014; Wang et al., 2016; Clark et al., 2011). Food represent the major contributor with more than 67% of human intake (Das et al., 2014) and the most frequently detected PAEs were reported to be DnBP and DEHP, found at highest levels in venous blood followed by breast milk, umbilical cord blood and urine (Wang et al., 2016; Chen et al., 2008).

The main concerns related to exposure to PAEs in humans are the effects on reproduction, including fertility problems (effect of endocrine disruption) (Han et al., 2014; Wang et al., 2016; Joensen et al., 2012; Mendiola et al., 2011), the development of newborns and carcinogenic character (Behnke et al., 1987).

5.1 Endocrine disruption effect

Endocrine disruptors (EDCs) are exogenous compounds with the potential to disturb hormonal regulation and the normal endocrine system, consequently affecting health and reproduction in animals and humans (U.S. EPA, 2014). Some of these chemicals bind to intracellular receptor proteins for steroid hormones and evoke hormonal effects in animals, humans and cell culture (Mariana et al., 2016). EDCs may possess multiple mechanisms of action, but because many EDCs are small lipophilic compounds, one privileged route is through their direct interaction with a nuclear receptors (NRs), which are activated by interaction with small lipophilic hormones such as sex steroid hormones (Casals-Casas and Desvergne, 2011). This presumably perturbs or modulates downstream gene expression.

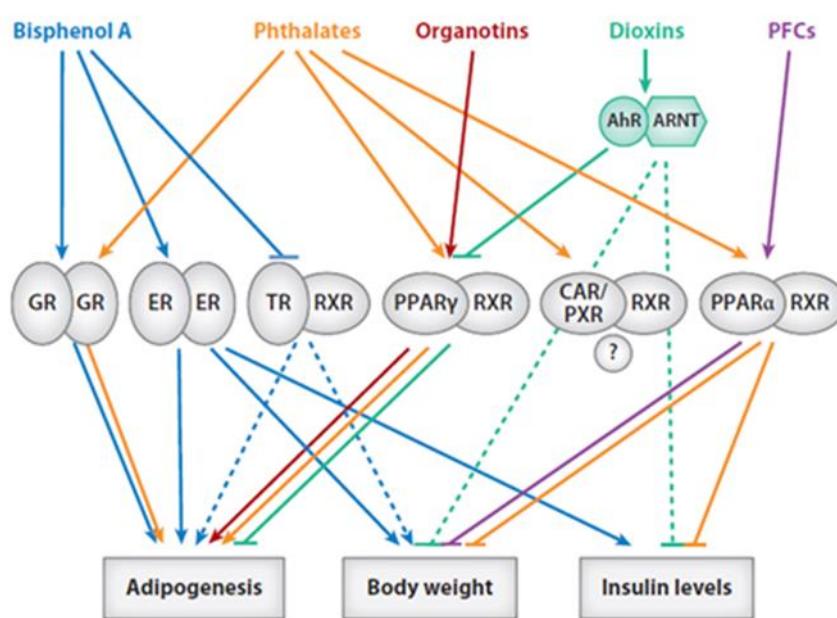


Figure 7. ECDs interaction with receptors. PAEs can influence three peroxisome proliferator-activated receptor (PPAR) interfering with adipogenesis, insulin levels and body weight (From Casals-Casas, C., Desvergne, 2001)

Laboratory experiments have demonstrated that exposure of fetuses to endocrine-disrupting chemicals can strongly disturb organ differentiation (Colborn et al., 1993), acting as hormone agonists or antagonists. Toxicology approaches have demonstrated that PAEs can directly influence peroxisome proliferator-activated receptor (PPAR) activity (Fig.7-8) and they can be considered as EDCs (Feige et al., 2007). PPARs potentially constitute important targets for environmental factors. They are lipid sensors that cooperate in different organs to adapt gene expression to a given metabolic status, as fat storage in the adipose tissue by promoting the differentiation and the survival of adipocytes, but also plays major roles in the control of insulin sensitivity (Feige et al., 2007).

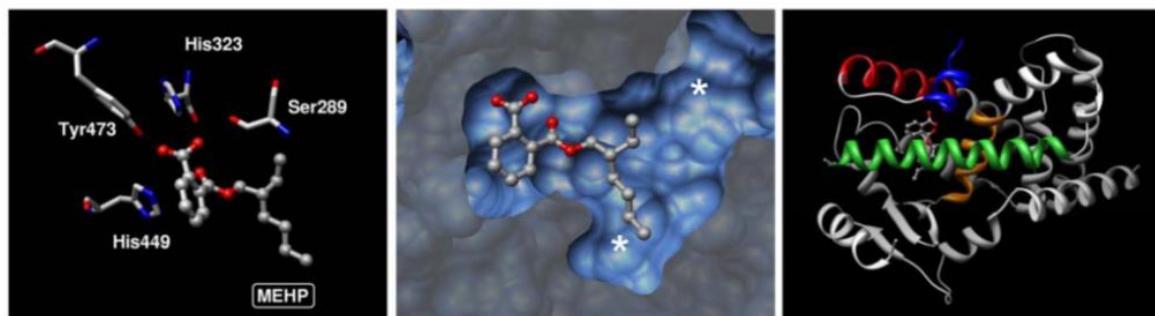


Figure 8. MEHP bind to the PPAR ligand-binding domain. Left panels represent interactions with key residues of the LBD. Middle panels describe the positioning in the LBD cavity where asterisks represent the two parts of the T-shaped ligand binding pocket. The right panels show the position of the ligand in the secondary structure of the receptor. From Feige et al., 2007.

PAEs, once incorporated into the human body, are short lived and are rapidly metabolized in a two phase process (Frederiksen et al., 2007). At first, diester phthalates are hydrolyzed into monoester phthalates and then, the conjugation process leads to the urinary excretion of the conjugated metabolites (Casals-Casas and Desvergne, 2011). Upon ingestion, pancreatic lipases present in the intestine convert DEHP to its monoester MEHP, which is preferentially absorbed (Huber et al., 1996). In addition, MEHP can also be

produced by plasmatic and hepatic lipases, which transform DEHP directly reaching the blood through absorption or medical contamination. This metabolite activates the three PPARs, among the NRs (Bility et al., 2004; Feige et al., 2007), and mediates the action of DEHP on hepatic peroxisome proliferation via PPAR (Fig. 7-8), inducing the expression of a subset of PPAR target genes required for adipogenesis (Feige et al., 2007; Lapinskas et al., 2005).

Experimental studies at low doses of DEHP exposure have demonstrated subtle reproductive toxicity in male rodents (Li et al., 1998). In marine environment, a recent study reported a strong decrease of cell abundance of dinoflagellate *Alexandrium pacifum* after one day of DEHP incubation (62 % of control values) (M'Rabet et al., 2018). Other reproductive outcomes include testicular dysgenesis together with permanent feminization and demasculinization (Foster, 2006). Some epidemiological studies reported an association between cord blood levels of MEHP and shorter gestational age of delivery. Maternal urine levels of metabolites of DEHP are associated with a higher risk of incomplete testicular descent for male human infants and are inversely correlated with the anogenital distance (Joensen et al., 2012; Wang et al., 2014; Mendiola et al., 2011). DnBP was detected for its estrogenic properties for the first time using mammalian estrogen screens in vitro (Jobling et al., 1995). The developmental toxicity of DnBP was evaluated using pregnant rats given DnBP at 250-750 mg/kg/day (Mylchreest et al., 1999). These studies found that the male offspring display an unusually high incidence of reproductive tract malformations, as decrease of anogenital distance, testicular and epididymal atrophy, widespread germ cell loss, absence of prostate gland and seminal vesicles. This was confirmed by recent studies in marine invertebrate and fish embryos (Lu et al., 2017; Ye et al., 2014). Other developmental effects of PAEs exposure may cause damage to the pulmonary system and may result in asthma (Gascon et al., 2015). More recently, several

studies have demonstrated a correlation between phthalates and metabolic disorders with deregulation of levels of serum insulin, blood glucose, liver glycogen (Wu et al., 2017; Mariana et al., 2016).

5.2 Regulations

The WHO recommends the concentration of DEHP in drinking water below 8 µg/L (WHO, 2004) and as well country such as U.S., Australia, Japan, and New Zealand have recommended a DEHP maximum value in drinking water to be 6 µg/L, 9, 100, and 10 µg/L respectively (Julinova and Slavic, 2012; Maycock et al., 2008). Serious questions have been raised about toy and childcare applications, especially if the toys are susceptible to being chewed or sucked by children (Wang et al., 2014; Marcilla et al., 2004). The use of PAEs in toys or objects that can be placed in the mouth of children is now restricted or prohibited in many countries such as UE, U.S., Canada, Argentina, Brazil, and Japan.

Six PAEs (DMP, DEP, DnBP, BBzP, DEHP, and DnOP) have been included in the list of priority pollutants compiled by both the U.S. (U.S. EPA, 2014), the EU (CEC, 2007) and on the list of priority pollutants in Chinese waters (National Standard of the People's Republic of China, Standard for drinking water quality GB 5749-2006.). The EU has included DnBP and DEHP in the list of substances suspected to cause endocrine disruption and DEHP has been classified as a substance causing toxic effects on fertility and development in humans. To minimize the health and environmental risk, DEHP has been replaced by DiNP and DiDP, which are considered not hazardous. Due to the possible endocrine disrupting effects of PAEs, environmental quality standards (EQSs), based on the annual average concentrations in aquatic environments, have been calculated ranging from 20 µg/L for DEHP to 800 µg/L for DMP (Butwell et a., 2001). However, EU proposed a guideline for environmental quality (NQE) of 1.3 µg/L for DEHP in fresh and marine waters.

6 Scope of the thesis

In this thesis, analytical strategies for the quantitative determination of phthalic acid esters in marine environmental samples are developed. The range of existing procedures for phthalate determination is very broad, from human to environmental samples, and the first scope of this work is to optimize a methodology for trace levels analysis at oceanographic scale, lowering contamination sources at all stages, from field collection to the process of the samples, and improving both the selectivity and sensitivity of detection of these compounds at low seawater concentrations. Then, this methodology has been applied for the detection of PAEs in the marine environment. Because of the lack of information on the occurrence of phthalates in seawater, especially in Mediterranean Sea, the second objective of this thesis is the determination of seasonal and vertical distribution of PAEs in both the Bay of Marseille and the Gulf of Lion (North Western Mediterranean Sea). Finally, the last objective of this work is the investigation of the potential release of phthalates from plastic fragments, through laboratory experiments, and the presence of PAEs in seawater.

In Chapter 1, the optimization of the method for PAEs analysis in seawater is reported, improving an existing methods, also describing its application to different marine environmental matrices such as seawater, river plumes and rivers. The chapter consists in the publication N° 1 (Paluselli et al., 2017, Progress in Oceanography, DOI:10.1016/j.pocean.2017.06.002).The optimized method was then applied to all other experiments.

In chapter 2, we describe the occurrence and the vertical and seasonal distributions of phthalates in seawater samples from the Bay of Marseille. The study is summarized in

the publication N°2 (Paluselli et al., 2018, STOTEN, DOI: 10.1016/j.scitotenv.2017.11.306).

Chapter 3 describes the results of the experiments focusing on PAEs migration from plastic fragments and PAEs biodegradation in seawater. Two common plastic materials were used for these experiments, the trash black plastic bags and the insulation layers of the electrical cables. This chapter consist in the publication N° 3 (Paluselli et al., in preparation).

At the end of the manuscript, we present our contributions to other studies on the topic, including two reviews on methodology and occurrence of phthalates in the environment, a study on the occurrence of microplastics at the surface waters of the Gulf of Lion and, finally, a comparative study on the occurrence of persistent organic pollutant in the marine aerosols around Marseille. This thesis was supported by PACA region (PhD scholarship to Andrea Paluselli), and funded by LABEX OT-Med, Plastic-Micro CNRS-EC2CO and the JPI-Ocean PLASTOX projects.

References

- Amir, S.; Hafidi, M.; Merlini, G.; Hamdi, H; Jouraiphy, A.; El Gharous, M.; Revel, J.C. Fate of phthalic acid esters during composting of both lagooning and activated sludges. *Process. Biochem.* **2005**, 40, 2183-2190.
- Andrade, A.L., Neal, M.A. Applications and societal benefits of plastics. *Philos. Trans. R. Soc. Lond. Ser. B Biol. Sci.* **2009**, 364, 1977-1984.
- Barnes, D.K.A., Galgani, F., Thompson, R.C., Barlaz, M. Accumulation and fragmentation of plastic debris in global environments. *Philos. Trans. R. Soc. Lond. Ser. B Biol. Sci.* **2009**, 364, 1985-1998.
- Behnke, W.; Nolting, F.; Zetzsche, C. An aerosol smog chamber for testing abiotic degradation. In Pesticide Science and Biotechnology, Proceedings of the International Congress of Pesticide Chemistry; Greenhalgh, R., Roberts, T.R. Eds. ; Blackwell Publishers: Oxford, UK, **1987**, 401-404.
- Bility, M.T., Thompson, J.T., McKee, R.H., David, R.M., Butala, J.H., Vanden Heuvel, J.P., Peters, J.M. Activation of mouse and human peroxisome proliferator-activated receptors (PPARs) by phthalate monoesters. *Toxicol. Sci.* **2004**, 82:170-82.
- Blair, J.D.; Ikonomou, M.G.; Kelly, B.C.; Surridge, B.; Gobas, F. Ultra-Trace Determination of Phthalate Ester Metabolites in Seawater, Sediments, and Biota from an Urbanized Marine Inlet by LC/ESI-MS/MS. *Environ. Sci. Technol.* **2009**, 43, 6262-6268.
- Brasche, S.; Bischof, W. Daily time spent indoors in German homes-Baseline data for the assessment of indoor exposure of German occupants. *Int. J. Hyg Environ. Health* **2005**, 208 (4), 247-253.
- Brossa, L.; Marcé, R.; Borrull, F.; Pocurull, E. Occurrence of twenty-six endocrine-disrupting compounds in environmental water samples from Catalogna, Spain. *Environ. Toxicol. Chem.* **2005**, 24, 261-267.
- Browne, M.A., Niven, S.J., Galloway, T.S., Rowland, S.J., Thompson, R.C. Microplastic moves pollutants and additives to worms, reducing functions linked to health and biodiversity. *Curr. Biol.* **2013**, 23, 2388-2392.
- Butwell, A. J.; Hetheridge, M.; James, H. A.; Johnson, A. C.; Young, W. F. Endocrine Disrupting Chemicals in Wastewater: A Review of Occurrence and Removal. Water Industry Research Limited (UKWIR): London, **2001**.
- Cartwright, C.D.; Owen, S.A.; Thompson, I.P.; Burns, R.G. Biodegradation of diethyl phthalate in soil by a novel pathway. *FEMS Microbiol. Lett.* **2000**, 186, 27-34.
- Casals-Casas, C., Desvergne. B. Endocrine Disruptors: From Endocrine to Metabolic Disruption. *Annu. Rev. Physiol.* **2011**, 73, 135-62.
- CEC (Commission of the European Communities): Brussels, **2007**. Commission Staff Working Document on the Implementation of the Community Strategy for Endocrine Disrupters A Range of Substances Suspected of Interfering with the Hormone Systems of Humans and Wildlife.

Introduction

Chang, B.V.; Yang, C.M.; Cheng, C.H.; Yuan, S.Y. Biodegradation of phthalate esters by two bacteria strains. *Chemosphere* **2004**, 55, 533-538.

Chang, B.V.; Liao, C.S.; Yuan, S.Y. Anaerobic degradation of diethyl phthalate, di-n-butyl phthalate, and di-(2-ethylhexyl) phthalate from river sediment in Taiwan. *Chemosphere* **2005**, 58, 1601-1607.

Chen, J.A.; Liu, H.; Qiu, Z.; Shu, W. Analysis of di-n-butyl phthalate and other organic pollutants in Chongqing women undergoing parturition. *Environ. Pollut.* **2008**, 156 (3), 849-853.

Chen, C.F., Chen, C.W., Ju, Y.R. Dong, C.D. Determination and assessment of phthalate esters content in sediments from Kaohsiung Harbor, Taiwan. *Mar. Pollut. Bull.* **2016**, 124 (2), 767-774.

Chen, C.F., Chen, C.W., Chen, T.M., Ju, Y.R., Chang, Y.K., Dong, C.D. Phthalate ester distributions and its potential-biodegradation microbes in the sediments of Kaohsiung Ocean Dredged Material Disposal Site, Taiwan. *Int. Biodegrad. Biodegradation*. **2017**.

Cheng, Z.; Nie, X.P.; Wang, H.S.; Wong, M.H. Risk assessments of human exposure to bioaccessible phthalate esters through market fish consumption. *Environ. Int.* **2013**, 54, 75-80.

Cizdziel, J.V.; Hodge, V.F. Attics as archives for house infiltrating pollutants: trace elements and pesticides in attic dust and soil from southern Nevada and Utah. *Microchem. J.* **2000**, 64 (1), 85-92.

Clara, M., Windhofer, G., Hartl, W., Braun, K., Simon, M., Gans, O., Scheffknecht, C., Chovanec, A. Occurrence of phthalates in surface runoff, untreated and treated wastewater and fate during wastewater treatment. *Chemosphere* **2010**, 78 (9), 1078-1084.

Clark, K.E.; David, R.M.; Guinn, R.; Kramarz, K.W.; Lampi, M.A.; Staples, C.A. Modeling human exposure to phthalate esters: A comparison of indirect and biomonitoring estimation methods. *Hum. Ecol. Risk Assess.* **2011**, 17 (4), 923-965.

Colborn, T., Vom Saal, F.S., Soto, A.M. Developmental effects of endocrine-disrupting chemicals in wildlife and humans. *Environ. Health Perspect.* **1993**, 101, 378-384.

Collignon, A., Hecq, J.H., Galgani, F., Voisin, P., Collard, F., Goffart, A. Neustonic microplastic and zooplankton in the North Western Mediterranean Sea . *Mar. Pollut. Bull.* **2012**, 64(4), 861-864.

Collignon, A., Hecq, J.H., Galgani, F., Collard, F., Goffart, A. Annual variation in neustonic micro- and meso-plastic particles and zooplankton in the Bay of Calvi (Mediterranean-Corsica). *Mar. Pollut. Bull.* **2014**, 79, 293-298

Cooper, D.A., Corcoran, P.L. Effects of mechanical and chemical processes on the degradation of plastic beach debris on the island of Kauai, Hawaii. *Mar. Pollut. Bull.* **2010**, 60 (5), 650-654.

Corton, J.C.; Lapinskas, P.J. Peroxisome proliferator-activated receptors: mediators of phthalate ester-induced effects in the male reproductive tract. *Toxicol. Sci.* **2005**, 83, 4-17.

Cousin, J.C.; Mackay, D.; Parkerton, T.F. Physical-Chemical properties and evaluative fate modeling of phthalate esters. *The Handbook of Environmental Chemistry* **2003**, 3, 57-84.

Cousins, I.; Mackay, D. Correlating the physical-chemical properties of phthalate esters using the ‘three solubility’ approach. *Chemosphere* **2000**, 41 (9), 1389-1399.

Cózar, A., Echevarría, F., González-Gordillo, J.I., Irigoien, X., Úbeda, B., Hernández-León, S., Palma, A.T., Navarro, S., García-de-Lomas, J., Ruiz, A., Fernández-de-Puelles, M.L., Duarte, C.M. Plastic debris in the open ocean. *PNAS* **2014**, 111 (28), 10239-10244.

Cózar, A., Sanz-Martín, M., Martí, E., González-Gordillo, J.I., Ubeda, B., Gálvez, J.Á., Irigoien, X., Duarte, C.M. Plastic accumulation in the mediterranean sea. *PLoS ONE* **2015**, 10 (4), 1-12.

Cuvillier-Hot, V.; Gaudron, S.M.; Massol, F.; Boidin-Wichlacz, C.; Pennel, T.; Lesven, L.; Net, S.; Papot, C.; Ravaux, J.; Vekemans, X.; Billon, G.; Tasiemski, A. Immune failure reveals vulnerability of populations exposed to pollution in the bioindicator species *Hediste diversicolor*. *Sci. Total Environ.* **2018**, 613, 1527-1542.

Das, M.T.; Ghosh, P.; Thakur, I.S. Intake estimates of phthalate esters for South Delhi population based on exposure media assessment. *Environ. Pollut.* **2014**, 189, 118-125.

Eaton, R.W.; Ribbons, D.W. Metabolism of dibutylphthalate and phthalate by *Micrococcus* sp strain 12b. *J. Bacteriol.* **1982**, 151, 48-57.

Elder, D.J.E.; Kelly, D.J. The bacterial degradation of benzoic-acid and benzenoid compounds under anaerobic conditions-unifying trends and new perspectives. *FEMS Microbiol. Rev.* **1994**, 13, 441-468.

Eriksen, M., Lebreton, L.C.M., Carson, H.S., Thiel, M., Moore, C.J., Borerro, J.C., Galgani, F., Ryan, P.G., Reisser, J. Plastic pollution in the world's oceans: more than 5 trillion plastic pieces weighing over 50,000 tons afloat at sea. *PLoS ONE* **2014**, 9 (12), 1-15.

Faure, F., Saini, C., Potter, G., Galgani, F., De Alencastro, L.F., Hagmann, P. An evaluation of surface micro- and mesoplastic pollution in pelagic ecosystems of the Western Mediterranean Sea. *Environ. Sci. Pollut. Res.* **2015**, 22 (16), 12190-12197.

Feige, J.N., Gelman, L., Rossi, D., Zoete, V., Metivier, R., Tudor, C., Anghel, S.I., Grosdidier, A., Lathion, C., Engelborghs, Y., Michielin, O., Wahli, W., Desvergne, B. The endocrine disruptor monoethylhexyl-phthalate is a selective peroxisome proliferator-activated receptor γ modulator that promotes adipogenesis. *J. Biol. Chem.* **2007**, 282, 19152-66.

Fischer, I., Schmitt, W.F., Porth, H., Allsopp, M.W., Vianello, G. Poly(vinyl chloride). *Ullmann's Encycl. Ind. Chem.* **2014**.

Fossi, M.C.; Panti, C.; Guerranti, C.; Coppola, D.; Giannetti, M.; Marsili, L.; Minutoli, R. Are baleen whales exposed to the threat of microplastics? A case of study of the Mediterranean fin whale (*Balaenoptera physalus*). *Mar. Pollut. Bull.* **2012**, 64, 2374-2379.

Fossi, M.C., Marsili, L., Baini, M., Giannetti, M., Coppola, D., Guerranti, C., Caliani, I., Minutoli, R., Lauriano, G., Finoia, M.G., Rubegni, F., Panigada, S., Berube, M., Ramírez, J.U., Cristina Panti, C. Fin whales and microplastics: The Mediterranean Sea and the Sea of Cortez scenarios. *Environ. Pollut.* **2016**, 209, 68-78.

Fossi, M.C., Romeo, T., Baini, M., Panti, C., Marsili, L., Campan, T., Canese; P., Galgani, F., Druon, J.N., Aioldi, S., Taddei, S., Fattorini, M., Brandini, C., Lapucci, C. Plastic Debris Occurrence, Convergence Areas and Fin Whales Feeding Ground in the Mediterranean Marine Protected Area Pelagos Sanctuary: A Modeling Approach. *Front. Mar. Sci.* **2017**, 4, 167.

Introduction

Foster, P.M. Disruption of reproductive development in male ratoffspring following in utero exposure to phthalate esters. *Int. J. Androl.* **2006**, 29, 140-147.

Frederiksen, H., Skakkebaek, N., Andersson, A. Metabolism of phthalates in humans. *Mol. Nutr. Food Res.* **2007**, 51, 899-911.

Fromme, H.; Kuchler, T.; Otto, T.; Pilz, K.; Muller, L.; Wenzel, A. Occurrence of phthalates and bisphenol A and F in the environment. *Water Res.* **2002**, 36, 1429-1438.

Fu, P.Q.; Kawamura, K.; Chen, J.; Charrière, B.; Sempéré, R. Organic molecular composition of marine aerosols over the Arctic Ocean in summer: Contributions of primary emission and secondary aerosol formation. *Biogeosciences* **2013**, 10, 653-667.

Gascon, M., Casas, M., Morales, E., Valvi, D., Gomez, A., Luque, N., Rubio, S., Monfort, N., Ventura, R., Martinez, D., Sunyer, J., Vrijheid, M. Prenatal exposure to bisphenol A and phthalates and childhood respiratory tract infections and allergy. *J. Allergy Clin. Immunol.* **2015**, 135 (2), 370-378.

Gao, J. and Chi, J. Biodegradation of phthalate acid esters by different marine microalgal species. *Mar. Pollut. Bull.* **2015**, 99, 70-75.

Gao, D.W., Wen, Z.D. Phthalate esters in the environment: A critical review of their occurrence, biodegradation, and removal during wastewater treatment processes. *Sci. Total Environ.* **2016**, 541, 986-1001.

Gavala, H.N.; Alatriste-Mondragon, F.; Iranpour, R.; Ahring, B.K. Biodegradation of phthalate esters during the mesophilic anaerobic digestion of sludge. *Chemosphere* **2003**, 52, 673-682.

Gu, J.D.; Li, J.; Wang, Y. Biochemical pathway and degradation of phthalate ester isomers by bacteria. *Water. Sci. Technol.* **2005**, 52, 241-248.

Gu, J.; Han, B.; Duan, S.; Zhao, Z.; Wang, Y. Degradation of the endocrine-disrupting dimethyl phthalate carboxylic ester by *Sphingomonas yanoikuyae* DOS01 isolated from the South China Sea and the biochemical pathway. *Int. Biodeterior. Biodegradation* **2009**, 63 (4), 450-455.

Guo, Y.; Kannan, K. Comparative assessment of human exposure to phthalate esters from house dust in China and the United States. *Environ. Sci. Technol.* **2011**, 45 (8), 3788-3794.

Guo, Y., Wang, L., Kannan, K. Phthalates and parabens in personal care products from China : concentration and human exposure. *Arch. Environ. Contam. Toxicol.* **2014**, 66-113-119.

Güven, K.C.; Coban, B. Phthalate pollution in fish *Sarda sarda*, *Engraulis encrasiculus*, *Mullus surmuletus*, *Merlangius merlangus* and shrimp *Parapenaeus longirostris*. *J. Black Sea/Mediterr. Environ.* **2013**, 19 (2), 185-189.

Han, X., Cui, Z., Zhou, N., Ma, M., Li, L., Li, Y. Urinary phthalate metabolites and male reproductive function parameters in Chongqing general population, China. *Int. J. Hyg. Environ. Health* **2014**, 217, 271-278.

Han, X., Liu, D. Detection of the toxic substance dibutyl phthalate in Antarctic krill. *Antarctic Science*, **2017**.

Introduction

Hashizume, K.; Nanya, J.; Toda, C.; Yasui, T.; Nagano, H.; Kojima, N. Phthalate esters detected in various water samples and biodegradation of the phthalates by microbes isolated from river water. *Biol. Pharm. Bull.* **2002**, 25, 209-214.

Huang, P.C.; Tien, C.J.; Sun, Y.M.; Hsieh, C.Y.; Lee, C.C. Occurrence of phthalates in sediment and biota: relationship to aquatic factors and the biota-sediment accumulation factor. *Chemosphere* **2008**, 73 (4), 539-544.

Huang, J., Nkrumah, P.N., Li, Y., Appiah-Sefah, G. Chemical behavior of phthalates under abiotic conditions in landfills. *Rev. Environ. Contam. Toxicol.* **2013**, 224, 39-52.

Huang, Q., Chen, Y., Chi, Y., Lin, Y., Zhang, H., Fang, C., Dong, S. Immunotoxic effects of perfluorooctane sulfonate and di(2-ethylhexyl) phthalate on marine fish Oryzias melastigma. *Fish Shellfish Immunol.* **2015**, 44, 302-306.

Huber, W.W., Grasl-Kraupp, B., Schulte-Hermann, R. Hepatocarcinogenic potential of di(2-ethylhexyl)phthalate in rodents and its implications on human risk. *Crit. Rev. Toxicol.* **1996**, 26, 365-481.

Hwang, H.M.; Park, E.K.; Young, T.M.; Hammock, B.D. Occurrence of endocrine-disrupting chemicals in indoor dust. *Sci. Total Environ.* **2008**, 404 (1), 26-35.

IARC. Monographs on the Evaluation of Carcinogenic Risks to Humans. Some Industrial Chemicals; International Agency for Research on Cancer: Lyon, France, **2000**, p. 77.

Iwaki, H.; Nishimura, A.; Hasegawa, Y. Isolation and characterization of marine bacteria capable of utilizing phthalate. *World J. Microbiol. Biotechnol.* **2012**, 28 (3), 1321-1325.

Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrade, A., Narayan, R., Law, K.L. Plastic waste inputs from land into the ocean. *Science* **2015**, 347, 768-771.

Jobling, S., Reynolds, T., White, R., Parker, M.G., Sumpter, J.P. A variety of environmentally persistent chemicals, including some phthalate plasticizers, are weakly estrogenic. *Environ. Health Perspect.* **1995**, 103, 582-587

Joensen, U.N., Frederiksen, H., Jensen, M.B., Lauritsen, M.P., Olesen, I.A., Lassen, T.H. Phthalate excretion pattern and testicular function: a study of 881 healthy Danish men. *Environ. Health Perspect.* **2012**, 120, 1397-1403.

Jonsson, S.; Baun, A. Toxicity of mono- and diesters of o-phthalic acid esters to a crustacean, a green alga, and a bacterium. *Environ. Toxicol. Chem.* **2003**, 22, 3037-3043.

Julinova, M., Slavik, R. Removal of phthalates from aqueous solution by different adsorbents: a short review. *J. J Environ Manage* **2012**, 94 (1), 13-24.

Kavlock, R.; Boekelheide, K.; Chapin, R.; Cunningham, M.; Faustman, E.; Foster, P.; Golub, M.; Henderson, R.; Hinberg, I.; Little, R.; Seed, J.; Shea, K.; Tabacova, S.; Tyl, R.; Williams, P.; Zacharewski, T. NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of butyl benzyl phthalate. *Reprod. Toxicol.* **2002**, 16, 453-487.

Introduction

Kim, Y.H.; Lee, J. Enzymatic degradation of dibutyl phthalate and toxicity of its degradation products. *Biotechnol. Lett.* **2005**, 27, 635-639.

Kim, D.S.; Um, H.J.; Lim, E.S.; Min, J.; Kim, Y.H. Degradation of diphenyl phthalate by Sphingomonas chungbukensis. *Biotechnol. Lett.* **2008**, 30, 93-96.

Kimber, I.; Dearman, R.J. An assessment of the ability of phthalates to influence immune and allergic responses. *Toxicology* **2010**, 271 (3), 73-82.

Koniecki, D.; Wang, R.; Moody, R. P.; Zhu, J. Phthalates in cosmetic and personal care products: concentrations and possible dermal exposure. *Environ. Res.* **2011**, 111 (3), 329-336.

Lapinskas, P.J., Brown, S., Leesnitzer, L.M., Blanchard, S., Swanson, C., Cattley, R.C., Corton, J.C. Role of PPARalpha in mediating the effects of phthalates and metabolites in the liver. *Toxicology* **2005**, 207, 149-163.

Lee, S.M.; Lee, J.W.; Koo, B.W.; Kim, M.K.; Choi, D.H.; Choi, I.G. Dibutyl phthalate biodegradation by the white rot fungus, *Polyporus brumalis*. *Biotechnol. Bioeng.* **2007**, 97, 1516-1522.

Li, C., Chen, J., Wang, J., Han, P., Luan, Y., Ma, X., Lu, A. Phthalate esters in soil, plastic film, and vegetable from greenhouse vegetable production bases in Beijing, China: Concentration, sources, and risk assessment. *Sci. Total Environ.* **2016**, 568, 1037-1043.

Li, B.; Chi, J.; Wu, W.X.; Wang, Z.K. Effect of nutrients and light on biodegradation of Dibutyl phthalate and di-2-ethylhexyl phthalate in haihe estuary. *Bull. Environ. Contam. Toxicol.* **2007**, 79, 80-83.

Li, L., Jester, W.J., Orth, J. Effects of relatively low levels of mono-(2-ethylhexyl) phthalate on cocultured Sertoli cells and gonocytes from neonatal rats. *Toxicol. Appl. Pharmacol.* **1998**, 153, 258-65.

Liang, D.W.; Zhang, T.; Fang, H.P.; He, J. Phthalates biodegradation in the environment. *Appl. Microbiol. Biotechnol.* **2008**, 80, 183-198.

Liu, S.M.; Chi, W.C. CO₂-H₂ dependent anaerobic biotransformation of phthalic acid isomers in sediment slurries. *Chemosphere* **2003**, 52, 951-958.

Lu, Y., Lin, M., Aitken, R.J. Exposure of spermatozoa to Dibutyl phthalate induces abnormal embryonic development in a marine invertebrate *Galeolaria caespitosa* (polychaeta: Serpulidae). *Aquat. Toxicol.* **2017**.

Lyman, W.J.; Reehl, W.F.; Rosenblatt, D.H. Handbook of Chemical Property Estimation Methods-Environmental Behavior of Organic Compounds, *American Chemical Society*: Washington, DC, **1990**, Vol. 960.

Maycock, D.; Fawell, J.; Merrington, G.; Watts, C. Review of England and Wales monitoring data for which a national or international standard has been set. *Guidel. Drinking Water Qual.* **2008**, 1-148.

Marcilla, A.; García, S.; García-Quesada, J.C. Study of the migration of PVC plasticizers. *J. Anal. Appl. Pyrolysis* **2004**, 71 (2), 457-463.

Introduction

Mariana, M., Feiteiro, J., Verde, I., Cairrao, E. The effects of phthalates in the cardiovascular and reproductive systems: a review. *Environ. Int.* **2016**, 94, 758-776.

Marttinen, S.K.; Kettunen, R.H.; Rintala, J.A. Occurrence and removal of organic pollutants in sewages and landfill leachates. *Sci. Total. Environ.* **2003**, 301, 1-12.

Mendiola, J., Jorgensen, N., Andersson, A.M., Calafat, A.M., Silave, M.J., Redmon, J.B. Associations between urinary metabolites of di(2-ethylhexyl) phthalate and reproductive hormones in fertile man. *Int. J. Androl.* **2011**, 34, 369-378.

Meng, X.Z., Wang, Y., Xiang, N., Chen, L., Liu, Z.G., Wu, B. Flow of sewage sludge-borne phthalate esters (PAEs) from human release to human intake: implication for risk assessment of sludge applied to soil. *Sci. Total Environ.* **2014**, 476, 242-249.

Moore, C.J. Synthetic polymers in the marine environment: a rapidly increasing, long-term threat. *Environ. Res.* **2008**, 108, 131-139

Morin, A. Distribution of phthalate esters in a marine mammal food chain from Canada's Eastern Arctic, **2003**.

M'Rabet, C., Pringault, O., Zmerli-Triki, H., Gharbia, H.B., Couet, D., Yahia, O.K.D. Impact of two plastic-derived chemicals, the Bisphenol A and the di-2-ethylhexyl phthalate, exposure on the marine toxic dinoflagellate *Alexandrium pacificum*. *Mar. Pollut. Bull.* **2018**, 126, 241-249.

Munshi, A.B.; Karim, N.; Shaukat, S.; Hashmi, D.; Boardman, G.D.; Flick, G.J. Toxicity of phthalates esters in fish and shellfish from Virginia Beach using matrix solid phase dispersion (MSPD) and GC-MS. *J. Chem. Soc. Pak.* **2013**, 36 (6), 1463-1471.

Mylchreest, E., Sar, M., Cattley, R.C., Foster, P.M. Disruption of androgen-regulated male reproductive development by di(n-butyl) phthalate during late gestation in rats is different from flutamide. *Toxicol. Appl. Pharmacol.* **1999**, 156, 81-95.

Nazaroff, W., Weschler, C.J., Little, J.C., Hubal, E.A.C. Intake to production ratio: a measure of exposure intimacy for manufactured chemicals. *Environ. Health Perspect.* **2012**, 120 (12), 1678-1683.

Naito, W.; Gamo, Y.; Yoshida, K. Screening-level risk assessment of di(2-ethylhexyl)phthalate for aquatic organisms using monitoring data in Japan. *Environ. Monit. Assess.* **2006**, 115, 451-471.

Neves, D., Sobral, P., Ferreira, J.L., Pereira, T. Ingestion of microplastics by commercial fish off the Portuguese coast. *Mar. Pollut. Bull.* **2015**, 101, 119–126.

Nomura, Y.; Nakagawa, M.; Ogawa, N.; Harashima, S.; Oshima, Y. Genes in pht plasmid encoding the initial degradation pathway of phthalate in *Pseudomonas putida*. *J. Ferm. Bioeng.* **1992**, 74, 333-344.

Oliver, R.; May, E.; Williams, J. The occurrence and removal of phthalates in a trickle filter STW. *Water Res.* **2005**, 39, 4436-4444.

Okamoto, Y.; Hayashi, T.; Toda, C.; Ueda, K.; Hashizume, K.; Itoh, K.; Nishikawa, J.; Nishihara, T.; Kojima, N. Formation of estrogenic products from environmental phthalate esters under light exposure. *Chemosphere* **2006**, 64 (10), 1785-1792.

Introduction

Orecchio, S.; Indelicato, R.; Barreca, S. Determination of selected phthalates by gas chromatography-mass spectrometry in mural paintings from Palermo (Italy). *Microchem. J.* **2014**, 114, 187-191.

Pei, X.Q., Song, M., Guo, M., Mo, F.F., Shen, X.Y. Concentration and risk assessment of phthalates present in indoor air from newly decorated apartments. *Atmos. Environ.* **2013**, 68, 17-23.

Peijnenburg, W.J.G.M.; Struijs, J. Occurrence of phthalate esters in the environment of the Netherlands. *Ecotoxicol. Environ. Saf.* **2006**, 63, 204-215.

Peng, X., Feng, L., Li,X. Pathway of diethyl phthalate photolysis in sea-water determined by gas chromatography-mass spectrometry and compound-specific isotope analysis. *Chemosphere* **2013**, 90, 220-226.

Plastics Europe, **2015**. Plastics - the Facts 2015: An analysis of European plastics production, demand and waste data. <<http://www.plasticseurope.org/Document/plastics—the-facts-2015.aspx>>

Porter, A.; Hayden, N. Nonylphenol in the Environment: A Critical Review. Department of Civil and Environmental Engineering, University of Vermont: Burlington, VT, **2002**.

Rudel, R.A.; Dodson, R.E.; Perovich, L.J.; Morello-Frosch, R.; Camann, D.E.; Zuniga, M.M.; Yau, A.Y.; Just, A.C.; Brody, J.G. Semivolatile endocrine-disrupting compounds in paired indoor and outdoor air in two Northern California communities. *Environ. Sci. Technol.* **2010**, 44 (17), 6583-6590.

Ruiz-Orejón, L.F., Sardá, R., Ramis-Pujol, J. Floating plastic debris in the Central and Western Mediterranean Sea. *Mar. Environ. Res.* **2016**, 120, 136–144.

Saido, K., Ocean Contamination Generated from Plastics. Comprehensive Water Quality and Purification, Elsevier Inc, **2014**, 1.

Sampath, S., Selvaraj, K.K., Shanmugam, G., Krishnamoorthy, V., Chakraborty, P., Ramaswamy, B.R. Evaluating spatial distribution and seasonal variation of phthalates using passive air sampling in southern India. *Environ. Pollut.* **2017**, 221, 407-417.

Sanchez-Avila, J.; Tauler, R.; Lacorte, S. Organic micropollutants in coastal waters from NW Mediterranean Sea: Sources distribution and potential risk. *Environ. Int.* **2012**, 46, 50-62.

Schreiber, A.; Fu, F.; Yang, O.; Wan, E.; Gu, E.; Le Blanc, Y. Increasing and Confidence in Detection When Analyzing Phthalates by LC-MS/MS, AB Sciex, **2011**.

Suaria, G., Avio, C.G., Mineo, A., Lattin, G.L., Magaldi, M.G., Belmonte, G., Moore, C.J., Regoli, F., Aliani, S. The Mediterranean Plastic Soup: synthetic polymers in Mediterranean surface waters. *Nature Sci. Rep.* **2016**, 6.

Subashchandrabose, S.R., Ramakrishnan, B., Megharaj, M. Mixotrophic cyanobacteria and microalgae as distinctive biological agents for organic pollutant degradation. *Environ. Int.* **2013**, 51, 59-72.

Suhrhoff, T.J., Scholz-Bottcher, B.M. Qualitative impact of salinity, UV radiation and turbulence on leaching of organic plastic additives from four common plastics- A lab experiment. *Mar. Pollut. Bull.* **2016**, 102, 84-94.

Introduction

Staples, C.A.; Peterson, D.R.; Parkerton, T.F.; Adams, W.J. The environmental fate of phthalate esters: a literature review. *Chemosphere* **1997**, 35, 667-749.

Swan, S., Main, K., Liu, F., Stewart, S., Kruse, R., Calafat, A.M., Mao, C.S., Redmon, J.B., Ternand, C.L., Sullivan, S., Teague, J.L. Decrease in anogenital distance among male infants with prenatal phthalate exposure. *Environ. Health Perspect.* **2005**, 113, 1056-61.

Tedetti, M.; Kawamura, K.; Narukawa, M.; Joux, F.; Charrière, B.; Sempéré, R. Hydroxyl radical-induced photochemical formation of dicarboxylic acids from unsaturated fatty acid (oleic acid) in aqueous solution. *J. Photochem. Photobiol. A Chem.* **2007**, 188, 135-139.

Teil, M-J.; Blanchard, M.; Chevreuil, M. Atmospheric fate of phthalate esters in an urban area (Paris-France). *Sci. Total Environ.* **2006**, 354, 212-223.

Turner, A.; Rawling, M.C. The behaviour of di-(2-ethylhexyl) phthalate in estuaries. *Mar. Chem.* **2000**, 68 (3), 203–217.

U.S. EPA (U.S. Environ. Prot. Agency). **2000**. Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC). Washington, DC: U.S. Environ. Prot. Agency. <http://www.epa.gov/scipoly/oscpendo/edspoview/edstac.htm>.

U.S. EPA (U.S. Environ. Prot. Agency) **2014**. United States Environmental Protection Agency, 40 CFR Part 423, Appendix A, December 2014. <https://www.epa.gov/sites/production/files/2015-09/documents/priority-pollutant-list-epa.pdf>.

Vione, D.; Minella, M.; Maurino, V.; Minero, C. Indirect photochemistry in sunlit surface waters: Photoinduced production of reactive transient species. *Chem. Eur. J.* **2014**, 20, 10590-10606.

Wang, J.L.; Liu, P.; Shi, H.C.; Qian, Y. Kinetics of phthalic acid ester degradation by acclimated activated sludge. *Process. Biochem.* **1997**, 32, 567-571.

Wang, J.L.; Chen, L.J.; Shi, H.C.; Qian, Y. Microbial degradation of phthalic acid esters under anaerobic digestion of sludge. *Chemosphere* **2000**, 41, 1245-1248.

Wang, Z.; Jing, M.; Lee, F.S.; Wang, X. Synthesis of 8-hydroxyquinoline Bonded Silica (SHQ) and its application in flow injection-inductively coupled plasma mass spectrometry analysis of trace metals in seawater. *Chin. J. Anal. Chem.* **2006**, 34 (4), 459-462.

Wang, P.; Wang, S.L.; Fan, C.Q. Atmospheric distribution of particulate- and gas-phase phthalic ester (PAEs) in a Metropolitan City, Nanjing, East China. *Chemosphere* **2008**, 72 (10), 1567-1572.

Wang, W.X.; Zhang, Y.L.; Wang, S.L.; Fan, C.Q.; Xu, H. Distributions of phthalic esters carried by total suspended particulates in Nanjing, China. *Environ. Monit. Assess.* **2012**, 184 (11), 6789-6798.

Wang, X.; Tao, W.; Xu, Y.; Feng, J.; Wang, F. Indoor phthalate concentration and exposure in residential and office buildings in Xi'an, China. *Atmos. Environ.* **2014**, 87, 146-152.

Wang, I.J., Lin, C.C., Lin, Y.J., Hsieh, W.S., Chen, P.C. Early life phthalate exposure and atopic disorders in children: a prospective birth cohort study. *Environ. Int.* **2014**, 62, 48-54.

Introduction

Wang, J.W., Luo, Z.H., Xu, W., Ding, J.F., Zheng, T.L. Transformation of dimethyl phthalate esters (DMPEs) by a marine red yeast Rhodotorula mucilaginosa isolated from deep sea sediment of the Atlantic Ocean. *Int. Biodeterior. Biodegradation.* **2016**, 109, 223-228.

Wang, Y.X., Zeng, Q., Sun, Y., You, L., Wang, P., Li, M., Yang, P., Li, J., Huang, Z., Wang, C., Li, S., Dan, Y., Li, Y.F., Lu, W.Q. Phthalate exposure in association with serum hormone levels, sperm DNA damage and spermatozoa apoptosis: A cross-sectional study in China. *Environ. Res.* **2016**, 150, 557-565.

WHO (World Health Organization). Guidelines for Drinking Water Quality, Geneva, **2004**, Vol. 1.

Wolfe, N.L.; Burns, L.A.; Steen, W.C. Use of linear free energy relationship and an evaluative model to assess the fate and transport of phthalate esters in the aquatic environment. *Chemosphere* **1980**, 9, 393-402.

Wu, X.L., Wang, Y.Y. Liang, R., Dai, Q.Y.Jin, D.C., Chan, W.I. Biodegradation of an endocrine-disrupting chemical di-n-butyl phthalate by newly isolated Agrobacterium sp. And the biochemical pathway. *Process Biochem.* **2011**, 46-1090-1094.

Wu, W., Zhou, F., Wang, Y., Ning, Y., Yang, J., Zhou, Y. Exposure to phthalates in children aged 5-7 years: Association with thyroid function and insulin-like growth factors. *Sci. Total. Environ.* **2017**, 579, 950-956.

Xiang, N., Zhao, C., Diao, X., Han, Q., Zhou, H. Dynamic responses of antioxidant enzymes in pearl oyster Pinactada martensii exposed to di(2-ethylhexyl) phthalate (DEHP). *Environ. Toxicol. Pharmacol.* **2017**, 54, 184-190.

Xie, Z.; Ebinghaus, R.; Temme, C.; Lohmann, R.; Cara, A.; Ruck, W. Occurrence and air-sea exchange of phthalates in the Arctic. *Environ. Sci. Technol.* **2007**, 41 (13), 4555-4560.

Xie, Z.; Ebinghaus, R.; Temme, C.; Caba, A.; Ruck, W. Atmospheric concentrations and air-sea exchanges of phthalates in the North Sea (German Bight). *Atmos. Environ.* **2005**, 39, 3209-3219.

Xu, G.; Li, F.S.; Wang, Q.H. Occurrence and degradation characteristics of dibutyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DEHP) in typical agricultural soils of China. *Sci. Total Environ.* **2008**, 393 (2), 333-340.

Yan, H.; Pan, G. Increase in biodegradation of dimethyl phthalate by *Closterium lunula* using inorganic carbon. *Chemosphere* **2004**, 55, 1281-1285.

Yan, H.; Pan, G.; Liang, P.L. Effect and mechanism of inorganic carbon on the biodegradation of dimethyl phthalate by *Chlorella pyrenoidosa*. *J. Environ. Sci. Health Part A* **2002**, 37, 553-562.

Ye, T., Kang,M., Huang,Q., Fanf, C., Chen, Y., Liu, L., Dong, S. Accumulation of Di(2-ethylhexyl) phthalate causes endocrine disruptive effects in Marine Medaka embryos. *Environ. Toxicol.* **2014**.

Yuwatini, E.; Hata, N.; Taguchi, S. Behavior of di-(2-ethylhexyl) phthalate discharged from domestic waste water into aquatic environment. *J. Environ. Monitor.* **2006**, 8, 191-196.

Zeng, F.; Cui, K.Y.; Xie, Z.Y.; Wu, L.N.; Luo, D.L.; Chen, L.X.; Lin, Y.J.; Liu, M.; Sun, G.X. Distribution of phthalate esters in urban soils of subtropical city, Guangzhou, China. *J. Hazard. Mater.* **2009**, 164 (2), 1171-1178.

Introduction

Zeng, F.; Lin, Y.; Cui, K.; Wen, J.; Ma, Y.; Chen, H.; Zhu, F.; Ma, Z.; Zeng, Z. Atmospheric deposition of phthalate esters in a subtropical city. *Atmos. Environ.* **2010**, 44 (6), 834-840.

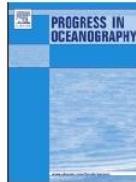
Zhang, Y.; Jiang, X.; Chen, B. Reproductive and developmental toxicity in F1 Sprague-Dawley male rats exposed to di-n-butylphthalate in utero and during lactation and determination of its NOAEL. *Reprod. Toxicol.* **2004**, 18, 669-676.

Zhang, L.; Wang, F.; Ji, Y.; Jiao, J.; Zou, D.; Liu, L.; Shan, C.; Bai, Z.; Sun, Z. Phthalate esters (PAEs) in indoor PM10/PM2.5 and human exposure to PAEs via inhalation of indoor air in Tianjin, China. *Atmos. Environ.* **2014**, 85, 139-146.

Zheng, X.; Zhang, B-T.; Teng, Y. Distribution of phthalate acid esters in lakes of Beijing and its relationship with anthropogenic activities. *Sci. Total Environ.* **2014**, 107-113.

CHAPTER I

METHOD



Occurrence of phthalate acid esters (PAEs) in the northwestern Mediterranean Sea and the Rhone River

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ABSTRACT

Phthalate acid esters (PAEs) which are mainly anthropogenic molecules with endocrine disrupting effects in animals and humans, have been detected in terrestrial and aquatic environments. However, little is known about their distribution in the Mediterranean Sea, mainly because of analytical difficulties and the high possibility of ambient sample contamination. Here, we report the optimization of an existing protocol for the determination of PAEs in seawater and freshwater samples, as well as the first estimation of the source and distribution of phthalates acid esters (PAEs) in coastal waters from the NW Mediterranean Sea. By passing 1 L of sample through glass cartridges packed with 200 mg of Oasis HLB and eluted with 6 mL of ethyl acetate followed by gas chromatography and mass spectrometry (GC/MS) analyses, the recoveries for DMP, DEP, DPP, DiBP, DnBP, BzBP, DEHP and DnOP were 101, 98, 115, 110, 99, 98, 103 and 95%, respectively, with acceptable blank values (below 0.4–4.0% of the masses measured in different seawater samples). By using this method, we detected PAEs in the Marseilles coastal area, offshore (2000 m depth) and in the Rhone River with total concentrations ranging from 75.3 ng/L offshore in surface water to 1207.1 ng/L a few meters above the bottom of the Marseilles Bay. High concentrations were also observed in deep waters offshore (310.2 ng/L) as well as in the Rhone River (615.1 ng/L). These results suggest that Marseilles urban area, Rhone River and sediment are potential sources of PAEs in the areas studied.

In the Rhone River, DEHP was the most abundant PAE (66.1%) followed by DiBP (20.5%) and DnBP (6.6%), whereas a gradual change was observed in the plume of the river with increasing salinity. In the Marseilles Bay, DiBP was the most abundant PAE at the surface (47.3% of total PAEs) followed by DEHP (22.7%) and DnBP (19.1%), whereas DnBP was predominant (38.6%) a few meters above the bottom. By contrast, DEHP was the dominant species in the first 50 m (66.9–76.7%) offshore followed by DnBP (10.9–15.2%), whereas DnBP was the most abundant (57.0–72.6%) followed by DEHP (20.1–33.1%) in the deepest waters. This study suggests that in addition to direct PAEs injection in marine waters, different processes regulate PAE distribution in Mediterranean Sea including photochemical oxidation reactions, bacterial degradation and possible diffusion following release from marine litter near the bottom.

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1. Introduction

Phthalates or phthalic acid ester (PAEs) with low volatility and low water solubility are colorless and odorless. They are mainly produced by anthropogenic activity such as the manufacture and processing of plastic products (Simoneit et al., 2005; Serôdio and Nogueria, 2006; Lyche et al., 2009). Their annual production reached 8 million tons in 2011 (Net et al., 2015a, 2015b and references therein) and they represent approximately 70% of the world

consumption of plasticizer in 2014 (CEH, 2015). The structure of PAEs consists of a di-alkyl ester of *o*-benzenedicarboxylic acid. The most commercially significant PAEs, sorted by increasing number of carbons in the ester side chains, are dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP), benzylbutyl phthalate (BzBP), di-ethylhexyl phthalate (DEHP) and di-n-octyl phthalate (DnOP) the later being the most abundant (Holahan and Smith, 2015). PAEs of lower molecular weight are used as essential components of solvents, adhesives, waxes, pharmaceutical products, insecticide materials and cosmetics, whereas PAEs of higher molecular weight are instead used to improve the flexibility and handling of industrial materials (IARC, 2000;

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As widely used compounds, PAEs are ubiquitous in terrestrial, marine and atmospheric environments (Xie et al., 2007; Fu et al., 2013; Dargnat et al., 2009; Gao et al., 2014; Staples et al., 1997; Net et al., 2014; 2015a-b; Wang et al., 2014). PAEs have been detected in surface seawater (Turner and Rawling, 2000; Horn et al., 2004; Brossa et al., 2005), in indoor air (Becker et al., 2004), in urban environments in soils (Ferreira and Morita, 2012), in urban lakes (Zeng et al., 2008), in drinking water (Yang et al., 2014), in terrestrial and marine remote aerosols (Xie et al., 2006, 2007; Fu et al., 2008, 2009, 2013),

and in marine sediment, as well as in biota, including several aquatic species (Wofford et al., 1981), algae (Gao and Chi, 2015), and the tissues of mammals (Staples et al., 1997) and humans (Liou et al., 2014). PAEs can be degraded by some microalgal species (Gao and Chi, 2015), fish and shellfish (Munshi et al., 2013), bacteria (Chang et al., 2004) and intracellular and extracellular algal enzymes (Gao and Chi, 2015) as well as by the combined action of UV and H₂O₂ (Xu et al., 2007). PAEs are of particular concern to humans since they are considered as emerging environmental contaminants due to the endocrine disruption and carcinogenic effects detected in laboratory animal experiments and in humans (Crisp et al., 1998; Latini, 2005; Kamrin, 2009; Meeker et al., 2009).

The Mediterranean Sea is a semi-enclosed basin covering an area of 2.5 million km² with a slow turnover time of ~ 80 years implying a sensitive response to anthropogenic impact (The Mermex group, 2011). Urbanization has been growing particularly along the coastline, with the result of a substantial modification of the coast and adverse effects on the quality of the environment (Pergent, 2012). There is a large range of industrial activities spread all along the Mediterranean basin, and a number of highly industrialized spots that are concentrated mainly in the northwestern Mediterranean Sea (Zorita et al., 2007). All these activities constitute a source of pollution through direct disposal, continental runoff and atmospheric transport (UNEP Chemicals, 2002; The Mermex group, 2011 and references therein). These industrial, agricultural and domestic activities generate a large volume of wastewater, which provides nutrients, trace metals (Cossa et al., 2017, this issue) organic matter, persistent organic pollutants (POPs) and related anthropogenic contaminants such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) (The Mermex group, 2011; Berrojalbiz et al., 2011; Guigue et al., 2011, 2014; Castro-Jiménez et al., 2008, 2010, 2012) that impact the coastal marine ecosystems. The Mediterranean Sea is also impacted

by marine litter and microplastics (Deudero and Alomar, 2015; C ózar et al., 2015; Faure et al., 2015; Pedrotti et al., 2016; Suaria et al., 2016 Schmidt et al., submitted), which can supply PAEs to surrounding waters during their degradation (Andrad y, 2011). Although PAEs have already been detected in aquatic environments (Xie et al., 2005; Net et al., 2015), only a few studies have reported the occurrence of individual phthalates in the Mediterranean Sea (Sanchez-Avila et al., 2012; Brossa et al., 2005), and there is no study dealing with the distribution of a complete series of PAEs in the Mediterranean basin, including the sea and rivers, mainly because of analytical difficulties.

Indeed, PAE analysis of environmental samples is a challenging task because of the low concentrations, which is associated with the risk of contamination during sampling and processing in relation with their ubiquity in the laboratory atmosphere, tools, glassware and various containers (Net et al., 2015b and references therein). For environmental waters, several extraction procedures have already been used, including liquid-liquid (EPA, 1996; Zeng et al., 2008a; Li et al., 2013; Gao et al., 2014), solid-liquid (SLE), solid phase (SPE), magnetic (MSPE) dispersive (DSPE), solid phase micro extraction (SPME) (Zhang et al., 2013; Liou et al., 2014; Yang et al., 2014) and high volume sample techniques with PAD-2 resin columns and Soxhlet extractor (Xie et al., 2005). SPE appears to be an appropriate technique for seawater because of its ease of implementation, its ability to save time and solvent (compared to liquid-liquid extraction) and the decreased contamination (Zhang et al., 2013; Liou et al., 2014; Yang et al., 2014; Net et al., 2015b). However, the SPE protocol uses a tube made of polyethylene or polypropylene, which can release DiBP, DnBP and DEHP (Tienpont, 2004, Fasano et al., 2012, Bonini et al., 2008; Paluselli unpublished results). This technique has been used by a great number of reported protocols, concerning the type, amount and conditioning of the phase (Liou et al., 2014; Sanchez-Avila et al., 2011-2012; Yang et al., 2014) and the sample volume as well as the

volume and type of solvent (He et al., 2013; Sanchez-Avila et al., 2011-2012; Yang et al., 2014; Liou et al., 2014). Previous protocols have shown a recovery variability ranging from 50-60% to 120-150% (Del Carlo et al., 2008; Wang et al., 2008; He et al., 2013, Sanchez-Avila et al., 2011), especially for DEHP, which ranges from 60-80% (He et al., 2013) to 151% (Sanchez-Avila et al., 2011).

The objectives of this study are to examine, for the first time, the concentration levels and distribution of a homologous series of PAEs in the coastal northwestern Mediterranean Sea. This environmental study was associated with an optimization of a detection protocol for PAEs at trace level in seawater. Based on previous studies (Liou et al., 2014; Gao and Chi, 2015; Yang et al., 2014), conditions for the SPE extraction of PAEs have been modified and optimized for seawater. The method we report here was tested in seawater spiked with authentic standards and then applied to coastal and offshore Mediterranean seawater as well as to Rhone River freshwater in the framework of the ‘Particule –MERMEX’ project.

2. Experimental section

2.1 Materials and reagents

The selected phthalates are dimethyl phthalate (DMP), diethyl phthalate (DEP), dipropyl phthalate (DPP), di-isobutyl phthalate (DiBP), di-n-butyl phthalate (DnBP), benzylbutyl phthalate (BzBP), di-ethylhexyl phthalate (DEHP) and di-n-octyl phthalate (DnOP). The deuterated internal standards were DEP-d4, DnBP-d4 and DEHP-d4. All native and labeled standards were of high purity grade (> 98 %) and were purchased from Supelco (Bellefonte, USA). Stock solutions were prepared in hexane and stored in the dark at 4 °C. Working solutions (unlabeled and labeled standards) were prepared by dilution of

these solutions to 20 mg/L. All solvents were glass-distilled grade and supplied by Rathburn Chemicals Ltd. (Walkerburn, UK). Ultra-pure water was produced on-site by a Milli-Q system, Millipore (Molsheim, France) with a specific resistivity of 18.2 MΩ.cm (25 °C) and a total organic carbon content of < 2 ppb. The extractions were carried out in controlled air conditions in an ISO class 6 cleanroom (temperature: 22 °C; SAS pressure: +15 Pa; SAS brewing rate: 30 vol/h; lab pressure: +30 Pa; brewing rate: 50 vol/h). All material was produced in borosilicate glass and that was previously kept in an acid bath overnight (10 % hydrochloric acid), rinsed with ultrapure water, combusted at 450 °C for 6 hours and rinsed with methanol and dichloromethane just before use.

2.2 Solid phase extraction (SPE)

The protocol was adapted from that of Yang et al. (2014) and Liou et al. (2014) and optimized for seawater in this study. The mentioned methods were modified in order to perform easy and rapid analysis on a large-scale with low contamination and to improve the recovery. The amount of Oasis HLB phase, the elution solvent type and volume, the sample volume, deuterated internal standards and glass materials were considered to improve the recoveries. Extraction cartridges were prepared in our laboratory with 200 mg of Oasis HLB sorbent (Waters Corporation, 30 µm, 100 g) in a precombusted 6 mL glass reaction tube equipped with methanol-precleaned Teflon frits (Supelco, Sigma-Aldrich). SPE was conducted on a Visiprep vacuum manifold from Sigma-Aldrich (Saint Quentin Fallavier, France). Before sample extraction, the SPE cartridges were sequentially cleaned three times with 5 mL of acetone and 5 mL of dichloromethane. The cartridges were then conditioned with 5 mL of ethyl acetate, 5 mL of acetone and 5 mL of ultrapure water prior to sample processing. Seawater samples were spiked with DEP-d4, DnBP-d4 and DEHP-d4 at 50, 200 and 400 ng/L, respectively, and percolated onto the cartridges under vacuum

at a flow rate of 1-2 drops per second. After percolation, the cartridge was washed with 5 mL of ultrapure water to remove the remaining salt and dried under vacuum for 1 h. The retained phthalates were then eluted with 2×3 mL of ethyl acetate into precombusted (450 °C, 6 hours) 10 mL vials. Ethyl acetate was then gently evaporated under a gentle stream of nitrogen (purity > 99,995 %) at room temperature to a final volume of 200 µL. The final samples were immediately closed with Teflon-lined screw caps, wrapped with Teflon ribbon and stored in the dark at -20 °C until analysis.

2.3 GC-MS analysis

Analysis was performed using an Agilent Technologies 6850 GC system coupled to an Agilent Technologies 5975C mass spectrometer (GC/MS) operated with electron impact ionization (70 eV). Chromatographic separation was achieved on an Agilent HP-5MS capillary column (30 m × 0.25 mm, 0.25 µm film thickness) with the GC oven programmed at 70 °C for 1 minute and then up to 230 °C at 30 °C/min, to 250 °C at 8 °C/min and to 280 °C at 30 °C/min with a final isothermal hold for 7.50 min. Helium was used as the carrier gas at a flow rate of 1.1 mL/min. The sample was manually injected (2 µL) in splitless mode at an injector temperature of 250 °C. A Merlin Microseal injector was used as a low carryover septum and a gas purifier (Charcoal, CP17972) was fitted on the carrier gas line to prevent contamination during injection. Data were acquired in selected ion monitoring (SIM) mode for increased sensitivity (SIM parameters given in Table 1) with a dwell time of 100 ms. Two fragment ions were monitored per compound, with the most abundant ion used for quantification, except for DMP, DPP, DiBP and DnBP, which were ionized in a unique fragment. Data were collected and analyzed with the Agilent ChemStation software. The PAEs were quantified by isotopic dilution of 3 deuterated PAEs. The use of internal standard homologues to the target molecules has been

shown to improve the recoveries by accurately compensating for loss of analyte during sample treatment (Aminot et al., 2015). The response factors were assessed for each analytical sequence from freshly prepared standards.

Table 1. Retention time and ions for selected ion monitoring (SIM) of PAEs by GC/MS.

Compound	Molar Mass (g mol ⁻¹)	Retention Time (min)	Quantifier ion (abundance)	Qualifier ion (abundance)
DMP	194.2	5.55	163 (100)	194, 135, 77
DEP	222.2	6.12	149 (100)	222, 121
DPP	250.0	6.84	149 (100)	209, 191
DiBP	278.4	7.22	149 (100)	223, 205
DnBP	278.4	7.65	149 (100)	223, 205
BzBP	312.4	9.72	149 (100)	206, 238
DEHP	390.6	10.62	149 (100)	279, 167
DnOP	390.6	11.76	149 (100)	279
DEP-d4	226.2	6.11	153 (100)	181
DnBP-d4	282.4	7.64	153 (100)	209
DnBP-d4	282.4	7.64	153 (100)	209
DEHP-d4	394.6	10.61	153 (100)	171, 283

2.4 Application to seawater and freshwater samples

Seawater samples were collected from SUNMEX station in the northwestern Mediterranean Sea, Bay of Marseilles (43°18'N, 05°22'E) in October 2014 and offshore at ‘Antares station’ (42° 47'856 N; 6° 04'395 E) in March 2015 (Fig. 1), with a 12 L GO-Flo bottle previously rinsed with 1% hydrochloric acid and ultrapure water to avoid contamination. The Go-Flo bottle tested with Milli-Q water showed only trace levels of PAEs which were not subtracted from our dissolved PAEs concentrations in this study. Immediately after collection, seawater samples were transferred into 5 L precombusted

glass bottles. Additional samples were directly collected in the Rhone River and Rhone River plume in March 2014 using 5 L precombusted glass bottles. General information on the Marseilles Bay, the Antares station and the Rhone River were given by Sempéré et al. (2015), Martini et al. (2016) and Sempéré et al. (2000), respectively. Less than two hours after collection, the samples were filtered through precombusted (450 °C for 6 h) GFF filters (47 mm filter diameter, rinsed with 2 L of Milli-Q water and 150 mL of sample prior to filtration) in a precombusted glass apparatus directly in a filtered-air clean laboratory. Milli-Q water rinse limit additional contamination (Yoro et al., 1999). After filtration, duplicate subsamples (10 mL) were poisoned with sulfuric acid to approximately pH 2 to avoid any biological activity and stored in the dark in precombusted Teflon-capped glass vials for dissolved organic carbon (DOC) analysis. DOC concentrations were measured using a Shimadzu TOC-5000 carbon analyzer (Sempéré et al., 2008). Some seawater samples (Bay of Marseilles) were spiked with authentic PAEs (from 5 to 800 ng/L final concentration) to perform recovery experiments. All the seawater analyses were conducted in duplicate in the laboratory in Marseilles.

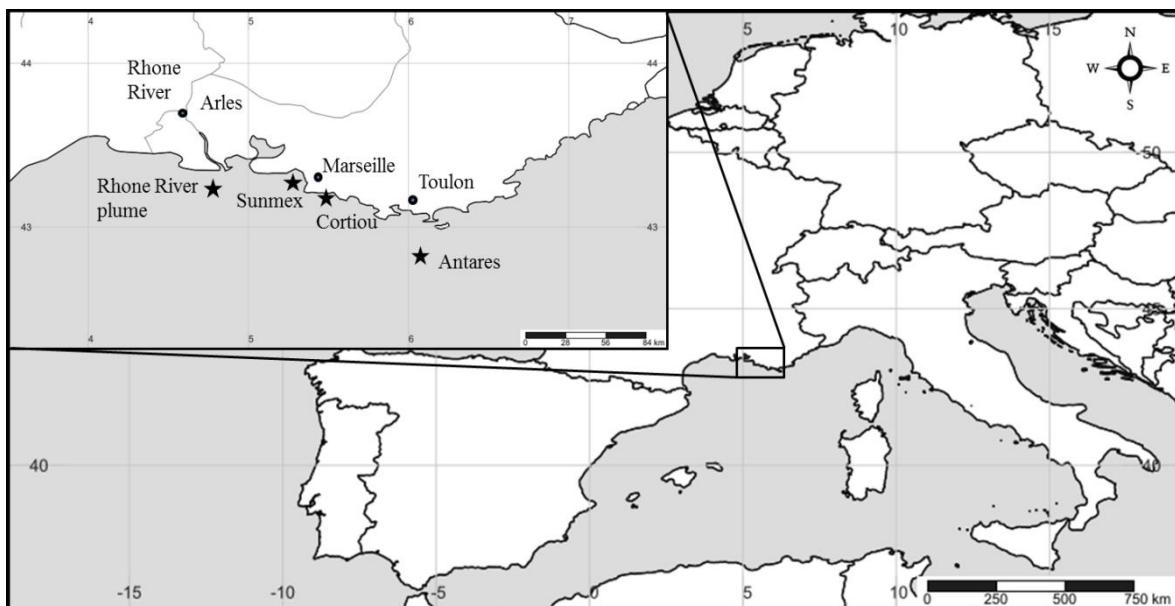


Figure 1. Area of study. The map shows the sampling stations: SUNMEX in the Bay of Marseilles (October 2014), offshore ‘Antares station’ (March 2015), Arles in Rhone River and the river plume (March 2014).

3. Results and Discussion

3.1 Extraction of PAEs in seawater samples (optimization of the method)

Numerous factors are known to significantly influence the efficiency of SPE extraction of phthalates from water. The most influential factors are elution solvent, sample volume and sorbent mass. To increase the recovery, the elution solvent, sample volume and sorbent mass were studied in order to optimize efficient and reliable conditions for SPE extraction of seawater samples.

a) Elution solvent effect

First, 10 µL of 20 mg/L PAE solution was passed through the cartridges, and two fractions of elution were collected. The first fraction was eluted with 5 mL of either acetone, dichloromethane, ethyl acetate, methanol or n-hexane, and the second fraction was systematically eluted with 5 mL of dichloromethane in order to elute the remaining PAEs off the cartridge. Internal standards were spiked directly in the eluted fraction. The repartition of PAEs between the two fractions is given in Fig. 2. Acetone, dichloromethane, ethyl acetate and methanol yielded acceptable recoveries ranging from 55 to 100 % while n-hexane was satisfactory only for DEHP and DnOP (79-85 %), with 12 % for DMP, 36 % for DEP and 1 % for BzBP. n-Hexane is a better solvent for aliphatic compounds, unlike DMP, DEP (short carbon chain) and BzBP (higher aromaticity).

Acetone and methanol showed a similar elution strength with recoveries of 80-100 % for DMP, DEP, DPP, DiBP, DnBP and BzBP in the first fraction and 70 % and 50 % for DEHP and DnOP, respectively. This result is consistent with the studies of Liou et al. (2014) and Yang et al. (2014), which performed the elution with 6 mL of methanol. Dichloromethane and ethyl acetate both indicated high recoveries for all PAEs in the first fraction and were the most appropriate elution solvents. Dichloromethane was the most

appropriate elution solvent for DMP (100 %), DEP (98 %) and DPP (97 %), whereas ethyl acetate was the most appropriate for the elution of DiBP (91 %), DnBP (92 %), BzBP (85 %) and DEHP (90 %). DnOP was efficiently eluted (100 %) with both solvents. Previously, published protocols used 10 mL of dichloromethane/n-hexane (He et al., 2013) or 10 mL of acetone/dichloromethane (Sanchez-Avila et al., 2011; 2012) as the elution solvent.

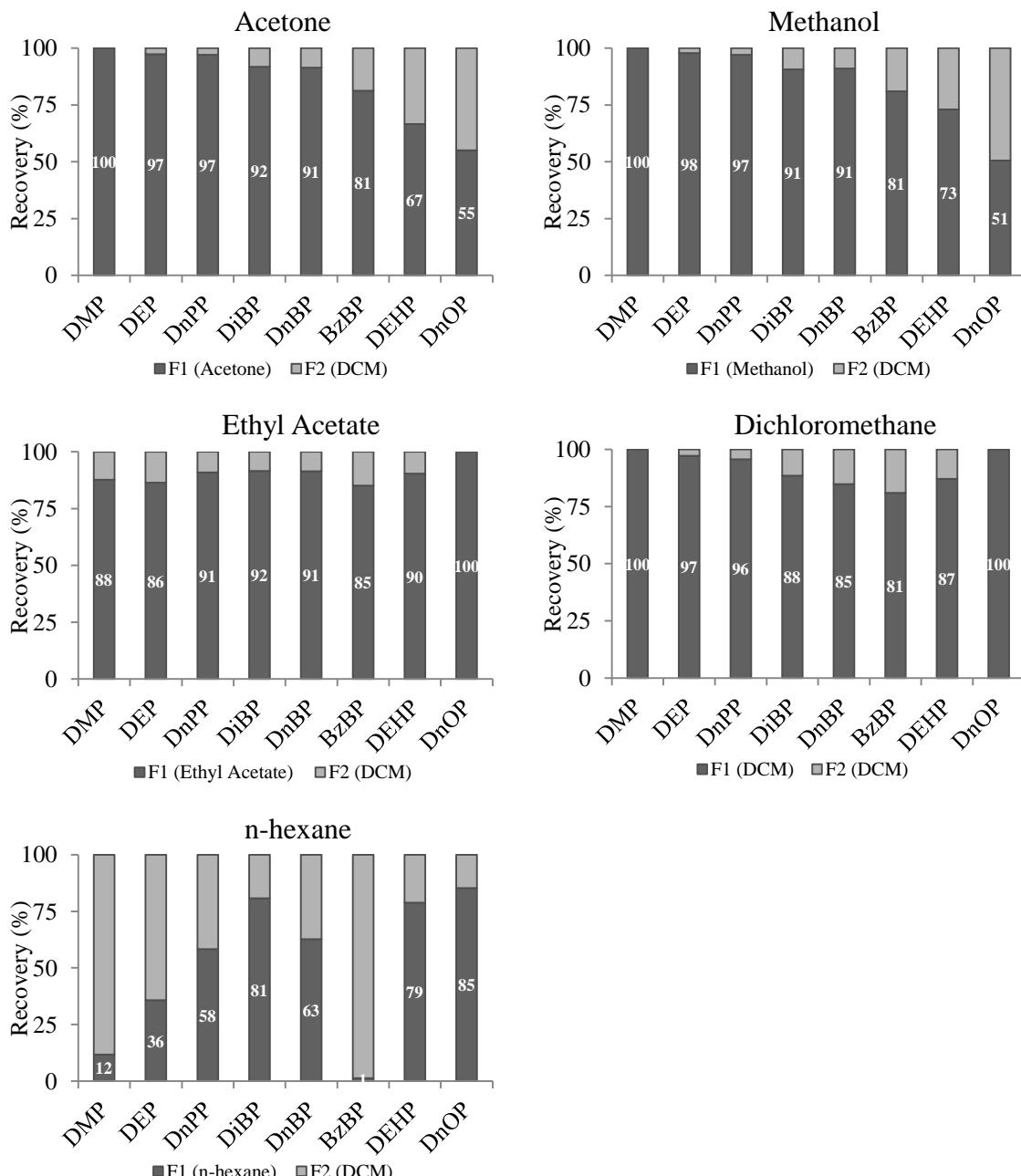


Figure 2. Recovery of PAEs obtained in two elution fractions carried out with five different organic solvents (F1) and dichloromethane (F2).

When comparing their recoveries and those from our developed protocol, the combination of dichloromethane with acetone seems to be more effective for PAE elution than its combination with n-hexane. In these protocols, the ability to elute PAEs from the cartridges was improved by increasing the elution solvent volume to 10 and 20 mL, respectively. According to our results, ethyl acetate is the best solvent for PAE elution.

b) Seawater volume and sorbent mass effects

As high SPE enrichment factors are required to compensate for the likely low PAE levels in seawater, it is important to ensure that the analytes do not breakthrough the sorbent at high percolation volumes. Increasing volumes (100 mL, 200 mL, 500 mL and 1000 mL) of seawater collected at Sunmex station at a 1.5 m depth were spiked with 10 µL of 20 mg/L PAEs and percolated through either 200 mg (Liou et al., 2014) or 400 mg of sorbent. For each experimental condition, two additional samples were kept unspiked and were processed in the same conditions (blank samples). The recoveries were calculated as the difference between the concentration in the spiked and unspiked samples. In this experiment, the deuterated internal standards DEP-d4, DnBP-d4 and DEHP-d4 were spiked after the elution of the solvent. The recoveries of the extractions obtained with 4 different volumes of spiked seawater for 200 and 400 mg of HLB sorbent are given in Table 2.

The volume of the sample does not significantly affect the recovery of most of the PAEs, indicating the absence of breakthrough. Only DEP and DnBP were marginally affected by increasing sample volumes. The recovery of DEP increased from 60 % with 100 mL to 93 % with all other volumes on 200 mg of sorbent. However, the recovery was stable between 93 and 100 % on 400 mg. DnBP showed the opposite trend, where the recovery decreased from 75-79 % with 100-200 mL to 63-66 % with 500-1000 mL on both 200 mg and 400 mg of sorbent. Acceptable recoveries (93-120 %) were determined for

DMP, DPP, DiBP and BzBP under all experimental conditions. The two most hydrophobic PAEs DEHP and DnOP exhibited lower recoveries regardless of the experimental conditions, attributed to their potential for adsorption onto glassware. Such losses were corrected for by the use of deuterated DEHP as an internal standard (Table 3).

Table 2. Recoveries of PAE extractions obtained with 4 different volumes of spiked seawater and 200 and 400 mg of HLB sorbent.

Compounds	Recoveries (%)							
	200 mg				400 mg			
	100 mL	200 mL	500 mL	1000 mL	100 mL	200 mL	500 mL	1000 mL
DMP	99	108	100	105	114	107	109	110
DEP	61	93	88	89	95	93	95	100
DPP	105	117	113	120	122	121	119	114
DiBP	96	122	111	123	121	100	107	115
DnBP	79	75	63	66	136	77	67	82
BzBP	102	125	94	106	126	104	87	97
DEHP	14	13	8	10	11	7	21	6
DnOP	8	10	15	10	10	6	24	6

Above all, the volume of the sample did not significantly influence the performance of the HLB sorbent toward PAEs. Similar results were observed for the sorbent mass. The DnOP concentration in seawater is expected to be low, indicating the need to increase the enrichment factor by extracting 1 L of sample. BzBP is also characterized by low concentrations in seawater and by relatively high instrumental detection limits, confirming the need for a large volume of sample. As the differences between 200 and 400 mg of sorbent did not justify the use of double the amount of sorbent, 200 mg of sorbent was

selected to reduce the price and time for a single extraction. Previously, published protocols reported the use of 1 L of matrix, but different amounts of solid phase, from 200 mg (Liou et al., 2014) to 500 mg (Yang et al., 2014). According to the results, our optimized conditions were 200 mg of HLB phase prepared in a combusted glass tube, 1 L of sample volume, and 6 mL of ethyl acetate as the elution solvent, split in two steps.

3.2 Method validation

Blank, response linearity and extraction validation

Procedural blank samples were examined by passing dry air and ethyl acetate directly through the precleaned cartridge and measuring the PAEs directly in the elution solution. Linearity was investigated over an eight-point calibration ranging from 50 to 6000 pg injected. Instrumental repeatability was measured through the relative standard deviation of 10 injections of the same standard solution, corresponding to 100 pg injected, whereas instrumental detection limits (IDLs) were extrapolated for a signal-to-noise ratio of 3. The noise region was equivalent to the width of the peak before the peak, and the noise value was taken as the average height (“RMS” mode). The recoveries were calculated from the spiked seawater samples (10 µL of 20 mg/L of PAEs in 1 L) after subtraction of the concentrations measured for the unspiked seawater samples (n=2). Such experiments were repeated with half the spiked concentration (5 µL of 20 mg/L of PAEs) in seawater samples (n=2) to study the influence of the concentration level.

The method was applied to 1 L seawater samples to minimize contamination and to allow the detection of low concentrations of BzBP and DnOP in seawater. The samples were passed through 200 mg of HLB sorbent, and the cartridges were eluted twice with 3 mL of ethyl acetate. A typical gas chromatogram of the PAEs isolated from the seawater

samples collected in the Marseilles Bay is given in Figure 3. Identification of the PAEs was confirmed by GC/MS. Despite the precautions taken to prevent contamination, DEP, DiBP and occasionally DnBP were detected in the blanks at levels that remained below 0.4-2 %, 2-3 % and 0-4 % of the masses measured in different seawater samples, respectively. The average recoveries of PAEs spiked in the seawater samples (Table 3) showed acceptable recoveries for all the phthalates, ranging from 97 % of DEP to 110 % of DiBP. The high recoveries obtained at low spiking levels also validated the appropriate performance of the protocol. To assess the influence of the concentration level on the recoveries, 1 L aliquots of seawater collected in the Bay of Marseilles were spiked at increasing concentration levels (standard addition technique). Different ranges of spiked concentrations were used depending on the initial concentration of the compound in seawater (from 5 to 40 ng/L for DMP, DEP, DPP, BzBP and DnOP and from 40 to 800 ng/L for DiBP, DiBP and DEHP). Excellent correlation coefficients ($R^2 > 0.96$) and recoveries (between 95 and 116 %) indicate that the method is linear and accurate for all compounds, including DEHP ($R^2=0.987$; n=7) and DnOP ($R^2=0.962$; n=5), in a range of environmentally realistic concentrations.

Table 3. Statistical data of the linear regression between the spiked concentration of PAEs and the measured peak areas. PAE recovery was reported.

Comp	spiked concentration (ng L ⁻¹)	n	R ²	slope (μ Vs/ng L ⁻¹)	y-intercept (μ Vs)	Recovery (%)	MDL (ng L ⁻¹)
DMP	0, 5, 10, 20, 40	5	0.98	11022	20671	101.2	0.11
DEP	0, 5, 10, 20, 40, 100	6	0.99	13978	40049	98.1	0.21
DPP	0, 5, 10, 20, 40	5	0.98	12072	2893	115.5	0.31
DiBP	0, 40, 100, 200, 400, 600, 800	7	0.99	11006	5477511	110.4	0.23
DnBP	0, 40, 100, 200, 400, 600	6	0.99	19424	1965660	99.7	0.28
BzBP	0, 5, 10, 20, 40	5	0.99	2718	1845	98.7	1.67
DEHP	0, 40, 100, 200, 400, 600, 800	7	0.99	1638	23076	103.8	0.93
DnOP	0, 5, 10, 20, 40	5	0.96	268	323	95.0	2.73

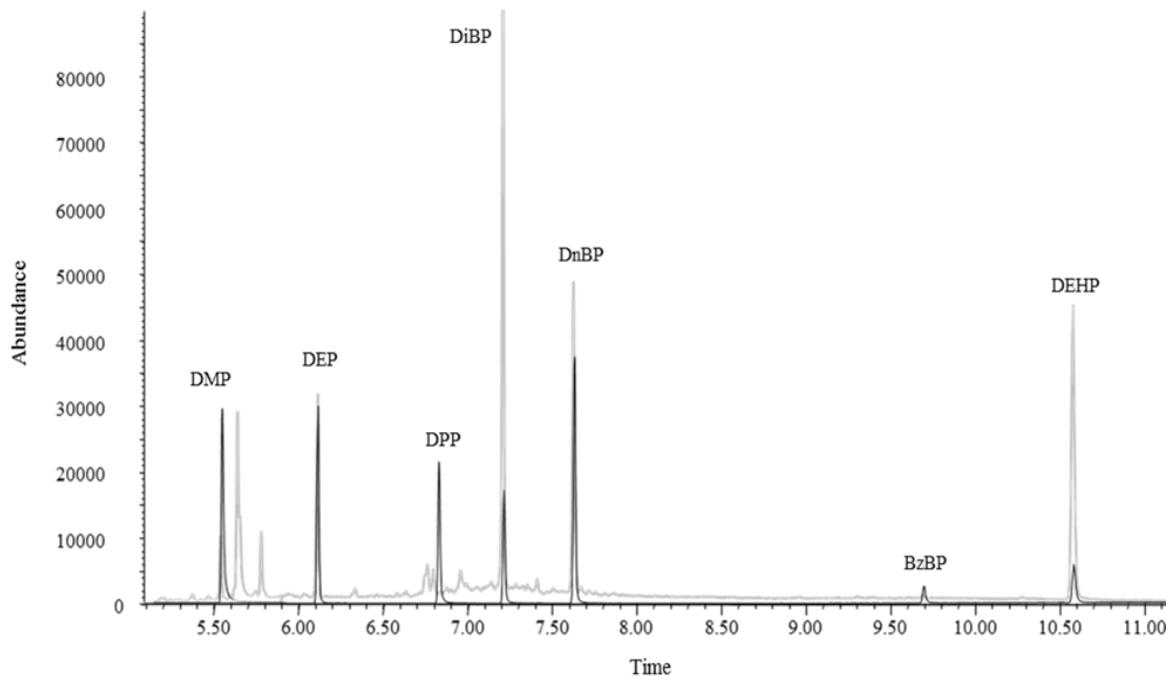


Figure 3. Typical capillary gas chromatogram of PAEs (DMP, DEP, DiBP, DnBP, BzBP and DEHP) isolated from the seawater sample (grey line) collected from the Marseilles Bay (northwestern Mediterranean Sea) in October 2014 and typical PAEs standard solution chromatogram (black line, 0.1 mg/L). The identification of PAEs was confirmed by GC/MS. The mass spectra of the PAEs (not presented here) were in accordance with those published in the literature. DPP and DnOP were not detected in this sample.

3.3 Concentration of PAEs in the northwestern Mediterranean Sea and Rhone River

All PAEs, excepted DPP and DnOP, were detected in the Mediterranean seawater and Rhone River samples (Table 4). We found that offshore (Antares site), the concentration of total PAEs ranged from 75.3 ng/L at the surface to 310.2 ng/L in the deepest water, from 244.5 ng/L to 1207.1 ng/L a few meters above the bottom in the Marseilles Bay and from 182.2 to 212.6 ng/L in the Rhone River plume and close to the Marseilles Cortiou water treatment plant outlet. Although particulate PAEs were not measured in this study, previous study indicated that DnBP, BzBP and DEHP particulate concentration may represent the 2, 29 and 43 %, respectively, of the dissolved

concentration in coastal seawater (North Sea, Xie et al., 2005). Very limited data are available for the occurrence and fate of dissolved PAEs in marine water, especially in the Mediterranean Sea. DEHP concentrations detected in the seawater samples in our study were in the range of 50.7-296.5 ng/L. These concentrations were in the same range reported by Sanchez-Avila et al. (2012) for Catalan coastal water (Spain, NW Mediterranean Sea) and by Turner and Rowling (2000) for the south coast of the UK, respectively, with range of 31-617 ng/L and 99-2200 ng/L. However, our results were 10 times lower than those reported by Brossa et al. (2005) for the Spanish coast. Lower concentrations have been only reported for North Sea with concentration ranges of 0.5-5.3 ng/L for DEHP and 0.02-4.0 ng/L for DMP and DEP (Xie et al., 2005).

Table 4. PAEs concentrations detected in different Mediterranean Sea samples: Surface Rhone River and associated Plume (March, 2014), Bay of Marseilles (October, 2014) and surface ‘Cortiou’ station (November, 2014).

Comp	Rhone River	Rhone River Plume			Bay of Marseille			Cortiou
	S=0	S=10	S=18	S=28	1.5 m	5 m	15 m	30 m
DMP	5.7	5.7	4.8	2.7	1.8	1.7	1.4	6.4
DEP	30.5	29.0	30.2	16.4	12.7	6.9	7.1	50.0
DPP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DiBP	125.9	48.6	67.0	136.4	215.7	56.5	77.0	383.4
DnBP	40.5	21.8	21.7	22.8	87.0	63.4	138.9	466.0
BzBP	5.4	2.7	2.6	2.5	3.5	3.2	4.0	4.8
DEHP	406.8	101.2	55.9	39.2	103.5	112.8	102.9	296.5
DnOP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total	615.1	209.0	182.2	220.0	424.2	244.5	331.3	1207.1
								212.6

In Marseilles Bay, the samples were characterized by high concentrations of PAEs in the surface waters, a slight decrease with the depth, probably because of microbial degradation, and then an increase close to the bottom (Table 4). DiBP was the most abundant at the surface (47.3 % of total PAEs) followed by DEHP (22.7 %) and DnBP (19.1 %), whereas DnBP was predominant (38.6 %) followed by DiBP (31.8 %) and DEHP (24.6 %) a few meters above the bottom. DMP, DEP and BzBP were detected as 0.5, 2.5 and 0.8 % of total PAEs, respectively (Table 5; Figure 4). The high concentration at the bottom suggests the resuspension of PAE-rich sediments. As marine litter has already been reported to be abundant near the bottom (M I O unpublished observations) of the Marseilles Bay, it is likely that PAEs in the surficial sediment were released during plastic debris aging through physico-chemical and biotic processes (Bakir et al., 2014). This seems to be more evident for DnBP, whose relative fraction showed a stronger variation. Different PAEs are usually used by industry during plastic polymer production in order to increase flexibility, transparency, durability and longevity of the different materials produced (Net et al., 2015b, and reference therein). DEHP and DnBP are used as plasticizer for soft PVC, PVA and rubber as well as fixative in paint and especially DnBP is essentially used for its viscosity reducing properties and compatibility with non-PVC mixture (ECHA, 2013). It is likely that the PAEs detected above the bottom depend on the type of material that accumulates in the sediment after sinking. In addition, microplastics could come from larger plastic debris that degrades into smaller pieces and microbeads, a type of microplastic that are added as exfoliants to health and beauty products and easily pass though water filtration systems and end up in the sea, could transfer attached pollutants and additive chemicals (Browne et al., 2007) in the water column. At Cortiou station, near the Marseilles wastewater treatment plant, the surface water PAE concentration averaged at 212.6 ng/L ($sd \pm 3.4$) (Table 4), detected 5-6 m from the Cortiou water treatment plant outlet, which was quite low during the studied period. DiBP was the

most abundant PAE (38.4 %), followed by DEHP (26.4 %), DEP (15.7 %) and DnBP (13.5 %), with DMP and BzBP representing minor fractions (3.5 and 2.5 %, respectively) (Table 5; Figure 4). The relative abundance was not very different from what we detected in Marseilles Bay, with the only exception of DEP.

Table 5. PAE relative abundances (%) detected in different Mediterranean Sea samples: Surface Rhone River and associated Plume (March, 2014), Bay of Marseilles (October, 2014) and surface ‘Cortiou’ station (November, 2014).

Compound	Rhone River	Rhone River Plume			Bay of Marseilles				Cortiou
	S=0	S=10	S=18	S=28	1.5 m	5 m	15 m	30 m	
DMP	0.9	2.7	2.6	1.2	0.4	0.7	0.4	0.5	3.4
DEP	5.0	13.9	16.6	7.5	2.8	2.8	2.1	4.1	15.7
DPP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DiBP	20.5	23.3	36.8	62.0	47.3	23.1	23.3	31.8	38.4
DnBP	6.6	10.4	11.9	10.4	19.1	25.9	42.0	38.6	13.5
BzBP	0.9	1.3	1.4	1.1	0.8	1.3	1.2	0.4	2.4
DEHP	66.1	48.4	30.7	17.8	22.7	46.0	31.1	24.6	26.4
DnOP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

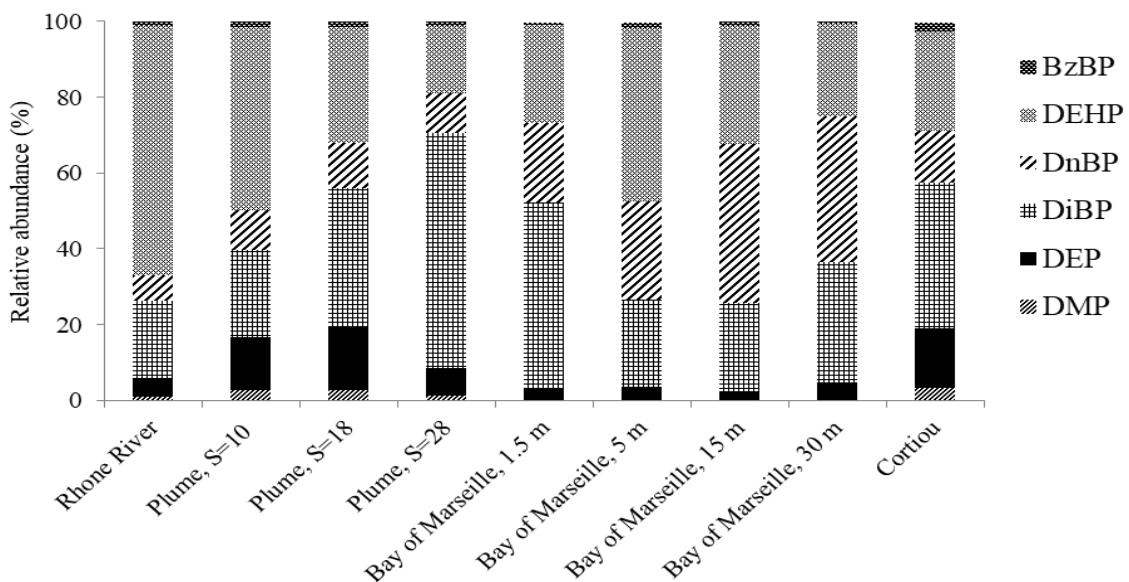


Figure 4. PAE relative abundances (%) detected in different Mediterranean Sea samples: Surface Rhone River and associated Plume (March, 2014), Bay of Marseilles (October, 2014) and surface ‘Cortiou’ station (November, 2014).

Five PAEs were detected offshore in the ‘Antares station’ water column (Figure 5-6; Table 6). DnBP was characterized by a large range of concentrations (8.2-225.5 ng/L), which reached a maximum in deep water (Figure 6). With the exception of DnBP, the vertical profiles seem to have similar trends. The surface samples were characterized by high concentrations that slightly decrease down to 200-500 m. Then, the concentration started to increase down to 1500 m, where the concentration was similar to that detected in the surface samples. The DnBP vertical profile was characterized by the same trend in the first meter of the water column, decreasing from 13.4 to 8.2 ng/L, but it was followed by a strongly increasing concentration in the deepest samples (87.3-225.5 ng/L). DEHP was the dominant species in the first 50 m (66.9-76.7 % of total PAEs) followed by DnBP (10.9-15.2 %). Between 100 and 250 m, the relative abundance of DEHP was slightly lower (56.9-65.4 %), whereas that of DnBP was higher (25.8-28.5 %) up to the maximum salinity and minimum temperature. Under 500 m, DnBP was the most abundant PAE (57.0-72.6 %) followed by DEHP (20.1-33.1 %). DiBP, DMP and DEP were detected as minor fractions of the total PAEs detected in offshore waters, representing 7.9, 5.7 and 4.4 % of total PAEs at the surface and 3.5, 2.3 and 1.5 % in deepest waters, respectively (Fig. 5; Tab. 6). Note that this offshore station area is influenced by the shallow depth Northern Current (NC) with high seasonal variability (Millot, 1991), which may penetrate into the shelf of the Gulf of Lions (Barrier et al., 2016 and references therein).

Table 6. PAE relative abundances (%) detected in offshore Antares station-samples collected at the surface and at depths of 5, 50, 100, 250, 500, 1000 and 1500 m.

Compounds	Depth (m)							
	0	5	50	100	250	500	1000	1500
DMP	5.7	5.1	5.0	3.5	7.9	4.6	3.5	2.3
DEP	4.4	2.3	2.0	1.9	2.3	1.6	1.7	1.5
DiBP	7.9	5.1	4.5	3.5	4.4	3.6	4.5	3.5
DnBP	15.2	10.9	15.2	25.8	28.5	57.0	61.0	72.6
DEHP	66.9	76.7	73.3	65.4	56.9	33.1	29.2	20.1

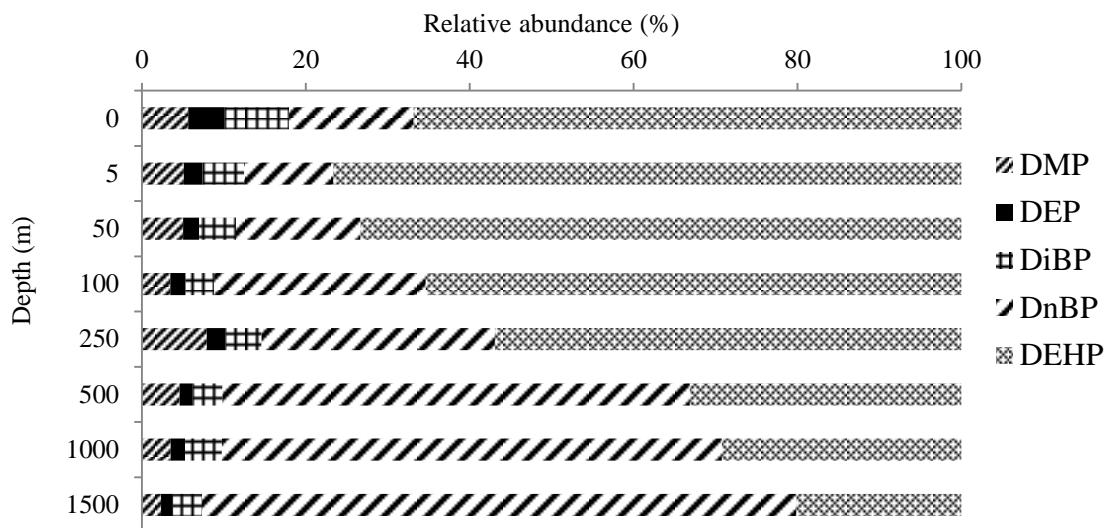


Figure 5. PAE relative abundances (%) detected in offshore Antares station-samples collected at the surface and at depths of 5, 50, 100, 250, 500, 1000 and 1500 m in March 2015.

This water originating eastward from the Italian coasts may carry plastic debris (Schmidt et al., submitted) and dissolved PAEs. The decrease in concentration in the first meter of the water column could be explained by biodegradation processes. The increase in concentration at 200-500 m suggests the production of PAEs from the aging of plastic debris, as was observed in Marseilles Bay. Indeed, the behavior of DnBP in the deepest water seems to reflect the same production observed close to the bottom of the Marseilles area. These data were the first attempt to investigate the vertical distribution of PAEs in the water column.

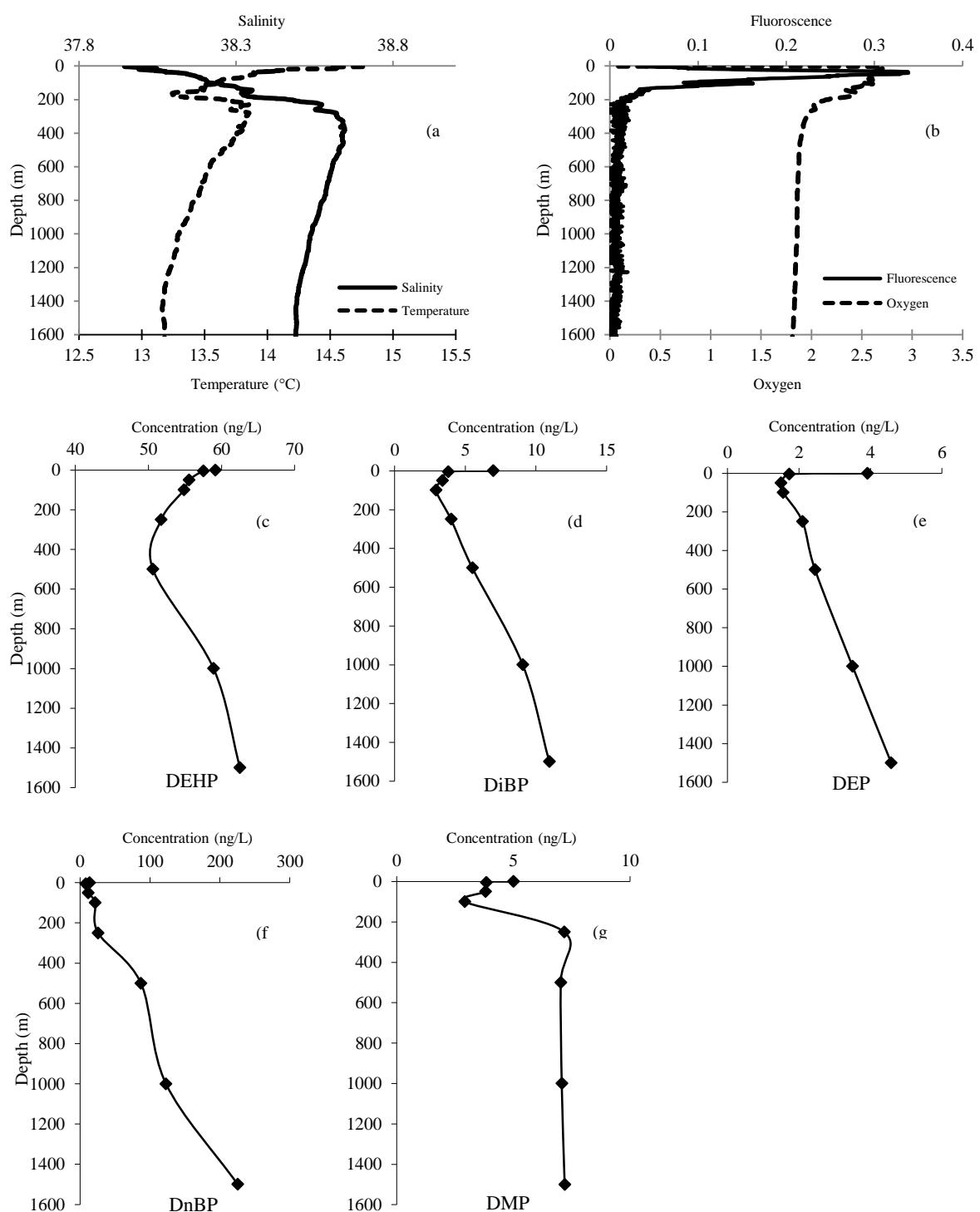


Figure 6. Vertical profile (0-1500 m) of 5 PAEs, along with salinity, temperature (a), fluorescence and oxygen (b) detected at offshore Antares station in March 2015. The compounds detected were: (c) di-ethylhexyl phthalate (DEHP), (d) di-iso-butyl phthalate (DnBP), (e) diethyl phthalate (DEP), (f) di-n-butyl phthalate (DnBP) and (g) dimethyl phthalate (DMP).

Rhone River and river mouth

The total PAE concentrations ranged from 615.1 ng/L to 182.2-220.0 ng/L in the Rhone River plume (Table 4) suggesting that the Rhone is clearly a source of PAEs in the coastal area. Previous studies dealing with individual PAEs reported DMP concentrations in the range of 2.5 – 5.5 ng/L (Sanchez-Avila et al., 2012) in six rivers in Spain (Muga, Fluvia, Ter, Besòs, Llobregat and Ebro River). DEP was detected in different studies in the Seine River (France) in a range slightly higher than our data, from 46-208 ng/L (Teil et al., 2007) to 71-181 ng/L (Dargnat et al., 2009), as well as 52-284 ng/L in Spain (Sanchez-Avila et al., 2012). BzBP was also reported at low concentration in the range of 5-23 ng/L (Dargnat et al., 2009; Sanchez-Avila et al., 2012). Dargnat et al. (2009) and Teil et al. (2007) found similar concentrations of DEHP, 161-314 ng/L and 323-779 ng/L, respectively, in the Seine River. We found that DEHP was the most abundant PAE (66.1 %) in the Rhone River followed by DiBP (20.5 %) and DnBP (6.6 %), whereas DMP, DEP and BzBP represented the smallest fractions (Table 5; Figure 4). The relative abundance of DEHP decreased from 66.1 % of the total PAEs in the river (S=0) to 48.4, 30.7 and 17.8 % in the plume stations (S=10-28). The opposite trend was observed for all other PAEs, especially for DnBP and DiBP, with DnBP values increasing from 6.6 to 11.9 % and from 20.5 to 62.0 % for DiBP. A similar trend was also observed for DMP and DEP. Changes in the relative abundance from the river to the plume could be due to different selective bacterial degradation and/or photodegradation processes occurring in the salty water. Only DiBP showed, after the concentration first decreased probably due to dilution effect, an increase in concentration and in relative abundance. This could be caused by some atmospheric input of this compound as it was already supposed in the Bay of Marseilles.

4. Conclusion

A reliable analytical technique for measuring PAEs in natural seawater samples at trace levels was slightly improved and allowed determination of PAEs in seawater. This technique consists of the adsorption on PAEs from acidified seawater samples onto 200 mg Oasis HLB glass cartridges followed by elution with ethyl acetate and determination by GC/MS. The recoveries of the PAEs from spiked seawater samples were found to be between 95-115 %, and the contamination was strongly reduced by using a number of precautions. Our results showed that the Rhone River was a source of PAE in estuary and in coastal area. Although DEHP was predominant in the river, its relative abundance decreased with increasing salinities, DiBP being predominant in the plume for a salinity of 28. We reported, for the first time, the PAE vertical profile (0-1500 m) from the offshore water, which had lower concentrations compared to the Bay of Marseilles. We observed that DEHP was also predominant in surface marine waters including offshore (0-250 m) and below the surface in Marseille Bay (5m). The opposite trend was found for DnBP for which concentrations significantly increased in mesopelagic waters. High concentrations of DnBP, DEHP and DiBP were detected close to the bottom (30 m) of the Bay of Marseilles. Such feature might be related to diffusion of PAEs released from the sediment surface very likely induced from plastic debris degradation and previously accumulated in the bottom. Precise origin of such material still needs to be determined. Other processes such as photochemical oxidation reactions in surface waters, bacterial degradation, are certainly important processes that regulate as well the distribution of PAEs in the water column. High PAE concentrations found in coastal area near Marseilles city strongly suggest that these organic compounds are very likely abundant in the whole Mediterranean that is surrounded by urbanized areas and that is submitted to relatively high inputs of rivers and atmospheric deposition compared to the global Ocean.

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References

- Aminot, Y., Litrico, X., Chambolle, M., Arnaud, C., Pardon, P., Budzindki, H., 2015. Development and application of a multi-residue method for the determination of 53 pharmaceuticals in water, sediment, and suspended solids using liquid chromatography-tandem mass spectrometry. *Analytical and Bioanalytical Chemistry* 407 (28), 8589-8604.
- Andrade, A.L., 2011. Microplastics in the marine environment. *Marine Pollution Bulletin* 62 (8), 1596–1605.
- Bakir, A., Rowland, S.J., Thompson, R.C., 2014. Enhanced desorption of persistent organic pollutants from microplastics under simulated physiological conditions. *Environmental Pollution* 185, 16-23.
- Barrier, N., Petrenko, A.A, Ourmières, Y., 2016. Strong intrusions of the Northern Mediterranean Current on the eastern Gulf of Lion: insights from in-situ observations and high resolution numerical modeling. *Ocean Dynamics* 66 (3), 313-327.
- Becker, K., Seiwert, M., Angerer, J., Heger, W., Koch, H.M., Nagorka, R., Roßkamp, E., Schluter, C., Seifert, B., Ullrich, D., 2004. DEHP metabolites in urine of children and DEHP in house dust. *International Journal of Hygiene and Environmental Health* 207, 409–417.
- Berrojalbiz, N., Dachs, J., Ojeda, M.J., Valle, M.C., Castro-Jimenez, J., Wollgast, J., Ghiani, M., Hanke, G., Zaldivar, J.M., 2011. Biogeochemical and physical controls on concentrations of polycyclic aromatic hydrocarbons in water and plankton of the Mediterranean and Black Sea. *Global Biogeochemical Cycle* 25 (4).
- Bonini, M., Errani, E., Zerbinati, G., Ferri, E., Girotti, S., 2008. Extraction and gas chromatographic evaluation of plasticizers content in food packing film. *Microchemical Journal* 90, 31-36.
- Brossa, L., Marcé, R., Borrull, F., Pocurull, E., 2005. Occurrence of twenty-six endocrine-disrupting compounds in environmental water samples from Catalogna, Spain. *Environmental Toxicology and Chemistry* 24, 261-267.
- Browne M.A., Galloway T., Thompson R., 2007. Microplastic—an emerging contaminant of potential concern?. *Integrated Environmental Assessment and Management* 3 (4), 559-566.
- Castro-Jimenez, J., Deviller, G., Ghiani, M., Loos, R., Mariani, G., Skejo, H., Umlauf, G., Wollgast, J., Laugier, T., Heas-Moisan, K., Leaute, F., Munsch, C., Tixier, C., Tronczynski, J., 2008. PCDD/F and PCB multi-media ambient concentrations, congener patterns and occurrence in a Mediterranean coastal lagoon (Etang de Thau, France). *Environmental Pollution* 156 (1), 123-125.
- Castro-Jimenez, J., Eisenreich, S.J., Ghiani, M., Mariani, G., Skejo, H., Umlauf, G., Wollgast, J., Zaldivar, J.M., Berrojalbiz, N., Reuter, H.I., Dachs, J., 2010. Atmospheric occurrence and deposition of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in the open Mediterranean Sea. *Environmental Science of Technology* 44 (14), 5456-5463.

- Castro-Jimenez, J., Berrojalbiz, N., Wollgast, J., Dachs, J., 2012. Polycyclic aromatic hydrocarbons (PAHs) in the Mediterranean Sea: Atmospheric occurrence, deposition and decoupling with settling fluxes in the water column. *Environmental Pollution* 166, 40-47.
- CEH, 2015. Acrylic Resins and Plastics. Chemical Economic Handbook.
- Chang, B.V., Yang, C.M., Cheng, C.H., Yuan, S.Y., 2004. Biodegradation of phthalates ester by two bacteria strains. *Chemosphere* 55 (4), 533-538.
- Cossa, D., Fanget, A.S., Chiffolleau, J.F., Bassetti, M.A., Buscail, R., Dennielou, B., Briggs, K., Arnaud, M., Guédron, S., Berné, S., 2017. Chronology of anthropogenic trace elements accumulation in the Rhone pro-delta sediments (northwestern Mediterranean) during the last 400 years. *MERMEX* special issue *Progress Oceanography*, this issue.
- Cozar, A., Sanz-Martin, M., Marti, E., Gonzalez-Gordillo, J.I., Ubeda, B., Galvez, J.A., Irigoien, X., Duarte, C.M., 2015. Plastic accumulation in the Mediterranean Sea. *PLoS ONE* 10 (4).
- Crisp, T.M., Clegg, E.D., Cooper, R.L., Wood, W.P., Anderson, D.G., Baetcke, K.P., Hoffmann, J.L., Morrow, M.S., Rodier, D.J., Schaeffer, J.E., Touart, L.W., Zeeman, M.G., Patel, Y.M., 1998. Environmental endocrine disruption: an effects assessment and analysis. *Environmental Health Perspectives* 106 (1), 11–56.
- Dargnat, C., Teil, M.J., Chevreuil, M., Blanchard, M., 2009. Phthalate removal throughout wastewater treatment plant: Case study of Marne Aval station (France). *Science of The Total Environment* 1235–1244.
- Del Carlo, M., Pepe, A., Sacchetti, G., Compagnone, D., Mastrolola, D., Cichelli, A., 2008. Determination of phthalate esters in wine using solid-phase extraction and gas chromatography–mass spectrometry. *Food Chemistry* 111, 771–777.
- Deudero, S., Alomar, C., 2015. Mediterranean marine biodiversity under threat: Reviewing influence of marine litter on species. *Marine Pollution Bulletin* 98 (1-2), 58-68.
- ECHA (European Chemicals Agency), 2013. Annex XV dossier proposal for identification of a substance as a CMR Cat 1 or 2.
- EPA (Environmental Protection Agency), 1996. Phthalates esters by gas chromatography with electron capture detection (GC/ECD). Method 506.
- Fasano, E., Bono-Blay, F., Cirillo, T., Montuori, P., Lacorte, S., 2012. Migration of phthalates, alkylphenols, bisphenol A and di(2-ethylhexyl)adipate from food packaging. *Food Control* 27 (1), 132-138.
- Faure, F., Demars, C., Wieser, O., Kunz, M., De Alencastro, L.F., 2015. Plastic pollution in Swiss surface waters: nature and concentrations, interaction with pollutants. *Environmental Chemistry* 12 (5), 582-591.
- Ferreira, I.D., Morita, D.M., 2012. Ex-situ bioremediation of Brazilian soil contaminated with plasticizers process wastes. *Brazilian Journal of Chemical Engineering* 29 (1), 77-86.

- Fu, P., Kawamura, K., Okuzawa, K., Aggarwal, S.G., Wang, G., Kanaya, Y., Wang, Z., 2008. Organic molecular compositions and temporal variations of summertime mountain aerosols over Mt. Tai, North China Plain. *Journal of Geophysical Research* 11.
- Fu, P., Kawamura, K., Barrie, L.A., 2009. Photochemical and other source of organic compounds in the Canadian high Arctic aerosol pollution during winter-spring. *Environmental Science and Technology* 43, 286-292.
- Fu, P., Kawamura, K., Chen, J., Charrière, B., Sempéré, R., 2013. Organic molecular composition of marine aerosols over the Arctic Ocean in summer: contributions of primary emission and secondary aerosol formation. *Biogeosciences* 10, 653–667.
- Gao, D., Li, Z., Wen, Z., Ren, N., 2014. Occurrence and fate of phthalate esters in full-scale domestic wastewater treatment plants and their impact on receiving waters along the Songhua River in China. *Chemosphere* 95, 24–32.
- Gao, J., Chi, J., 2015. Biodegradation of phthalate acid esters by different marine microalgal species. *Marine Pollution Bulletin* 99, 70–75.
- Guigue, C., Tedetti, M., Giorgi, S., Goutx, M., 2011. Occurrence and distribution of hydrocarbons in the surface microlayer and subsurface water from the urban coastal marine area off Marseilles, Northwestern Mediterranean Sea. *Marine Pollution Bulletin* 62 (12), 2741-2752.
- Guigue, C., Tedetti, M., Ferretto, N., Garcia, N., Goutx, M., 2014. Spatial and seasonal variabilities of dissolved hydrocarbons in surface waters from the Northwestern Mediterranean Sea: Results from one year intensive sampling. *Science of the Total Environment* 466-467, 650-662.
- Halden, R.U., 2010. Plastics and Health Risks. *Annual Review of Public Health* 31, 179-194.
- He, W., Qin, N., Kong, X., Liu, W., He, Q., Ouyang, H., Yang, C., Jiang, Y., Wang, Q., Yang, B., Xu, F., 2013. Spatio-temporal distributions and the ecological and health risks of phthalate esters (PAEs) in the surface water of a large, shallow Chinese lake. *Science of the Total Environment* 461–462, 672–680.
- Holahan, M.R., Smith, C.A., 2015. Phthalates and neurotoxic effects on hippocampal network plasticity. *NeuroToxicology* 48, 21–34.
- Horn, O., Nalli, S., Cooper, D., Nicell, J., 2004. Plasticizer metabolites in the environment. *Water Research* 38, 3693–3698.
- IARC, 2000. Monograph on the evaluation of carcinogenic risk to humans: some industrial chemicals, di(2-ethylhexyl) phthalate. *IARC Monographs* 77, 41-148.
- Kamrin, M.A., 2009. Phthalate Risks, Phthalate Regulation, and Public Health: A Review. *Journal of Toxicology and Environmental Health* 12 (2), 157-174.
- Latini, G., 2005. Monitoring phthalate exposure in humans. *Clinica Chimica Acta* 361 (1-2), 20–29.

- Li, J., Su, Q., Li, K., Sun, C., Zhang, W., 2013. Rapid analysis of phthalates in beverage and alcoholic samples by multi-walled carbon nanotubes/silica reinforced hollow fibre-solid phase microextraction. *Food Chemistry* 141 (4), 3714–3720.
- Liou, S., Yang, G.C.C., Wang, C., Chiu, Y., 2014. Monitoring of PAEMs and beta-agonists in urine for a small group of experimental subjects and PAEs and beta-agonists in drinking water consumed by the same subjects. *Journal of Hazardous Materials* 277, 169–179.
- Lyche, J.L., Gutleb, A.C., Bergman, A., Eriksen, G.S., Murk, A.J., Ropstad, E., Saunders, M., Skaare, J.U., 2009. Reproductive and Developmental Toxicity of Phthalates. *Journal of Toxicology and Environmental Health* 12 (4), 225-249.
- Martini, S., Michotey, V., Casalot, L., Bonin, P., Guasco, S., Garel, M., Tamburini, C., 2016. Bacteria as part of bioluminescence emission at the deep ANTARES station (North-Western Mediterranean Sea) during a one-year survey. *Deep-Sea Research I* 116, 33-40.
- Meeker, J.D., Sathyanarayana, S., Swan, S.H., 2009. Phthalates and other additives in plastics: human exposure and associated health outcomes. *Philosophical transaction of The Royal Society B* 364 (1526), 2097-2113.
- Millot, C., 1991. Mesoscale and seasonal variabilities of the circulation in the western Mediterranean. *Dynamics of Atmospheres and Oceans* 15 (3-5), 179-214.
- Munshi, A.B., Karim, N., Shaukat, S., Hashmi, D., Boardman, G.D., Flick, G.J., 2013. Toxicity of Phthalate Esters in Fish and Shellfish from Virginia Beach Using Matrix Solid Phase Dispersion (MSPD) and GC-MS. *Journal of The Chemical Society Of Pakistan* 35 (6), 1463-1471.
- Net, S., Dumoulin, D., El-Osmani, R., Rabodonirina, S., Ouddane, B., 2014. Case study of PAHs, Me-PAHs, PCBs, Phthalates and Pesticides Contamination in the Somme River water, France. *International Journal of Environmental Research* 8(4), 1159-1170.
- Net, S., Delmont, A., Sempéré, R., Paluselli, A., Ouddane, B. Reliable quantification of phthalates in environmental matrices (air, water, sludge, sediment and soil): A review. 2015 a. *The Science of Total Environment*. 515–516 , 162–180. <http://dx.doi.org/10.1016/j.scitotenv.2015.02.013>.
- Net, S., Sempéré, R., Delmont, A., Paluselli, A., Ouddane, B., 2015 b. Occurrence, Fate, Behavior and Ecotoxicological State of Phthalates in Different Environmental Matrices. *Environmental Science of Technology* 49 (7), 4019–4035.
- Para, J., Coble, P.G., Charrière, B., Tedetti, M., Fontana, C., Sempéré, R., 2010. Fluorescence and absorption properties of chromophoric dissolved organic matter (CDOM) in coastal surface waters of the northwestern Mediterranean Sea, influence of the Rhône River. *Biogeosciences* 7, 4083-4103.
- Pedrotti, M.L., Petit, S., Elineau, A., Bruzaud, S., Crebassa, J.C., Dumontet, B., Marti, E., Gorsky, G., Cozar, A., 2016. Changes in the floating plastic pollution of the Mediterranean Sea in relation to the distance to land. *PLoS ONE* 11 (8).
- Pergent, G., Bazairi, H., Bianchi, C.N., Boudouresque, C.F., Buia, M.C., Clabaut, P., Harmelin, M., Mateo, M.A., Montefalcone, M., Morri, C., Orfanidis, S., Pergent-Martini, C., Semroud, R.,

Serrano, O., Verlaque, M., 2012. Mediterranean seagrass meadows: resilience and contribution to climate change mitigation. A short summary. IUCN.

Sanchez-Avila, J., Fernandez-Sanjuan,M., Vicente, J., Lacorte, S., 2011. Development of a multi-residue method for the determination of organic micropollutants in water, sediment and mussels using gas chromatography–tandem mass spectrometry. *Journal of Chromatography A* 1218, 6799–6811.

Sanchez-Avila, J., Tauler, R., Lacorte, S., 2012. Organic micropollutants in coastal waters from NW Mediterranean Sea: Sources distribution and potential risk. *Environment International* 46, 50–62.

Schmidt, N., Thibault, D., Galgani, F., Paluselli, A., Sempéré, R., 2017. Occurrence of microplastics and potential contribution of phthalates in the surface waters of the Gulf of Lion(NW Mediterranean Sea). *Progress in Oceanography*, Mermex special issue.

Sempéré, R., Charrière, B., Van Wambeke, F., Cauwet, G., 2000. Carbon inputs of the Rhône River to the Mediterranean Sea: Biogeochemical implications. *Global Biogeochemical Cycles* 14 (2), 669-681.

Sempéré, R., Tedetti, M., Panagiotopoulos, C., Charrière, B., Van Wambeke, F., 2008. Distribution and bacterial availability of dissolved neutral sugars in the South East Pacific. *Biogeosciences* 5, 1165–1173.

Sempéré, R., Para, J., Tedetti, M., Chattiére, B., Mallet, M., 2015. Variability of Solar radiation and CDOM in Surface Coastal Waters of the Northwestern Mediterranean Sea. *Photochemistry and Photobiology* 91 (4), 851-561.

Serôdio, P., Nogueria, J.M.F., 2006. Considerations on ultra-trace analysis of phthalates in drinking water. *Water Research* 40 (13), 2572–2582.

Simoneit, B.R.T., Medeiros, P.M., Didyk, B.M., 2005. Combustion Products of Plastics as Indicators for Refuse Burning in the Atmosphere. *Environmental Science of Technology* 39 (18), 6961–6970.

Staples, C.A., Peterson, D.R., Parkerton, T.F., Adams, W.J., 1997. The environmental fate of phthalate esters: a literature review. *Chemosphere* 35 (4), 667-749.

Suaria, G., Avio, C. G., Mineo, A., Lattin, G. L., Magaldi, M.G., Belmonte, G., Moore, C. J., Regoli, F., Aliani, S. 2016. The Mediterranean Plastic Soup: synthetic polymers in Mediterranean surface waters. *Nature Scientific Reports* 6, 37551 (2016), doi:10.1038/srep37551

The Mermex Group, 2011. Marine ecosystems responses to climatic and anthropogenic forcings in the Mediterranean. *Progress in Oceanography* 91, 97–166.

Teil, M., Blanchard, M., Dargnat, C., Larcher-Tiphagne, K., Chevreuil, M., 2007. Occurrence of phthalates diesters in river of the Paris district (France). *Hydrological Processes* 21, 2515-2525.

Tienpont, B., 2004. Determination of Phthalates in Environmental, Food and Biomaterials. An Analytical Challenge. PhD Thesis. Department of Organic Chemistry Ghent University.

- Turner, A., Rawling, M.C., 2000. The behaviour of di-(2-ethylhexyl) phthalate in estuaries. *Marine Chemistry* 68 (3), 203–217.
- UNEP Chemicals, 2002. Regionally based assessment of persistent toxic substances. *Mediterranean Regional Report*, UNEP, Geneve.
- Wang, I., Lin, C., Lin, Y., Hsieh, W., Chen, P., 2014. Early life phthalate exposure and atopic disorders in children: A prospective birth cohort study. *Environment International* 62, 48–54.
- Wang, F., Xia, X., Sha, Y., 2008. Distribution of Phthalic Acid Esters in Wuhan section of the Yangtze River, China. *Journal of Hazardous Materials* 154, 317–324.
- Wofford, H.W., Wilsey, C.D., Neff, G.S., Giam, C.S., Neff, J.M., 1981. Bioaccumulation and metabolism of phthalate esters by oysters, brown shrimp, and sheepshead minnows. *Ecotoxicology and Environmental Safety* 5 (2), 202-210.
- Xie, Z., Ebinghaus, R., Temme, C., Caba, A., Ruck, W., 2005. Atmospheric concentrations and air-sea exchanges of phthalates in the North Sea (German Bight). *Atmospheric Environment* 39, 3209–3219.
- Xie, Z., Selzer, J., Ebinghaus, R., Caba, A., Ruck, W., 2006. Development and validation of a method for the determination of trace alkylphenols and phthalates in the atmosphere. *Analytica Chimica Acta* 565, 198–207.
- Xie, Z., Ebinghaus, R., Temme, C., Lohmann, R., Caba, A., Ruck, W., 2007. Occurrence and Air-Sea Exchange of Phthalates in the Arctic. *Environmental Science of Technology* 41, 4555-4560.
- Xu, B., Gao, N., Sun, X., Xia, S., Rui, M., Simonnot, M., Causserand, C., Zhao, J., 2007. Photochemical degradation of diethyl phthalate with UV/H₂O₂. *Journal of Hazardous Materials* 139 (1), 132–139.
- Yang, G.C.C., Yen, C., Wang, C., 2014. Monitoring and removal of residual phthalate esters and pharmaceuticals in the drinking water of Kaohsiung City, Taiwan. *Journal of Hazardous Materials*, 277 53–61.
- Yoro, S.C., Panagiotopoulos C., Sempere, R., 1999. Dissolved organic carbon contamination induced by filters and storage bottles. *Water Research* 33 (8), 1956-1959.
- Zeng, F., Cui, K., Xie, Z., Liu, M., Li, Y., Lin, Y., Zeng, Z., Li, F., 2008. Occurrence of phthalate esters in water and sediment of urban lakes in a subtropical city, Guangzhou, South China. *Environment International* 34, 372–380.
- Zhang, X., Zhang, L., Li, L., Feng, Y., Chen, B., Ma, J., Huynh, E., Shi, Q., De Felici, M., Shen, W., 2013. Diethylhexyl phthalate exposure impairs follicular development and affects oocyte maturation in the mouse. *Environmental and Molecular Mutagenesis* 54 (5), 354–361.
- Zorita, I., Apraiz, I., Ortiz-Zarragoitia, M., Orbea, A., Cancio, I., Soto, M., Marigomez, I., Cajaraville, M.P., 2007. Assessment of biological effects of environmental pollution along the NW Mediterranean Sea using mussels as sentinel organisms. *Environmental Pollution* 148 (1), 236-250.

ANNEXE

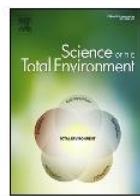
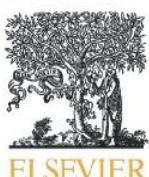
CHAPTER I

Vertical PAEs concentrations at Antares site

Depth (m)	DMP (ng L ⁻¹)		DEP (ng L ⁻¹)		DiBP (ng L ⁻¹)		DnBP (ng L ⁻¹)		DEHP (ng L ⁻¹)	
	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.
0	5.0	0.5	3.9	0.4	7.0	1.2	13.4	0.9	59.1	2.5
5	3.8	0.4	1.7	0.5	3.8	1.4	8.2	1.2	57.5	3.2
50	3.8	0.4	1.5	0.9	3.4	1.5	11.5	1.5	55.5	4.5
100	2.9	0.3	1.6	0.4	2.9	0.9	21.7	0.9	54.9	1.9
250	7.2	0.4	2.1	0.6	4.0	1.2	25.9	1.2	51.7	1.5
500	7.0	0.4	2.5	0.7	5.5	1.6	87.1	1.1	50.6	2.2
1000	7.1	0.2	3.5	0.6	9.1	0.5	122.9	2.5	58.9	2.6
1500	7.2	0.4	4.6	0.5	10.9	1.4	225.5	2.4	62.5	2.8

CHAPTER II

Occurrence



Distribution of phthalates in Marseille Bay (NW Mediterranean Sea)



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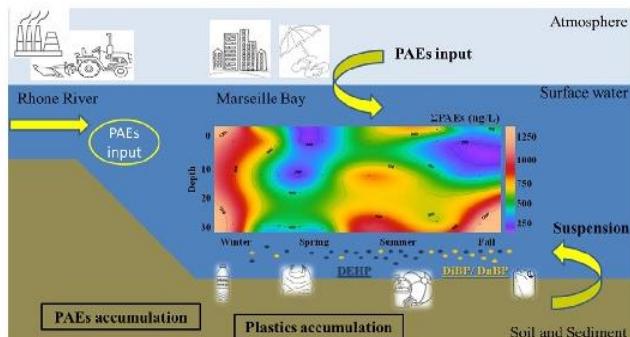
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HIGHLIGHTS

- Estimation of DMP, DEP, DiBP, DnBP, BzBP and DEHP concentration at Bay of Marseille.
- One year PAEs observations (2014) in the Bay of Marseille.
- Variation of PAE composition from surface to the bottom water.
- High PAEs concentration close to deep and bottom water.

GRAPHICAL ABSTRACT



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ABSTRACT

Phthalic Acid Esters (PAEs) are a group of emerging organic contaminants that have become a serious issue because of their ubiquitous presence and hazardous impact on the marine environment worldwide. Seawater samples were collected monthly from December 2013 to November 2014 in the northwestern Mediterranean Sea (Marseille Bay). The samples were analyzed for dissolved organic carbon (DOC) as well as the molecular distribution of dissolved PAEs by using solid phase extraction followed by gas chromatography and mass spectrometry (GC/MS) analyses. The results demonstrated the occurrence of six PAEs, including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-isobutyl phthalate (DiBP), di-n-butyl phthalate (DnBP), benzylbutyl phthalate (BzBP) and diethylhexyl phthalate (DEHP), with total concentrations ranging from 130 to 1330 ng L⁻¹ (av. 522 ng L⁻¹). In Marseille Bay, the highest concentrations were detected in the bottom water from June to November 2014 and in the whole water column during the winter mixing period. This result suggests that resuspension of PAE-rich sediment, in relation to the accumulation of plastic debris above the seabed, or the higher degradation rate in the upper layer of the water column, plays a significant role in the PAE dynamics in coastal water. DEHP was the most abundant PAE in all of the surface samples and the summer bottom samples, followed by DiBP and DnBP, which also represent the largest fractions in the other bottom samples.

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1. Introduction

Phthalates or phthalic acid esters (PAEs) are widely used in the manufacture and processing of plastic products such as plasticizers in a very broad range of industrial applications (Serôdio and Nogueria, 2006; Net

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Distribution of phthalates in Marseille Bay (NW Mediterranean Sea)

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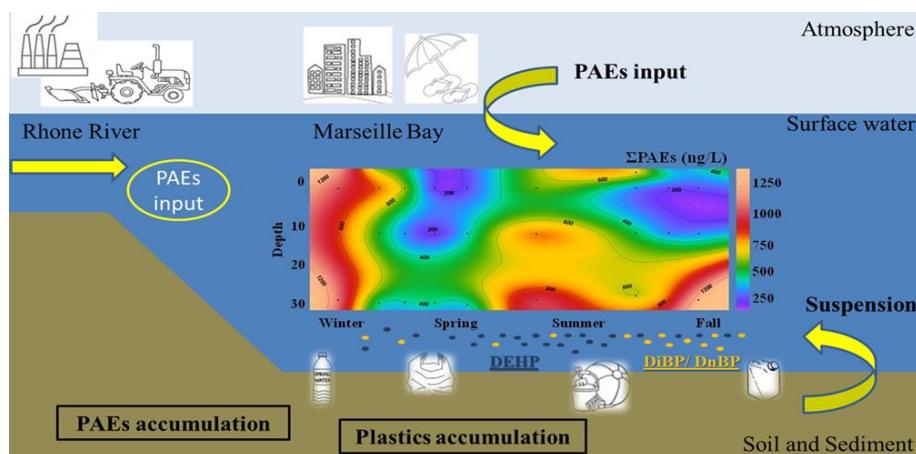
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Abstract:

Phthalic Acid Esters (PAEs) are a group of emerging organic contaminants that have become a serious issue because of their ubiquitous presence and hazardous impact on the marine environment worldwide. Seawater samples were collected monthly from December 2013 to November 2014 in the northwestern Mediterranean Sea (Marseille Bay). The samples were analyzed for dissolved organic carbon (DOC) as well as the molecular distribution of dissolved PAEs by using solid phase extraction followed by gas chromatography and mass spectrometry (GC/MS) analyses. The results demonstrated the occurrence of six PAEs, including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-isobutyl phthalate (DiBP), di-n-butyl phthalate (DnBP), benzylbutyl phthalate (BzBP) and diethylhexyl phthalate (DEHP), with total concentrations ranging from 130 to 1330 ng L⁻¹ (av. 522 ng L⁻¹). In Marseille Bay, the highest concentrations were detected in the bottom water from June to November 2014 and in the whole water column during the winter mixing period. This result suggests that resuspension of PAE-rich sediment, in relation to the accumulation of plastic debris above the seabed, or the higher degradation rate in the upper layer of the water column, plays a significant role in the PAE dynamics in coastal water. DEHP was the most abundant PAE in all of the surface samples and the summer bottom samples, followed by DiBP and DnBP, which also represent the largest fractions in the other bottom samples.



1 Introduction

Phthalates or phthalic acid esters (PAEs) are widely used in the manufacture and processing of plastic products such as plasticizers in a very broad range of industrial applications.¹⁻² PAEs account for approximately 92% of produced plasticizers and represent the most produced and consumed plasticizers worldwide³⁻⁴ since these compounds are used to improve the flexibility of polyvinyl chloride (PVC) resins.⁵⁻⁶ Other industrial applications include the manufacturing of cosmetics, insect repellents, insecticide carriers and propellants.^{2,6-7} PAEs of lower molecular weight (LMW-PAEs: C3-C6) are used as essential components of solvents, adhesives, waxes, pharmaceutical products, insecticide materials and cosmetics, whereas PAEs of higher molecular weight (HMW-PAEs: C7-C13) are instead used as additives to improve the flexibility and handling of industrial materials.⁸⁻¹⁰ These compounds are suspected to enter the environment directly as emissions from household and industrial products, as released by wastewater from production and processing activity or the use and disposal of materials¹¹ as well as from plastic polymer migration.¹²

Previous studies have shown that PAEs are endocrine-disrupting chemicals with the capability of inducing significant effects on the reproduction of various organisms, including protozoans, mollusks, crustaceans, fishes and invertebrates,¹² on the ecosystem functioning¹³ and on human obesity and cancer development.¹⁴⁻¹⁷ Therefore, PAEs have become a matter of concern for their potential risk to health and the environment. Six PAEs (dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP), benzylbutyl phthalate (BzBP), diethylhexyl phthalate (DEHP) and di-n-octyl phthalate (DnOP)) have been included as priority pollutants of the US-EPA¹⁸, the European Union (EU)¹⁹ and the Chinese water list.²⁰ Accordingly, monitoring PAEs in the major environmental matrices has become a priority. After their introduction in the environment,

they can reach marine water by wastewater and riverine inputs, and end up in the sediment via association with humic acid and adsorption onto particles and finally end up in the sediment.²¹ Due to the physiochemical properties and biogeochemical cycling of PAEs, they have been detected in food, air, water, soil and sediment^{6,22-32}. However, there is a lack of data related to their sources, distribution in the whole water column as well as their transfer mechanisms from the molecular state to different living species.

The Mediterranean Sea being a semi-enclosed basin with slow turnover time of ~ 80 years implies a sensitive response to anthropogenic impact.³⁶ Mediterranean rivers and primarily the Rhone River supply large amounts of freshwater, particles and organic carbon to the Mediterranean Sea.³⁷⁻³⁸ There is extensive urbanization particularly along the coastline as well as a number of highly industrialized spots all along the Mediterranean basin that are concentrated mainly in the northwestern Mediterranean Sea. All these activities as well as agricultural and domestic activities^{36,39} generate a large volume of wastewater, which provides marine litter, microplastics,⁴⁰⁻⁴⁷ anthropogenic molecules,⁴⁸⁻⁴⁹ persistent organic pollutants (POPs) and related contaminants such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs)^{36,50-51} that impact the coastal marine ecosystems in unknown proportion. However, only a few studies have reported the occurrence of individual phthalates in the Mediterranean Sea,^{25,52} and there is only one study dealing with the distribution of a series of PAEs in the Mediterranean basin.⁵³ The objectives of the present study are to investigate the composition and distribution of PAEs in the NW Mediterranean coastal seawater column and to ascertain their temporal trends on an annual basis.

2 Materials and Methods

2.1 Study area, sampling, and dissolved organic carbon analyses

Seawater samples ($n=72$) were collected with R/V Antedon from the SUNMEX station (Fig. 1) in the northwestern Mediterranean Sea in Marseille Bay ($43^{\circ}18'N$, $05^{\circ}22'E$) from December 2013 to November 2014 at 1.5, 5, 15 and 30 m (with a bottom depth of 32–33 m) with a 12-L GO-FLO[©] (GENERAL OCEANICS) bottle previously rinsed with 1% hydrochloric acid and ultrapure water to avoid contamination. Immediately after sampling, the seawater samples were directly transferred from the GO-FLO[©] into 5-L precombusted ($450^{\circ}C$ for 6 h) glass bottles closed with PTFE (polytetrafluoroethylene) lined screw caps, wrapped with aluminum foil and brought back to the laboratory within 4 hours for processing. Four samples collected in October 2014 at Marseille Bay were already published.⁵³ The samples were filtrated through precombusted ($450^{\circ}C$ for 6 h) GFF filters (47-mm filter diameter, rinsed with 2 L of Milli-Q water and 150 mL of sample prior to filtration) in a glass apparatus directly and transferred into 1-L glass bottles. After filtration, duplicate subsamples (10 mL) were collected for dissolved organic carbon (DOC) analyses with precombusted Pasteur pipettes, transferred into precombusted glass vials, poisoned with sulfuric acid to pH ~ 2 to avoid any biological activity, closed with PTFE-lined screw caps and stored in the dark at $4^{\circ}C$. DOC concentrations were measured using a Shimadzu TOC-5000 carbon analyzer.⁵⁴ The nominal analytical precision of the procedure was within 2%. The accuracy of the instrument and the system blank were determined by analyzing reference materials (D. Hansell, Rosenstiel School of Marine and Atmospheric Science, Miami, USA), including the Deep Seawater reference (DSR) and low carbon water (LCW) reference materials. The average DOC concentrations in the DSR and LCW reference standards were $45 \pm 2 \mu\text{M C}$, $n = 24$ and $1 \pm 0.3 \mu\text{M C}$, $n = 24$, respectively.

All glassware including Pasteur pipettes, glass bottles and glass filtration apparatus was previously cleaned in 1% hydrochloric acid bath, rinsed with ultrapure water and combusted at 450 °C for 6 h. All the GC/MS and DOC seawater analyses were conducted in duplicate in the MIO laboratory in Marseille within 6 months. Filtration of samples was conducted in the MIO ISO class 6 chemistry cleanroom (temperature: 22 °C; SAS pressure: +15 Pa; SAS brewing rate: 30 vol/h; lab pressure: +30 Pa; brewing rate: 50 vol/h).

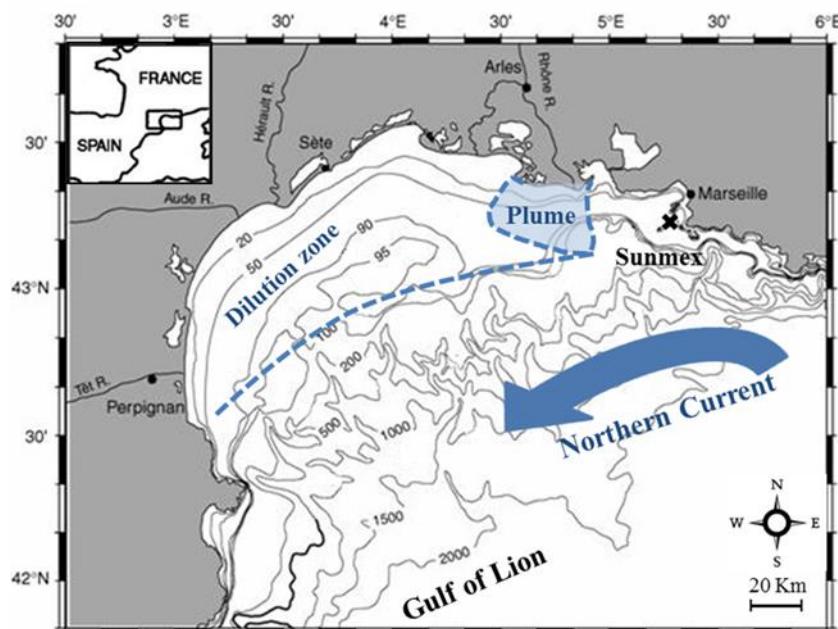


Figure 1. Area of study. The map (adapted from Fraysse et al.⁵⁵) shows the sampling stations in the Gulf of Lyon: SUNMEX ($43^{\circ}18'N$, $05^{\circ}22'E$; depth 32 m) in the Bay of Marseille (December 2013–November 2014). Northern current is the main general circulation feature influencing the Gulf of Lyon with a geostrophic flux (calculated to 700 dbar) that varies throughout the year in a range of 0.9–1.8 Sv with its maximum in November or December³⁷. The Rhône River is the main fresh water supplier of the Mediterranean Sea with an average flow rate of $54 \pm 12 \text{ km}^3 \text{ year}^{-1}$ with maximum values in the fall period³⁷. In the studied period, the Rhône River flux ranged from 1300 to $2800 \text{ m}^3 \text{ s}^{-1}$.

2.2 Phthalates analyses

Seven phthalates were studied including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-isobutyl phthalate (DiBP), di-n-butyl phthalate (DnBP), benzylbutyl phthalate (BzBP), diethylhexyl phthalate (DEHP) and di-n-octyl phthalate (DnOP) (Fig. 2). The deuterated internal standards were: DEP-d4, DnBP-d4, DEHP-d4. All native and labeled standards were of high purity grade (> 98%, 2000 µg mL⁻¹ Supelco). Stock solutions were prepared in hexane and stored in the dark at 4°C. Working solutions (unlabeled and labeled standards) were prepared by dilution of these solutions at 20 mg L⁻¹. All solvents were glass-distilled grade and supplied by Rathburn Chemicals Ltd. (Walkerburn, UK). Milli-Q water was produced on-site on a Milli-Q system, Millipore (Molsheim, France) with resistivity higher than 18.2 MΩ cm (25°C) and Total Organic Carbon < 2 µg L⁻¹.

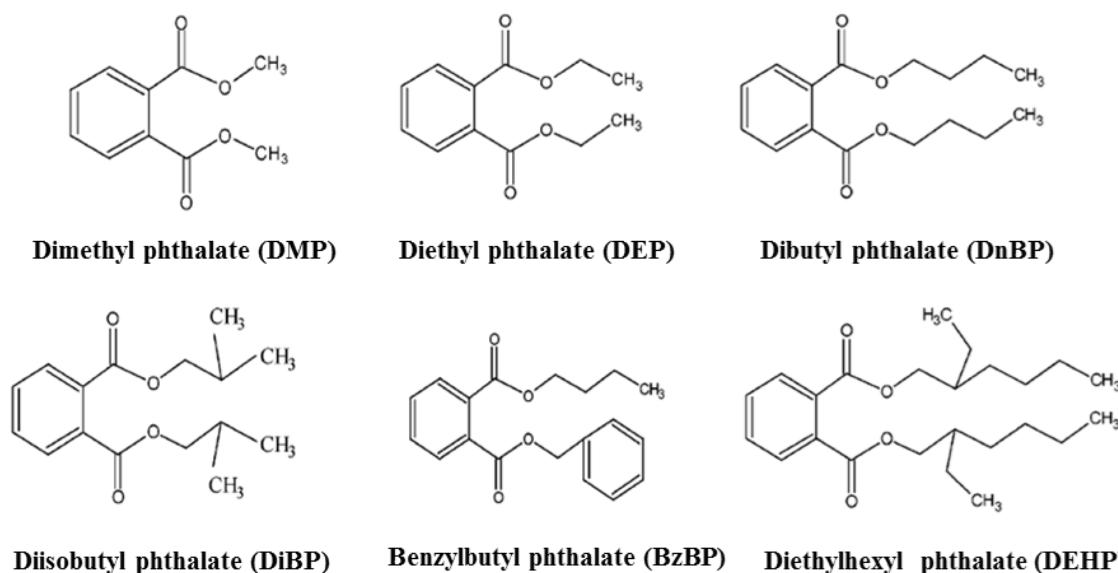


Figure 2. Chemical structure of the 6 detected PAEs. Dimethyl phthalate (DMP; MW = 194.18), Diethyl phthalate (DEP; MW = 222.24), Dibutyl phthalate (DnBP; MW = 278.34), Diisobutyl phthalate (DiBP; MW = 278.34), Benzylbutyl phthalate (BzBP; MW = 312.36) and Diethylhexyl phthalate (DEHP; MW = 390.56). Figure adapted from Xie et al.⁷

The extractions were performed following the method optimized for seawater PAE detection at trace levels.⁵³ PAEs were extracted by solid phase extraction (SPE) from seawater using a precombusted 6-mL glass reaction tube containing 200 mg of Oasis® HLB sorbent (Waters Corporation, 30 µm, 100 g). SPE was conducted on a Visiprep vacuum manifold from Sigma-Aldrich (Saint Quentin Fallavier, France). Before sample extraction, SPE cartridges were three times sequentially cleaned with 5 mL of acetone, 5 mL of dichloromethane, conditioned with 5 mL of ethyl acetate, 5 mL of acetone and 5 mL of ultrapure water prior sample processing. Seawater samples were spiked (for recovery estimate) with DEP-d4, DnBP-d4 and DEHP-d4 at 50, 200 and 400 ng L⁻¹, respectively, prior to loading onto SPE cartridges under vacuum at a flow rate of 5 to 10 mL min⁻¹. Then, 5 mL of ultrapure water was percolated to remove the remaining salt and air-dried for around 1 h under vacuum. PAEs were eluted into precombusted 10 mL-vials by a 2-step percolation of 3 mL of ethyl acetate. Ethyl acetate was gently evaporated to a final volume of 200 µL at room temperature under a gentle stream of nitrogen (purity > 99,995 %). Then, samples were immediately closed with PTFE lined screw caps rubbed with PTFE ribbon and stored before injection in the dark at -20 °C.

Analysis was performed using an Agilent Technologies 6850 GC system coupled to an Agilent Technologies 5975C mass spectrometer (GC/MS) operated with electron impact ionization (70 eV). Chromatographic separation was achieved on an Agilent HP-5MS capillary column (30 m x 0.25 mm, 0.25 µm film thickness) with the GC oven programmed at 70°C for 1 min and then up to 230°C at 30°C min⁻¹, to 250°C at 8°C min⁻¹ and to 280°C at 30°C min⁻¹ with a final isotherm hold for 7.50 min. Helium was used as a carrier gas at a flow rate of 1.1 mL min⁻¹. Samples were manually injected (2 µL) on a splitless mode injector with a temperature set at 250°C. The injector (Merlin Microseal system) was used as a low carryover septum and a gas purifier (Charcoal, CP17972) to

prevent contamination during the injection. Data were acquired in single ion monitoring (SIM) mode for increased sensitivity with a dwell time of 100 ms. Data were collected and analyzed with the Agilent ChemStation software.

2.3 Quality control and quality assurance

For each batch of 12 samples, a method blank, a spiked blank and a sample duplicate were processed. The retention time and the response factors of GC/MS were assessed for each analytical sequence from daily control standards to ensure the most appropriate quantification. The average recoveries of PAEs spiked in seawater samples showed acceptable recovery for all phthalates, ranging from $97\% \pm 3\%$ for DEP to $110\% \pm 7\%$ for DiBP. Internal standard recoveries were estimates as $94\% \pm 2\%$ for DEP-d4, $77\% \pm 3\%$ for DnBP-d4 and $14\% \pm 2\%$ for DEHP-d4. All material was produced in borosilicate glass previously kept in an acidic bath overnight (10% hydrochloric acid), rinsed with ultrapure water, combusted at 450°C for 6 hours and rinsed with methanol and dichloromethane before use. Extractions were carried out in controlled air conditions in an ISO class 6 chemistry cleanroom (temperature: 22°C ; SAS pressure: +15 Pa; SAS brewing rate: 30 vol/h; lab pressure: +30 Pa; brewing rate: 50 vol/h). Although precautions were considered to prevent sample contamination during the protocol, DEP, DiBP and occasionally DnBP were detected in the blanks at levels that remained below $0.07 \pm 0.02 \text{ ng L}^{-1}$, $0.8 \pm 0.3 \text{ ng L}^{-1}$ and $0.7 \pm 0.2 \text{ ng L}^{-1}$, respectively. DEHP was occasionally detected in blanks between the method detection limit (MDL) and the quantification detection limit (QDL). Limits of detection (LOD) were derived from the blanks and quantified as mean blanks plus three times the standard deviation of blanks, and they ranged from 0.11 ng L^{-1} for DMP to 1.67 ng L^{-1} for DEHP.

2.4 Statistics

Principal component analysis (PCA) was applied to reduce the multidimensional nature of the dataset and to evaluate the interrelationships among the PAEs, sites and sampling periods. PCA was performed using the individual phthalate concentrations (i.e. DEHP, DiBP) as PCA parameters. This data set was transformed in two smaller matrices that are linear combinations of the original data set. The number of observations in this study is 216, which permits the use of this statistical approach. The PCA statistics were performed using the statistical package XLSTAT 2010.2 (Addinsoft). Time series maps were made using the latest Ocean Data View version: ODV 4.7.4.

3 Results and discussion

3.1 General characteristics of the water column

The hydrological data (Fig. 3) are in line with previous well-known features in Marseille Bay and the local coastal area indicating that (1) the water column was well mixed during winter and fall periods, most of the time under the action of wind,⁵⁵⁻⁵⁷ whereas (2) the water began warming in May (16–17°C) causing water stratification. It is noteworthy that lower salinity was observed in October-November 2014 probably in association with freshwater intrusion (Fig. 3b). The DOC distribution (Fig. 3e) showed a clear seasonal trend with a concentration range of 62.5-72.5 µM in winter-spring and 72.5-90 µM during summer-fall. Higher DOC values (79-81 µM) were observed in the spring water column as well as above the bottom in winter. As a byproduct of primary production, the DOC distribution highlighted higher concentrations in spring-summer following phytoplankton growth (Fig. 3d). The high DOC concentrations near the bottom and in the whole water column during winter might instead be explained by resuspension of rich

organic sediment and subsequent mixing under the action of wind as previously reported from CDOM (colored dissolved organic matter) and DOC time series studies.⁵⁸⁻⁵⁹ Such low DOC concentrations were comparable to those previously reported in open waters of the Mediterranean Sea,⁶⁰⁻⁶⁴ with a stable annual mean of $67 \pm 7 \mu\text{M}$ at 2 m and $63 \pm 6 \mu\text{M}$ at 5 m.

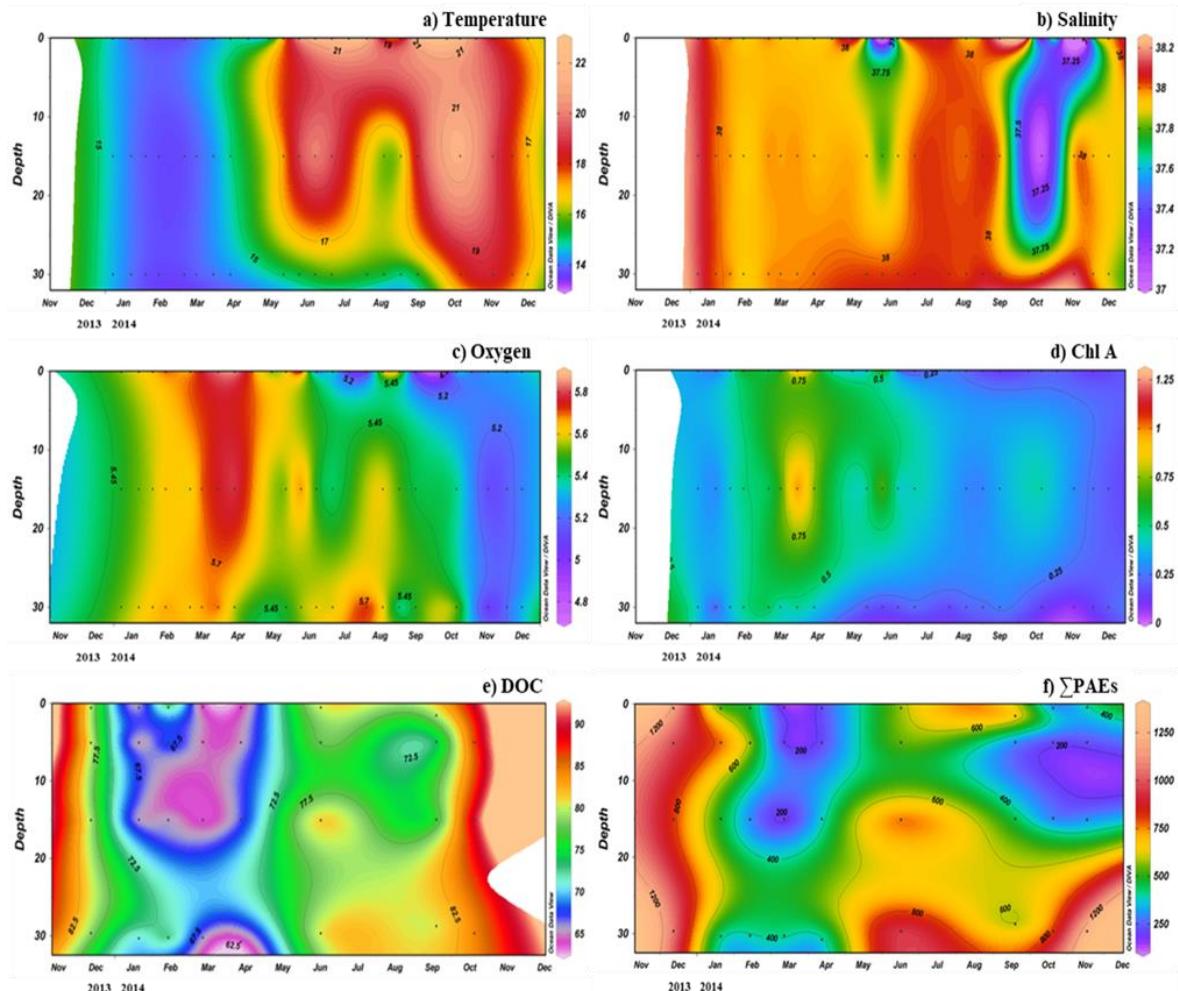


Figure 3. a) Temperature ($^{\circ}\text{C}$), b) salinity (PSU), c) oxygen (ml L^{-1}), d) chlorophyll A ($\mu\text{g L}^{-1}$), e) DOC (μM) and f) $\sum\text{PAEs}$ (ng L^{-1}) time-series at SUNMEX station (Bay of Marseille) from December 2013 to November 2014. Samples were collected at 1.5, 5, 15 and 30 m.

Table 1. Concentration ranges, average concentrations and relative abundance of PAEs in Marseille Bay (n = 72). Samples were collected at 0.5, 5, 15 and 30 m depth.

Depth (m)	Concentrations (ng L ⁻¹)		Relative abundance (%)	
	Range	Av. ± SD	Range	Av. ± SD
<i>Bay of Marseilles (Dec 2013-Nov 2014)</i>				
0.5	0.9-6.9	2.8 ± 2.2	0.2-1.4	0.6 ± 0.3
Dimethyl phthalate (DMP) 5	0.8-6.8	2.9 ± 2.0	0.3-1.1	0.7 ± 0.4
15	0.8-7.7	2.7 ± 2.3	0.2-0.9	0.6 ± 0.3
30	2.1-11.9	4.5 ± 2.1	0.2-1.2	0.7 ± 0.3
Total	0.8-11.9	3.2 ± 2.4	0.2-1.4	0.6 ± 0.3
0.5	3.4-25.7	11.8 ± 7.6	1.1-4.9	2.6 ± 1.4
Diethyl phthalate (DEP) 5	6.3-27.2	11.9 ± 7.9	1.1-10.2	3.4 ± 2.7
15	3.3-45.5	13.9 ± 13.4	0.9-9.9	3.3 ± 2.7
30	8.9-50.0	25.3 ± 12.6	0.9-5.1	3.8 ± 1.3
Total	3.3-50.0	15.7 ± 12.5	0.9-10.2	3.3 ± 2.1
0.5	34.2-215.7	89.5 ± 70.3	4.3-68.0	24.3 ± 21.9
Diisobutyl phthalate (DiBP) 5	30.1-155.3	62.0 ± 37.9	3.8-78.0	23.3 ± 23.1
15	29.4-155.1	71.1 ± 39.6	4.7-64.2	20.2 ± 18.6
30	50.8-383.4	188.5 ± 124.8	5.0-42.5	28.0 ± 11.5
Total	27.5-383.4	102.7 ± 90.5	3.8-78.0	23.9 ± 18.7
0.5	12.0-314.6	76.7 ± 66.7	2.6-26.3	11.1 ± 7.9
Dibutyl phthalate (DnBP) 5	14.0-196.5	58.3 ± 50.9	2.7-26.1	11.1 ± 7.3
15	12.0-178.6	61.4 ± 48.9	2.8-42.1	14.2 ± 12.0
30	21.0-596.0	173.8 ± 165.0	2.1-44.8	19.4 ± 13.7
Total	12.0-596.0	83.2 ± 75.2	2.1-44.8	13.9 ± 10.7
0.5	2.7-4.9	3.7 ± 0.7	0.4-2.0	1.0 ± 0.6
Benzylbutyl phthalates (BzBP) 5	2.6-4.6	3.6 ± 0.6	0.5-1.8	1.1 ± 0.5
15	2.6-4.6	3.6 ± 0.6	0.5-1.8	1.0 ± 0.4
30	3.6-6.1	4.4 ± 0.9	0.4-1.5	0.8 ± 0.4
Total	2.6-6.1	3.8 ± 0.7	0.4-2.0	0.9 ± 0.5
0.5	42.3-802.0	331.4 ± 257.1	18.5-89.3	61.0 ± 23.8
Diethylhexyl phthalate (DEHP) 5	15.8-714.0	317.0 ± 274.1	9.3-90.2	61.1 ± 24.7
15	51.3-525.0	291.9 ± 221.5	21.2-91.1	61.4 ± 24.1
30	130.0-923.8	328.6 ± 257.9	18.3-91.6	48.1 ± 23.9
Total	15.8-923.8	317.2 ± 242.7	9.3-91.6	57.9 ± 23.8
Total PAEs	131-1331	522.7 ± 313.3	100	

3.2 Concentration and relative abundance of PAEs in Marseille Bay

All targeted PAEs were detected in all samples collected at SUNMEX station except DnOP. During the studied period, the sum of the 6 PAEs' concentrations in the water column (Σ PAEs) ranged from 130 to 1330 ng L⁻¹ (av. 520 ng L⁻¹; Table 1; Fig. 3f) in Marseille Bay. The highest Σ PAEs concentrations were observed all along the well mixed water column in winter 2013 as well as near the bottom in the May-August and September-December 2014 periods (Figs. 3). By contrast, the lowest Σ PAEs concentrations were found in shallower waters between 0.5 and 15 m by the end of winter and in October-November 2014 where low salinities were observed (Fig. 3b). Note that the October-November 2014 period corresponds to possible freshwater intrusion into Marseille Bay⁵⁶ as suggested by lower salinity values (Fig. 3b). In Marseille Bay, for 62 out of 72 samples, DEHP (9.3-91.6%) was the most abundant PAE, followed by DiBP (3.8-78%) and DnBP (2.1-44.8%) (Fig. 4-5; Tab. 1). By contrast, DMP, DEP and BzBP were the least abundant (0.2-2%) and can be considered minor species here.

Very limited data are available for the occurrence and fate of PAEs as a simultaneous series in marine waters and more specifically in both the Mediterranean Sea and river waters, making any comparison of Σ PAEs data with existing studies difficult. However we found that our data are consistent with literature. Indeed, examination of already published individual PAEs, indicated that our DEHP concentrations (20-920 ng L⁻¹; Tab. 1) were in the same range as values reported for NW Spanish coastal seawater (30-620 ng L⁻¹;⁵²) and the southern coast of the UK (100-2200 ng L⁻¹;²²) but one order of magnitude lower than that for the Northern Mediterranean Spanish coast.²⁵ Noteworthy lower values were also reported in the North Sea for DEHP (0.5-5.3 ng L⁻¹), DMP as well as DEP (0.02-4.0 ng L⁻¹).^{26,65} Similar concentrations of DEHP, 161-314 and 323-779 ng L⁻¹, were found in the Seine River whereas DMP concentrations were reported in the range of 2.5-5.5 ng L⁻¹ in six Spanish rivers including Ebro River.⁵² DEP was detected in different studies in the

Seine River (France) in a range slightly higher than our data, from 46-208 ng L⁻¹²⁶ to 71-181 ng L⁻¹,⁶⁵ as well as 52-284 ng L⁻¹ in 6 Spanish rivers.⁵² BzBP was also reported at low concentration in the range of 4.8-23 ng L⁻¹.^{52,65} Limited data are available for the distribution of PAEs in coastal seawater

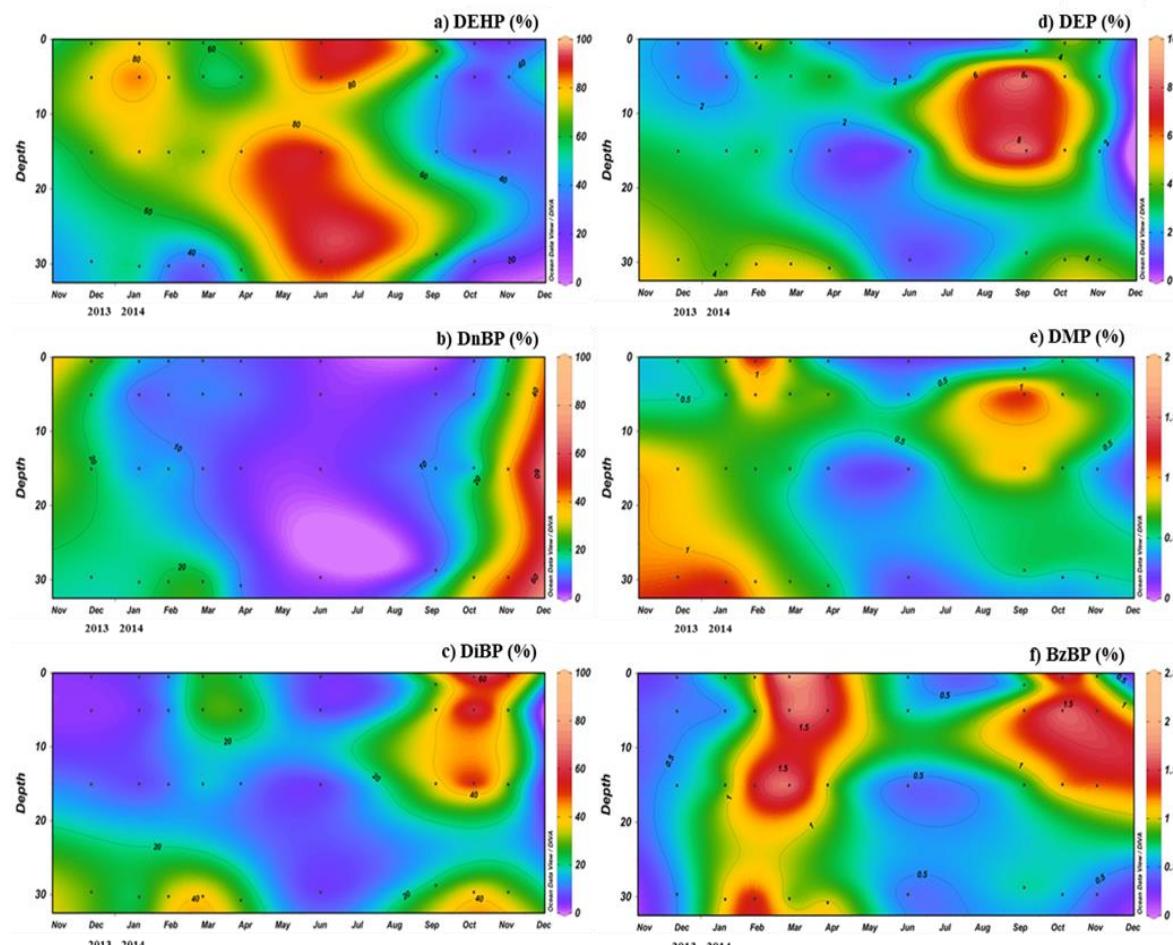


Figure 4. Relative abundances for DEHP (a), DnBP (b), DiBP (c), DEP (d), DMP (e) and BzBP (f) at SUNMEX station in Marseille Bay from December 2013 to November 2014.

The contribution of carbon from PAEs to the DOC pool (PAE-C) accounted for 10-60 ppm. A comparison with other organic compounds within the DOC pool identified in the coastal Mediterranean Sea indicated that our PAE concentrations are in the same order of magnitude as the reported values of dissolved water phase PAHs (3-120 ng L⁻¹;⁵⁰), one of the most abundant classes of organic contaminants in the marine environment. Lower

concentration range was reported for other organic pollutant as PFCs ($0.07\text{-}4.55 \text{ ng L}^{-1}$ ^{1,52,66}) in NW Mediterranean Sea, PCB ($2.2\text{-}82.4 \text{ pg L}^{-1}$ ⁵⁰) in surface water of Mediterranean Sea and PBDE, another group of compounds used as additives in polymer, detected in Aegean Sea with concentration range of $4\text{-}6 \text{ pg L}^{-1}$ ⁶⁷. PCDD/Fs was reported with two orders of magnitude lower than PAEs concentration ($42.5\text{-}64.0 \text{ fg L}^{-1}$).⁶⁸ However, PAE concentrations are nevertheless two orders of magnitude lower than the sum of α,ω -dicarboxylic acids ($20.7 \pm 10.6 \mu\text{g L}^{-1}$) and ω -oxoacids ($11.7 \pm 6.2 \mu\text{g L}^{-1}$) in the Marseille coastal area⁶⁹ or in the Rhone River close to the Marseille Bay.⁴⁹

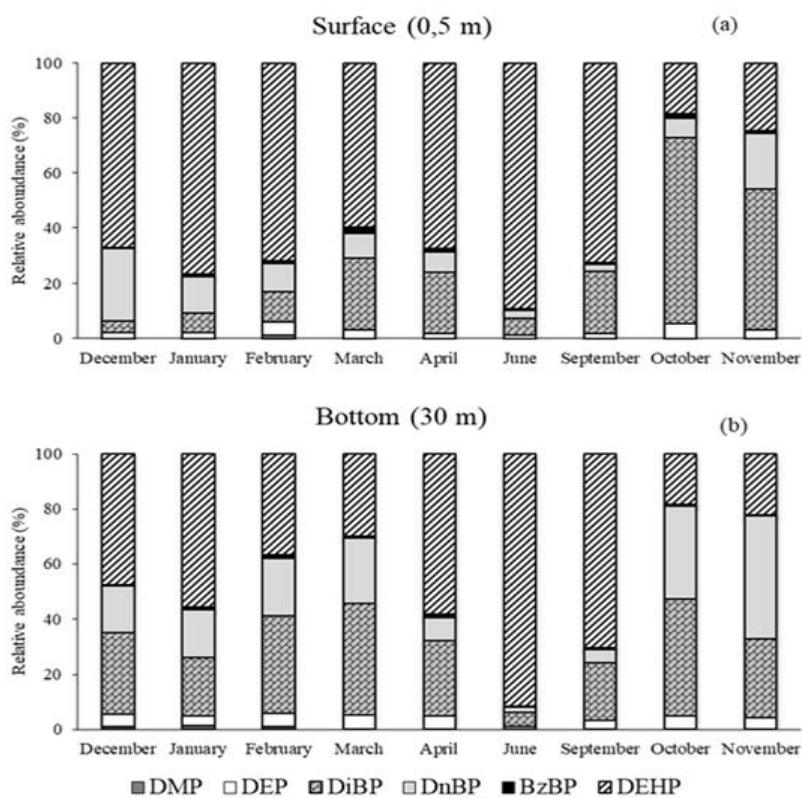


Figure 5. Relative abundance of PAEs in surface (0.5 m; a) and bottom (30 m; b) seawater samples collected at SUNMEX station in Marseille Bay from December 2013 to November 2014.

3.3 PCA analysis

The grouping of samples by depth and season using principal component analysis (PCA) formed several clusters (samples scores, Fig. 6a) over PC1 and PC2 that represent 79.7% of the total information. Samples collected at Marseille Bay formed five well-identified clusters (Fig. 6a) including the fall samples in the lower left quadrant, the spring in the central left, the summer in the upper left, winter samples in the upper right quadrant and the bottom samples in the right quadrant. Of the biomarkers plotted, DMP, DEP and DnBP being positive on PC1 and most negative on PC2 form a compact cluster on the central-right quadrant and separated from DEHP located in the upper quadrant (positive on PC1 and PC2 factors) and from DiBP in the lower quadrant (positive on PC1 and negative on PC2). DEHP is a plasticizer used in the manufacture of PVC and other plastic products. On the other hand, the presence of LMW-PAEs in the same group is related to their common use as components of solvents, adhesives, pharmaceutical products, insecticide materials and cosmetics.

In brief, the PCA score plot therefore highlights that i) summer and winter groups have a similar pattern i.e. highest concentrations of DEHP, DMP and DEP, together with lowest concentrations of DiBP; ii) fall and spring groups are also very close on Figure 6a: their intensity on both PC1 and PC2 axis are low and negative, meaning low Σ PAEs concentration rather than a specific PAE mix; and iii) bottom samples are mainly driven by DiBP concentration, and are thus clearly separated from upper water layers whatever the season.

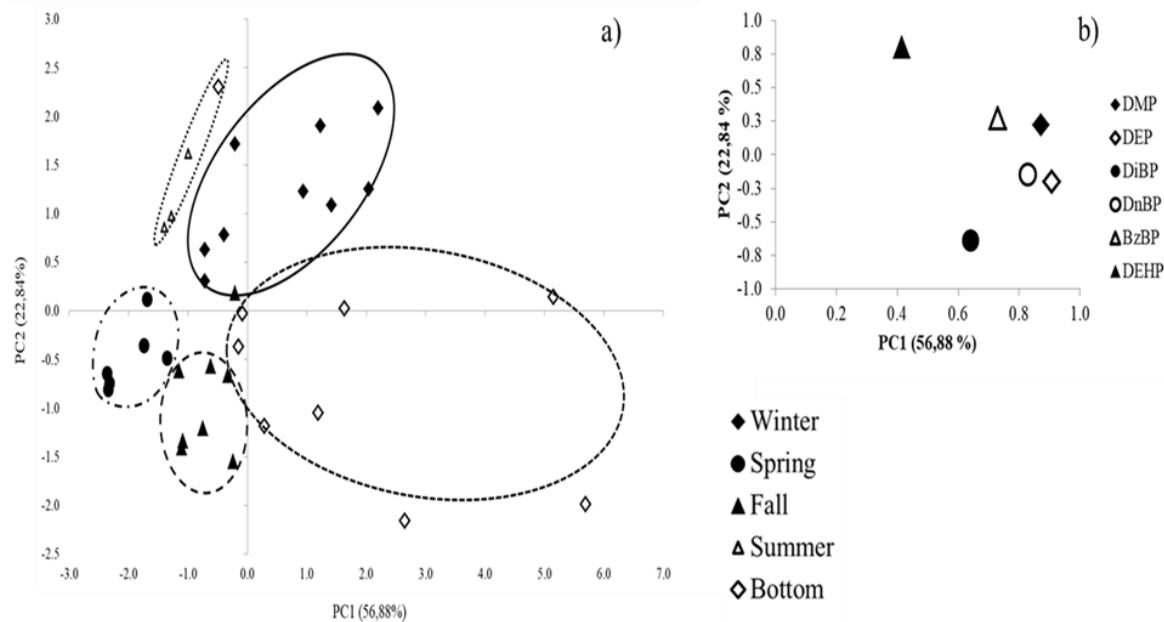


Figure 6. Principal components analysis (PCA) for PAEs in the study area was applied to reduce the multidimensional nature of the dataset and to evaluate the interrelationships among the PAEs, sites and sampling periods. The PCA statistics were performed using the statistical package XLSTAT 2010.2 (Addinsoft). In (a) the sample scores, whereas in (b) the variable loadings of the PCA. The variance accounted for by each principal component is shown in parentheses after the axis label.

3.4 Potential sources and sinks of PAEs in the water column

The averaged concentrations of PAEs found in Marseille Bay ($522.7 \pm 313.3 \text{ ng L}^{-1}$) samples are significantly higher than that previously found offshore (maximum depth 2500 m) ($135 \pm 74 \text{ ng L}^{-1}$,⁵³) suggesting that the freshwater input and urban area provide a significant amount of PAEs to Marseille Bay. Our results also indicated i) significant seasonal variations of ΣPAEs in Marseille Bay suggesting variability in sources, degradation processes of PAEs occurring in coastal seawaters, and/or partitioning of PAEs onto particulate matter; ii) heterogeneous vertical distribution by the end of winter/spring and homogenous concentration in the whole water column in the winter period with a large ΣPAEs increase of concentration above the sea floor at different periods of the year.

Seasonal variation

Concerning seasonal variation in Marseille Bay, it is interesting to note that elevated concentration of PAEs (Fig. 3f) in summer coastal seawater nearby the Marseille urban area is concomitant with (1) the intense recreational coastal activities that reach their maximum during the summer on the beaches of Marseille, as well as (2) the elevated maritime traffic occurring during the tourist season between the ports of the coastal study area. As DEHP is predominant during the summer period (Figs. 4-5), it is likely that such summer activities preferentially generate inputs of DEHP-rich PAE into coastal seawater. It should be noticed that DEHP is the most abundant plasticizer for PVC, PVA and rubber materials that are widely used at sea through surfing, diving and swimming or left on the beaches such as food packaging, bags and sunscreen containers. The high turnover of cruise ships could also represent a significant source of DEHP for the coastal area. In Marseille Bay, the large variations of PAE concentrations in the first 25 m of the water column could be connected to variation of input and degradation processes as well. Few PAE-degrading bacteria have been isolated from marine environments⁷⁰ and a recent study suggests that the ability to degrade phthalate and its monoesters is widespread in Japanese seawater from bacteria related to 11 different genera.⁷¹ It is likely that prokaryotic degradation processes regulate the PAE concentration in the water column as well.

Higher concentration near the bottom

Interestingly, we found that PAE concentrations are quite elevated above the bottom being, in most cases, higher than the corresponding concentration on the sea surface (Fig. 3f-7), with the exclusion of winter 2013 and September for which PAE concentrations are similar in the whole water column probably because of winter mixing under the action of Mistral wind.⁵⁵ Such an accumulation of ΣPAEs near the bottom has already been reported in a previous study in offshore Mediterranean seawater at 2000 m

depth.⁵³ A gradient in the PAE concentration might be either due to i) preferential photochemical and/or prokaryotic degradation in the surface water column rather than in deeper seawater, giving rise to accumulation of PAEs above the seafloor, or ii) PAE input directly from the bottom by pure chemical diffusion and/or advection phenomena (resuspension of sediment or bioturbation).

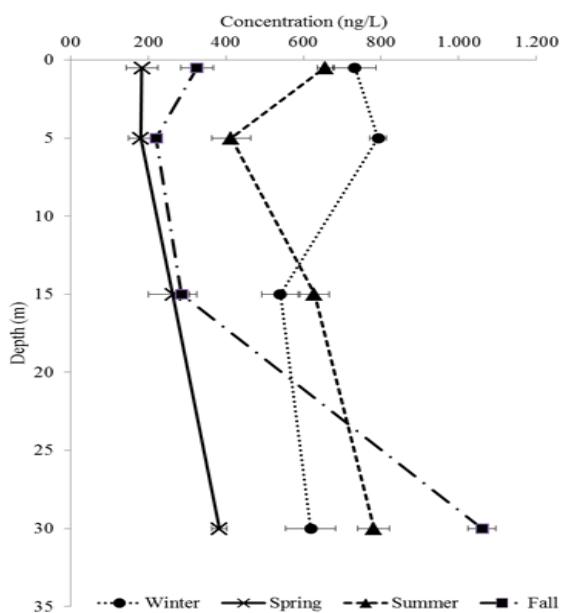


Figure 7. Σ PAEs vertical profile at Bay of Marseille in 4 seasons (average values) of 2014.

Surface water column photochemical degradation is certainly more effective in the first meters of the water column whereas prokaryotic degradation is likely to be more efficient above the sediment. Although PAE-degrading bacteria have been isolated from marine environments,⁷⁰⁻⁷¹ preferential biodegradation in the water column rather than above the bottom is very unlikely. Therefore, only photochemical degradation may explain such PAE concentration gradient along the vertical gradient.

This vertical gradient might also be connected to a concentration of plastic debris above the sea floor that may releases various chemical additives including phthalates into

surrounding waters during their degradation as stated before. Indeed, accumulation of debris with a large proportion of plastic material has been observed several times, by trawling sampling and by video quantification based on recordings at the sea floor of the French Mediterranean coast including Marseille Bay,⁷²⁻⁷⁴ the Rhone River plume area as well as canyons and continental slopes in the northwestern Mediterranean.⁷⁵ In most cases, plastic bags accounted for more than 90% of the total debris⁷² and in particular in the eastern canyons of the Gulf of Lion⁷⁴ close to Marseille. Such debris are likely PAE-producer candidates. Chemical diffusion from sediment, or sediment resuspension/bioturbation could though explain higher PAE concentration close to the sediment. Resuspension episodes of PAE-rich sediment in the water column (originating from wind-driven turbulence and hydrodynamic features⁷⁶ such as upwelling above the seafloor as previously reported for CDOM and DOC in Marseille Bay⁵⁸) are possible. However, higher DOC concentrations were not observed close to the sediment (Fig. 3e), supporting poor physical transport from the sediment toward the water column. Transport by chemical diffusion would therefore be predominant, in case PAEs input came from the sediment.

Interestingly, in Marseille Bay bottom samples, DiBP and DnBP relative abundance values were predominant over DEHP or higher (compared to surface waters) and match the period of high concentration of total PAEs. Indeed, in surface water samples, the relative abundance of DEHP, DnBP and DiBP averaged $66 \pm 18\%$, $11 \pm 6\%$ and $21 \pm 15\%$, respectively, whereas these values averaged $48 \pm 21\%$, $21 \pm 12\%$ and $32 \pm 14\%$, respectively, in bottom samples during the year (Fig. 5). A possible explanation would be a higher degradation rate of LMW-PAEs close to the atmosphere/water interface due to higher organisms' density, as suggested by Yuan et al.⁷⁷ The predominance (or higher relative abundance) of DnBP and DiBP *versus* DEHP in deepwater samples is in line with previous observations at a deep offshore station ($z = 2400$ m).⁵³ The variation of

PAE relative abundance near the bottom could also be explained considering the higher hydrophobicity of DEHP ($\log K_{ow} = 7.54$, SPARC) compared with DnBP and DEP ($\log K_{ow} = 4.63$ and 2.51, respectively, SPARC), which could determine different grades of PAE repartition between sediment and water, making available a smaller dissolved fraction of DEHP and suggesting that DEP and even DnBP mainly exist under freely dissolved phase compared with DEHP. The higher desorption rate of these phthalate, with the exception of DEHP and DMP, in the interface sediment/water was already observed in a previous study⁷⁸

Surprisingly, a significant decrease of DEHP concentration and relative abundance was observed after the summer (October/November 2014) (Figs. 4-5). The change in relative abundance during fall, even on the surface, was due to an increase of DiBP and to a lesser extent DnBP and could be associated with potential resuspension as we observed only high PAE concentration in bottom samples. Note that the variable intensity of the resuspension processes might be favored by the Northern Current entering into the Gulf of Lyon and being particularly high from October to May⁷⁶ intensifying the inputs and shelf/slope exchange processes including turbulent mixing and vertical flux on the continental slope.^{76,79} In these circumstances exchange with the deep bottom, already observed to be rich in plastic debris, could represent a seasonal source of PAEs for the Bay of Marseille at the end of the stratification season, especially in the eastern canyons close to Marseille. This area was already noticed to accumulate most of the debris in the Gulf of Lyon, especially plastic bags.⁷²⁻⁷³ Our data together with others studies, suggest sediment resuspension as an important process explaining the heterogeneous vertical distribution. However, additional specific experiments are needed to confirm such hypothesis.

4 Conclusion

This study provides the first complete data on PAEs concentration levels in the Bay of Marseille (NW Mediterranean Sea). In addition, the first estimation of the PAEs annual occurrence and PAEs vertical distribution were reported here. The Marseille Bay, which is highly populated, displays levels of contamination of the same order of magnitude as other coastal area (NW Spanish coast, UK southern coast, Seine River;^{22,25-26,52,65}). DEHP was detected as the predominant PAE congener in spring/summer season at Marseille area in the whole water column, whereas DiBP and DnBP were found to be abundant when close to the seafloor and especially in fall/winter season in the study areas. DMP, DEP and BzBP represent a minor fraction of PAEs pool and DnOP was never detected in the analyzed samples. The highest PAEs concentrations were detected close to the bottom and we have hypothesized a connection with the plastic debris accumulated over the seafloor and with PAEs in the sediment.

More research regarding PAEs input from plastic, and PAEs presence in the sediment should be implemented in the future to better identify the sources of the PAEs in the water column. Furthermore, more investigation is needed on the level of PAEs transfer to food web, for a better risk assessment and management policy.

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References

- (1) Serôdio, P.; Nogueria, J.M.F. Considerations on ultra-trace analysis of phthalates in drinking water. *Water Res.* **2006**, *40* (13), 2572–2582.
- (2) Net, S.; Delmont, A.; Sempéré, R.; Paluselli, A.; Ouddane, B. Reliable quantification of phthalates in environmental matrices (air, water, sludge, sediment and soil): A review. *Sci. Total Environ.* **2015** a, 515–516 , 162–180.
<http://dx.doi.org/10.1016/j.scitotenv.2015.02.013>.
- (3) Rahman, M.; Brazel, C.S. The plasticizer market: an assessment of traditional plasticizers and research trends to meet new challenges. *Prog. Polym. Sci.* **2004**, *29*, 1223-1248.
- (4) He, W.; Qin, N.; Kong, X.; Liu, W.; He, Q.; Ouyang, H.; Yang, C.; Jiang, Y.; Wang, Q.; Yang, B.; Xu, F. Spatio-temporal distributions and the ecological and health risks of phthalate esters (PAEs) in the surface water of a large, shallow Chinese lake. *Sci. Total Environ.* **2013**, *461–462*, 672–680.
- (5) Kimber, I.; Dearman, R.J. An assessment of the ability of phthalates to influence immune and allergic responses. *Toxicol.* **2010**, *271* (3), 73–82.
- (6) Net, S.; Sempéré, R.; Delmont, A.; Paluselli, A.; Ouddane, B. Occurrence, Fate, Behavior and Ecotoxicological State of Phthalates in Different Environmental Matrices. *Environ. Sci. Technol.* **2015** b, *49* (7), 4019–4035.
- (7) Xie, Z.; Ebinghaus, R.; Temme, C.; Lohmann, R.; Caba, A.; Ruck, W. Occurrence and Air-Sea Exchange of Phthalates in the Arctic. *Environ. Sci. Technol.* **2007**, *41*, 4555-4560.
- (8) Holahan, M.R.; Smith, C.A. Phthalates and neurotoxic effects on hippocampal network plasticity. *NeuroToxicology* **2015**, *48*, 21–34.
- (9) IARC. Some industrial chemicals, di(2-ethylhexyl) phthalate. *IARC Monogr. Eval. Carcinog. Risks Hum.* **2000**, *77*, 41-148.
- (10) Halden, R.U. Plastics and Health Risks. *Annu. Rev. Public Health* **2010**, *31*, 179-194.
- (11) Staples, C.A.; Peterson, D.R.; Parkerton, T.F.; Adams, W.J. The environmental fate of phthalate esters: a literature review. *Chemosphere* **1997**, *35* (4), 667-749.
- (12) Andrade, A.L. Microplastics in the marine environment. *Mar. Pollut. Bull.* **2011**, *62* (8), 1596–1605.
- (13) Kolena, B.; Petrovivova, I.; Pilka, T.; Pucherova, Z.; Munk, M.; Matula, B.; Vankova, V.; Petlus, P.; Jenisova, Z.; Rozova, Z.; Wimmerova, S.; Trnovec, T. Phthalate exposure and health-related outcomes in specific types of work environment. *Int. J. Environ. Res. Publ. Health* **2014**, *11*(6), 5628-5639.
- (14) Okamoto, Y.; Ueda, K.; Kojima, N. Potential risks of phthalates esters: acquisition of endocrine-disrupting activity during environmental and metabolic processing. *J. Health Sci.* **2011**, *57*, 497-503.
- (15) Howdeshell, K.I.; Rider, C.V.; Wilson, V.S.; Gray Jr, L.E. Mechanisms of action of

- phthalate esters, individually and in combination, to induce abnormal reproductive development in male laboratory rats. *Environ. Res.* **2008**, 108 (2), 168-176.
- (16) Buckley, J.P.; Engel, S.M.; Mendez, M.A.; Richardson, D.B.; Daniels, J.L.; Calafat, A.M.; Wolff, M.S.; Herring, A.H. Prenatal phthalate exposures and childhood fat mass in a New York City cohort. *Environ. Health Perspect.* **2016**, 124 (4), 507-513.
- (17) Wang, Y.; Zeng, Q.; Sun, Y.; You, L.; Wang, P.; Li, M.; Yang, P.; Li, J.; Huang, Z.; Wang, C.; Li, S.; Dan, Y.; Li, Y. Phthalate exposure in association with serum hormone levels, sperm DNA damage and spermatozoa apoptosis: A cross-sectional study in China. *Environ. Res.* **2016**, 150, 557-565.
- (18) United States Environmental Protection Agency, 40 CFR Part 423, Appendix A, December 2014. <https://www.epa.gov/sites/production/files/2015-09/documents/priority-pollutant-list-epa.pdf>.
- (19) *Commission staff working document on the implementation of the community strategy for endocrine disrupters-A range of substances suspected of interfering with the hormone system of humans and wildlife*; CEC (Commission of the European Communities): Brussels, **2007**.
- (20) National Standard of the People's Republic of China, *Standard for drinking water quality GB 5749-2006*.
- (21) Bauer, M.J.; Herrmann, R.; Martin, A.; Zellmann, H. Chemodynamics, transport behavior and treatment of phthalic acid esters in municipal landfill leachates. *Water Sci. Technol.* **1998**, 38 (2), 185-192.
- (22) Turner, A.; Rawling, M.C. The behaviour of di-(2-ethylhexyl) phthalate in estuaries. *Mar. Chem.* **2000**, 68 (3), 203–217.
- (23) Fromme, H.; Kuchler, T.; Otto, T.; Pilz, K.; Muller, L.; Wenzel, A. Occurrence of phthalates and bisphenol A and F in the environment. *Water Res.* **2002**, 36, 1429-1438.
- (24) Horn, O.; Nalli, S.; Cooper, D.; Nicell, J. Plasticizer metabolites in the environment. *Water Res.* **2004**, 38, 3693–3698.
- (25) Brossa, L.; Marcé, R.; Borrull, F.; Pocurull, E. Occurrence of twenty-six endocrine-disrupting compounds in environmental water samples from Catalogna, Spain. *Environ. Toxicol. Chem.* **2005**, 24, 261-267.
- (26) Teil, M.; Blanchard, M.; Dargnat, C.; Larcher-Tiphagne, K.; Chevreuil, M. Occurrence of phthalates diesters in river of the Paris district (France). *Hydrol. Process.* **2007**, 21, 2515-2525.
- (27) Xie, Z.; Ebinghaus, R.; Temme, C.; Caba, A.; Ruck, W. Atmospheric concentrations and air-sea exchanges of phthalates in the North Sea (German Bight). *Atmos. Environ.* **2005**, 39, 3209–3219.

- (28) Xie, Z.; Selzer, J.; Ebinghaus, R.; Caba, A.; Ruck, W. Development and validation of a method for the determination of trace alkylphenols and phthalates in the atmosphere. *Anal. Chim. Acta* **2006**, 565, 198–207.
- (29) Zeng, F. ; Cui, K. ; Xie, Z. ; Liu, M. ; Li, Y. ; Lin, Y. ; Zeng, Z. ; Li, F. Occurrence of phthalate esters in water and sediment of urban lakes in a subtropical city, Guangzhou, South China. *Environ. Int.* **2008**, 34, 372–380.
- (30) Ferreira, I.D.; Morita, D.M. Ex-situ bioremediation of Brazilian soil contaminated with plasticizers process wastes. *Braz. J. Chem. Eng.* **2012**, 29 (1), 77-86.
- (31) Fu, P.; Kawamura, K.; Barrie, L.A.. Photochemical and other source of organic compounds in the Canadian high Arctic aerosol pollution during winter-spring. *Environ. Sci. Technol.* **2009**, 43, 286-292.
- (32) Fu, P.; Kawamura, K.; Chen, J.; Charrière, B.; Sempéré, R. Organic molecular composition of marine aerosols over the Arctic Ocean in summer: contributions of primary emission and secondary aerosol formation. *Biogeosciences* **2013**, 10, 653–667.
- (33) Ye, T.; Kang, M.; Huang, Q.; Fang, C.; Chen, Y.; Shen, H.; Dong, S. Exposure to DEHP and MEHP from hatching to adulthood causes reproductive dysfunction and endocrine disruption in marine medaka (*Oryzias melastigma*). *Aquat. Toxicol.* **2014**, 149, 115-126.
- (34) Gao, J.; Chi, J. Biodegradation of phthalate acid esters by different marine microalgal species. *Mar. Pollut. Bull.* **2015**, 99, 70–75.
- (35) Chen, X.; Xu, S.; Tan, T.; Lee, S.T.; Cheng, S.H.; Lee, F.W.F.; Xu, S.J.I.; Ho, K.C. Toxicity and estrogenic disrupting activity of phthalates and their mixtures. *Int. J. Environ. Res. Publ. Health* **2014**, 11 (3), 3156-3168.
- (36) The Mermex Group. Marine ecosystems responses to climatic and anthropogenic forcings in the Mediterranean. *Progr. Oceanogr.* **2011**, 91, 97–166.
- (37) Sempéré, R.; Charrière, B.; Van Wambeke, F.; Cauwet, G. Carbon inputs of the Rhône River to the Mediterranean Sea: Biogeochemical implications. *Global Biogeochem. Cycles* **2000**, 14 (2), 669-681.
- (38) Panagiotopoulos, C.; Sempéré, R.; Para, J.; Raimbault, P.; Rabouille, C.; Charrière, B. The composition and flux of particulate and dissolved carbohydrates from the Rhone River into the Mediterranean Sea. *Biogeosciences* **2012**, 9, 1827-1844.
- (39) UNEP Chemicals. Regionally based assessment of persistent toxic substances. Mediterranean Regional Report, *UNEP* **2002**, Geneve.
- (40) Deudero, S.; Alomar, C. Mediterranean marine biodiversity under threat: Reviewing influence of marine litter on species. *Mar. Pollut. Bull.* **2015**, 98 (1-2), 58-68.
- (41) Collignon, A.; Hecq, J.-H.; Galgani, F.; Voisin, P.; Collard, F; Goffart, A. Neustonic microplastic and zooplankton in the North Western Mediterranean Sea. *Mar. Pollut. Bull.* **2012**, 64, 861-864.

- (42) Cozar, A.; Sanz-Martin, M.; Marti, E.; Gonzalez-Gordillo, J.I.; Ubeda, B.; Galvez, J.A.; Irigoien, X.; Duarte, C.M. Plastic accumulation in the Mediterranean Sea. *PLoS ONE* **2015**, 10 (4).
- (43) Faure, F.; Demars, C.; Wieser, O.; Kunz, M.; De Alencastro, L.F. Plastic pollution in Swiss surface waters: nature and concentrations, interaction with pollutants. *Environ. Chem.* **2015**, 12 (5), 582-591.
- (44) Pedrotti, M.L.; Petit, S.; Elineau, A.; Bruzaud, S.; Crebassa, J.C.; Dumontet, B.; Marti, E.; Gorsky, G.; Cozar, A. Changes in the floating plastic pollution of the Mediterranean Sea in relation to the distance to land. *PLoS ONE* **2016**, 11 (8).
- (45) Suaria, G.; Avio, C. G.; Mineo, A.; Lattin, G. L.; Magaldi, M.G.; Belmonte, G.; Moore, C. J.; Regoli, F.; Aliani, S. The Mediterranean Plastic Soup: synthetic polymers in Mediterranean surface waters. *Nat. Scient. Rep.* **2016**, 6, 37551.
- (46) Ruiz-Orejon, L.F.; Sarda, R.; Ramis-Pujol, J. Floating plastic debris in the Central and Western Mediterranean Sea. *Mar. Environ. Res.* **2016**, 120, 136-144.
- (47) Schmidt, N.; Thibault, D.; Galgani, F.; Paluselli, A.; Sempéré, R. Occurrence of microplastics and potential contribution of phthalates in the surface waters of the Gulf of Lion (NW Mediterranean Sea). *Progr. Oceanogr.* Submitted.
- (48) Sicre, M.A.; Fernandes, M.B.; Pont, D. Poly-aromatic hydrocarbon (PAH) inputs from the Rhone River to the Mediterranean Sea in relation with the hydrological cycle: Impact of floods. *Mar. Pollut. Bull.* **2008**, 56 (11), 1935-1942.
- (49) Sempéré, R.; Charrière, B.; Castro-Jimenez, J.; Kawamura, K.; Panagiotopoulos, C. Occurrence of α , ω -dicarboxylic acids and ω -oxoacids in the surface waters of the Rhone River and fluxes into the Mediterranean Sea. *Progr. Oceanogr.* **2017**, in press. <https://doi.org/10.1016/j.pocean.2017.07.002>.
- (50) Berrojalbiz, N.; Dachs, J.; Ojeda, M.J.; Valle, M.C.; Castro-Jimenez, J.; Wollgast, J.; Ghiani, M.; Hanke, G.; Zaldivar, J.M. Biogeochemical and physical controls on concentrations of polycyclic aromatic hydrocarbons in water and plankton of the Mediterranean and Black Sea. *Global Biogeochem. Cycles* **2011**, 25 (4).
- (51) Castro-Jimenez, J.; Eisenreich, S.J.; Ghiani, M.; Mariani, G.; Skejo, H.; Umlauf, G.; Wollgast, J.; Zaldivar, J.M.; Berrojalbiz, N.; Reuter, H.I.; Dachs, J. Atmospheric occurrence and deposition of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in the open Mediterranean Sea. *Environ. Sci. Technol.* **2010**, 44 (14), 5456-5463.
- (52) Sanchez-Avila, J.; Tauler, R.; Lacorte, S. Organic micropollutants in coastal waters from NW Mediterranean Sea: Sources distribution and potential risk. *Environ. Int.* **2012**, 46, 50–62.

- (53) Paluselli, A.; Aminot, Y.; Galgani, F.; Net, S.; Sempéré, R. Occurrence of phthalate acid esters (PAEs) in the northwestern Mediterranean Sea and the Rhone River. *Progr. Oceanogr.* **2017**, in press. DOI: 10.1016/j.pocean.2017.06.002.
- (54) Sempéré, R.; Tedetti, M.; Panagiotopoulos, C.; Charrière, B.; Van Wambeke, F. Distribution and bacterial availability of dissolved neutral sugars in the South East Pacific. *Biogeosciences* **2008**, *5*, 1165–1173.
- (55) Fraysse, M.; Pairaud, I.; Ross, O.N.; Faure, V.M.; Pinazo, C. Intrusion of Rhone River diluted water into the Bay of Marseille: Generation processes and impacts on ecosystem functioning. *J. Geophys. Res.* **2014**, *119* (10), 6535-6556.
- (56) Gatti, J.; Petrenko, A.; Devenon, J.L.; Leredde, Y.; Ulles, C. The Rhone River dilution zone present in the northeastern shelf of the Gulf of Lion in December 2003. *Cont. Shelf Res.* **2006**, *26* (15), 1794-1805.
- (57) Barrier, N.; Petrenko, A.A; Ourmières, Y. Strong intrusions of the Northern Mediterranean Current on the eastern Gulf of Lion: insights from in-situ observations and high resolution numerical modeling. *Ocean Dyn.* **2016**, *66* (3), 313-327.
- (58) Para, J.; Coble, P.G.; Charrière, B.; Tedetti, M.; Fontana, C.; Sempéré, R. Fluorescence and absorption properties of chromophoric dissolved organic matter (CDOM) in coastal surface waters of the northwestern Mediterranean Sea, influence of the Rhône Rive not completer. *Biogeosciences* **2010**, *7*, 4083-4103.
- (59) Sempéré, R.; Para, J.; Tedetti, M.; Chattiére, B.; Mallet, M. Variability of Solar radiation and CDOM in Surface Coastal Waters of the Northwestern Mediterranean Sea. *Photochem. Photobiol.* **2015**, *91* (4), 851-561.
- (60) Doval, M.D.; Perez, F.F.; Berdalet, E. Dissolved and particulate organic carbon and nitrogen in the Northwestern Mediterranean. *Deep-Sea Res. Part I Oceanogr. Res. Pap.* **1999**, *46* (3), 511-537.
- (61) Dafner, E; Sempéré, R.; Bryden, H.L. Total organic carbon distribution and budget through the Strait of Gibraltar in April 1998. *Mar. Chem.* **2001**, *73* (3-4), 233-252.
- (62) Santinelli, C.; Sempéré, R.; Van-Wambeke, F.; Charriere, B.; Seritti, A. Organic carbon dynamics in the Mediterranean Sea: an integrated study. *Global Biogeochem. Cycles* **2012**, *26*.
- (63) Sempéré, R.; Panagiotopoulos, C.; Lafont, R.; Marroni, B.; Van Wambeke, F. Total organic dynamics in the Aegean Sea. *J. Mar. Syst.* **2002**, *33-34*, 355-364.
- (64) Sempéré, R.; Dafner, E.; Van Wambeke, F.; Lefevre, D.; Magen, C.; Allegre, S.; Bruyant, F.; Bianchi, M.; Prieur, L. Distribution and cycling of total organic carbon across the Almeria-Oran Front in the Mediterranean Sea: implications for carbon cycling in the western basin. *J. Geophys. Res.* **2003**, *108*.

- (65) Dargnat, C.; Teil, M.J.; Chevreuil, M.; Blanchard, M. Phthalate removal throughout wastewater treatment plant: Case study of Marne Aval station (France). *Sci. Total Environ.* **2009**, 407 (4), 1235–1244.
- (66) Ahrens, L.; Gerwinski, W.; Theobald, N.; Ebinghaus, R. Sources of polyfluoroalkyl compounds in the North Sea, Baltic Sea and Norwegian Sea: evidence from their spatial distribution in surface water. *Mar. Pollut. Bull.* **2010**, 60 (2), 255-260.
- (67) Lammel, G.; Audy, O.; Besis, A.; Efstathiou, C.; Eleftheriasis, K.; Kohoutek, J.; Kukucka, P.; Mulder, M.D.; Pribylova, P.; Prokes, R.; Rusina, T.P.; Samara, C.; Sofuooglu, A; Sofuooglu, S.; Tasdemir, Y.; Vassilatou, V.; Voutsas, D.; Vrana, B. Air and seawater pollution and air-sea gas exchange of persistent toxic substances in the Aegean Sea: spatial trends of PAHs, PCBs, OCPs and PBDEs. *Environ. Sci. Pollut. Res.* **2015**, 22(15), 11301-11313.
- (68) Castro-Jimenez, J.; Deviller, G.; Ghiani, M.; Loos, R.; Mariani, G.; Skejo, H.; Umlauf, G.; Wollgast, J.; Laugier, T.; Heas-Moisan, K.; Leaute, F.; Munsch, C.; Tixier, C.; Tronczynski, J. PCDD/F and PCB multi-media ambient concentrations, congener patterns and occurrence in a Mediterranean coastal lagoon (Etang de Thau, France). *Environ. Pollut.* **2008**, 156 (1), 123-125.
- (69) Tedetti, M.; Kawamura, K.; Charriere, B.; Chevalier, N.; Sempéré, R. Determination of low molecular weight dicarboxylic and ketocarboxylic acids in seawater samples. *Anal. Chem.* **2006**, 78, 6012-6018.
- (70) Gu, J.; Han, B.; Duan, S.; Zhao, Z.; Wang, Y. Degradation of the endocrine-disrupting dimethyl phthalate carboxylic ester by *Sphingomonas yanoikuyae* DOS01 isolated from the South China Sea and the biochemical pathway. *Int. Biodegradation Biodegradation* **2009**, 63 (4), 450-455.
- (71) Iwaki, H.; Nishimura, A.; Hasegawa, Y. Isolation and characterization of marine bacteria capable of utilizing phthalate. *World J. Microbiol. Biotechnol.* **2012**, 28 (3), 1321-1325.
- (72) Galgani, F.; Jaunet, S.; Campillo, A.; Guenegen, X.; His, E. Distribution and abundance of debris on the continental shelf of the north-western Mediterranean Sea. *Mar. Pollut. Bull.* **1995**, 30 (11), 713-717.
- (73) Galgani F.; Souplet, A.; Cadiou, Y. Accumulation of debris on the deep sea floor off the French Mediterranean coast. *Mar. Ecol. Prog. Ser.* **1996**, 142(1-3), 225-234.
- (74) Galgani F.; Leaute, J.P.; Moguedet, P.; Souplet, A.; Verin, Y.; Carpentier, A.; Goraguer, H.; Latrouite, D.; Andral, B.; Cadiou, Y.; Mahe, J.C.; Poulard, J.C.; Nerisson, P. Litter on the sea floor along European coasts. *Mar. Pollut. Bull.* **2000**, 40 (6), 516-527.
- (75) Fabri, M-C.; Pedel, L.; Beuck L.; Galgani, F.; Hebbeln D.; Freiwald A. Megafauna of vulnerable marine ecosystems in French mediterranean submarine canyons: Spatial

- distribution and anthropogenic impacts. *Deep Sea Res. Part 2 Top. Stud. Oceanogr.* **2014**, 104, 184-207.
- (76) Lapouyade, A.; Durrieu de Madron, X. Seasonal variability of the advective transport of particulate matter and organic carbon in the Gulf of Lion (NW Mediterranean). *Oceanol. Acta* **2001**, 24 (3), 295-312.
- (77) Yuan, S.; Huang, I.; Chang, B. Biodegradation of dibutyl phthalate and di-(2-ethylhexyl) phthalate and microbial community changes in mangrove sediment. *J Hazard Mater* **2010**, 184 (1-3), 826-831.
- (78) Mackintosh, C.; Maldonado, J.; Ikonomou, M.A.; Gobas, P.C. Sorption of Phthalate Esters and PCBs in a Marine Ecosystem. *Environ. Sci. Technol.* **2006**, 40,3481-3488.
- (79) Monaco, A.; Durrieu de Madron, X.; Radakovitch, O.; Heussner, J.; Carbone, J. Origin and variability of downward biogeochemical fluxes on the Rhone continental margin (NW Mediterranean). *Deep-Sea Res. Part I Oceanogr. Res. Pap.* **1999**, 46 (9), 1483-1511.

ANNEXE

CHAPTER II

PAEs concentration detected in the Bay of Marseille from December 2013 to Novemeber 2014

Sample		DMP (ng L ⁻¹)		DEP (ng L ⁻¹)		DiBP (ng L ⁻¹)	
Month	Depth (m)	Avr.	St. dev.	Avr.	St. dev.	Avr.	St. dev.
December 2013	30	11.9	0.2	49.0	0.3	320.1	27.1
	15	7.7	0.2	24.5	0.9	85.8	6.2
	5	4.8	0.2	18.4	1.0	37.1	7.5
	0.5	5.9	0.0	21.5	0.3	51.3	0.6
January 2014	30	4.6	0.0	13.7	0.0	79.4	4.7
	15	3.5	0.1	12.1	0.2	33.8	1.8
	5	3.7	0.1	9.8	0.6	40.3	2.5
	0.5	3.3	0.2	8.5	0.2	34.3	2.7
February 2014	30	3.8	0.1	20.7	1.4	144.5	19.7
	15	1.9	0.1	10.1	0.1	29.4	2.0
	5	6.8	0.4	19.4	1.2	63.3	2.4
	0.5	6.9	0.1	25.7	0.2	58.3	3.9
March 2014	30	3.0	0.1	20.1	0.2	177.0	2.1
	15	0.8	0.1	3.3	0.2	27.5	3.8
	5	0.8	0.1	3.4	0.2	40.0	1.0
	0.5	0.9	0.1	3.4	0.1	34.2	0.7
April 2014	30	2.2	0.1	14.7	0.3	90.7	1.9
	15	1.0	0.1	4.4	0.2	47.6	3.7
	5	1.7	0.1	8.7	0.1	62.1	0.1
	0.5	0.9	0.1	4.2	0.1	52.1	4.5
June 2014	30	2.1	0.1	8.9	0.3	50.8	1.7
	15	1.8	0.1	7.3	0.1	37.2	2.1
	5	1.4	0.1	6.3	0.3	30.1	2.0
	0.5	1.4	0.1	6.0	0.3	35.1	0.1
September 2014	30	3.5	0.2	15.0	0.5	115.6	9.4
	15	5.1	0.1	45.5	1.4	146.2	1.7
	5	3.8	0.1	27.2	0.3	73.1	2.2
	0.5	3.2	0.1	13.0	0.2	168.9	2.1
October 2014	30	2.8	0.2	35.7	2.2	335.3	13.6
	15	1.3	0.1	10.7	0.1	155.1	13.3
	5	1.1	0.1	7.4	0.2	155.3	3.5
	0.5	1.4	0.1	11.0	0.8	155.6	7.7
November 2014	30	6.4	0.3	50.0	4.2	383.4	40.9
	15	1.4	0.1	7.2	0.5	77.0	7.8
	5	1.7	0.1	7.0	0.1	56.5	7.6
	0.5	1.7	0.1	12.7	0.2	215.7	7.8

PAEs concentration detected in the Bay of Marseille from December 2013 to November 2014

Sample		DnBP (ng L ⁻¹)		BzBP (ng L ⁻¹)		DEHP (ng L ⁻¹)	
Month	Depth (m)	Avr.	St. dev.	Avr.	St. dev.	Avr.	St. dev.
December 2013	30	187.1	15.9	5.2	0.5	517.0	56.8
	15	178.6	16.9	4.6	0.3	525.0	52.1
	5	196.5	12.3	4.6	0.3	714.0	39.8
	0.5	314.6	16.1	4.7	0.3	802.0	48.4
January 2014	30	65.4	2.5	3.8	0.3	209.5	1.2
	15	49.0	2.4	4.0	0.1	384.3	86.8
	5	51.1	2.6	4.0	0.1	675.4	37.5
	0.5	63.8	4.3	3.6	0.3	371.8	43.7
February 2014	30	85.6	5.0	6.1	0.2	150.3	38.1
	15	48.3	1.2	4.3	0.2	226.7	12.1
	5	61.7	0.3	4.3	0.1	475.9	43.9
	0.5	54.5	3.8	4.9	0.1	377.9	64.6
March 2014	30	103.5	4.2	3.6	0.1	130.0	24.6
	15	12.0	1.9	2.6	0.1	102.4	2.7
	5	14.0	0.3	2.6	0.1	80.6	5.2
	0.5	12.0	0.3	2.7	0.1	78.4	3.5
April 2014	30	28.8	1.0	3.7	0.1	194.9	22.2
	15	15.5	0.4	3.3	0.1	309.4	35.7
	5	20.8	0.9	3.4	0.2	126.9	3.9
	0.5	17.6	0.2	3.4	0.2	159.9	8.5
June 2014	30	21.0	0.3	3.9	0.1	923.8	39.6
	15	22.3	1.9	3.6	0.1	724.4	89.4
	5	15.1	0.9	3.6	0.1	507.0	37.0
	0.5	15.6	0.9	3.4	0.2	502.6	84.1
September 2014	30	28.2	0.6	3.6	0.2	391.3	91.4
	15	66.2	2.2	3.1	0.1	200.4	27.2
	5	21.1	1.2	3.1	0.1	141.6	1.8
	0.5	19.4	0.3	3.5	0.1	544.5	55.2
October 2014	30	268.4	16.9	4.4	0.3	144.4	49.7
	15	21.5	1.6	3.2	0.1	51.3	4.9
	5	14.4	3.4	3.6	0.1	18.5	4.3
	0.5	15.9	0.1	3.8	0.1	42.3	3.6
November 2014	30	596.0	10.3	4.8	0.1	296.4	12.2
	15	138.9	1.4	4.0	0.1	102.9	28.7
	5	63.4	0.3	3.2	0.1	112.8	34.6
	0.5	87.0	18.4	3.5	0.2	103.5	22.7

CHAPTER III

Release and Degradation

Phthalate release and degradation from plastic fragments in seawater

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Abstract:

Plastic debris in the marine environment, including resin pellets, macro- and microplastic fragments, contain organic contaminants, such as phthalic acid esters (PAEs), that were added during plastic manufacture or adsorbed from the surrounding seawater. In this study, two common plastic materials as trash plastic bags (PB, 50 µm thickness) and insulation layer of electric cables (EC, 2 mm thickness) were incubated in natural seawater in controlled laboratory conditions and studied for PAEs migration under different conditions including temperature, light/dark and bacteria. Our results showed migration of distinct PAEs with varying release kinetics depending of the plastic type. Dimethyl phthalate (DMP) and diethyl phthalate (DEP) migrated from the insulation layer of EC up to 9.5 ± 1.4 and 68.9 ± 10.3 ng g⁻¹ of plastic, respectively, after one months of incubation. Otherwise, disobutyl phthalate (DiBP) and di-n-butyl phthalate (DnBP) were the main PAEs able to migrate out of PB, reaching the highest migration rate after only one week with values of 333.4 ± 50.3 and 480.5 ± 72.1 ng g⁻¹ of plastic, respectively. Light and bacteria increased significantly the total amount of PAE released from EC material. This was however not observed in the case of PB, highlighting the crucial role of thickness in the PAEs release process from plastic piece in a marine environment.

1 Introduction

The worldwide production of plastics has increased considerably since the development of synthetic polymers in the middle of the 20th century (Andrady, 2011; Plastic Europe, 2015). The amount of plastic manufactured has increased rapidly, with 311 million tons of plastic produced globally in 2014 (Plastics Europe, 2015), giving rise to large emission and transport of plastics debris (Eriksen et al., 2014; Saido, 2014) through rivers, sewage and atmosphere to the Ocean (Barnes et al., 2009; Alder et al., 2005). Plastic materials are dispersed by wind and currents, and significant amounts may either sink into the water column (Ter Halle et al., 2016; Moore et al., 2001), incorporate into the sediments (Woodall et al., 2014; Cooper and Corcoran, 2010) or be assimilated by organisms (Neves et al., 2015). Although degradation processes are extremely slow (Barnes et al., 2009; Browne et al., 2011), plastics debris in aquatic systems are subjected to a series of physical, chemical and biological degradations (Andrady and Neal, 2009; Cózar et al., 2014), which is intensified in coastal environments due to higher seawater dynamic, abrasion and sand/coastline (Corcoran et al., 2009; Rios et al., 2011). Most plastics contain a number of additives such as phthalic acid esters or phthalates (PAEs) used as plastic softeners (Serodio and Nogueira, 2006; Net et al., 2015) that are considered as priority pollutants of US-EPA, the European Union (EU) and Chinese water list (CEC, 2007) due to the endocrine disruption and carcinogenic (Crisp et al., 1998; Latini, 2005; Kamrin, 2009; Meeker et al., 2009). Importantly, they are not covalently bound to the plastic polymer and are likely to migrate out of the plastic into the environment or inside an animal's stomach or tissue (Andrady, 2011) during aging.

Although PAEs have been detected in aquatic environments (Fossi et al. 2017; Net et al., 2015, 2014; Paluselli et al., 2017, 2018; Wang et al., 2014; Xie et al., 2007), there is a paucity of data dealing with the preferential pathway driving their introduction in the

aqueous marine media and kinetic of release from various plastic materials as well as with degradation processes (Gao and Chi, 2015; Munshi et al., 2013). Here, we report a study dealing with the potential of selected plastic materials to release phthalates into Mediterranean seawater under the action of light, temperature and natural bacteria. The Mediterranean Sea is a semi-enclosed basin with high solar radiation (Sempéré et al., 2015) and high atmospheric inputs (Castro et al., 2017; Theodosi et al., 2017), with a slow turnover time of ~ 80 years (The Mermex Group, 2011 and references therein) and a strong urbanization with a large range of industrial activities spread all along the Mediterranean basin (Zorita et al., 2007) that is greatly affected by marine litter (Cozar et al., 2014, 2015; Faure et al., 2015; Collignon et al., 2014; Eriksen et al., 2014; Fossi et al., 2016, 2017).

In this paper, we investigate the potential for plastics to release phthalates in the marine environment in laboratory controlled conditions by following PAE potential migration from two commercially available plastic materials, diluted in Mediterranean seawater. Furthermore, the impact of oceanographic parameters such as temperature, light/night conditions and bacterial degradation on migration processes were included in simplified basic attempts.

2. Materials and Methods

2.1 Sampling and experimental conditions

For PAEs and plastic incubations, about one hundred liters of seawater were collected in Marseille Bay (NW Mediterranean Sea: 43°16'N; 05°20'E) in June 2015 at 3 m depth by using a 12 L-GO-FLO© (GENERAL OCEANICS) bottle, previously rinsed with 1 % hydrochloric acid and ultrapure water (MQ, resistivity > 18.2 MΩ), to prevent contamination, transferred in 5 and 10 L glass bottles and brought back in the laboratory

within one hour. Then, seawater was directly filtrated in an ISO class 6 cleanroom (temperature: 22 °C; SAS pressure: +15 Pa; SAS brewing rate: 30 vol h⁻¹; lab pressure: +30 Pa; brewing rate: 50 vol h⁻¹) through precombusted (450 °C for 6 h) GFC filters (1.2 µm pore size, 47-mm diameter, rinsed with 2 L of MQ and 150 mL of sample prior to filtration) in a precombusted glass apparatus and transferred into 1 L-glass bottles stored for 2-3 hours at 4 °C for further experiments.

a) PAE bacterial degradation experiment

For PAEs biodegradation, 700 mL of filtered seawater was transferred into preccombusted 1-L glass bottles, spiked with a mixture of 7 PAEs solution (grade > 98 %, Supelco, Bellefonte) reaching a final concentration of 1 ug L⁻¹, wrapped up with aluminum paper, and incubated in duplicate at 22 °C for two months in the dark in temperature controlled laboratory. Bottles were filled to 70% of the bottle volume to ensure well oxygenated conditions. Control samples were prepared in duplicates, poisoned with sulfuric acid to pH ~ 2 to avoid any biological activity and taken at the end of the experiments. Subsamples were collected by using precombusted Pasteur pipettes at 0, 1, 2, 4, 7, 13, 21, 28, 35, 42, 49 and 60 days.

b) PAE releases from plastic material experiments

For PAEs release experiments, i) one pieces of 2 cm × 2 cm × 50 µm (total mass of 0.4 g, 8.1 cm² surface area) of commercially available black plastic ordinary garbage bag (PB) ii) the insulation layer of electrical cable (EC, total mass of 1.5 g, tube 1cm length, 9 mm O.D., 5 mm ID, 4.8 cm² surface area) were transferred into separated 1-L glass bottles previously filled with 600 mL of filtrated seawater. The Plastic fragments were incubated for two months in the dark in temperature controlled laboratory. Bottles were filled to 60% of the bottle volume to ensure well oxygenated conditions. Before experiment, the plastic

material surfaces were cleaned with MQ and cut into pieces with metal scissors previously cleaned with organic solvent and MQ. Twelve experiments were carried out in controlled thermostatic rooms and consisted of evaluating two types of plastic at three different temperatures: 1) in-situ temperature (22°C); 2) 27°C and 12°C. Highest and lowest temperatures were used to explore possible effect of extreme summer warming in surface water (27°C) and Mediterranean deep seawater conditions (12 °C), respectively. For each temperature, four experimental conditions were set up: dark biotic (DB), dark abiotic (DA), light biotic (LB) and light abiotic (LA). The artificial light inside the thermostatic room was left on for light samples whereas dark samples were wrapped up with aluminum paper and kept in cardboard boxes. The abiotic condition was obtained poisoning the samples with 1 mL of 10 g L⁻¹ HgCl₂. Two replicates for each condition were performed. The experiment was performed for 3 months and bottle samples were gently swirled for few seconds three times a day and twice during week end. The subsamples for PAE analyses were collected at 0, 1, 2, 4, 7.5, 10, 12 weeks and about 400 mL of water were transferred to glass bottles, poisoned with sulfuric acid to pH ~ 2 to avoid any biological activity, closed with polytetrafluoroethylene-lined (PTFE) screw caps and stored in the dark at 4 °C.

From the subsamples of all the experiments, an aliquot in duplicate (10 mL) were collected for dissolved organic carbon (DOC) determination with precombusted Pasteur pipettes, transferred into precombusted glass vials, poisoned with sulfuric acid to pH ~ 2, closed with PTFE-lined screw caps and stored in the dark at 4 °C. DOC concentrations were measured using a Shimadzu TOC-5000 carbon analyzer (Sempéré et al., 2008). An additional aliquot of subsample (1.8 mL) was collected for prokaryote abundance determination, transferred into cryovials and fixed with 2% (w/v final dilution)

formaldehyde solution. Samples were stored in freezer (-60 °C) until analysis in the laboratory.

2.2 Phthalates analyses

Seven phthalates were studied in this study including dimethyl phthalate (DMP), diethyl phthalate (DEP), dipropyl phthalate (DPP), di-isobutyl phthalate (DiBP), di-n-butyl phthalate (DnBP), benzylbutyl phthalate (BzBP) and di-(2-ethylhexyl) phthalate (DEHP). The deuterated internal standards were: DEP-d4, DnBP-d4, DEHP-d4. All native and labeled standards were of high purity grade (> 98 %). Stock solutions were prepared in hexane and stored in the dark at 4 °C. Working solutions (unlabeled and labeled standards) were prepared by dilution of these solutions at 20 mg L⁻¹. All solvents were glass-distilled grade and supplied by Rathburn Chemicals Ltd. (Walkerburn, UK). MQ was produced on-site on a Milli-Q system, Millipore (Molsheim, France). Water extractions were carried out in controlled air condition of a purified air room. All the glassware was previously kept in acid bath overnight (10 % hydrochloric acid), rinsed with MQ, combusted at 450 °C for 6 h and rinsed with methanol and dichloromethane immediately prior the use.

Water extractions were performed following the method optimized for seawater PAEs detection at trace level by Paluselli et al. (2017). Briefly, PAE were SPE extracted from seawater by using precombusted 6 mL-glass reaction tube equipped with methanol-precleaned PTFE frits (Supelco, Sigma-Aldrich) and containing 200 mg of Oasis HLB sorbent (Waters Corporation, 30 µm, 100 g). SPE was conducted on a Visiprep vacuum manifold from Sigma-Aldrich (Saint Quentin Fallavier, France). Before sample extraction, SPE cartridges were three times sequentially cleaned with 5 mL of acetone, 5 mL of dichloromethane, then conditioned with 5 mL of ethyl acetate, 5 mL of acetone and 5 mL of MQ prior the sample processing. Seawater samples, which were spiked with DEP-d4,

DnBP-d4 and DEHP-d4 at 50, 200 and 400 ng L⁻¹, respectively for internal standard quantification, were percolated onto the cartridges under vacuum at a flow rate of about 10 mL min⁻¹. Then, 5 mL of MQ was percolated to remove the remaining salt and air-dried for around 1 h under vacuum. PAEs were eluted into precombusted 10 mL-vials by a 2-step percolation of 3 mL of ethyl acetate. Ethyl acetate was gently evaporated up to a final volume of 200 µL at room temperature directly in the vial under a gentle stream of nitrogen (purity > 99,995 %), immediately closed with PTFE-lined screw caps rubbed with PTFE ribbon and stored before injection in the dark at -20 °C. Extractions were carried out in controlled air conditions in an ISO class 6 chemistry cleanroom. All glassware was made of borosilicate glass and that was previously kept in an acid bath overnight (10 % hydrochloric acid), rinsed with ultrapure water, combusted at 450 °C for 6 hours and rinsed with methanol and dichloromethane just before use.

2.3 GC/MS condition

Analysis was performed using an Agilent Technologies 6850 GC system coupled to an Agilent Technologies 5975C mass spectrometer (GC/MS) operated with electron impact ionization (70 eV). Chromatographic separation was achieved on an Agilent HP-5MS capillary column (30 m x 0.25 mm, 0.25 µm film thickness) with the GC oven programmed at 70 °C for 1 minute and then up to 230 °C at 30 °C min⁻¹, to 250 °C at 8 °C min⁻¹ and to 280 °C at 30 °C min⁻¹ with a final isotherm hold for 7.50 min. Helium was used as the carrier gas at a flow rate of 1.1 mL min⁻¹. The sample was manually injected (2 µL) on a splitless mode with an injector temperature of 250 °C. The injector (Merlin Microseal system) was used as a low carryover septum and a gas purifier (Charcoal, CP17972) in order to prevent contamination during the injection. Data were acquired in single ion monitoring mode for increased sensitivity with a dwell time of 100 msec.

Retention time and response factors were assessed for each analytical sequence from daily control standards to ensure the most appropriate quantification. Data was collected and analyzed with the Agilent ChemStation software. Although caution was paid to prevent contamination, DEP, DiBP and occasionally DnBP were detected in the procedural blanks at levels that remained however below 0.4-2 %, 2-3 % and 0-4 % of the masses measured in different seawater samples, respectively.

2.4. Heterotrophic prokaryotes

For heterotrophic prokaryote determination, seawater aliquots of 1.8cm³ were fixed with 2% (w/v final dilution) formaldehyde solution, quickly frozen in liquid nitrogen and stored in the deep freezer onboard (-60°C) until analysis at the flow cytometry core facility PRECYM of the Mediterranean Institute of Oceanology (<http://precym.mio.osupytheas.fr>). In the PRECYM, samples were thawed at room temperature and stained using SYBR Green II (Molecular Probes®) (Girault et al., 2015). The analyses were performed on a FACSCalibur flow cytometer (BD Biosciences®) equipped with an air-cooled argon laser (488 nm, 15 mW).

3. Results and discussion

3.1 PAEs biodegradation in seawater

PAEs concentrations in the dark under abiotic conditions (controls) were only affected by hydrolysis and adsorption on glass walls and their degradation was negligible even after 60 days for all compounds (Fig. 1). Under biotic conditions, 4 of the 7 target PAEs in seawater, DnBP, DiBP, BzBP and DEHP degraded almost completely (> 85 %) within 49 days of incubation (Fig. 1). A first order nonlinear regression (Eq 1) was applied

to the data to estimate degradation rate (i.e., k) and half-life ($t_{1/2}$, Eq 2) and the values are shown in Table 1. $C_{(t)}$ and $C_{(t=0)}$ are the PAE concentrations at each time t or $t = 0$, respectively.

$$C_{(t)} = C_{(t=0)} \times e^{-kt} \quad (1)$$

$$t_{1/2} = \frac{\ln 2}{k} \quad (2)$$

DnBP was characterized by the highest degradation rate ($k = 0.046 \pm 0.009 \text{ d}^{-1}$), with a half-life of 15 days, followed by BzBP with $t_{1/2}$ of 21 days. DiBP, DEHP and DPP showed higher $t_{1/2}$ of 29, 26 and 29 days, respectively. In contrast, DEP and DMP showed a slower and gradual degradation down to 51 and 40 %, respectively, of the original concentration after 2 months (end of the experiment) with estimated half-lifes of 79 and 53 days, respectively.

Table 1. Degradation rates (k) and half-lifes ($t_{1/2}$) of 6 PAEs under dark biotic conditions. First order regression was fitted to experimental data using XLSTAT software. RSD (relative standard deviation) is applicable for both k and $t_{1/2}$

Compound	$k (\text{d}^{-1})$	$t_{1/2} (\text{d})$	RSD (%)	R^2
DMP	0.013	53	11.4	0.905
DEP	0.009	79	9.2	0.932
DPP	0.024	29	20.1	0.727
DiBP	0.024	29	20.1	0.822
DnBP	0.046	15	10.2	0.964
BzBP	0.034	21	20.8	0.824
DEHP	0.027	26	8.3	0.963

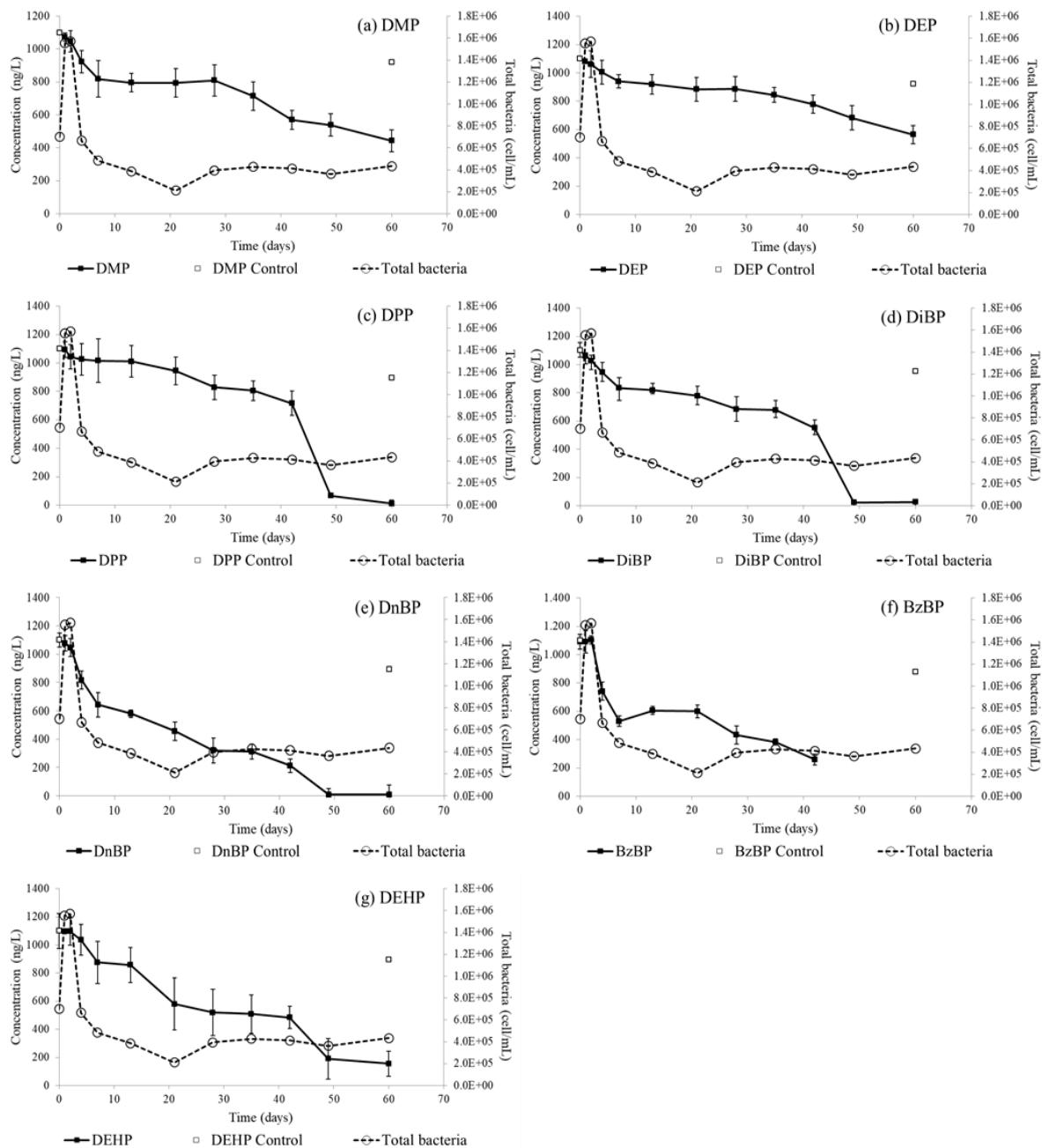


Figure 1. Degradation of 7 PAEs in seawater at 22 °C (*in situ* temperature) and in dark condition. (a) DMP, (b) DEP, (c) DPP, (d) DiBP, (e) DnBP, (f) BzBP and (g) DEHP kinetics of degradation. Control samples were used as a comparison in this study at t_0 and t_{final} .

The differences observed between degradation of 6 PAEs in natural seawater could be due to a selective degradation by the bacterial community. Probably the butanol hydrolyzed by de-esterification from one of the ester groups of DnBP served as carbon and energy source

of growth by bacteria preferentially than the methyl or ethyl group of DMP and DEP. PAEs with longer side chains, as DiBP, DnBP and DEHP are converted to those with shorter chains by β -oxidation, which removes one ethyl group each time until getting DEP (Amir et al., 2005) or/and by trans esterification (demethylation), replacing an ethyl group from DEP with a methyl group in each step, producing ethyl-methyl phthalate and then DMP (Cartwright et al., 2000).

3.2 Release from plastic fragments

PAEs release was observed in all the experiments performed from both plastics studied. However, only DMP and DEP migration were detected from EC experiments (Fig. 2, 3, 4) whereas only DiBP and DnBP were released from PB experiments (Fig. 2, 3, 4). DPP, BzBP and DEHP were never detected. This could be explained by: i) their absence from the selected polymers; ii) the low release rate implying concentrations below our detection limits in the surrounding water phase; iii) the thermodynamically unfavorable migration of heaviest PAEs to the water compartment (PAEs having highest $\log K_{ow}$). In all experiments, the larger migration was detected in first weeks of incubation with specific magnitude and trend for each individual treatment. Processes involved in these experiments were physical mixing, light effect, bacteria, temperature, as well as adsorption and hydrolysis after two months.

3.2.1 Light effect

The influence of the artificial light was investigated for both PB and EC plastics materials at the three temperatures and under biotic and abiotic experimental conditions, and PAEs release was observed in all the samples treated. All data are normalized to the mass of plastic incubated. LA conditions were compared to DA, in order to isolate the

effect of light. Fig. 1 illustrates typical release kinetics observed at 22 °C for both EC (release of DMP and DEP) and PB (release of DiBP and DnBP) experiments.

In the 12 EC experiments, a large migration was observed during the first 1-2 weeks, whereas the measured concentration reached a plateau and remained stable, in both LA and DA treatments, for the following 6 weeks. After 8-10 weeks, the measured concentration started a slight decrease most probably due to adsorption or hydrolysis phenomena. Overall, a significant difference was observed on the magnitude of DMP and DEP migrations between the DA and LA conditions. In DA treatments, the release after 2 weeks reached up the values of $2.6 \pm 0.4 \text{ ng g}^{-1}$ for DMP and $11.1 \pm 2.4 \text{ ng g}^{-1}$ for DEP, while in the presence of the artificial light (LA) it increased up to $6.7 \pm 1.0 \text{ ng g}^{-1}$ and $23.3 \pm 3.5 \text{ ng g}^{-1}$, respectively. Therefore, in the presence of light, twice higher quantities of PAEs were released from EC under our experimental conditions.

In the PB experiments, the migration of DiBP and DnBP was detected in the first week for all 12 experimental conditions. Differently from EC experiments, the differences observed between DA (DiBP: $333.4 \pm 50.3 \text{ ng g}^{-1}$; DnBP: $480.5 \pm 72.1 \text{ ng g}^{-1}$) and LA (DiBP: $414.5 \pm 62.2 \text{ ng g}^{-1}$; DnBP: $555.2 \pm 83.2 \text{ ng g}^{-1}$) were not significant during the time course experiment (Fig. 2). Thus, in the case of PAEs release from PB, no differences were measurable under our experimental varying light conditions, whether for release velocity or maximum mass reached.

The different patterns observed for both EC and PB could rather be linked to the 3-dimension configuration of each plastic pieces (i.e., 2 mm vs. 50 µm thickness respectively). Indeed, the very thin PB could release all of its PAE burden either with or without light. In contrast, light could help degrading the surface layer of EC, making more PAE quantities water-accessible.

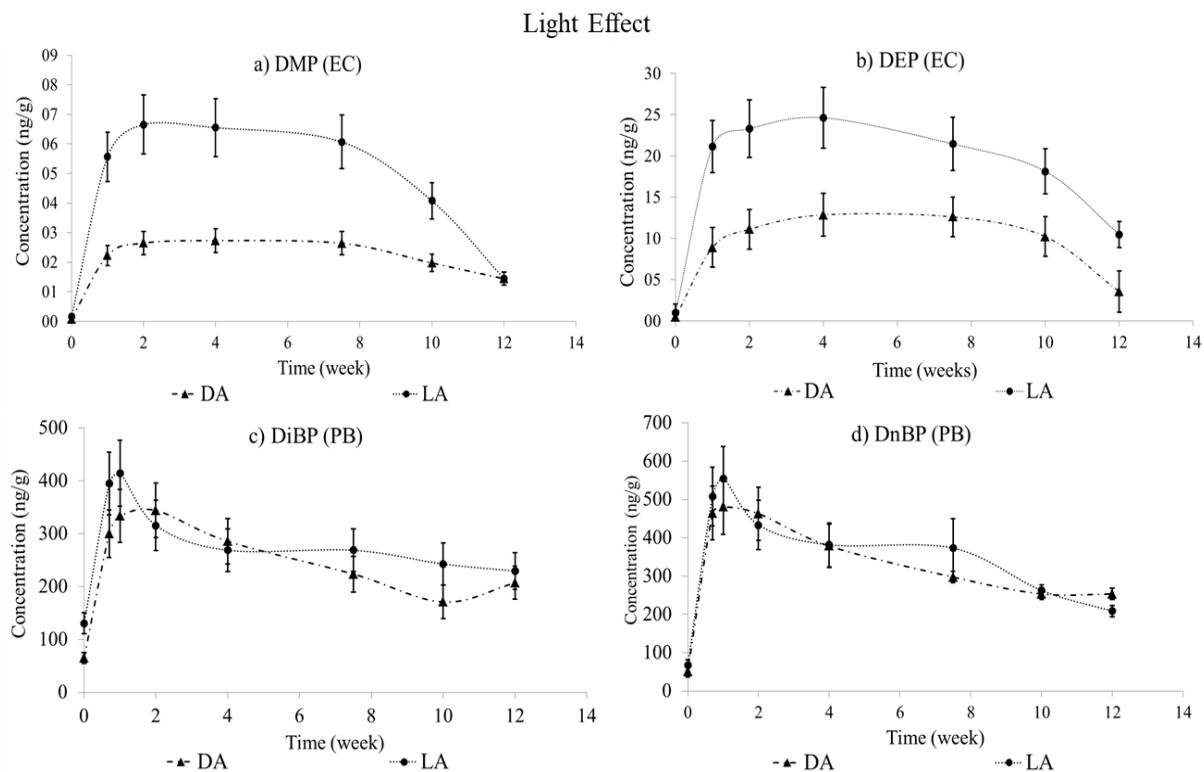


Figure 2. Graphical representation of the release kinetics of DMP (a) and DEP (b) from EC experiments and of DiBP (c) and DnBP (d) from PB experiments. The two experimental conditions were Dark Abiotic (DA) and Light Abiotic (LA) incubated at 22°C (in-situ temperature). Curves are given to assist in reading and do not represent data modeling.

3.2.2 Biotic effect

Among all experiments, the highest PAEs migration was observed under biotic conditions. DB conditions were compared to DA, in order to isolate the effect of bacteria. Fig. 3 shows typical release kinetics observed at 22 °C for both EC (release of DMP and DEP) and PB (release of DiBP and DnBP) experiments. In the 6 EC biotic experiments, the DMP and DEP migrations were observed for all the first month of incubation, followed by a sharp decrease down to almost zero after 10 weeks. In these DB conditions, releases measured after 4 weeks (DMP: $9.5 \pm 1.4 \text{ ng g}^{-1}$; DEP: $68.9 \pm 10.3 \text{ ng g}^{-1}$), were around 5 times higher than those observed under abiotic conditions. Differently, migrations from the DB (DiBP: $364.7 \pm 54.7 \text{ ng g}^{-1}$; DnBP: $464.4 \pm 69.7 \text{ ng g}^{-1}$) and DA PB experiments were characterized by i) a similar initial increase in concentration and ii) a faster decrease of this

concentration, down to almost zero after 4 weeks in DB conditions. As for light effect, a PAEs release catalyzed by bacterial communities seems to be more effective for EC than PB. Indeed, as the plateau value is much higher in the case of EC, it is likely that bacteria made water-accessible a larger amount of PAE, whereas PB is so thin that most PAEs were already able to migrate toward the water phase, without the help of bacteria. Thus, thickness of each plastic pieces should again play an important role in the release of their PAEs content.

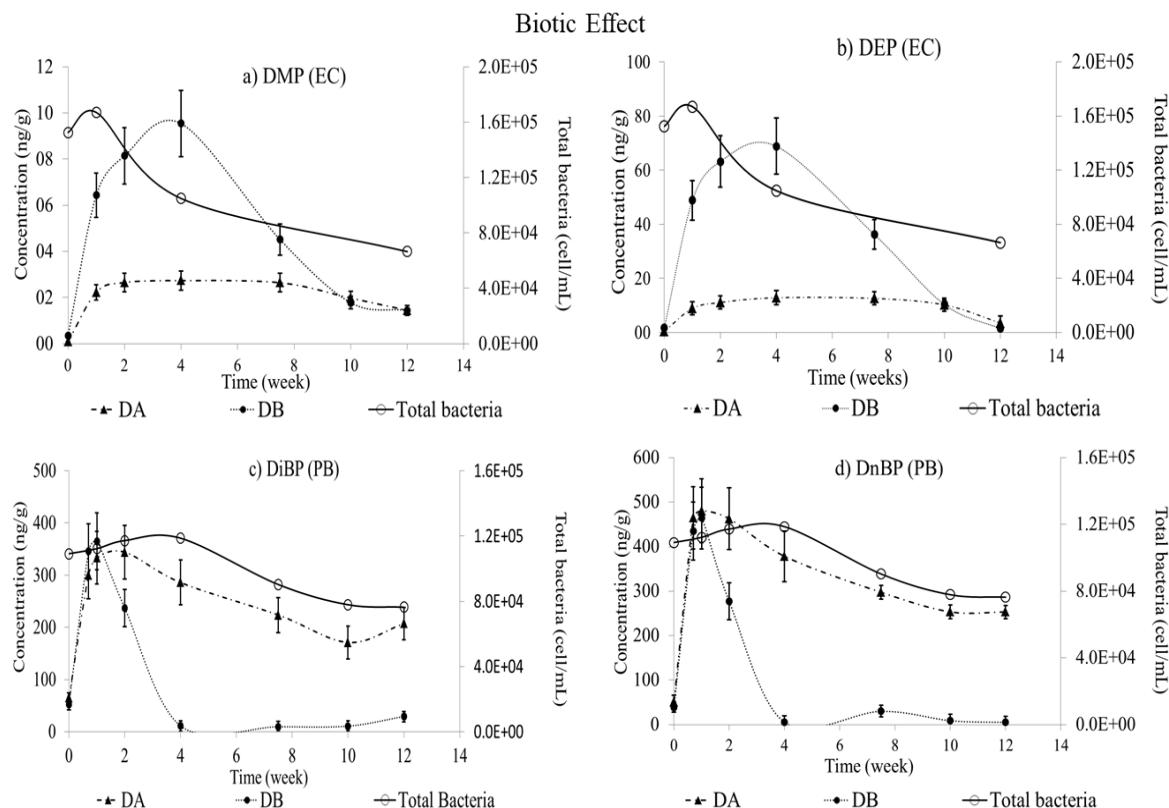


Figure 3. Graphical representation of the release kinetics of DMP (a) and DEP (b) from EC experiments and of DiBP (c) and DnBP (d) from PB experiments. The two experimental conditions were Dark Abiotic (DA) and Dark Biotic (DB) incubated at 22°C (in-situ temperature). Curves are given to assist in reading and do not represent data modeling.

3.2.3 Temperature effect

Three temperatures were considered in these experiments: 12 °C, 22 °C and 27 °C.

In Fig 4, the DA experimental conditions at 3 temperatures are shown. In EC experiments, an extremely high release was observed in the 12 °C condition for both DMP and DEP compared to 22 and 27 °C experiments. In addition, the highest value of $13.8 \pm 2.1 \text{ ng g}^{-1}$ and $84.8 \pm 12.7 \text{ ng g}^{-1}$ for DMP and DEP, respectively, was reached after 2 months of incubation. At 27 °C, the observed release was similar to the DA condition at 22 °C with $2.3 \pm 0.3 \text{ ng g}^{-1}$ for DMP and $9.0 \pm 1.8 \text{ ng g}^{-1}$ for DEP. At 12 °C, the 87 % of DMP and 81 % of DEP amount of migration were probably caused by the decreasing of temperature compared with the results obtained at 22 °C (Paragraph 3.2 a).

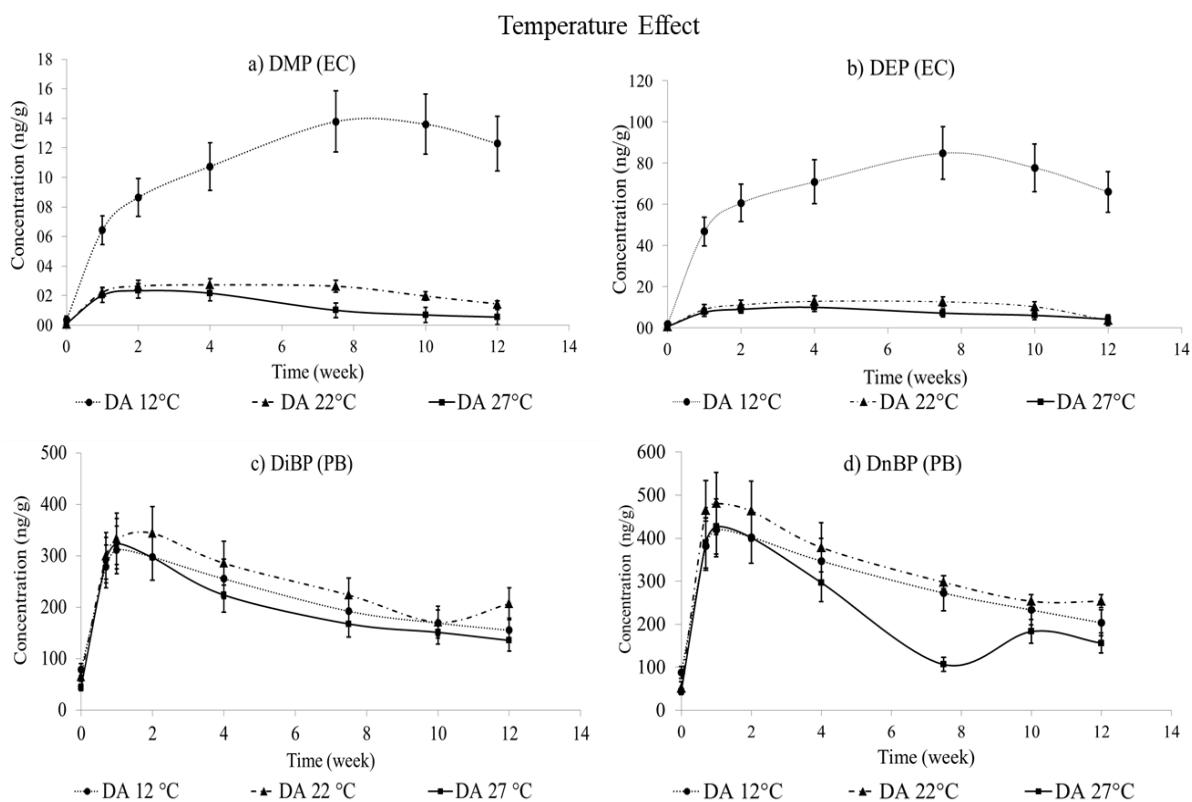


Figure 4. Graphical representation of the release kinetics of DMP (a) and DEP (b) from EC experiments and of DiBP (c) and DnBP (d) from PB experiments. The three experimental conditions were Dark Abiotic (DA) at 22°C, Dark Abiotic (DA) at 27°C and Dark Abiotic (DA) at 12°C. Curves are given to assist in reading and do not represent data modeling.

This unexpected finding is otherwise confirmed by the other three set of experimental conditions (DB; LA; LB, data not shown). This large release observed at 12 °C from EC would therefore be related to the nature of the plastics. Indeed, one purpose of this material is to support the higher temperatures of the electrical cables without any degeneration. It could be that at lower temperatures the structure of this polymer undergoes small changes that allows higher migration of the two PAEs of smaller size and highest solubility in water (e.g., tightening of the polymer structure implying higher porosity and pore size). In PB experiments, temperature does not seem to affect the magnitude of the DiBP and DnBP release process and the differences between the three temperatures were small or even not significant during the 3 months of incubation.

3.2.4 Material effect

These results showed how two different common plastic materials could be considered as potential source of PAEs in marine environment. None of the plastics investigated were chemically inert and releases of phthalates were observed in all cases during time course experiments. In this study, two common plastic products as trash plastic bags and electrical cables were found to release distinct PAEs in different ways. Trash bags are commonly manufactured of polyethylene, transforming plastic beads in bags. They are made from low density polyethylene (LDPE) which is purported to be flexible, soft, airtight and waterproof. High density polyethylene (HDPE) is also used to provide strength to the bags. The insulation sheath of electric cables is made of a polymer composition comprising a polymer base resin of polyethylene, ethylene-propylene rubber (EPR) or polyvinyl chloride (PVC). In addition, the insulation layers usually contain further additives to improve the physical proprieties and to increase cables resistance to different surrounding conditions, ranging from 0.3 to 5 % by weight of total polymer composition.

PAEs migration from plastic materials was already well documented in cases concerning the potential release in food and water from bottles, packaging materials and disposable tableware. Even when a polymer (without additives) such as PE or PVC does not exhibit plasticizer, commercial resins and the final products from these polymers often release additives. Different PETE products release different amounts of PAEs because different PETE copolymer manufacturers choose different monomers, additive packages and synthetic processes to produce PETE copolymer resins (Yang et al., 2011). Despite some claims that phthalates are not used in manufacturing PETE food packaging, several phthalates have been extracted from PETE water bottles. PAEs (DMP, DEP, DiBP, DnBP and DEHP) migration was reported to be significantly higher ($p<0.001$) in plastic mineral bottles, made of PETE and Tetra Pak®, compare with the contamination in glass bottles (Hahladakis et al., 2017; Wagner and Oehlmann, 2009; Montuori et al., 2008; Biscardi et al., 2003; Bosnir et al., 2003, Kim et al., 1990). Migration of 5 PAEs was observed from tableware to drinking water, with DiBP and DEHP concentration (10.1 ng mL^{-1} and 5.8 ng mL^{-1} , respectively) exceeded the limit levels regulated by some organizations (Li et al., 2016). The migration after an incubation of 10 days at 40°C was reported to be higher in PE bread-bag than in PE film (Fasano et al., 2012) and DMP, DEP, DnBP and DEHP were detected at higher concentration after 10 weeks of incubation in PETE storing bottles (Casajuana and Lacorte, 2003). The exposition to one or more stresses often increases the leaching of plasticizers (Yang et al., 2011) as confirmed by baby bottles experiments under hot fill conditions of 70°C , where large migration was observed, after 2 hours, of DiBP and DnBP ($50\text{-}150 \mu\text{g kg}^{-1}$) and DEHP ($25\text{-}50 \mu\text{g kg}^{-1}$) (Simoneau et al., 2012). Another study has estimated the PAEs migration at different temperatures and to different liquid media (water/cooking oil) and in this experiments DnBP was the PAE with the highest migration rate in water (Xu et al., 2010). Similar results were obtained in migration experiments to water ($\text{pH}>5$) and soft drinks ($\text{pH}<3$), in which DnBP, followed by DEHP,

were characterized by the highest release rate in water (Bosnir et al., 2009). High transfer rate was also detected from PVC gasket material for closures to oily foods, estimating an average transfer of 46% (Fankhauser-Noti and Grob, 2006; Ezerskis et al., 2016). A recent study has estimated the migration process to seawater from plastic material made in PVC or PETE and they have detected migration of DEHP from PVC and DnBP from PETE for 3.8% and 0.4%, respectively, of the original content (Suhrhoff and Scholz-Bottcher, 2016).

The migration of an additive in a polymer depends on several parameters. The polymer has a three-dimensional porous structure in which the additives are dispersed and pore diameter and additive size are important parameters (Teuten et al., 2009) that could determine a selective release of the lower molecular weight additives, in this case DMP and DEP. In addition, the depletion of these PAEs from the resin surface and a negative concentration gradient from the inside to the surface may causes the migration (Teuten et al., 2009). In contrast, DEHP, the highest molecular weight phthalate target in this study and the other HMW-PAEs are more resistant to migration owing to their hydrophobicity and higher partitioning coefficient. The nature of the polymer of the insulation layer of electrical cables, compact and dense, and the tube-shape of the fragments used for the incubation experiments could be two factors involved as well in PAEs selective migration in the surrounding medium. DMP and DEP could be better candidates for migration process from this fragment of plastic if compared with DiBP, DnBP and DEHP. On the other hand, a significant DiBP and DnBP release was observed from the plastic bags. This material was made by a different polymer structure, resulting less compact and more flexible, and the fragments used for the incubation were characterized by a larger surface to mass ratio. In addition, the two plastic materials could be made of different amount of plasticizers since the purpose for which they have been produced and necessary features are different. The release may take place during the service life of plastics or their production or after their disposal and since the easiness of DMP and DEP to pass through

larger pore of the polymer, it could be possible that this material has already lost most of LMW-PAEs content before the incubation experiments.

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References

- Andrade, A.L., Neal, M.A. Applications and societal benefits of plastics. *Phil. Trans. R. Soc. B* **2009**, 364, 1977–1984.
- Andrade, A.L. Microplastics in the marine environment. *Mar. Pollut. Bull.* **2011**, 62 (8), 1596–1605.
- Barnes, D.K.A., Galgani, F., Thompson, R.C., Barlaz, M. Accumulation and fragmentation of plastic debris in global environments. *Phil. Trans. R. Soc. B* **2009**, 364 (1526), 1985–1998.
- Biscardi, D., Monarca, S., De Fusco, R., Senatore, F., Poli, P., Buschinie, A., Rossie, C., Zani, C. Evaluation of the migration of mutagens/carcinogens from PET bottles into mineral water by Tradescantia/micronuclei test, Comet assay on leukocytes and GC/MS. *Sci. Total Environ.* **2003**, 302 (1-3), 101-108.
- Bosnir, J., Puntaric, D., Skes, I., Klaric, M., Simic, S., Zoric, I. Migration of Phthalates from Plastic Products to Model Solutions. *Coll. Antropol.* **2003**, 27, 23-30.
- Bosnir, J., Puntaric, D., Galic, A., Skes, I., Dijanic, T., Klaric, M., Grgic, M., Curkovic, M., Smit, Z. Migration of Phthalates from Plastic Containers into Soft Drinks and Mineral Water. *Food Technol. Biotechnol.* **2007**, 45 (1), 91-95.
- Browne, M.A., Crump, P., Niven, S.J., Teuten, E.L., Tonkin, A., Galloway, T., Thompson, R.C. Accumulations of microplastic on shorelines worldwide: sources and sinks. *Environ. Sci. Technol.* **2011**, 45, 9175–9179.
- Casajuana, N. and Lacorte, S. Presence and release of phthalic esters and other endocrine disrupting compounds in drinking water. *Chromatographia* **2003**, 57, 649-655
- Castro-Jiménez, J., Barhoumi, B., Paluselli, A., Tedetti, M., Jiménez, B., Muñoz-Arnanz, J., Wortham, H., Driss, M.D., Sempére, R. Occurrence, Loading, and Exposure of Atmospheric Particle-Bound POPs at the African and European Edges of the Western Mediterranean Sea. *Environ. Sci. Technol.* **2017**.
- Cooper, D.A., Corcoran, P.L. Effects of mechanical and chemical processes on the degradation of plastic beach debris on the island of Kauai, Hawaii. *Mar. Pollut. Bull.* **2010**, 60 (5), 650-654.
- Corcoran, P.L., Biesinger, M.C., Grifi, M. Plastics and beaches: a degrading relationship. *Mar. Pollut. Bull.* **2009**, 58, 80–84.

Cozar, A., Echavarria, F., Gonzalez-Gordillo, J.I., Irigoien, X., Ubeda, B., Hernandez-Leon, S., Palma, A.T., Navarro, S., Garcia-de-Lomas, J., Tuiz, A., Fernandez-de-Puelles, M.L., Duarte, C.M. Plastic debris in the open ocean. *PNAS* **2014**, 111(28), 10239-10244.

Cozar, A., Sanz-Martin, M., Marti, E., Gonzalez-Gordillo, J.I., Ubeda, B., Galvez, J.A., Irigoien, X., Duarte, C.M. Plastic accumulation in the Mediterranean Sea. *PLoS ONE* **2015**, 10 (4).

Crisp, T.M., Clegg, E.D., Cooper, R.L., Wood, W.P., Anderson, D.G., Baetcke, K.P., Hoffmann, J.L., Morrow, M.S., Rodier, D.J., Schaeffer, J.E., Touart, L.W., Zeeman, M.G., Patel, Y.M. Environmental endocrine disruption: an effects assessment and analysis. *Environ. Health Perspect.* **1998**, 106 (1), 11–56.

Eriksen, M., Lebreton, L.C.M., Carson, H.S., Thiel, M., Moore, C.J., Borrero, J.C., Galgani, F., Ryan, P.G., Reisser, J. Plastic pollution in the World's Ocean; More than 5 Trillion Plastic Peaces Weighing over 250.000 Tons Afloat at Sea. *PLOS ONE* **2014**, 9 (12).

Ežerskis, Z., Morkūnas, V., Suman, M., Simoneau, C. Analytical screening of polyadipates and other plasticisers in poly(vinyl chloride) gasket seals and in fatty food by gas chromatography–mass spectrometry, *Anal. Chim. Acta* **2007**, 604, 29-38.

Fankhauser-Noti, A., Grob, K. Migration of plasticizers from PVC gaskets of lids for glass jars into oily foods: Amount of gasket material in food contact, proportion of plasticizer migrating into food and compliance testing by simulation. *Trends Food Sci. Technol.* **2006**, 17 105-112.

Fasano, E., Bono-Blay, F., Cirillo, T., Montuori, P., Lacorte, S. Migration of phthalates, alkylphenols, bisphenol A and di(2-ethylhexyl)adipate from food packaging. *Food Control* **2012**, 27 (1), 132-138.

Fossi, M.C., Marsili, L., Baini, M., Giannetti, M., Coppola, D., Guerranti, C., Caliani, I., Minutoli, R., Lauriano, G., Finolia, M.G., Rubegni, F., Panigada, S., Berude, M., Ramirez, J.U., Panti, C. Fin whales and microplastics: The Mediterranean Sea and the Sea of Cortez scenarios. *Environ. Pollut.* **2016**, 209,68-78.

Fossi, M.C., Romeo, T., Baini, M., Panti, C., Marsili, L., Campan, T., Canese, S., Galgani, F., Druon, J.N., Airoldi, S., Taddei, S., Fattorini, M., Brandini, C., Lapucci, C. Plastic debris occurrence, convergence areas and fin whales feeding ground in the Mediterranean marine protected area Pelagos Sanctuary: A modeling approach. *Front. Mar. Sci.* **2017**, 4, 1-15.

Faure, F., Demars, C., Wieser, O., Kunz, M., De Alencastro, L.F. Plastic pollution in Swiss surface waters: nature and concentrations, interaction with pollutants. *Environ. Chem.* **2015**, 12 (5), 582-591.

Gao, J., Chi, J. Biodegradation of phthalate acid esters by different marine microalgal species. *Mar. Pollut. Bull.* **2015**, 99, 70–75.

Girault, M., Arakawa, H., Barani, A., Ceccaldi, H.J., Hashihama, F., Gregori, G. Heterotrophic prokaryote distribution along a 2300 km transect in the North Pacific subtropical gyre during a strong La Niña conditions: relationship between distribution and hydrological conditions. *Biogeosciences*, **2015**, 12.3607-3621

Hahladakis, J.N., Velis, C.A., Weber, R., Iacovidou, E., Purnell, P. An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling. *J. Hazard. Mater.* **2017**.

Kamrin, M.A. Phthalate Risks, Phthalate Regulation, and Public Health: A Review. *J. Toxicol. Environ. Health* **2009**, 12 (2), 157-174.

Kim, H., Gilbert, S.G., Johnson, J.B. Determination of Potential Migrants from Commercial Amber Polyethylene Terephthalate Bottle Wall. *Pharm. Res.* **1990**, 7, 176-179

Latini, G. Monitoring phthalate exposure in humans. *Clin. Chim. Acta* **2005**, 361 (1-2), 20–29.

Li, C., Chen, J., Wang, J., Han, P., Luan, Y., Ma, X., Lu, A. Phthalate esters in soil, plastic film, and vegetable from greenhouse vegetable production bases in Beijing, China: Concentration, sources, and risk assessment. *Sci. Total Environ.* **2016**, 568, 1037-1043.

Montuori, P., Jover, E., Morgantini, M., Bayona, J.M., Triassi, M. Assessing human exposure to phthalic acid and phthalate esters from mineral water stored in polyethylene terephthalate and glass bottles. *Food Addit. Contam.* **2008**, 25, 511-518.

Moore, C.J., Moore, S.L., Leecaster, M.K., Weisberg, S.B. A comparison of plastic and plankton in the North Pacific Central Gyre. *Mar. Pollut. Bull.* **2001**, 42 (12), 1297–1300.

Meeker, J.D., Sathyanarayana, S., Swan, S.H. Phthalates and other additives in plastics: human exposure and associated health outcomes. *Phil. Trans. R. Soc. B* **2009**, 364 (1526), 2097-2113.

Munshi, A.B., Karim, N., Shaukat, S., Hashmi, D., Boardman, G.D., Flick, G.J. Toxicity of Phthalate Esters in Fish and Shellfish from Virginia Beach Using Matrix Solid Phase Dispersion (MSPD) and GC-MS. *J. Chem. Soc. Pak.* **2013**, 35 (6), 1463-1471.

Net, S., Dumoulin, D., El-Osmani, R., Rabodonirina, S., Ouddane, B. Case study of PAHs, Me-PAHs, PCBs, Phthalates and Pesticides Contamination in the Somme River water, France. *Int. J. Environ. Res.* **2014**, 8(4), 1159-1170.

Net, S., Sempéré, R., Delmont, A., Paluselli, A., Ouddane, B. Occurrence, Fate, Behavior and Ecotoxicological State of Phthalates in Different Environmental Matrices. *Environ. Sci. Technol.* **2015**, 49 (7), 4019–4035.

Neves, D., Sobral, P., Ferreira, J.L., Pereira, T. Ingestion of microplastics by commercial fish off the Portuguese coast. *Mar. Pollut. Bull.* **2015**, 101, 119–126.

Plastics Europe. *Plastics- the facts 2015 An Analysis of European Plastics Production, Demand and Waste Data*. **2015** Bruxelles: Plastics Europe.

Paluselli, A., Aminot, Y., Galgani, F., Net, S., Sempéré, R. Occurrence of phthalate acid esters (PAEs) in the northwestern Mediterranean Sea and the Rhone River. *Progr. Oceanogr.* **2017**, in press. DOI: 10.1016/j.pocean.2017.06.002.

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

Saido, K., Koizumi, K., Sato, H., Ogawa, N., Kwon, B.G., Chung, S.Y., Kusui, T., Nishimura, M., Kodera, Y. New analytical method for the determination of styrene oligomers formed from polystyrene decomposition and its application at the coastlines of the North-West Pacific Ocean. *Sci. Total Environ.* **2014**, 473-474, 490-495.

Sempéré, R.; Para, J.; Tedetti, M.; Chattiére, B.; Mallet, M. Variability of Solar radiation and CDOM in Surface Coastal Waters of the Northwestern Mediterranean Sea. *Photochem. Photobiol.* **2015**, 91 (4), 851-561.

Serôdio, P., Nogueria, J.M.F. Considerations on ultra-trace analysis of phthalates in drinking water. *Water Res.* **2006**, 40 (13), 2572–2582.

Simoneau, C., Van den Eede L., Valzacchi, S. Identification and quantification of the migration of chemicals from plastic baby bottles used as substitutes for polycarbonate. *Food Additives & Contaminants: Part A* **2012**, 29, 469-480.

Suhrhoff, T.J., Scholz-Bottcher, B.M. Qualitative impact of salinity, UV radiation and turbulence on leaching of organic plastic additives from four common plastics- A lab experiment. *Mar. Pollut. Bull.* **2016**, 102, 84-94.

Ter Halle, A., Ladirat, L., Gendre, X., Goudouneche, D., Pusineri, C., Routaboul, C., Tenailleau, C., Dupoyer, B., Perez, E. Understanding the fragmentation pattern of marine plastic debris. *Environ. Sci. Technol.* **2016**, 50, 5668-5675

Teuten, E.L., Saquing, J.M., Knappe, D.R.U., Barlaz, M.A., Jonsson, S., Bjorn, A., Rowland, S.J.,

Thompson, R.C., Galloway, T.S., Yamashita, R., Ochi, D., Watanuki, Y., Moore, C., Viet, P.H., Tana, T.S., Tana, T.S., Prudente, M., Boonyatumanond, R., Zakaria, M.P., Akkhavong, K., Ogata, Y., Hirai, H., Iwasa, S., Mizukawa, K., Hagino, Y., Imamura, A., Saha, M., Takada, H. Transport and release of chemicals from plastics to the environment and to wildlife. *Phil. Trans. R. Soc. B* **2009**, 364, 2027-2045.

Theodosi, C., Panagiotopoulos, C., Nouara, A., Zarmpas, P., Nicolaou, P., Violaki, K., Kanakidou, M., Sempéré, R., Mihalopoulos, N. Sugars in atmospheric aerosols over the Eastern Mediterranean. 19th EGU General Assembly, EGU2017, proceedings from the conference held April, **2017** in Vienna, Austria., p.409.

The Mermex Group. Marine ecosystems responses to climatic and anthropogenic forcings in the Mediterranean. *Progr. Oceanogr.* **2011**, 91, 97–166.

Wagner, M., Oehlmann, J. Endocrine disruptors in bottled mineral water: total estrogenic burden and migration from plastic bottles. *Environ. Sci. Pollut. Res. Int.* **2009**, 16, 278-286.

Wang, I., Lin, C., Lin, Y., Hsieh, W., Chen, P. Early life phthalate exposure and atopic disorders in children: A prospective birth cohort study. *Environ. Int.* **2014**, 62, 48–54.

Woodall, L.C., Sanchez-Vidal, A., Canals, M., Paterson, G.L.J., Coppock, R., Sleight, V., Calafat, A., Rogers, A.D., Narayanaswamy, B.E., Thompson, R.C. The deep sea is a major sink for microplastic debris. *R. Soc. Open Sci.* **2014**, 1, 140317.

Xie, Z., Ebinghaus, R., Temme, C., Lohmann, R., Caba, A., Ruck, W. Occurrence and Air-Sea Exchange of Phthalates in the Arctic. *Environ. Sci. Technol.* **2007**, 41, 4555-4560.

Xu, Q., Yin, X., Wang, M., Wang, H., Zhang, , H., Shen, Y., Xu, S., Zhang, L., Gu, Z. Analysis of Phthalate Migration from Plastic Containers to Packaged Cooking Oil and Mineral Water. *J. Agr. Food Chem.* **2010**, 58, 11311-11317.

Yang, C.Z., Yaniger, S.I., Jordan, V.C., Klein, D.J., Bittner, G.D. Most Plastic Products Release Estrogenic Chemicals: A Potential Health Problem that Can Be Solved. *Environ. Health Perspect.* **2011**, 119, 989-996.

Zorita, I., Apraiz, I., Ortiz-Zarragoitia, M., Orbea, A., Cancio, I., Soto, M., Marigomez, I., Cajaraville, M.P. Assessment of biological effects of environmental pollution along the NW Mediterranean Sea using mussels as sentinel organisms. *Environ. Pollut.* **2007**, 148 (1), 236-250.

ANNEXE

CHAPTER III

Release of DnBP (ng g⁻¹) from Plastic Bag fragment experiments

Time (Week)	Dark Biotic (DB) 22 °C		Dark Abiotic (DA) 22 °C		Light Biotic (LB) 22 °C		Light Abiotic (LA) 22 °C		Dark Abiotic (DA) 12 °C		Dark Abiotic (DA) 27 °C	
	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.
0	39.4	11.0	51.1	15.0	33.7	5.1	67.1	15.0	88.0	13.2	44.1	6.6
0.7	435.4	65.3	464.5	69.7	395.2	59.3	508.0	76.2	382.0	57.3	389.2	58.4
1	464.4	69.7	480.5	72.1	430.7	64.6	555.2	83.3	419.3	62.9	427.0	64.0
2	276.8	41.5	462.9	69.4	345.9	51.9	433.5	65.0	402.5	60.4	401.3	60.2
4	5.3	15.0	378.5	56.8	214.7	32.2	381.7	57.3	347.0	52.0	296.8	44.5
7.5	30.1	12.5	297.4	16.5	87.9	5.4	373.2	76.0	272.5	40.9	106.6	16.0
10	9.0	3.2	253.6	15.4	37.2	8.9	262.6	16.8	233.3	35.0	183.0	27.5
12	5.1	1.5	253.3	14.8	16.7	4.2	208.6	14.5	203.5	30.5	156.1	23.4

Release of DiBP (ng g⁻¹) from Plastic Bag fragment experiments

Time (Week)	Dark Biotic (DB) 22 °C		Dark Abiotic (DA) 22 °C		Light Biotic (LB) 22 °C		Light Abiotic (LA) 22 °C		Dark Abiotic (DA) 12 °C		Dark Abiotic (DA) 27 °C	
	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.
0	52.5	10.0	65.2	9.8	59.7	9.0	131.0	19.6	79.0	11.9	44.2	6.6
0.7	346.0	51.9	300.0	45.0	355.7	53.4	394.9	59.2	279.5	41.9	291.6	43.7
1	364.7	54.7	333.4	50.0	383.9	57.6	414.5	62.2	311.7	46.8	323.8	48.6
2	237.2	35.6	344.1	51.6	292.9	43.9	315.8	47.4	297.8	44.7	296.9	44.5
4	11.3	3.5	285.9	42.9	252.2	37.8	269.1	40.4	255.5	38.3	224.1	33.6
7.5	9.8	4.8	223.8	33.6	170.6	29.4	269.0	40.3	192.5	28.9	167.9	25.2
10	10.9	4.5	171.2	31.5	123.6	18.5	242.9	39.5	169.4	25.4	151.4	22.7
12	29.3	10.5	207.3	31.1	85.8	12.9	229.8	34.5	155.4	23.3	135.7	20.4

Release of DEP (ng g⁻¹) from Electrical Cable fragment experiments

Time (Week)	Dark Biotic (DB) 22 °C		Dark Abiotic (DA) 22 °C		Light Biotic (LB) 22 °C		Light Abiotic (LA) 22 °C		Dark Abiotic (DA) 12 °C		Dark Abiotic (DA) 27 °C	
	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.
0	1.8	0.3	0.4	1.6	1.1	0.2	1.0	0.1	1.7	0.3	0.6	0.2
1	48.8	7.3	8.9	2.4	65.6	9.8	21.1	3.2	46.8	7.0	7.5	1.1
2	63.2	9.5	11.1	2.4	77.0	11.6	23.3	3.5	60.6	9.1	9.0	1.3
4	68.9	10.3	12.9	2.6	86.0	12.9	24.6	3.7	70.9	10.6	9.9	2.1
7.5	36.2	5.4	12.6	2.4	82.2	12.3	21.4	3.2	84.8	12.7	7.1	1.9
10	10.4	1.6	10.2	2.4	68.1	10.2	18.1	2.7	77.7	11.7	6.0	2.4
12	1.4	0.2	3.5	2.5	38.0	5.7	10.5	1.6	66.0	9.9	4.2	0.6

Release of DMP (ng g⁻¹) from Electrical Cable fragment experiments

Time (Week)	Dark Biotic (DB) 22 °C		Dark Abiotic (DA) 22 °C		Light Biotic (LB) 22 °C		Light Abiotic (LA) 22 °C		Dark Abiotic (DA) 12 °C		Dark Abiotic (DA) 27 °C	
	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.
0	0.3	0.1	0.1	0.1	0.2	0.1	0.2	0.0	0.4	0.1	0.1	0.2
1	6.4	1.0	2.2	0.3	10.5	1.6	5.6	0.8	6.4	1.0	2.0	0.8
2	8.1	1.2	2.6	0.4	11.7	1.8	6.7	1.0	8.6	1.3	2.3	0.3
4	9.5	1.4	2.7	0.4	14.3	2.1	6.6	1.0	10.7	1.6	2.2	0.7
7.5	4.5	0.7	2.6	0.4	12.9	1.9	6.1	0.9	13.8	2.1	1.0	0.1
10	1.8	0.3	2.0	0.3	10.1	1.5	4.1	0.6	13.6	2.0	0.7	0.2
12	1.4	0.2	1.4	0.2	1.4	0.2	1.4	0.2	12.3	1.8	0.6	0.2

PAEs degradation occurring in the biodegradation experiment

Time (Day)	DMP (ng L ⁻¹)		DEP (ng L ⁻¹)		DPP (ng L ⁻¹)		DiBP (ng L ⁻¹)		DnBP (ng L ⁻¹)		BzBP (ng L ⁻¹)		DEHP (ng L ⁻¹)	
	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.	Avg	ST. Dev.
0	1108	84	1124	98	1102	107.0	1127	156	1182	154	1107	87	1249	95
1	1073	89	1082	101	1093	109	1061	159	1077	124	1100	96	1097	132
2	1048	78	1062	106	1043	103	1028	137	1046	148	1114	89	1097	124
4	924	66	1006	91	1026	94	946	134	817	98	748	101	1037	114
7	819	71	941	93	1016	92	834	123	643	128	533	78	877	94
13	796	63	920	97	1012	98	819	117	579	126	611	73	858	56
21	794	89	885	88	945	99	779	125	457	85	605	82	581	78
28	810	74	887	74	829	93	685	88	320	53	437	56	520	68
35	715	58	845	52	806	108	678	75	313	59	387	24	509	51
42	571	49	778	67	717	54	551	89	213	28	262	32	484	62
49	539	56	683	64	67	8	23	9	8	2	nd	nd	191	35
60	444	54	564	59	11	2	27	4	9	2	nd	nd	155	39.0

CONCLUSION AND PROSPECTIVES

This thesis is a contribution to the study of the dynamics of phthalates in the marine environment. Further research is needed however for a better understanding of the impact of PAEs on the environment. This project was divided in three parts: firstly, an analytical method was optimized in order to analyse PAEs at trace levels in seawater; in a second part, this new method was applied to aquatic samples to estimate the occurrence of phthalates mainly at the Bay of Marseille as well in the Rhone River plume, at the WWTP outlet of Cortiou and finally, in water offshore Toulon. The last part of the thesis was dedicated to the experimental estimation of the release of PAE from plastic fragments in seawater.

Analytical methods for PAEs detection in several matrices have been already described, with large number of techniques and protocols that are hardly applied to seawater matrices, because of a possible contamination of samples interfering with the analysis of low concentrations of phthalates in the marine environment. Only a few studies reported PAE concentrations in seawater. In this thesis, the method has been optimized in ISO class 6 cleanroom from previously published techniques testing several organic solvents for elution, different volumes of sample and sorbent masses in order to decrease phthalates contamination prior to PAE determination in seawater. This SPE extraction technique consists of the adsorption on PAEs from 1-L acidified seawater eluted onto 200 mg Oasis HLB glass cartridges followed by elution with 6 mL of ethyl acetate and determination by GC/MS (Fig. 1). The recovery of the PAEs from spiked seawater samples ranged from 95 to 115 % and the contamination was strongly reduced by using a number of precautions. The samples were tested for low PAEs concentration using GO-Flo bottles and the complete protocol, in order to obtain the first vertical profile of the water column at the Bay of Marseille (0-30 m) and off-shore (0-1500 m) a large number of samples was collected and analyzed. Moreover, the method was successfully applied on samples along

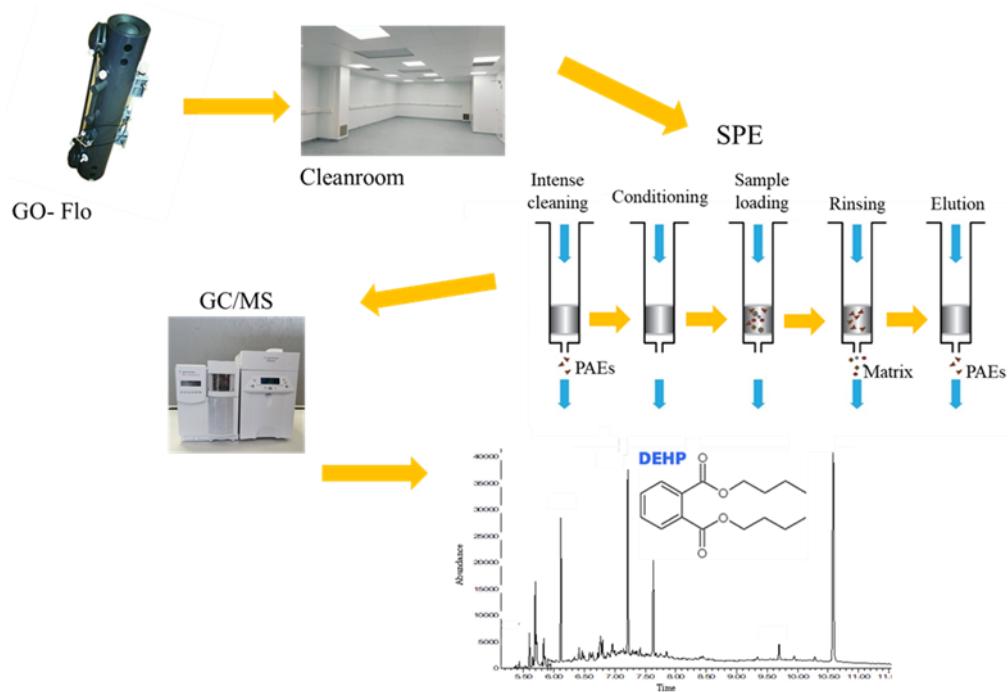


Figure 1. Method for PAE detection in seawater (Paluselli et al., 2017).

gradients of salinity in the plume of Rhone River and the WWTP outlet of Cortiou (Paluselli et al., 2017).

PAEs distribution was measured on annual basis at Marseille Bay, from December 2013 to November 2014 and from surface to bottom water (0.5, 5, 15 and 30 m) (Fig. 2). Σ PAEs ranged from 130 to 1330 ng L⁻¹ (av. 520 ng L⁻¹), with the highest concentration in winter 2013 in the mixed water column and close to the bottom in summer/fall 2014. DEHP was the most abundant PAEs in most of the samples, especially in summer (up to 92%), followed by DiBP and DnBP. High concentrations were detected close to the seafloor in most of the sampling periods, when slight changes in the relative abundance were detected with a relative increase of DiBP, DnBP and DEP. DMP, DEP and BzBP was

detected at lower concentration, as already observed in other study area. The high concentration of DEHP is probably connected to the strong impact of the anthropic activity around the city of Marseille, since this compound is the most common plasticizer used in the process of plastic products. Indeed, the peak of concentration was observed during the summer season, when recreational activities on the beaches and the maritime traffic between islands are increased by tourism. The use and disposal of materials such as PVC, food packaging, personal-care products, medical devices and detergents is more common along the coast during the touristic season increasing the amount of DEHP released. Moreover, high concentrations of PAEs were observed close to the bottom and we hypothesized a more intense degradation in upper layer of the water column or a resuspension of PAEs rich sediment. Indeed, accumulation of debris with a large proportion of plastic material, PAE-producer, has been observed several times in the Gulf of Lion.

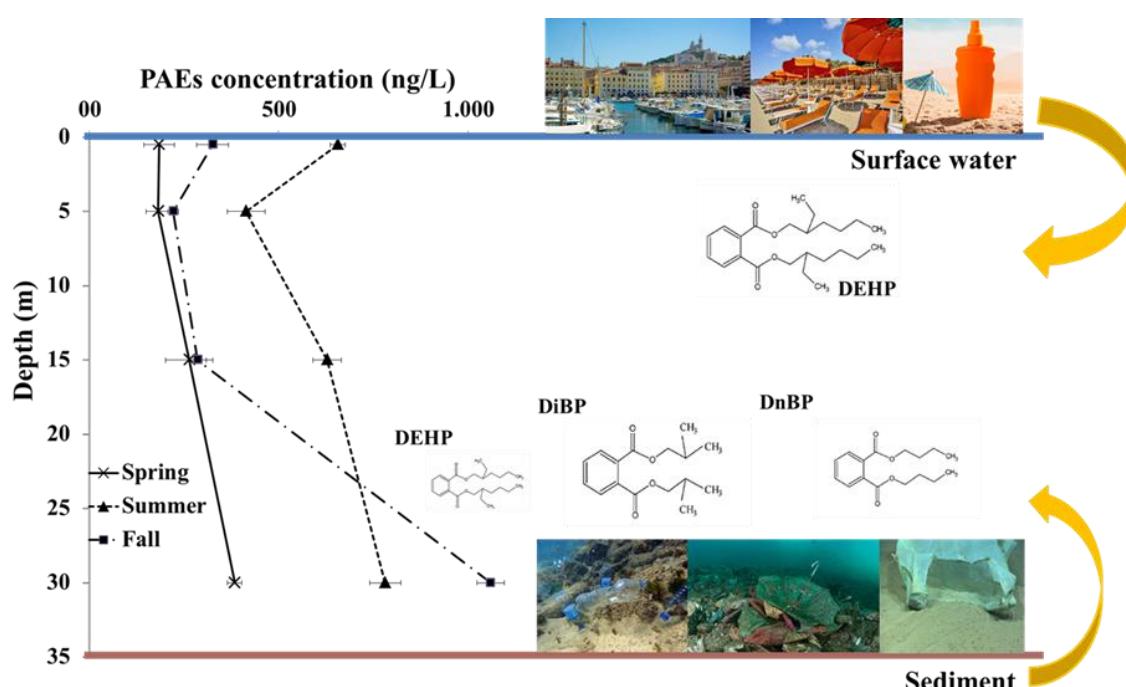


Figure 2. Σ PAEs vertical profile at Bay of Marseille (Paluselli et al., 2018).

Plastic bags and the insulation layer of the electrical cables were tested to estimate the release of PAEs to seawater. These two materials have been chosen because of their common used and dispersal in the environment. The effects of light, bacteria and temperature have been also studied as potential factors that affect the release of PAEs from plastics. During the first 1-3 weeks of the experiments, only DiBP and DnBP were released from plastic bags without any effects of tested parameters. A large amount of DMP and DEP were released, however, from electrical cable, also favored by both light and free bacteria (Fig. 3). In addition, these results confirmed the possible resuspension of PAEs from Marseille sediments polluted by plastic debris.

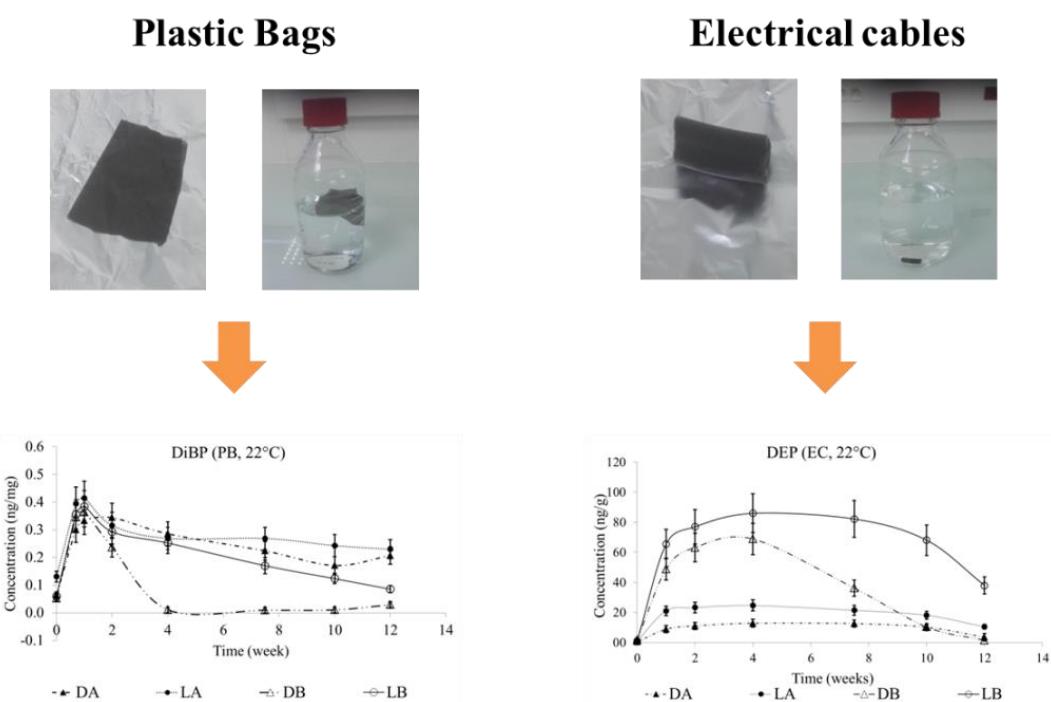


Figure 3. PAEs release experiments from two common plastic products (Paluselli et al., in preparation).

More research regarding PAEs distribution in seawater and, especially, in Mediterranean coastal area is needed to improve our knowledge on the sources and the extent of pollution by PAEs and to support a better risk assessment and management measures. The recent techniques and the implementation of the old protocols allow the reduction of PAEs background levels to obtain reliable measurements. A future implementation could be focused on higher degree of automation of the analytical procedures of sample treatments and analysis in order to shorten the times of analysis, allowing the treatment of a larger amount of samples for a large scale research as on oceanographic scale. Because of the lack of data in seawater, the creation of a PAEs dataset in seawater could be a necessary tool considering the high level of micro and macro-plastics accumulation in the Ocean. Integrated and concurrent studies on sediment, seawater column and marine aerosol and as well reparation between particulate and dissolved/gas phases could support more correct evaluations of exchange-fluxes between the different environmental compartments and a better understanding of the composition and fate of PAEs in the Mediterranean Sea. The confirmation of our hypothesis of PAEs resuspension from marine sediment could be the first step of this research pathway. Indeed, a recent research conducted in China (Zhang et al., 2018) seems to confirm this hypothesis, detecting higher PAEs concentration in bottom water than in surface. However, these are only the first steps for the future phthalates observations in marine environment. Additional future research will include detailed analysis of phthalate monoesters in the environment, first metabolites that are involved in the endocrine disruption mechanisms of the phthalate diesters.

More investigations are needed on the level of PAEs transfer and bioaccumulation on the food web in marine environment. This could be implemented through concurrent individual PAE analysis at all levels of trophic chain, from phyto and zooplankton to

predator organisms tissues, and including PAEs and microplastic determination in the surrounding seawater in order to estimate phthalates transfer to biota. These studies should be part of ecological and toxicological studies to evaluate the impact on marine ecosystem. Moreover, PAEs catabolic pathways in biota should be fully investigated and future research activities will probably focus as well on the secondary metabolites of phthalates. Finally, the number of organisms potentially used as bioindicator should be increased for the implementation of monitoring the PAEs impact on the ecosystem.

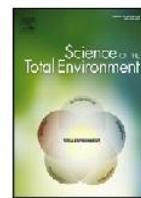
Finally, understanding the interactions between PAEs and plastic pollution will support a better understanding of impacts of PAEs on both human and environment health. For this, investigating the release of PAEs from common plastic materials, in different experimental conditions, has become critical. Sunlight, bacteria, wave action, sand, salt and natural leaching are potential factors to studies. In addition, these evaluations must be performed in different other compartments of the environment, such as rivers or river plumes. Experiments through plastic incubation in sediment samples, may bring key information and confirm our hypothesis of PAEs resuspension from seafloor. Improving our knowledge will also enable to estimate PAEs kinetics for the release from plastics and conceptualize and predict or estimate the global impact of phthalates as consequence of the plastic pollution in the Ocean.

PUBLICATIONS

LIST OF PUBLICATIONS:

- **Paluselli, A.**, Aminot, Y., Galgani, F., Net, S., Sempere, R. Occurrence of phthalate acid esters (PAEs) in the northwestern Mediterranean Sea and the Rhone River. *Progress In Oceanography* 2017, DOI: 10.1016/j.pocean.2017.06.002.
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- Net, S., Sempere, R., Delmont, A., **Paluselli, A.**, Ouddane, B. Occurrence, Fate, Behavior and Ecotoxicological State of Phthalates in Different Environmental Matrices. *Environmental Science & Technology* 2015, 49(7). DOI: 10.1021/es505233b.
- Net, S., Delmont, A., Sempere, R., **Paluselli, A.**, Ouddane, B. Reliable quantification of phthalates in environmental matrices (air, water, sludge, sediment and soil): A review. *Science of The Total Environment* 2015, DOI: 10.1016/j.scitotenv.2015.02.013.
- Schmidt, N., Thibault, D., Galgani, F., **Paluselli, A.**, Sempéré, R. Occurrence of microplastics and potential contribution of phthalates in the surface waters of the Gulf of Lion (NW Mediterranean Sea). *Progress In Oceanography* 2017. DOI: 10.1016/j.pocean.2017.11.010.
- Castro-Jimenez, X., Barhoumi, B., **Paluselli, A.**, Tedetti, M., Jimenez, B., Munoz-Arnaz, J., Wortham, H., Driss, M., Sempere, R. Occurrence, loading and exposure of atmospheric particle-bound POPs at the African and European edges of the western Mediterranean Sea. *Environmental Science and Technology* 2017, DOI: 10.1021/acs.est.7b04614.

+ **Paluselli et al.** (in preparation). Phthalate release and degradation from plastic fragments in seawater.



Review

Reliable quantification of phthalates in environmental matrices (air, water, sludge, sediment and soil): A review



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HIGHLIGHTS

- Reliable quantification of phthalates in environmental matrices
- Phthalates (PAEs) can be analyzed by either GC/MS or LC/MS.
- Phthalates in the environment can be extracted by LLE, SPE, SPME, Soxhlet, and ASE.
- Contamination during sample preparation is one of the main problems in PAE analysis.
- Some useful information to avoid overestimating PAE concentrations was reported.

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ABSTRACT

Because of their widespread application, phthalates or phthalic acid esters (PAEs) are ubiquitous in the environment. Their presence has attracted considerable attention due to their potential impacts on ecosystem functioning and on public health, so their quantification has become a necessity. Various extraction procedures as well as gas/liquid chromatography and mass spectrometry detection techniques are found as suitable for reliable detection of such compounds. However, PAEs are ubiquitous in the laboratory environment including ambient air, reagents, sampling equipment, and various analytical devices, that induces difficult analysis of real samples with a low PAE background. Therefore, accurate PAE analysis in environmental matrices is a challenging task. This paper reviews the extensive literature data on the techniques for PAE quantification in natural media. Sampling, sample extraction/pretreatment and detection for quantifying PAEs in different environmental matrices (air, water, sludge, sediment and soil) have been reviewed and compared. The concept of "green analytical chemistry" for PAE determination is also discussed. Moreover useful information about the material preparation and the procedures of quality control and quality assurance are presented to overcome the problem of sample contamination and these encountered due to matrix effects in order to avoid overestimating PAE concentrations in the environment.

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1. Introduction

Phthalates or phthalic acid esters (PAEs) are widely used since 1920s in the manufacture and processing of plastic products as plasticizers in a very broad range of industrial applications (Serôdio and Nogueira, 2006). PAEs have been detected throughout the worldwide environment, including atmospheric aerosols and air (Xie et al., 2007; Fu et al., 2009; Barreca et al., 2014; Wang et al., 2014), municipal solid waste compost, sludge (Dargnat et al., 2009; Reid et al., 2009), river and marine waters/sediments (Xie et al., 2007; Blair et al., 2009; Net et al., 2014), wastewater (Gao et al., 2014) and drinking water (Gao et al., 2014; Liou et al., 2014). Their individual concentrations are ranging from lower than limit of quantification (<LOQ) to tens µg/L but can be up to 500 mg/L in surface water; from <LOQ to tens mg/kg dw in sediment; from <LOQ to few hundred mg/kg dw in sludge; from <LOQ to few thousands ng/m³ in air and from <LOQ to few thousands mg/kg in air dust phase according to the location and the activities nearby (Net et al., 2015).

Field and laboratory studies reveal high exposure and evident toxicity of PAEs affecting human health and ecosystem functioning (Kolena et al., 2014). The main concerns related to PAE exposure in human and wildlife are the effects on reproduction, including fertility problems, the development of newborns and the carcinogenic character (Howdeshell et al., 2008). PAEs are toxic for many species including alga, protozoan, molluscs, crustaceans, fishes and invertebrates (Staples et al., 1997; Chen et al., 2014). The developmental toxicity of BBzP and DnBP and the estrogenic endocrine disrupting activity of BBzP, DnBP, DEHP and DiNP on intact organisms have been highlighted (Chen et al., 2014). For instance, exposure to DEHP from hatching to adulthood accelerated the start of spawning and decreased the egg production of exposed marine madaka females whereas exposure to both DEHP and MEHP resulted in a reduction of the fertilization rate of oocytes spawned by untreated females paired with treated males (Chen et al., 2014). DMP, DnBP, BBzP and DEHP affect reproduction in annelids (both aquatic and terrestrial), molluscs, crustaceans, insects, fishes and amphibians, to impair development in crustaceans and amphibians and to induce genetic aberrations.

Due to their potential health and environmental risks, PAEs have become a matter of worldwide concern. Six PAEs (DMP, DEP, DnBP, BBzP, DEHP and DnOP) have been included as priority pollutants of US-EPA, the European Union (EU) and Chinese waters list. The WHO recommends the concentration of DEHP in drinking water below 8 µg/L (WHO, 2004). USA, Australia, Japan and New Zealand have recommended a DEHP maximum value in drinking water at 6, 9, 100 and 10 µg/L respectively (Maycock et al., 2008). EU proposed a guideline for environmental quality of 1.3 µg/L for DEHP in fresh and marine waters. While Australian and New Zealand guidelines proposed trigger values of 5100, 1300 and 64.6 µg/L respectively for DMP, DEP and DnBP as threshold values for the protections of 80% of species in freshwater. EU has established the limit value for DEHP in sludge for disposal onto farmland at 100 mg/kg dw (JOUE, 2013), while Danish Ministerial fixed the value at 50 mg/kg dw (Danish Ministerial Order, 1996). Many other regulations and guidelines have been proposed for soil, water, sediment and sludge and the data has been compiled in Net et al. (2015).

Accordingly, the monitoring of PAEs in various environmental matrices has become a necessity. However, PAEs are ubiquitous in the laboratory (air, material, chemicals); analysis of real samples with a low PAE background can be difficult. PAE quantification with good precision and reliability is a real challenge. Large variety of methods can be applied for PAE extraction and quantification. However, some pretreatment techniques (LLE, Soxhlet) are simple to implement but requires the use of a large volume of organic solvents and time consuming. Some others are environmentally friendly techniques (SPME, TD). This review provides a synthesis of the literature data on the efficient methods for PAE quantification in different environmental matrices. Green analytical chemistry (GAC) will also be discussed and compared with conventional techniques. As blank problem is one of the main concerns in PAE quantification, this paper covers few reliable procedures and useful information to avoid overestimating PAE concentrations. Table 1 presents the physicochemical properties of PAEs and a list of abbreviations used in this review is provided in Table 1S in Supporting information (SI).

2. Quality control (QC) and quality assurance (QA)

One of the main problems for PAE analysis is the risk of contamination, as PAEs could be present in water, organic solvents, ambient air, glassware and plastic material used for the analysis. Thus, the primary issue for PAE quantification is not the trace analysis itself but the risk of contamination during the analytical procedure, which can often lead to false positive or overestimated results (Fankhauser-Noti and Grob, 2007; Marega et al., 2013). In real samples, a high background can be observed for the PAE analysis. Sample contamination can occur at different stages of the procedure including field sampling, storage, preparation and chromatographic analysis itself. All the steps must be subjected to strict quality control procedures. In this section, useful information about the material preparation, procedural blanks, storage, recoveries studies and the reliable PAE quantification are presented.

2.1. Materials and chemical preparation

Contamination from the ambient air of the laboratory can be significant, levels of DnBP, DiBP and DEHP have been reported between 0.37 and 3.0 µg/m³ (Baram et al., 2000; Fankhauser-Noti and Grob, 2007), which can cause contamination of glassware and solvents. Ideally, a room dedicated to PAE analysis with a purified air filter should be used. All the materials handled during sampling and sample treatment should be made of glass, Teflon, polytetrafluoroethylene (PTFE), aluminum or stainless steel. Rigorous procedures are required to minimize sample contamination and to maintain a low background concentration. These procedures include prewashing the laboratory material and equipment. All laboratory glassware should be washed with an appropriate organic solvent such as cyclohexane, n-hexane, isoctane, methanol or 2,2,4-trimethylpentane (Hashizume et al., 2002; Tienpont,

2004). An acidic solution such as hydrochloric acid, sulfochromic or ammonium persulfate/sulfuric acid mixtures (Cincinelli et al., 2001; Dargnat et al., 2009; Mousa et al., 2013) or a potassium hydroxide solution (Baram et al., 2000) can also be used. The glassware and quartz or glass fiber filters (QFFs, GF/Fs) should be calcinated at 450–550 °C overnight to remove organic materials and adsorbed PAEs (Fankhauser-Noti and Grob, 2007; Blair et al., 2009; Dévier et al., 2013; Félix-Cañedo et al., 2013; Marega et al., 2013). All glassware, apparatus, sampling jars, tubes and columns should be washed as previously reported and kept in an appropriate box with a lid (glass or PTFE) and/or calcinated aluminum foil to avoid PAE adsorption from ambient air (Tienpont, 2004). Given PAEs contained in plastic materials (10–60%), the use of plastic materials is absolutely prohibited throughout the procedure, with the exception of PAE-free nitrile gloves (Cousins et al., 2014). SPE cartridges, filters, vial caps, syringes and septa should also be checked for PAE-free.

PAEs have been reported in some organic solvents. DnBP and DEHP have been detected in the order of 100 µg/L in hexane (Fankhauser-Noti and Grob, 2007). For this reason, all solvents used should be of high quality (i.e., Suprasolv, ultra residue, HPLC or pico grades) and should be checked for free-PAEs. To increase their purity, organic solvents can be distilled (Cincinelli et al., 2001; Xie et al., 2005) and/or pre-baked aluminum oxide can be added (3% w/v) (Fankhauser-Noti and Grob, 2007; Luo et al., 2012; Wu et al., 2013a). Attention should also be given to the use of ultrapure water from Milli-Q® system (18.2 MΩ/cm resistivity), which can sometimes induce contamination (Hashizume et al., 2002; Cao, 2008). Other chemicals including aluminum oxide, silica, sodium carbonate, sodium chloride and sodium sulfate should be decontaminated by calcination at 400–550 °C from 4 h to overnight (EPA, 1995a; Cincinelli et al., 2001; Cao, 2008; Dargnat et al., 2009; Adewuyi, 2012). Moreover, the use of personal care products such

Table 1
Physicochemical properties of some PAEs and MPEs.

PAEs	CAS N°	Mw (g/mol)	Carbone atom per chain	d (g/mL)	Boiling point (°C)	pKa ^b	Sw ^{a,b} (mg/L)	Vp (Pa) ^a	Log Kow ^{a,b}
Dimethyl phthalate	DMP	131-11-3	194.2	1	1.192	284	5220	0.263	1.61
Diethyl phthalate	DEP	84-66-2	222.2	2	1.118	298	591	6.48×10^{-2}	2.54
Diallyl phthalate	DAIP	131-17-9	246.3	3			165	2.71×10^{-2}	3.11
Di-n-propyl phthalate	DnPrP	131-16-8	250.3	3	1.078	317.5	77	1.74×10^{-2}	3.40
Di-n-butyl phthalate	DnBP	84-74-2	278.4	4	1.042	340	9.9	4.73×10^{-3}	4.27
Diisobutyl phthalate	DiBP	84-69-5	278.4	4			9.9	4.73×10^{-3}	4.27
Di-n-pentyl phthalate	DnPp	131-18-0	306.4	5	1.025		1.3	1.28×10^{-3}	5.12
Butyl benzyl phthalate	BBzP	85-68-7	312.4	4,6	1.111	370	3.8	2.49×10^{-3}	4.70
Di-n-hexyl phthalate	DnHxP	84-75-3	334.4	6			0.159	3.45×10^{-4}	6.00
Butyl 2-ethylhexyl phthalate	BOP	85-69-8	334.4	4,8			0.385	5.37×10^{-4}	5.64
Di-n-heptyl phthalate	DiHpP	41451-28-9	362.5	7			2.00×10^{-2}	9.33×10^{-5}	6.87
Di (n-hexyl, n-octyl, n-decyl) phthalate	610P	68-648-93-1	557	6,8,10			8.76×10^{-4}	1.31×10^{-5}	8.17
Di(2-ethylhexyl) phthalate	DEHP	117-81-7	390.6	8	0.985	386	2.49×10^{-3}	2.52×10^{-5}	7.73
Di-n-octyl phthalate	DnOP	117-84-0	390.6	8	0.980	390	2.49×10^{-3}	2.52×10^{-5}	7.73
Diisoctyl phthalate	DiOP	27554-26-3	390.6	8			2.49×10^{-3}	2.52×10^{-5}	7.73
Diisonyl phthalate	DiNP	28553-12-0	418.6	9		423.5	3.08×10^{-4}	6.81×10^{-6}	8.60
Di-n-nonyl phthalate	DnNP	84-76-4	418.6	9			3.08×10^{-4}	6.81×10^{-6}	8.60
Di-n-decyl phthalate	DnDP	84-75-5	446.7	10			3.08×10^{-4}	6.81×10^{-6}	8.60
Diisodecyl phthalate	DiDP	26761-40-0	446.7	10		>400	3.81×10^{-4}	1.84×10^{-6}	9.46
Di (heptyl, nonyl, undecyl) phthalate	D711P	68515-42-4	557	7,9,11			3.08×10^{-4}	6.81×10^{-6}	8.60
Diundecyl phthalate	DUP	3648-20-2	474.7	11			4.41×10^{-6}	4.97×10^{-7}	10.33
Ditridecyl phthalate	DTDP	119-06-2	530.8	13			7.00×10^{-8}	3.63×10^{-8}	12.06
Monomethyl phthalate	MMP	180	1			3.6	3738		1.37
Monethyl phthalate	MEP	194	2			4.2	1212		1.86
Mono-n-butyl phthalate	MnBP	222	4			4.2	126		2.84
Monobenzyl phthalate	MBzP	256	6			4.2	52		3.07
Mono-iso-hexyl phthalate	MiHxP	250	6			4.2	12.8		3.85
Mono-iso-heptyl phthalate	MiHpP	264	7			Na	3.01		Na
Mono-2-ethylhexyl phthalate	MEHP	278	8			4.2	1.49		4.73
Mono-n-octyl phthalate	MnOP	278	8			Na	0.97		Na
Mono-iso-nonyl phthalate	MnNP	292	9			4.2	0.408		5.30
Mono-iso-decyl phthalate	MnDP	306	10			4.2	0.129		5.79

^a Cousins and Mackay, 2000 for PAEs.

^b Blair et al. (2009) for MPEs.

as hand creams, perfumes, deodorants, and any cosmetic products that contain PAEs must be avoided during sample handing (Félix-Cañedo et al., 2013; Cousins et al., 2014).

2.2. Method and field blanks

Analytical blanks should be performed to track the source of sample contamination and thus find an appropriate solution, if required. A blank must be used at each step of sample treatment or, at least; one blank for the entire analytical procedure could be performed in triplicate. The blank should be free from any targeted PAEs to ensure that no significant contamination occurs during the procedure. Moreover, to minimize the error of quantification, procedural blanks should be extracted together with each set of samples and measured in triplicate. Method and field blanks are strongly recommended for each environmental sample batch. Nevertheless, DnBP and DEHP are found frequently in procedural blanks. The common background contamination was estimated at 0.02, 0.15, 0.005 and 0.49 µg/L for DEP, DnBP, BBzP and DEHP, respectively (Prokúpková et al., 2002). The DEHP concentrations in blanks can be contained between 0.090 and 1.64 µg/L, with a mean value of approximately 0.5 µg/L (11 laboratories) (INERIS, 2009). PAEs in blanks should be ≤ LOQ and if they are present at significant levels (>LOQ), they must be eliminated. If impossible to eliminate, they must be subtracted from sample measurement.

2.3. Quantification

PAE quantification can be performed either with an external or internal standard. Nevertheless, the use of internal standard(s) (IS) is strongly recommended because of the numerous steps required between field sampling and final analysis. The loss of targeted compounds could be significant during the extraction, purification, pre-concentration, transfer and storage. For example, PAEs with short alkyl chain lengths (i.e., DMP, DEP) are quite volatile, and thus their

loss during the preconcentration step could be significant. Spiking an IS to the samples prior to extraction enables to correct both the eventual loss during the procedure and the error caused by variations of the injected volume and the detector response. In addition, the IS allows one to monitor matrix effects. The choice of an appropriate IS is important for accurate and precise quantification. For these reasons, it is recommended to use isotopically labeled (with ^{13}C or ^2H (hereafter d4) analogs of the targeted compounds as IS. The IS that are most often used and proved to be efficient for the GC quantification of PAEs are: DiPhP, DnPhP, DnBzP, dimethyl isophthalate DMIP, benzyl benzoate or deuterated PAEs (DMP-d4, DEP-d4, DnBP-d4, BBzP-d4, DEHP-d4, DiDP-d4, BEHP-d4, DHxP-d4, DnPhP-d4, DnOP-d4 and DiNP-d4) (Table 3). The linear range and LOD/LOQ should be studied initially. Generally, the LOD of PAEs is ranging from <1 µg/kg to dozens of µg/kg dw for soil, sludge and sediment, and from <10 ng/L to dozens ng/L for liquid matrices (i.e., marine and fresh surface water, wastewater) (Table 3). For more precise measurements, a procedural blank and a spiked matrix sample are strongly recommended, and both should be performed at least in duplicate with each set of samples.

2.4. Recovery studies

Recoveries of each targeted PAE and IS (if any) in the matrix of interest should be evaluated by spiking a certain amount of standard mixture, with a concentration similar to those found in the real samples, into the matrix and performing the entire analytical procedure. Spike recovery rates should be within acceptable limits to ensure either good efficiency and no significant loss or interference during the procedure. The recoveries of PAEs in real sample can be different from one PAE to another, which might be affected by the organic contents of blank matrices and the extraction efficiency of the method used. To date, many performance methods for quantifying PAEs in different environmental matrices have been developed, and the extraction yield are generally very satisfactory (Table 3).

Table 2
Standard methods for the PAE analysis.

Matrices	Methods	Extraction/concentration	Instrumental analysis	Targeted compounds
Drinking water	EPA Method 506 (EPA, 1995a)	LLE or LSE	GC-PID (capillary)	DMP, DEP, DnBP, BBzP, DEHP, DnOP
	EPA Method 525 (EPA, 1995b)	LSE	GC/MS (capillary)	DMP, DEP, DnBP, BBzP, DEHP
	ISO 18856:2004	SPE	GC/MS	
Wastewater	EPA Method 606 (municipal/industrial wastewater) (EPA, 2007a)	LLE	GC-ECD	DMP, DEP, DnBP, BBzP, DEHP, DnOP
	EPA Method 625 (EPA, 2007b)	LLE	GC/MS	DMP, DEP, DnBP, BBzP, DEHP, DnOP
Surface water	ISO 18856:2004	SPE	GC/MS	
	ISO 18856:2004	SPE	GC/MS	
Groundwater	EPA Methods 8060, 8061, 8250, 8270 (EPA, 1986, 1996)	LLE	GC or GC/MS	
	ISO 18856:2004	SPE	GC/MS	
Water	HJ/T 72-2001		HPLC-UV	
Soil, sediment, sludge, hazardous waste	EPA Method 8060 (EPA, 1986)	Sonication or soxhlet extraction	GC-ECD or GC-FID	DMP, DnBP, DnOP DMP, DEP, DnBP, BBzP, DEHP, DnOP
	EPA Method 8061 (EPA, 1996)	Sonication or soxhlet extraction	GC-ECD (capillary)	DMP, DEP, DnBP, BBzP, DEHP, DnOP
	EPA Method 8250	Sonication or soxhlet extraction	GC/MS	DMP, DEP, DnBP, BBzP, DEHP, DnOP
Organic liquids	EPA Method 8270 (EPA, 1998)	Sonication or soxhlet extraction	GC/MS (capillary)	DMP, DEP, DnBP, BBzP, DEHP, DnOP
	EPA Method 8060 (EPA, 1986)	Waste dilution or direct injection	GC-ECD or GC-FID	
Air	NIOSH Method 5020	Collected over cellulose ester membrane and desorbed into CS2	GC-FID	DBP, DEHP

3. Sampling, storage and transport of PAE samples

3.1. Sampling

3.1.1. Water sampling

- a) Active sampling: Traditional monitoring programs consist of collecting water samples in 1–10 Lamber glass or aluminum bottles (Zeng et al., 2008a; Dargnat et al., 2009; Net et al., 2014) in any depth of water column in order to study the distribution of PAEs in deep profile. The clear glass can be also used for sampling. However, it should be wrapped with calcinated aluminum foil to limit photochemical oxidation reactions (EPA, 1995a; Fromme et al., 2002; Cai et al., 2007). For seawater sampling, the use of a pre-washed (with 0.1% HCl and Milli-Q water before each cruise) Go-Flo bottle rather than a Niskin bottle is strongly recommended. This Go-Flo bottle, which is coated with Teflon is closed when it is immersed in the water column to avoid interaction with the atmosphere and subsurface water, and automatically open to a depth of 10 m (Caroli et al., 2001; Wurl, 2009). Ideally, water samples should be transferred directly from the Go-Flo bottle into precalcinated glass bottles closed with Teflon lined screw caps, and acidified ($\text{pH} = 2$) with sulfuric acid. Handling must be preferably performed with nitrive gloves (INERIS, 2011). It is recommended to avoid any plastic material except PTFE, and more generally the use of intermediate materials (funnels, ladles) for filling bottles (INERIS, 2011).
- b) Passive sampling: On the other hand, two types of in situ passive integrative samplers, POCIS (Polar Organic Chemical Integrative Sampler) and SPMD (SemiPermeable Membrane Device) (Steele and Hardy, 2009a,b; Alvarez et al., 2014a,b) can be used for monitoring at ultra trace—(i.e. $<1 \text{ ppt}$), and trace-levels of PAEs from the dissolved phase. SPMD covers a wide range of hydrophobic organic compounds with $\log K_{\text{OW}}$ higher than 3 (Huckins et al., 2006), whereas POCIS is efficient with hydrophilic compounds ($\log K_{\text{OW}} < 3$) (Table 1). Such material provides time-weighted average concentrations of compounds over deployment periods ranging from weeks to months (Alvarez et al., 2005, 2008, 2014a,b) and produces information on their bioconcentration potential. Both devices consist of a receiving phase (sorbent or lipid) enclosed in a diffusion membrane. They receive widespread recognition and are used as tools for point pollution source identification, screening the nature of pollutants, monitoring of temporal pollution trends, toxicity screening, investigative or comparative monitoring and water quality assessment. Accumulated PAEs are extracted from these samplers in the laboratory and measured using suitable techniques.

A standard SPMD consists of 91.4 cm long, 2.5 cm wide layflat tube of low density polyethylene (LDPE) membrane and 1 ml of $\geq 95\%$ purity triolein. It can be made of various lengths provided they maintain the standard $460 \text{ cm}^2/\text{mL}$ surface area to volume ratio consisting of approximatively 20% triolein. The SPMD uses a membrane (e.g., in silicone polycarbonate called SSP-M213; Steele and Hardy, 2009a) through which the PAEs permeate, diffuse and are collected onto an adsorbent, e.g. amberlite XAD-16 (Steele and Hardy, 2009a), Tenax TA (Steele and Hardy, 2009b). After a known period (days-months), the samplers are removed from the water and the PAEs are extracted from the adsorbent using organic solvent(s) for example DCM/hexane (50:50 v/v) (Steele and Hardy, 2009a) or directly thermally desorbed with a gas stream (helium) into a GC (Steele and Hardy, 2009b), and then analyzed by GC apparatus. An advantage of the SPMD sampling is that it can be a solventless method (thermodesorption) for sample preparation. While, POCIS consists of a solid-phase adsorbent trapped between two hydrophilic microporous membranes with 41 cm^2 of effective sampling surface area (Alvarez et al., 2004, 2008). The PAE configuration uses the Oasis HLB (phase: divinylbenzene (DVB) copolymer and n-pyrrolidone)

sorbent. The membranes act as a semipermeable membrane, allowing chemicals of interest to pass through to the sorbent, while excluding particulate matter, biogenic material, and other large, potentially interfering substances. The polyethersulfone (PES) membrane contains water-filled pores, $0.1 \mu\text{m}$ in diameter, to facilitate transport of the hydrophilic chemicals. Each POCIS disk can potentially sample tens to hundreds of liters of water. After sampling, the POCIS is disassembled and the sorbent is transferred into glass gravity-flow chromatography column and PAE residues are recovered from the sorbent by organic solvent elution.

Above all, active sampling (grab samples) is simple to implement and not expensive which allows quantification of both dissolved and particulate phases of water. It gives the immediate situation at the given time and suitable for PAE quantification from trace level to high level (accidental pollution). However, it cannot represent an integrated estimate of the time-averaged exposure. Thus passive sampling has been developed as an alternative protocol which enables estimation of time-weighted concentrations. Thanks to their greater ability to concentrate ultra-trace PAEs, passive samplers allow to increase the sensitivity of the analysis and thus to achieve low detection limits. However, passive sampling could not be used for monitoring accidental pollution (industrial effluent, structural damage, severe weather conditions, collision...). Moreover, SPMD and POCIS technique can be vandalism. Indeed, SPMD/POCIS devices are left for several days or weeks in the environment (coastal, lake, river, estuary water) and thus 25% of the devices are often damage or lost.

3.1.2. Sludge, sediment, SSM and soil sampling

Sludge and sediment grab samples can be collected with stainless steel sampler, and the top 10-cm layer of the samples is scooped using a precleaned stainless steel scoop into solvent-rinsed aluminum containers. SSM is the particulate fraction that is separated from the dissolved phase by water sample filtration and retained on GF/F filter (with an effective retention size of $0.7 \mu\text{m}$; Zeng et al., 2008a). For soil sampling, surface soil (0–5 cm depth) can be collected using a pre-cleaned stainless steel scoop into precleaned aluminum foil envelopes, a steel spatula or with stainless steel rings (7.5 cm in diameter, 5 cm depth).

3.1.3. Air sampling (gas and particulate phases)

Air samples can be collected on calcinated QFFs ($25 \times 25 \text{ cm}$) or by adsorption to XAD-2 resin (Fu et al., 2013; Das et al., 2014). PAEs can be collected either by air pumping (1–200 L) through ethylene glycol or over a $0.8 \mu\text{m}$ cellulose ester membrane, or directly through an activated Florisil column. Air can also be collected by passive sampling on charcoal. This technique is less expensive than active sampling but requires much more sampling times (~2 days). The SPMD is an effective passive air-sampling device (Huckins et al., 2006). However, its deployment requires an appropriate protective canister (Alvarez, 2010). While PAEs can be collected in the gas phase on polyurethane foam plugs (PUFs), atmospheric deposition from dust phase can be collected by deposition on QFFs or aluminum bottles (Das et al., 2014).

3.2. Sample storage and transport

There are no reliable methods to carry out in situ analysis of PAEs in the environment. After sampling, the water samples should be immediately poisoned (to prevent biotic degradation) by using either sodium azide (500 mg/L) (Furtmann, 1994; Fromme et al., 2002; Tienpont, 2004) or acidified to pH 2–3 with hydrochloric, formic, nitric or sulfuric acid (Blair et al., 2009; Adewuyi, 2012; Félix-Cañedo et al., 2013) and transported within 24 h in aluminum or stainless steel containers at 4°C (Furtmann, 1994; Caroli et al., 2001; Wu et al., 2013a). Liquid samples should be stored at 4°C in darkness and treated as soon as possible within a maximum period of 14 days to reduce losses by adsorption on the walls of the container (EPA, 1995a). Solid matrices-samples

Table 3
Extraction technique and quantification method for the measurement of PAEs and MPes in environmental matrices.

Target PAEs	Extraction/pretreatment	Technique		Identification and quantification		Column	Analyze	Yields (%)	LOD (ng/L or ng/g or ng/m ³)	Ref.
		Solvent (eluent)	Internal standards/surrogate							
Water samples 7PAEs ^a	DCM	LLE	—	DB-5	GC-FID GC-MS (full scan)	—	—	—	—	[1]
16PAEs ^b	DCM	LLE	DnPhP, DnPhP, DnBzP, Benzyl benzoate	DB-5MS GC-MS (SIM)	78–113	1–9 pg	—	—	—	[2]
15PAEs ^c	DCM	LLE	DnPhP, DnPhP, DnBzP, Benzyl benzoate	DB-35MS GC-MS (full scan)	62–112	6–30	—	—	—	[3]
DMP, DEP, DnBP, DEHP 15PAEs ^d	DCM DCM	LLE LLE	Benzyl benzoate External calibration	Col-Elite 5 DB-5MS (full scan)	82–91 81–104	1–20	—	—	—	[4] [5]
6PAEs ^e	DCM/Hexane	LLE	Benzyl benzoate	XLB GC-MS (SIM)	72–108	LOQ: 10	—	—	—	[6]
DnBP, DChxP, DEHP 6PAEs ^f	Ethyl acetate	LLE	DnBP-d4	DB-5MS (SIM)	>75	DEHP: 4 pg	—	—	—	[7]
6PAEs ^g	Hexane	LLE	DnPhP-d4	—	86–114	51–130	—	—	—	[8]
DMP, DEP, BBzP 7PAEs ^f	n-Tetradecane 1-Dodecane	HF-LLEME UPME	Ascentis-ODS Benzyl benzoate	DB-5MS (SIM)	91–102 84–115	10–20 20–50	—	—	—	[9] [10]
DnBP, BBzP, DEHP, DnOP 16PAEs ^b	Toluene Acetone	MLLE MSPE	External standard	DB-5 RXi®-5MS (SIM)	54–110 80–125	200–10,000 3.1–38	—	—	—	[11] [12]
DnBP, DEHP, BBzP ^g	Acetone	SPE	DnBP-d4, BBzP-d4, DEHP-d4	DB-XLB GC-MS (MS/MS, MRM)	82–106	20–30	—	—	—	[13]
15PAEs ^d	Acetone	DSPE	Triphenyl phosphate	HP-5MS (SIM)	71–117	2,000–7,000	—	—	—	[14]
15 PAEs ^d	DCM/Acetone/MeOH	SPE	—	DB-5MS (SIM)	71–98	24–772	—	—	—	[15]
6PAEs ^e 6PAEs ^e	DCM/Ethyl acetate DCM/Hexane	SPE SPE	—	DB-5MS HP-5MS (SIM)	79–97 61–108	45–500 LOQ: 0.5–1	—	—	—	[16] [17]
11PAEs ^g	Ethyl acetate	SPE	DAIP	HP-1 (SIM)	91–108	10–30	—	—	—	[18]
SPAEs ^h , 11 MPes	MeOH	SPE	DMP-d4, DEP-d4, DnBP-d4, BBzP-d4, DEHP-d4, DiNP-d4, DiOP-d4, DiDP-d4 External calibration	Eclipse-plus-C18 UHPLC-MS (MS/MS, MRM, ESII)	65–135	LOQ: PAEs; 1; MPes; 2000–17,000	—	—	—	[19]
SPAEs ^h	MeOH	SPE	DBP, DiOP	C18 RP-18 DB-5MS (SIM)	—	1	—	—	—	[20]
BBzP, DEHP DMP, DAIP, DnBP, BBzP, DChxP, DEHP	MeOH/DCM C ₆ H ₅ Cl	SPE DLME	—	LC-UV GC-MS (SIM)	99–104 68–89	50–100 2–8	—	—	—	[21] [22]
6PAEs ⁱ 6PAEs ^j	Solvent-free Solvent-free Solvent-free	SPME SPME SMPE	Benzyl benzoate External calibration External calibration	DB-5MS DB-35 DB-35 (SIM)	—	—	—	—	—	[23] [24] [25]
6PAEs, 4MPes ^j	Solvent-free	SPME	—	HP-5MS (SIM)	—	20–400, 1,00–4,400	—	—	—	[26]
11PAEs ^j	Solvent-free	SPME	—	HP-5MS-U (SIM)	—	LOQ: 10–30	—	—	—	[27]
6PAEs ^k	DCM/ Hexane	SPME	—	DB-5 GC-FID	78–116	20–400	—	—	—	[28]

(continued on next page)

Table 3 (continued)

Target PAEs	Extraction/pre-treatment		Identification and quantification				Yields (%)	LOD (ng/L or ng/g or ng/m ³)	Ref.
	Solvent (eluent)	Technique	Internal standards/surrogate		Column	Analyze			
DnBP	Without pre-treatment	-(POCIS)	Benzyl benzoate	C18	LC-UV	-	-	-	[23]
DEHP	DCM/MTBE	-(POCIS)	p-terphenyl-d14	-	GC-MS (full scan)	-	-	-	[29]
DEP, DEHP	DCM/MTBE	-(POCIS)	-	HP5-MS	GC-MS (full scan)	-	-	-	[30]
Groundwater and drinking water (tap, bottled water) samples									
6PAEs ^c	DCM	LLE	DnOP-d4	Rtx-5MS	GC-MS (SIM)	70-94	DMP: 30	-	[31]
5PAEs ^j	DCM	LLE	-	TG-5MS	GC-MS (SIM)	-	1.62-16.3	-	[32]
6PAEs ^c	DCM, hexane	LLE, SPE	-	DB1, DB-5	GC/FID	840-11,820	-	-	[33]
DnOP	MeOH	LLE	-	C18 gold	LC-MS (MS/MS, MRM)	96-99	20	-	[34]
BBzP, DDEHP	Acetone	SPE	Internal calibration	DB1	GC-MS (SIM)	-	500	-	[35]
DBP, BBzP, DEHP, DnOP,	DCM	SPE (disk, cartridge)	-	TG-1MS	GC-ECD	89-113	-	-	[36]
DnP, DiDP	Etyl acetate	DnP-d4	-	Rxi-5MS	GC-MS (full scan)	49-83	LOQ: 100	-	[37]
5PAEs ^m	Solvent-free	SPME	DMP -d4; DEP-d4, DnBP d4; DEHP d4; DnOP-d4	DB-5MS	GC-MS (SIM)	-	3-85	-	[38]
Wastewater samples									
6PAEs ^c	Hexane/DCM	LLE	External calibration	HT8	GC-ECD	68-84	-	-	[39]
6PAEs ^c	Hexane/DCM	LLE	External calibration	HT8	GC-ECD	68-84	-	-	[40]
5PAEs ^o	DCM	LLE	n-Butyl benzoate	Zorbax Eclipse	LC-UV	57-97	600-1230	-	[41]
DEP, DnBP, DiBP, DEHP	MeOH	SPE	-	XDB C18	GC-MS (full scan)	-	-	-	[42]
6PAEs ^c	MeOH/Diethyl ether	SPE	Internal calibration	-	GC-MS (SIM)	95-106	25-400	-	[43]
6PAEs, 4 MPEs ⁱ	Solvent-free	SPME	MEP-d4; MBP-d4; DEP-d4; DBP-d4	2B-5MS	GC-MS (SIM)	-	20-400, 100-4400	-	[26]
DEP, DEHP	Hexane, DCM, MeOH	SSPE	External calibration	HP-5MS	GC-MS (SIM)	69-71	13,000-15,000	-	[44]
DEP, DEHP	MeOH	-(POCIS)	Internal standard	Hypersil Green	LC-MS (SIM, ESI)	-	-	-	[45]
Seawater samples									
DnBP, DHxP, DchxP, DEHP	Ethyl acetate	LLE	DnBP-d4, DEHP-d4	Ultra II	GC-MS (full scan)	-	-	-	[7]
DEP, MEIP	Hexane	LLE	-	DB5-MS	GC-MS (SIM)	>75	-	-	[46]
1,5PAEs ^c	Acetone	DSPE	Triphenyl phosphate	HP-5	GC-FID/GC-MS (full scan)	-	-	-	[14]
DEP, DnPrP, DiBP, DchxP	Acetone	SPE	-	HP-5MS	Zorbax Eclipse	71-117	2000-7000	-	[47]
10MPes ^p	Ethyl acetate, ACN	SPE	MEP- ¹³ C4, MnBP- ¹³ C4, MEHP- ¹³ C4, MnNP- ¹² C4	XDB C8	Synergis RP-MAX	50-72	0.19-3.9	-	[48]
DEHP	Methanol	SPE	-	C12	LC-MS (MS/MS, MRM)	70	-	-	[49]
DEP, DnBP, BBzP	EE-SPME	-	-	Cl-UV	GC-MS (SIM)	74-93	4-150	-	[50]
DEHP	DCM/MTBE	-(POCIS)	-	HP-1	GC-MS (full scan)	-	-	-	[51]

5PAEs ^a	ASE	DCM/Acetone	—	Pinnacle™ II	LC-6 AD	83–92	—	[52]
6PAEs ^e	ASE	Ethyl acetate	DBzP, Benzyl benzoate	Phenyl DB-5MS	GC-MS (SIM)	77–102	6–11	[53]
10MPAEs ^b	ASE/SPE	AcOH/MeOH	MEP- ¹³ C4, MnBP- ¹³ C4, MEHP- ¹³ C4, MnNP- ¹³ C4	Syntegri RP-MAX C12 DB-5MS	LC-MS (MS/MS, MRM)	83–99	0.01–0.20	[48]
15PAEs ^c	MAE	—	—	GC-MS (SIM)	GC-MS (MS/MS, MRM)	84–109	24–772	[15]
DnBP, DEHP BBzP 16PAEs ^b	Cyclodhexane/Ethyl acetate	Soxhlet	DnBP-d4, BBzP-d4, DEHP-d4, DiPhP, DnPhP, Benzyl benzoate	DB-XLB DB-5MS	GC-MS (MS/MS, MRM)	71–102	20–50	[13]
DCM	—	Soxhlet	DiPhP, Benzyl benzoate	—	GC-MS (SIM)	71–108	1–9	[2]
DMP, DEP, DnBP, DEHP 16PAEs ^b	DCM	Soxhlet	Butyl benzoate	DB-5MS	GC-HD GC/MS	89–90	1–20	[4]
DCM	DCM	Soxhlet	DiPhP, DnPhP, DnBzP, benzyl benzoate	—	GC/MS (SIM)	77–109	0.44–55	[54]
6PAEs ^e	Hexane/DCM	USE	DMP-d4, DnBP-d4, DnOP-d4	C8 DB-5	LC-MS (ESI) GC/MS	71–106	—	[55]
Sludge samples 5PAEs ^a	ASE	DCM/Acetone	—	Pinnacle™ II	LC-6 AD	83–92	—	[52]
DEHP	Hexane	SAE	tert-butylphenol	Phenyl HP-5MS	GC-MS (SIM)	105 ± 8	LOQ: 65	[56]
DnBP, BBzP, DEHP	Cyclodhexane/Ethyl acetate	Soxhlet	DnBP-d4, BBzP-d4, DEHP-d4	DB-XLB	GC-MS (MS/MS, MRM)	71–102	20–50	[13]
16PAEs ^b	DCM	Soxhlet	DMP-d4, DEP-d4, DnBP-d4, DEHP-d4	HP-5MS HT8	GC-MS (GC-ECD)	74–100	—	[57]
6PAEs ^e	DCM	Volatilisation/condensation	External calibration	—	68–84	—	[40]	[40]
Soil samples 12PAEs ^f	ACN	—	2-Methylanthracene	LiChroCART RP-18 ZB-5MS	LC-UV GC-MS	82–92	—	[58]
DEHP	DCM	ASE	DEHP-d4	Pinnacle™ II Phenyl DB-5	GC-MS (LC-6 AD)	90	50	[59]
5PAEs ^a	DCM/Acetone	ASE	—	DnBP-MS DB-5	GC-MS (GC-MS)	83–92	—	[50]
6PAEs ^e	Centrifugation	DnBP-d4	DnBP-d4, BBzP-d4, DEHP-d4, DnOP-d4	DB-5MS DB-5MS	GC-MS (GC-MS)	80–113	—	[61]
7PAEs ^w	DCM	SLE	DiPhP, DnPhP, DnBzP	—	DB-5MS (SIM)	76–111	—	[62]
16PAEs ^b	Soxhlet	—	—	DB-5MS	GC-HD	≥98	—	[63,64]
DnBP, DEHP	USE	—	—	—	—	—	—	[65]
Air samples DEHP, DiNP DEHP, BBzP	ASE	n-Hexane DCM	DEHP-d4	Rxi-5 ms DB-5MS	GC-MS (GC-MS)	99 ± 11	0.5–2	[60]
6PAEs ^e	Soxhlet	—	—	HP-5	GC-MS	—	2–8	[22]
DiBP, DEHP, DNP	DCM	(QFFs, PUFs)	—	HP-5MS	GC-MS (SIM)	>71	—	[66]
6PAEs ^e	DCM	Soxhlet	DEHP-d4	DB-5MS	GC-MS (GC-MS)	75	3.4	[67]
16PAEs ^b	DCM	—	—	HP-5MS	GC-MS	72–121	—	[68]
17PAEs ^c	Soxhlet	DnBzP, Benzyl benzoate	—	HP-5MS	GC-MS (GC-MS)	73–94	—	[69]
6PAEs ^c	DCM ⁺⁺	—	—	HP-5MS	GC-MS (MS/MS)	86–118 ^{**}	0.2–13	[70]
14PAEs ⁱⁱ	DCM	DBzP	DBzP	HP-5MS	GC-MS	80–140 [*]	—	[71]
6PAEs ⁱ	Soxhlet	DnBP-d4, DEHP-d4	—	HP-5MS	GC-MS	72–105 [*]	—	[68]
Acetone	—	¹³ C-DnPeP	—	DB-5MS	GC-MS	82–105 ^{**}	—	[72]
DnBP, DEHP	Acetone/Hexane/MeOH/Carbon disulfide	Sep-Pak PS Air cartridge	External calibration	HP-5MS	GC-MS	>90–100	—	[73]
6PAEs ^e	DCM	USE	Benzyl benzoate	HP-5MS	GC-MS	78–116	0.002–0.016	[74]

(continued on next page)

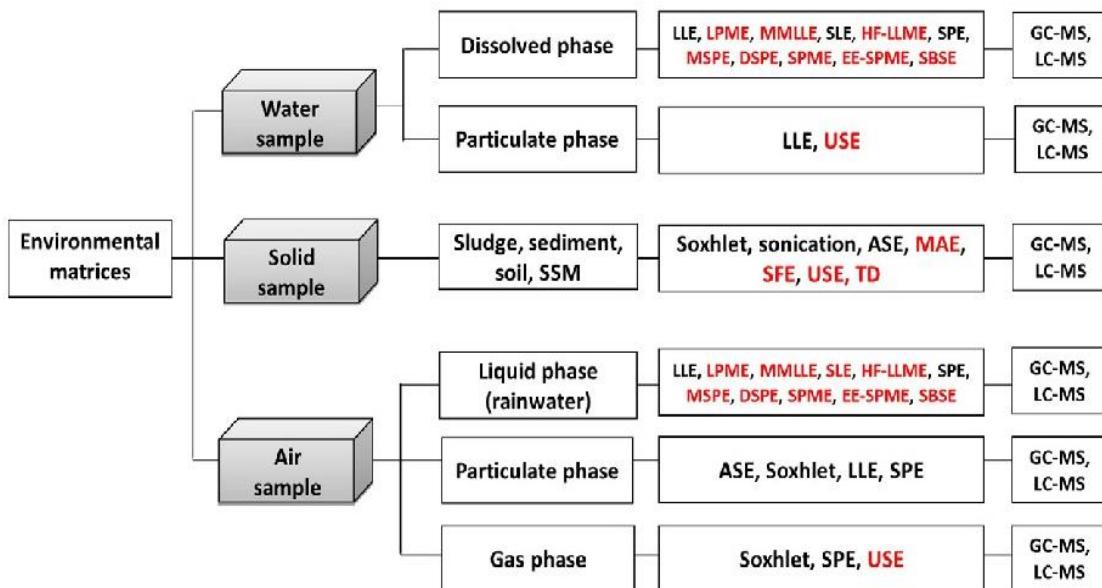


Fig. 1. Schematic illustration of typical analytical procedure used for analysis of PAEs from environmental sample (in red are techniques considered as green technique methodology).

including soil, sediment, sludge, SSM, atmospheric particle retained on filter should be stored in precleaned closed aluminum containers, kept cold with ice or in a refrigerator ($0\text{ }^{\circ}\text{C}$) during sampling and transport, and stored at the laboratory at $-20\text{ }^{\circ}\text{C}$ until further analysis (Rhind et al., 2013; Sun et al., 2013a; Liou et al., 2014; Meng et al., 2014). For air samples, both QFFs and PUFs should be transferred into calcinated glass jars with Teflon lined screw caps or wrapped in aluminum foil, stored in Teflon bags and kept at $-20\text{ }^{\circ}\text{C}$ until the analysis is performed.

4. Extraction or pretreatment techniques

Extraction, preconcentration and cleanup are the important steps to improve the LOQs. There are large varieties of sample pretreatment techniques (Lv et al., 2013) and the most efficient is discussed in this section. Fig. 1 presents the diagram of milestones of PAE quantification for different environmental matrices. Table 2 summarizes the standard analytical methods for the PAE analysis and Table 7 compares the different extraction techniques.

4.1. Water sample

There is a large variety of methods for PAE extraction from dissolved phases. The most often used presenting acceptable efficiency are discussed in this section. PAEs are adsorbed on SSM, approximately 70% of DnOP, 55% of DEHP and 10–20% of other PAEs (Furtmann, 1994). Consequently, PAE quantification should be performed both in dissolved and particulate phases to better represent the global contamination and their distribution in the water column.

4.1.1. Liquid-liquid extraction (LLE)

LLE consists of adding organic solvent (50–500 mL) into the aqueous sample (500–1000 mL), shaking the contents and PAEs are collected in organic phase after decantation. Propanol can be good solvent for PAE extraction from water. However, propanol is miscible with water, organic salts, so ideally ammonium sulfate must be added to the mixture to separate the two phases (Cai et al., 2007). Good efficiency can also be obtained with hexane and/or DCM, which are non-miscible with water (Liu et al., 2013; Gao et al., 2014; Net et al., 2014). The addition of an organic modifier (e.g., 50% methanol) can improve the extraction of most apolar PAEs such as DEHP and DnOP (Bergström et al., 2007). For successive extractions of the same sample ($n = 1\text{--}3$),

recovery yields above 80% can be generally obtained (Table 3). LLE can be performed with water sample without SSM separation from water. The eventual emulsion involving water and SSM can be removed by various techniques including EPA-Method 506 (EPA, 1995a) including centrifugation, NaCl addition (20–150 g/L) (Hashizume et al., 2002; Adewuyi, 2012), ultrasound, freezing or vigorous stirring. However, the presence of emulsions can affect the extraction efficiency of PAEs in the SSM. Addition of NaCl does not always improve it (Farahani et al., 2008).

Using non-miscible organic solvent allows one to avoid the addition of organic salt. This approach saves time and involves less preparatory steps, thus minimizing the source of contaminations. In this regard, EPA Method 8061 (EPA, 1996) is the most often used approach (Zeng et al., 2008a,b; Liu et al., 2013; Gao et al., 2014). For this method, 2 L of water should first be filtered with $0.7\text{ }\mu\text{m}$ GF/F, spiked with the IS, and then extracted with 3×100 mL of DCM. Traces of water can be eliminated with sodium sulfate then solvent exchanged to 1 mL hexane prior to GC-MS analysis. Overall, the LLE technique is simple to implement but requires the use of a large amount of organic solvents and thus expensive. Additionally, it is labor intensive and time consuming.

4.1.2. Solid supported LLE (SLE), liquid-phase microextraction (LPME), microporous membrane LLE (MMLLE), dispersive liquid-liquid microextraction (DLLME)

Few techniques have been developed as alternatives to LLE. Solid supported LLE (SLE) is a technique in which the aqueous sample containing PAEs is passed through a cartridge packed with high purity, finely divided, inert, diatomaceous earth sorbent. PAEs are then eluted with an immiscible organic solvent. SLE allows minimizing the matrix interferences. Farahani et al. (2008) miniaturized the system of PAE extraction using liquid-phase microextraction (LPME). Only $100\text{ }\mu\text{L}$ of 1-dodecanol is needed to extract PAEs from 10 mL of water. Microporous membrane LLE (MMLLE) has been also developed and enables automation of the process of micro-LLE to a blank card (Bergström et al., 2007). This card consists of a PP membrane doubled grooved for entrance of the aqueous phase and the organic solvent. The extraction is governed by the partition between the two phases and the diffusion of analytes; and toluene has been proved efficient extraction solvent. The microextraction by liquid-liquid dispersion (DLLME) can be also used for PAE extraction (Yan et al., 2010; Xue et al., 2014). In this technique, an appropriate dispersive solvent (e.g., ACN, methanol) is added

Table 4

Ions for selected ion monitoring (SIM) of PAEs by GC/MS-El.

Analyte	Quantifier ion (abundance)	Qualifier ions (abundance)	Reference	Analyte	Quantifier ion (abundance)	Qualifier ions (abundance)	References
DMP	163 (100)	194, 135, 77 194(15), 135(15) 194, 133 194, 77 194 77	[12] [31] [43] [38] [10,26,80] [37,79,82] [27]	DEHP	167 (36) 149 (100)	279 (9.8), 149 (100) 279, 167, 113 279 (8.8), 167 (34) 279 167, 57 167	[7] [12] [13,31,35,38] [10,43] [32] [27,37,26] [79]
DEP	149 (100)	222, 177, 121 222 (1.6), 177 (23) 177, 76 177 (28) 177, 65	[12] [83,84] [38] [10,26,27,31,43,79,80,82] [32] [37]	DPhP DBzP BBzP	225 149 149 (100)	197, 153, 77 108 312(1), 206(22) 238, 206, 91 238 (5), 206 (25) 206, 91 206	[12] [27] [84] [12] [83] [34,80] [10,13]
BMEP	59	251, 193, 149	[12]			205 (21.5), 91 (71.5)	[31]
BEPP	45	149, 121, 72	[12]			205	[43]
BBEP	149	249, 193, 57	[12]			91, 65	[32]
DnPrP	149 (100)	209 (5.9), 191 (6.9)	[84]			91	[27,79,82]
DiPrP	149		[27]			265	[80]
DnBP	149 (100)	278 (1.0), 223 (7.4), 205, 121 223 (5.5), 205 (4.4) 223, 104 223 205 150 147, 73	[12] [13,26,31,83] [81] [10,80] [82] [79] [32] [26,37]	DiHpP DnOP	149 149 (100)	279, 261, 179 279 (6.6), 207 (4.4) 279, 150 279 (18.0) 167 149, 71, 57 149	[12] [84] [38,43,79] [31,82] [27] [12] [80]
DiBP	149 (100)	223, 205, 167 223 (7.4), 205 (1.9) 223, 57 223 57, 41	[12] [84] [38] [80] [32] [37]	DiDcP DUP DMIP DMP-d4 DEP-d4	307 149 (100) 149 (100) 163 167 153	307 (6.4) 321 (5.4) 194, 133 181	[84] [84] [81] [27,38] [26] [27,38]
DPeP	149	237, 219, 167 237	[12] [80]	DiPrP-d4	153	153	[27]
BMPP	149	251, 167, 121	[12]	DnBP-d4	153 (100)	209, 227 227 (6.3)	[13,26] [7,27,38,80]
DAIP	149	189	[10,80]	DnHxP-d4	153		[27]
DnHxP	149 (100)	251 (11), 233 (3.3) 251, 104, 76 251, 43	[7] [12] [38] [27]	DEHP-d4	153 (100)	171 (31), 283 (14) 171 (41)	[13] [7,37] [27,38]
DcHxP	149 (100)	269, 167, 83 249 (17), 167 (32) 167 (32), 249 (5.5) 167	[12] [7,80] [84] [10,27]	DBzP-d4 BBzP-d	153 153	210	[27] [13] [27] [31,80] [38]
				DnOP-d4	153 (100)	283 (17)	

References: see indication in Table 3.

to extraction solvent (e.g., CCl_4) increasing the contact surface between phases and this binary mixture is injected rapidly into an aqueous sample by syringe to form a cloudy solution. To improve this process, ultrasounds have been used (Yan et al., 2010) that permit to accelerate the formation of fine cloudy solution with less disperser solvent, which is increased the extraction efficiency and reduced the equilibrium time.

4.1.3. Solid phase extraction (SPE)

SPE receives increasing attention because of its ease of implementation, its ability to save time and solvent, its possible semi-automation (Zhang et al., 2013), and its ability to eliminate the emulsions. In addition, high enrichment factors are usually obtained with SPE. To date, SPE has been shown to be a powerful method for the extraction, preconcentration and cleanup of water samples. It can be semi-automatic which allows to simultaneous extraction up to 12–24 water samples. SPE can also be used on-line, i.e. directly connected to a chromatograph allowing its full automation (Brossa et al., 2003). Briefly, PAEs are transferred from the water sample (100–1000 mL) to an activated solid phase and are recovered by elution with organic solvent (Loos et al., 2008). The SPE devices can be either cartridges or disks (Amalric et al., 2011) and has been used in France as standardized

extraction method NF EN ISO 18856 (AFNOR, 2005). Moreover, standardized EPA methods 506 and 525 (EPA, 1995a,b) based on SLE have been replaced by the SPE. Typical cartridge devices consist of short columns; conventionally, an open syringe barrel contains the sorbent with different particulate sizes (50–60 μm). Octadecylsilane (ODS) C18, HLB, and a mixture of LiChrolut RP18 and Lichrolut EN (2.5/1 by weight) have been proved to be efficient cartridge types for PAEs (Kerené et al., 2011; He et al., 2013; Liou et al., 2014; Zheng et al., 2014). Sequential SPE (SSPE) can also be used to isolate and extract PAEs (Castillo and Barcelo, 1999).

PAEs in water can be extracted directly without filtration if $\text{SSM} \leq 1 \text{ g/L}$ (Du et al., 2013), but in most cases, filtration with GF/F is a necessity step to avoid clogging, especially when the sample contains a high level of SSM ($> 1 \text{ g/L}$). Moreover, the SPE implementation with unfiltered waters does not allow a quantitative extraction of PAEs attached to SSM (Amalric et al., 2011). Nevertheless if the water sample is filtered on a GF/F, the particulate phase is not then considered, causing a bias in the total concentration by about 20% (Isobe et al., 2001). MeOH, DCM, hexane and acetone are commonly used as eluting solvent, either as individual or mixtures (Table 3). Most of SPE cartridges are made of polyethylene (PE) or polypropylene (PP), which can release 3–14 ng of DiBP, DnBP and DEHP for 500 mg ODS sorbent (Tienpont, 2004). The use of

Table 5

Analyte	Quantifier ion Q1	Qualifier ion Q3	Reference
<i>Positive mode</i>			
DMP	195	163, 133	[85]
DEP	149	177, 223	[49]
	223	149, 177	[85]
BMEP	283	207, 59	
BEEP	311	221, 149	
DnPrP	251	149, 191	
DiPrP	251	149, 191	
DnBP	279	149, 205	
	149		[87]
DiBP	279	149, 205	[85]
DnPeP	307	219, 149	
DiPeP	307	219, 149	
BMPP	335	167, 251	
DAIP	247	189, 149	
BBEP	367	101, 249	
DnHxP	335	149, 233	
DcHP	331	167, 249	
DEHP	149	167, 391	[49,87]
	391	167, 279	[85]
	413.8	414.8	[86]
DPhP	319	225, 77	[85]
BBzP	313	149, 205	
DiHpP	363	149, 233	
DnOP	391	261, 149	
DiNP	419	275, 149	
DiDcP	447	149, 289	
<i>Negative mode</i>			
DEHP	277		[80]

References: see indication in Table 3.

glass SPE cartridges or extraction disks is recommended (Furtmann, 1994). Two examples of the SPE method for the extraction and cleanup of PAEs from water samples are presented in Fig. 1S in SI.

4.1.4. Magnetic SPE (MSPE), dispersive SPE (DSPE)

MSPE is classified as GAC technique. A dispersed iron-based magnetic carbon nanotube solution can be used as an alternative to SPE with very good sensibility. MSPE coupled with GC/MS-SIM allows low LOQs in the range 3.1–37 ng/L for 16 PAEs (Luo et al., 2012). Cai et al. (2003) used also carbon nanomaterial (multi-walled carbon nanotubes) but directly packed into a cartridge. Recently two new methods based on graphene-dispersive SPE (DSPE) have been developed to extract PAEs from water and plastic bottled beverage samples (Wu et al., 2013a; Qiao et al., 2014). The first method uses graphene as carbon nanomaterial because it possesses an ultra-high specific surface area (theoretically of 2630 m²/g), while the second one consists of a magnetic dummy molecularly imprinted microsphere (MAG-MIM) adsorbent. Desorption organic solvents most often used are ACN, acetone, ethyl acetate and n-hexane (Wu et al., 2013a). Compared with conventional method, graphene-DSPE is a simple, rapid and cost-effective method, but with low sensibility (LODs ranging from 2 to 7 µg/L with GC/MS-SIM analysis) for PAE extraction from water samples (Wu et al., 2013a).

Table 6

Ions for SIM of the corresponding silyl derivatives of phthalic esters by GC/MS-EI (Kim et al., 2007).

Analyte	Quantifier ion (abundance)	Qualifier ion (abundance)
DBP-SE	131 (100)	103 (23), 145 (72)
DHP-SE	159 (100)	103 (42), 115 (5.0)
DCHP-SE	157 (97)	129 (100), 172 (23)
DEHP-SE	187 (80)	103 (100), 202 (0.1)
DBP-d4	295 (17)	147 (100), 310 (2.0)
DEHP-d4	153 (100)	227 (6.3)

Table 7

Comparison of sampling, extraction and analysis techniques for PAE determination (in red, "green" techniques).

Sampling devices	Advantages/specificities	Inconvenients
Active sampling with (Go-Flo) bottle, sediment sampler, air impactor	Timely monitoring Coated with Teflon which minimize adsorption and contamination	Time-consuming, not very easy sampling Require a qualified staff
POCIS	Specific (hydrophilic contaminants) Easy installation Long-term sampling (accumulation)	Not allow accidental pollution Vandalism
SPMD	Specific (hydrophobic contaminants) Easy installation Long-term sampling (accumulation) Solventless method	Not allow accidental pollution Vandalism
Extraction techniques	Advantages/specificities	Inconvenients
LLE	Easy implementation Possible automation of stirring	Require large amounts of organic solvents Require a large amount of sample Possible emulsions if SSM
SLE	Alternative of SLE Minimize the matrix interferences	Expensive, labor intensive and time consuming technique
LPME	Alternative mode of LLE	
MMLE	Miniaturization of LLE	
DLLME	Alternative mode of LLE Automation of micro-LLE With ultrasons, less disperser solvent volume (increase the extraction efficiency, reduce the equilibrium time)	Use of another solvent (dispenser solvent)
SPE	Alternative of LLE Two types of material: glass cartridge, disk Less sample volume than for LLE Relatively easy implementation Possible automation or on-line	Time-consuming, relatively expensive technique but less than LLE Use SPE cartridges with an additional risk of contamination Presence of SSM can disturb physically the processus
MSPE	Alternative mode of SPE Easy operation Short extraction time High efficiency	
DSPE	Alternative mode of SPE Simple, cost-effective technique	Low efficiency
SPME	Alternative of SPE Require a small sample volume Solventless technique Short-term sampling Easy implementation Great adaptability Possible automation Obtaining of low LODs Solventless technique Small water sample volume	Only extraction of pollutants (e.g. PAEs) in dissolved and gaseous phases Low reproducibility Not very efficiency Difficult quantification due to adsorption competition
SBSE		
Soxhlet		Large amount of solvent Time-consuming, labor-intensive and expensive technique
USE	Easy implementation (shaking, ultrasonic bath)	
MAE	No cleanup	Expensive Not very widespread technique

(continued on next page)

Table 7 (continued)

Sampling devices	Advantages/specificities	Inconvenients
SFE	No cleanup	Not very common technique Not appropriate for widespread application
ASE or PLE	Simple, fast technique Possible automation Addition of dispersing agent to prevent aggregation	
TD	Direct analysis No sample preparation High reproducibility	
Analysis techniques	Advantages	Inconvenients
GC	EI: high ionization efficiency PCI: for isomer PAE determination Tandem MS: high sensitivity HRMS: discrimination of PAEs and their degradation products	Analytes from DMP to DDP No separation of PAE isomers with capillary column Necessary to derivatize MPEs and PA prior analysis Lower sensitivity, low dynamic range
HPLC	Analysis of PAE isomeric mixtures Better separation if thermostated column oven	
UHPLC	Alternative of HPLC Reduction of run time	
IMS	Direct analysis without separation Very fast, lower cost analysis Positive mode: distinguishing of each PAE	
MEKC	High efficiency, high resolution, rapid analysis Low amount of reagents	Not very widespread technique Low sensitivity
FTIR	Simple technique Qualitative analysis	No very quantitative

4.1.5. Solid phase micro extraction (SPME)

SPME is a GAC technique. It involves the use of a fiber coated with an extracting phase, which can be a liquid (polymer) or a solid (sorbent) that extracts PAEs from water. After extraction/concentration, the SPME fiber is transferred to the injection port of GC, where thermal desorption of PAEs occurs and analysis is performed. The extraction involves the equilibrium sorption of analytes onto a microfiber coated with a hydrophilic polymer. There are numerous fiber coatings available based on the solid sorbents. Poly(dimethylsiloxane) (PDMS), which is relatively non-polar and the most frequently used fiber. Among a large variety of fiber coatings, polydimethylsiloxane and divinyl benzene (PDMS-DVB), hand-made polyaniline, and polyacrylate fibers have been successfully used to analyze the 6 PAEs listed in the priority list of the US-EPA (Prokúpková et al., 2002; Li et al., 2006a,b,c). The advantage of SPME is organic solvent-free technique, which avoids the risk of secondary contamination that may occur during the pretreatment step. Further, the fiber can be reused (100–300 cycles). However, it appears that the SPME method for PAE quantification remains in the development phase. To date, very few reported data are available in the literature on this technique and most of them did not mention good efficiency for all of the selected PAEs. Indeed it is difficult to quantify PAEs due to adsorption competition often observed when solid materials are used. However, with optimal conditions, SPME allows to obtain lower LODs than other extraction techniques for some PAEs (Wu et al., 2013b). SPME procedure can be also automated by using an autosampler like CombiPal (Liu, 2008).

4.1.6. Stir-bar sorptive extraction (SBSE)

SBSE is a GAC extraction method that has been used for PAE extraction (Abamou et al., 2013). This technique is based on the sorption of dissolved PAEs on a 20 mm magnetic stirrer coated glass and covered with an adsorbent phase (PDMS polymer of 0.5–1 mm thickness) directly immersed in the water sample, then directly introduced into the analytical instrument for PAE desorption (Baltussen et al., 1999). The extraction yields of PAEs depend on their K_{ow} . SBSE might be used at room temperature, for one to several hours, at 500–1000 rpm stirring (Kawaguchi et al., 2005; Serôdio and Nogueira, 2006; Tan et al., 2008) or with both higher temperature and agitation (50 °C and 1200 rpm) (Tan et al., 2008). The parameters which influence the efficiency are temperature, agitation speed (Baltussen et al., 1999; Leon et al., 2003), NaCl addition (5%) (Amalric et al., 2011) and MeOH content (0%) (Serôdio and Nogueira, 2006). An advantage of the use of SBSE is the small water sample volume (2–10 mL) required for analysis (Kawaguchi et al., 2004, 2005).

4.2. Sludge, sediment, SSM and soil samples

The soil, sludge and sediment should be first lyophilized or dried at room temperature in a storage room separated from the laboratory, ground and sieved (0.5–2 mm) prior extraction (Aparicio et al., 2007; Cai et al., 2007; Ma et al., 2014). The extraction of PAEs from the solid matrix generally includes extraction, cleanup, column fractionation and chromatographic separation. Large variety of organic solvents, such as acetone, ACN, DCM, hexane, ethyl acetate have been reported as efficient for PAE extraction from aquatic SSM, soil, sediment and sludge (Zeng et al., 2008a,b, 2009; Reid et al., 2009) (Table 3). The extraction of PAEs from solid environmental matrices is conventionally performed by the Soxhlet extraction technique that offers high extraction yields (Meng et al., 2014; Wang et al., 2008, 2014). However, other extraction techniques have also been developed not only to reduce the solvent volume and extraction times but also to improve the precision of the recovery. Such techniques include microwave-assisted extraction (MAE), supercritical fluid extraction (SFE), ultrasonic (USE) and accelerated solvent extractions (ASE) (Table 3). The extracted solution requires subsequent cleanup process by using centrifugation or filtration that will remove any remaining solid material (Guo and Kannan, 2012). Two protocols for analyzing PAEs from solid matrices are presented in Fig. 2S in SI.

4.2.1. Soxhlet, microwave-assisted extraction (MAE), supercritical fluid extraction (SFE) and ultrasonic extraction (USE)

Although Soxhlet extraction is recognized as a traditional method for PAE extraction from solid samples, such method is a time-consuming and labor-intensive procedure (4–72 h) that requires large amounts of solvent (100–500 mL) and induces PAE contamination. EPA method 8061A (EPA, 1996) indicates that even after the heating, the Soxhlet extractor under reflux with acetone for three days, DEHP remained in the Soxhlet apparatus at a level of ~500 ng. Moreover, it is not environmentally friendly. GAC methodology USE has also been developed for PAE quantification. USE is performed by simply shaking the sample with solvent or by ultrasonication. Moreover its higher boiling point makes ethyl acetate more suitable for ultrasonication if a thermostatic ultrasonic bath is not available. Another technique characterized by MAE is a GAC methodology, but is expensive and not very widespread (Chee et al., 1996). There is no recent work reported using this technique. SFE is also a GAC methodology (McDowell and Metcalfe, 2001) and allows to extract PAEs from sludge and sediment with carbon dioxide. In both cases (MAE, SFE) the samples did not require further cleanup. However, the use of SFE is not very common and not appropriate for widespread application.

4.2.2. Accelerated solvent extraction (ASE)

ASE is another technique for PAE extraction from solid matrices. Also known as pressurized liquid extraction (PLE), ASE is a simple and fast method that allows high pressure extraction and received recently increased attention. This means that solvents can be heated to temperatures above their boiling points, which make them much more efficient to dissolve target compounds from their matrix. Moreover, ASE maintains constant extraction conditions and its automation provides reliable repeatability (Hubert et al., 2001; Schantz, 2006). In general, solid matrices should be dried, finely ground and sieved at 0.2–2 mm prior to extraction for better efficiency (Zeng et al., 2008a; Wang et al., 2013; Ma et al., 2014; Meng et al., 2014). For coastal and harbor samples, the optimum extraction yield was obtained when sediments were sieved at 0.2 mm (Muñoz-Ortuño et al., 2014). Indeed, reducing the particle size improves the extraction yield by providing better contact of the solvent with the sample. A hydromatrix or diatomaceous earth dispersing agent can be added to the sample to prevent aggregation of sample particles (Reid et al., 2009).

4.2.3. Thermodesorption (TD)

TD is a GAC technique that do not necessitate sample preparation step and allows to direct analysis of the sample with high reproducibility and provides high data quality. This technique is often used for PAE quantification from food packaging, medical devices or plastic toys. For example, ASTM D782 describes the quantitative analysis of six regulated PAEs in polyvinylchloride (PVC) (ASTM, 2013). The sample is heated to desorb PAEs from the solid matrices. It is vaporized and enters through the tube, then PAEs can be detected with MS. The entire analytical sequence is performed in a single step: a known weight of sample (i.e., a known weight of solid sample or a known volume of a quantitative solution is placed in a sample cup which in turn is placed in the autosampler carousel).

4.3. Air samples (gas and particulate phases)

For air sample, PAEs retained on QFFs, PUFs or adsorb to XAD-2 resin can be extracted using the many different techniques as previously reported for solid matrices (i.e., TS, Soxhlet, USE).

5. Chromatographic analysis

Tables 2 and 3 present respectively various regulated methods and other different methods for PAE quantification from environmental matrices. The advantages and inconvenients of each technique are listed in Table 7.

5.1. Direct analysis

The identification and quantification of PAEs and mono-alkyl phthalate esters (MPEs) in environmental matrices require an appropriate pretreatment step, as reported previously, followed by an analysis using different separation and detection techniques. PAEs can be quantified using chromatographic techniques such as liquid chromatography (LC) or gas chromatography (GC). GC equipped with mass spectrometry (MS) is the most commonly used technique for PAE determination (Table 3). A mass spectrometer is the most common detector used; it is an efficient tool for the simultaneous identification and quantification of each targeted PAE with low LOD (ng/L or <ng/g). To achieve accurate quantification, compounds must be fully resolved from each other with a low signal-to-noise background.

5.1.1. Gas chromatography

- Separation:** The majority of PAEs can be analyzed with high efficiency using capillary gas chromatography (CGC) with split/splitless (SSL) injector in splitless mode (with or without pulsed mode) as they are sufficiently volatile and thermostable. Nevertheless, some

authors (Brossa et al., 2003; Warden, 2007) tested a programmable temperature vaporizing (PTV) injection in splitless mode with a good sensitivity. The injection in splitless mode increases the amount of sample introduced to the capillary column than in split mode, so better LODs will be obtained. However, with this type of injection, more sample matrix and solvent are introduced into the column and detector may require more frequent maintenance. PAE separation in GC-MS is commonly performed on a 30 m × 0.25 mm ID, non-polar capillary column with 0.25 μm film of 5% phenyl-95% methyl polysiloxane such as DB-5MS and HP-5MS. This column provides good resolution, higher maximum operating temperature and lower bleeding than columns coated with polar stationary phases like polyethylene glycols (Wax columns) or cyanopropyls. Other columns such as DB-XLB, Rxi-5MS, SLB-5MS, Phenomenex XLB, Ultra-2 and DB-35 can be also used with good efficiency (Table 3). A stainless steel column (2 m × 3 mm) containing 5% OV-101 on 100/120 Chromosorb W-HP has been used in the NIOSH Method 5020 (NIOSH, 1994) for DnBP and DEHP from air samples. To our knowledge, there is no capillary column that can separate DNP from DDP. The quantification of these isomers can be done only from the extracted ion chromatograms with the sum of the peak areas of each group.

- Identification and quantification:** After GC separation, PAEs can be detected with electron capture (ECD), photoionization (PID) or MS detectors and some standard methods used them (Table 2). Although ECD is relatively sensitive for PAEs (Jaworek and Czaplicka, 2013), the specificity is restricted since ECD responds much more towards halogenated compounds. The MS appears to be the most selective for PAE analysis. All types of MS analyzers including quadrupole, triple quadrupole, ion trap and magnetic sector have been used. Benchtop quadrupole systems are generally preferred due to their robustness, stability, linear dynamic range and low cost. Ion trap detectors have similar sensitivity, but lower dynamic range (Blair et al., 2009; Net et al., 2014). With MS detector, each PAE can be ionized by electronic impact (EI) or more rarely by chemical ionization (CI) (Berset and Etter-Holzer, 2001), and be detected in full scan, single ion monitoring (SIM), selected ion storage (SIS), tandem MS (MS/MS) or multiple reaction monitoring (MRM) mode. The splitless injection and/or SIM, SIS, MS/MS and MRM functions enable to increase the LODs of PAEs. Table 4 presents the quantifier/qualifier ions of PAEs using a Rxi®-5 ms capillary column. MS/MS is not widely adopted in US-EPA methodology, especially as GC/tandem MS applications (Table 2). The high specificity of tandem MS involves a determination at very low levels of PAEs and MS/MS can be chosen when excessive cleanup operations are required.

High resolution MS (HRMS) coupled to GC for PAE determination from sewage sludge (Berset and Etter-Holzer, 2001), soil (Vikelsøe et al., 1999) allows to discriminate PAEs and their degradation products with a high selectivity due to accurate masses, but do not offer any advantage for routine PAE analysis because it presents lower sensitivity and dynamic range than low resolution classical MS (Segura et al., 2012). PAEs in environmental matrices can also be characterized with high sensitivity by ion mobility spectrometry (IMS), an analytical technique emerged in 1970 (Li et al., 2002). This direct monitoring do not necessitate separation technique before, is very fast (several minutes) and lower cost. In the positive mode, a characteristic reduced mobility is obtained for each PAE, thus they can be distinguished.

5.1.2. Liquid chromatography (LC)

According to the literature data, PAEs can also be quantified using the LC. However, compared to GC-MS, a lower sensitivity is obtained with LC-MS. Indeed, LC is more appropriate for analyzing MPEs and degradation products of PAEs than PAEs themselves. However, high pressure liquid chromatography (HPLC), or more recently ultra HPLC

(UHPLC) (Liou et al., 2014; Yang et al., 2014), is useful for the determination of PAE isomeric mixtures (e.g. DiNP, DiDP) that are not sufficiently separated by GC. PAEs are dissolved first in a mobile phase, pass through a column packed with a stationary phase where they are separated. PAE separation with LC is commonly achieved on an apolar C18 ODS analytical column, using a mobile phase containing an organic solvent such as methanol or ACN and Milli-Q water, both generally buffered (e.g., with 10 mM ammonium formate, ammonium acetate) or acidified (0.05–0.1% AcOH or TFA). However, a C8 column provides better separation peaks for the isomeric mixtures, with well defined and narrower peaks than on a classical C18. Better separation can be obtained when the column is thermostated between room temperature to 80 °C. Table 2S in SI presents the columns commonly used in LC for PAE analysis. UHPLC allows notably to reduce the run time. MS or UV detector can perform the detection of PAEs using LC. Table 4 presents the quantifier and qualifier ions of PAEs with MS detector. With MS detector, PAEs can be analyzed with electrospray (ESI) (Masia et al., 2013) or atmospheric pressure chemical (APCI) (Castillo and Barcelo, 2001) ionization in positive mode (Table 5).

5.1.3. Micellar electrokinetic capillary chromatography (MEKC)

MEKC is an alternative to HPLC, GC for PAE analysis owing to its high efficiency, rapid analysis and low consumption of reagents, but not very widespread. This technique, which can provide high resolution, is performed with the same apparatus as capillary electrophoresis although its principle of separation is based on chromatography, i.e. the difference in the distribution between an aqueous buffer solution (mobile phase) and micelles of ionic surfactants (pseudo-stationary phase). In MEKC, it is possible to estimate distribution coefficients and thermodynamic parameters in micellar solubilization. MEKC has been used for PAE determination from landfill leachate and water samples (Sun et al., 2013b), soil (Guo et al., 2005; Lin et al., 2010) and their migration order agreed with that of log K_{ow}. However, to date, their resolution is poor and this technique is not very sensitive (LOD of several µg/L or µg/g for water and soil samples, respectively). Addition of methanol (20%, v/v) as buffer modifier to aqueous migration buffer solution containing 0.05 M sodium dodecyl sulfate (SDS) as common surfactant can improve the resolution of their separation (Takeda et al., 1993). To improve a bit, Sun et al. (2013b) developed an SPE-β-cyclodextrin (β-CD)-MECC method with UV detection where coal cinder is employed as adsorbent for SPE and β-CD as electrophoresis additive. The coupling of MECC to MS-APCI with on-line sample concentration was investigated by Isoo et al. (2001) for the analysis of environmental samples and also improved the method sensitivity.

5.1.4. Fourier transform infrared spectroscopy (FTIR)

FTIR is a simple technique allowing to obtain an infrared spectrum of e.g. absorption, emission of a matrix. The spectrometer simultaneously collects high spectral resolution data over a wide spectral range and the Fourier transform process converts the raw data into a spectrum generated by an interferometer. This technique uses unique fingerprint of materials and is very useful in qualitative analysis. It is based on the principle that a compound that has a covalent bond and a dipole moment can absorb frequencies of electromagnetic radiation. Each

compound absorbs at different energies/frequencies and thus has different absorption patterns. There are two common types of spectrophotometers, dispersive and Fourier transform (FT) instruments, but the latter is more interesting due to a very fast analysis and a better response. They are benchtop or portable apparatus. Different ways exist to do PAE analysis depending of the state of the matrix. If it is a liquid, a cuvette is used or a drop is placed on a handmade crystal, however for solid or liquid samples it is also possible to employ universal attenuated total reflectance (UATR) for the measurement. In the case of solid, the process consists to manufacture a film by heat and/or pressure from powder or solid piece and then analyze it.

The leaching of PAEs from plasticized polymers is often examined by FTIR (Zhang and Chen, 2014). FTIR can be also used to obtain a pre-screening to determine gross PAE contamination with accurate measurements as low as 0.1% (Higgins, 2013; Thermo Scientific, 2013). To date, applications are limited but the couplings are possible with separation techniques (eg, GC) or a second detection for considering new applications. Indeed, FTIR alone is not very sensitive.

5.2. Derivatization method

Generally, PAEs can be easily identified and quantified by direct analysis as reported in the previous section. They are sufficiently volatile to be analyzed directly by GC/MS. Nevertheless, their derivatization can make them more volatile. Although this step facilitates their GC analysis, there is paucity of reports dealing with such method. The peaks of silylated derivatives in the GC chromatograms are more symmetrical and less broad than those of corresponding PAEs, and the retention times are shorter. For the derivatization technique, PAEs are first hydrolyzed using an alkaline solution of NaOH or KOH. Following by the acidification step the obtained phthalic acid (PA) and alcohols are then extracted with organic solvent(s) and finally derivatized (e.g., by silylation as showed in Fig. 2) prior to GC/MS analysis.

For PAE derivatization, first, alkaline hydrolysis can be performed with 1 M NaOH, or at pH ≥ 12, at 90 °C for 30 min or at room temperature (Kim et al., 2007; Peng et al., 2013). Then the solution can be acidified with HCl to pH ≤ 2 to convert carboxylates into carboxylic acids. PA and alcohols obtained are usually extracted with ethyl acetate according to Kim et al. (2007). Under anhydrous conditions, these analytes can be derivatized by silylation. The derivatizing agent most commonly used is pentafluorobenzyl chloride (PFBCl). However, other derivatization reagents such as N-Methyl-N-tert-butyltrimethylsilyltrifluoroacetamide (MTBSTFA) and N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) can be used (Ballesteros et al., 2006; Schreiber et al., 2011; Félix-Cafredo et al., 2013; Fu et al., 2013). The quantifier and qualifier ions of silyl derivatives of phthalic esters are presented in Table 6. This method enables to quantifying the total PAEs with good efficiency and low LOQ, but does not allow the determination of individual PAEs, while individual MPE concentrations can be obtained. Thus, to determine the real contamination level of PAEs, they must be analyzed without derivatization as previously described. As they contain free acid function(s), they require derivatization stage before GC analysis or on-line, e.g. with SPME-diazomethane on-fiber (Alzaga et al., 2003).

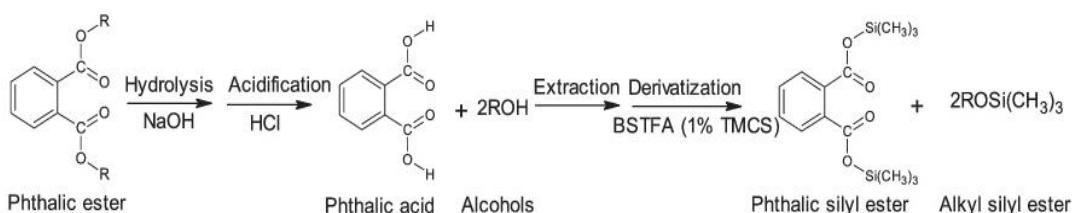


Fig. 2. Hydrolysis reaction and the derivatization of PAEs by silylation (Kim et al., 2007).

6. Conclusions

To date, PAEs are the most common chemicals that humans are in contact with daily. For PAE monitoring in aquatic and atmospheric environments, passive samplers offer an attractive alternative to traditional grab sampling methods because they have no volume limitation and can accumulate pollutants in ultra-trace level. Because of their ubiquity in the laboratory environment, reagents and equipment, accurate and precise PAE determination in environmental samples can be a challenging task. For reliable quantification, nitrile gloves and handling in a filtrated air room are highly recommended. Simplification of analytical steps and exercise of adequate precautions with QA/QC procedures are important in reliable PAE quantification from environmental matrices.

During these last few decades, there has been considerable improvement in PAE extraction and analysis techniques. Numerous pretreatment and detection techniques can be now applied for identifying and quantifying PAEs present at the low concentration level in different environmental matrices throughout the worldwide environment, including atmospheric aerosols, indoor and outdoor air, in municipal solid waste compost, sludge, river and marine water/sediment, SSM and drinking water. Generally, they can be easily identified and quantified by common techniques of extraction (i.e., LLE, SPE, SPME, ASE, Soxhlet, sonication...) and analysis (i.e., GC/MS, LC/MS). There is now increasing interest in developing on-line hyphenated techniques (e.g. on-line SPE) for environmental PAE analysis that combine sample preparation, separation and detection. Some methods are simple to implement but organic solvents and time consuming, labor intensive, vandalism, expensive and require qualified staff. Moreover, some conventional methods are not environmentally friendly technologies. Other methods are GAC techniques that can present certain disadvantages. Many techniques of extraction and analysis can be applied for reliable PAE quantification. The method of choice depends on the availability of materials and devices of each of the laboratory. However, by respect to the environment, choosing the green analytical chemistry (GAC) methodologies such as SMPE for solid extraction and USE or TD for solid matrices is recommended.

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Appendix A. Supplementary data

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References

- Abamou, A., Bocquené, G., Champin, M., Durand, G., Gonzalez, J.-L., Le Moigne, M., Masson, J.-C., Priou, P., Tixier, C., 2013. Rapport de l'étude prospective sur les contaminants émergents dans les eaux littorales de la métropole et de DOM. Convention ONEMA/Ifremer du 29 juin 2012, p. 52.
- Adeniyi, A.A., Okedeyi, O.O., Yusuf, K.A., 2011. Flame ionization gas chromatographic determination of phthalate esters in water, surface sediments and fish species in the Ogun river catchments, Ketu, Lagos, Nigeria. Environ. Monit. Assess. 172 (1), 561–569.
- Adewuyi, G.O., 2012. High performance liquid chromatographic identification and estimation of phthalates in sewer waste and a receiving river in Ibadan city, Southwest Nigeria. J. Water Resour. Protect. 4, 851–858.
- AFNOR (Association Française de Normalisation) NF EN ISO 18856, 2005. Qualité de l'eau - Dosage de certains phthalates par chromatographie en phase gazeuse/spectrométrie de masse. pp. T90-T186.
- Aguayo, S., Munoz, M.J., de la Torre, A., Roset, J., de la Pena, E., Carbalo, M., 2004. Identification of organic compounds and ecotoxicological assessment of sewage treatment plants (STP) effluents. Sci. Total Environ. 328, 69–81.
- Al Khatib, A.J., Habib, I.Y., Muhammad, M., Danladi, F.I., Bala, S.S., Adamu, A., 2014. Analysis of phthalate plasticizer in Jordanian bottled waters by liquid chromatography-tandem mass spectrophotometry (LC-MS/MS). Eur. Sci. J. 10 (18), 271–282.
- Alvarez, D.A., 2010. Guidelines for the use of the semipermeable membrane device (SPMD) and the polar organic chemical integrative sampler (POCIS) in environmental monitoring studies. U.S. Geological Survey, Techniques and Methods 1-D, p. 28.
- Alvarez, D.A., Petty, J.D., Huckins, J.N., Jones-Lepp, T.L., Getting, D.T., Goddard, J.P., Manahan, S.E., 2004. Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments. Environ. Toxicol. Chem. 23 (7), 1640–1648.
- Alvarez, D.A., Stackelberg, P.E., Petty, J.D., Huckins, J.N., Furlong, E.T., Zaug, S.D., Meyer, M.T., 2005. Comparison of a novel passive sampler to standard water-column sampling for organic contaminants associated with wastewater effluents entering a New Jersey stream. Chemosphere 61, 610–622.
- Alvarez, D.A., Cranor, W.L., Perkins, S.D., Clark, R.C., Smith, S.B., 2008. Chemical and toxicologic assessment of organic contaminants in surface water using passive samplers. J. Environ. Qual. 37, 1024–1033.
- Alvarez, D.A., Maruya, K.A., Dodder, N.G., Lao, W., Furlong, E.T., Smalling, K.L., 2014a. Occurrence of contaminants of emerging concern along the California coast (2009–2010) using passive sampling devices. Mar. Pollut. Bull. 81 (2), 347–354.
- Alvarez, D., Perkins, S., Nilsen, E., Morace, J., 2014b. Spatial and temporal trends in occurrence of emerging and legacy contaminants in the Lower Columbia River 2008–2010. Sci. Total Environ. 484, 322–330.
- Alzaga, R., Pena, A., Bayona, J.M., 2003. Determination of phthalate monoesters in aqueous and urine samples by solid-phase microextraction-diazomethane on-fibre derivatization-gas chromatography-mass spectrometry. J. Sep. Sci. 26, 87–96.
- Amalric, L., Cabillie, J., Lardy-Fontan, S., Strub, M.P., 2011. Compatibilité des méthodes d'analyse des substances organiques avec les exigences des programmes de surveillance de la DCE. Rapport final, BRGM/RP-59499-FR, p. 94 (Fév).
- Amiridou, D., Voutsas, D., 2011. Alkylphenols and phthalates in bottled waters. J. Hazard. Mater. 185, 281–286.
- Aparicio, I., Santos, J.L., Alonso, E., 2007. Simultaneous sonication-assisted extraction, and determination by gas chromatography-mass spectrometry, of di-(2-ethylhexyl) phthalate, nonylphenol, nonylphenol ethoxylates and polychlorinated biphenyls in sludge from wastewater treatment plants. Anal. Chim. Acta 584 (2), 455–461.
- Aragón, M., Borrull, F., Marcé, R.M., 2013. Thermal desorption-gas chromatography-mass spectrometry method to determine phthalate and organophosphate esters from air samples. J. Chromatogr. A 1303, 76–82.
- ASTM D7823, 2013. Standard Test Method for the Determination of Low Level, Regulated Phthalates in Poly(vinyl chloride) Plastics by Thermal Desorption-Gas Chromatography/Mass Chromatography.
- Bach, C., Dauchy, X., Severini, I., Munoz, J.F., Etienne, S., Chagnon, M.C., 2013. Effect of temperature on the release of intentionally and non-intentionally added substances from polyethylene terephthalate (PET) bottles into water: chemical analysis and potential toxicity. Food Chem. 139, 672–680.
- Ballesteros, O., Zafra, A., Navalón, A., Vilchez, J.L., 2006. Sensitive gas chromatography-mass spectrometric method for the determination of phthalate esters, alkylphenols, bisphenol A and their chlorinated derivatives in wastewater samples. J. Chromatogr. A 1121, 154–162.
- Baltussen, E., Sandra, P., David, F., Cramers, C., 1999. Stir bar sorptive extraction (SBSE), a novel extraction technique for aqueous samples: theory and principles. J. Microcolumn Sep. 11 (10), 737–747.
- Baram, G.I., Azarova, I.N., Gorshkov, A.G., Vereshchagin, A.L., Lang, B., Kiryukhina, E.D., 2000. Determination of bis(2-ethylhexyl) phthalate in water by high-performance liquid chromatography with direct on-column preconcentration. J. Anal. Chem. 55, 750–754.
- Barreca, S., Indelicato, R., Orecchio, S., Pace, A., 2014. Photodegradation of selected phthalates on mural painting surfaces under UV light irradiation. Microchem. J. 114, 192–196.
- Battle, R., Neñín, C., 2004. Application of single-drop microextraction to the determination of dialkyl phthalate esters in food simulants. J. Chromatogr. A 1045 (1–2), 29–35.
- Bell, J., Barsh, R., 2010. Development and Application of a Method for the Analysis of Diethylhexyl Phthalate (DEHP) in San Juan County Waters. Report, p. 9.
- Bergé, A., 2012. Identification des sources d'alkylphénols et de phthalates en milieu urbain –Comparaison des rejets à dominante urbaine (domestique) par rapport à des rejets purement industriels. (Thèse).
- Bergh, C., Torgrip, R., Emenius, G., Ostman, C., 2011. Organophosphate and phthalate esters in air and settled dust—a multi-location indoor study. Indoor Air 21 (1), 67–76.
- Bergström, S., Barri, T., Norberg, J., Jönsson, J.A., Mathiasson, L., 2007. Extracting syringe for extraction of phthalate esters in aqueous environmental samples. Anal. Chim. Acta 394, 240–247.
- Berset, J.D., Etter-Holzer, R., 2001. Determination of phthalates in crude extracts of sewage sludges by high-resolution capillary gas chromatography with mass spectrometric detection. J. AOAC Int. 84 (2), 383–391.
- Blair, J.D., Ikonomou, M.G., Kelly, B.C., Surridge, B., Gobas, F.A.P.C., 2009. Ultra-trace determination of phthalate ester metabolites in seawater, sediments, and biota from an urbanized marine inlet by LC/ESI-MS/MS. Environ. Sci. Technol. 43 (16), 6262–6268.
- Brossa, L., Marcé, R.M., Borrull, F., Pocurull, E., 2003. Determination of endocrine-disrupting compounds in water samples by on-line solid-phase extraction-programmed-temperature vaporization-gas chromatography-mass spectrometry. J. Chromatogr. A 998, 41–50.
- Cai, Q.K., Jiang, G.B., Liu, J.F., Zhou, Q.X., 2003. Multi-walled carbon nanotubes packed cartridge for the solid-phase extraction of several phthalate esters from water

- samples and their determination by high performance liquid chromatography. *Anal. Chim. Acta* 494, 149–156.
- Cai, Y., Cai, Y., Shi, Y., Liu, J., Mou, S., Lu, Y., 2007. A liquid–liquid extraction technique for phthalate esters with water-soluble organic solvents by adding inorganic solvents. *Microchim. Acta* 157 (1–2), 73–79.
- Cao, X.L., 2008. Determination of phthalates and adipate in bottled water by headspace solid-phase microextraction and gas chromatography/mass spectrometry. *J. Chromatogr. A* 1178, 231–238.
- Caroli, S., Cescon, P., Walton, D.W.H., 2001. Environmental contamination in Antarctica: a challenge to analytical chemistry, book. Kindle Editionp. 420.
- Castillo, M., Barcelo, D., 1999. Identification of polar toxicants in industrial wastewaters using toxicity-based fractionation with liquid chromatography/mass spectrometry. *Anal. Chem.* 71, 3769–3776.
- Castillo, M., Barcelo, D., 2001. Characterisation of organic pollutants in textile wastewaters and landfill leachate by using toxicity-based fractionation methods flooded by liquid and gas chromatography coupled to mass spectrometric detection. *Anal. Chim. Acta* 426, 253–264.
- Chang, M.S., Shen, J.Y., Yang, S.-H., Wu, G.J., 2011. Subcritical water extraction for the remediation of phthalate ester-contaminated soil. *J. Hazard. Mater.* 192, 1203–1209.
- Chao, Y.Y., Jian, Z.X., Tu, Y.M., Huang, Y.L., 2013. Rapid on-line microextraction of neutral analytes in plastic-bottled beverages through ultrasound-assisted push/pull perfusion hollow-fiber liquid–liquid microextraction. *Microchem. J.* 110, 386–394.
- Chee, K.K., Wong, M.K., Lee, H.K., 1996. Microwave extraction of phthalate esters from marine sediment and soil. *Chromatographia* 42 (7), 378–384.
- Chen, X., Xu, S., Tan, T., Lee, S.T., Cheng, S.H., Lee, F.W.F., Xu, S.J.L., Ho, K.C., 2014. Toxicity and estrogenic endocrine disrupting activity of phthalates and their mixtures. *Int. J. Environ. Res. Public Health* 11 (3), 3156–3168.
- Choi, H., Schmidbauer, N., Spengler, J., Bornehag, C.G., 2010. Sources of propylene glycol and glycol ethers in air at home. *Int. J. Environ. Res. Public Health* 7, 4213–4237.
- Cincinelli, A., Stortini, A.M., Perugini, M., Checchini, L., Lepri, L., 2001. Organic pollutants in sea-surface microlayer and aerosol in the coastal environment of Leghorn (Tyrrhenian Sea). *Mar. Chem.* 76, 77–98.
- Cousins, A.P., Holmgren, T., Remberger, M., 2014. Emissions of two phthalate esters and BDE 209 to indoor air and their impact on urban air quality. *Sci. Total Environ.* 470–471, 527–535.
- Danish Ministerial Order. No. 823, 1996. Application of Waste Products for Agricultural Purposes (September 16, 1996).
- Dargnat, C., Teil, M.J., Chevreuil, M., Blanchard, M., 2009. Phthalate removal throughout wastewater treatment plant: case study of Marne Aval station (France). *Review. Sci. Total Environ.* 407 (4), 1235–1244.
- Das, M.T., Ghosh, P., Thakur, I.S., 2014. Intake estimates of phthalate esters for South Delhi population based on exposure media assessment. *Environ. Pollut.* 189, 118–125.
- Dévier, M.H., Le Menach, K., Viglino, L., Di Gioia, L., Lachassagne, P., Budzinski, H., 2013. Ultra-trace analysis of hormones, pharmaceutical substances, alkylphenols and phthalates in two French natural mineral waters. *Sci. Total Environ.* 443, 621–632.
- Du, X., Li, X., Luo, T., Matssur, N., Kadokami, K., Chen, J., 2013. Occurrence and aquatic ecological risk assessment of typical organic pollutants in water of Yangtze River estuary. *Procedia Environ. Sci.* 18, 882–889.
- Dumitrescu, I., 2013. Method validation for phthalate analysis from water, advances in environmental sciences. *Int. J. Bioflux Soc.* 5 (2), 63–69.
- EPA (Environmental Protection Agency), 1986. Phthalate Esters. Method 8060, Rev. 0.
- EPA (Environmental Protection Agency), 1995a. Determination of phthalate and adipate esters in drinking water by liquid–liquid extraction or liquid–solid extraction and gas chromatography with photoionization detection. Method 506. Rev. 1.1.
- EPA (Environmental Protection Agency), 1995b. Determination of organic compounds in drinking water by liquid–solid phase extraction and capillary column chromatography/mass spectrometry. Method 525.2, Rev. 2.0.
- EPA (Environmental Protection Agency), 1996. Phthalate esters by gas chromatography with electron capture detection (GC/ECD). Method 806 1a, Rev 1.
- EPA (Environmental Protection Agency), 1998. Semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS). Method 8270d, Rev. 4.
- EPA (Environmental Protection Agency), 2007a. Methods for organic chemical analysis of municipal and industrial wastewater. Method 606–Phthalate ester, Appendix A to part 136.
- EPA (Environmental Protection Agency), 2007b. Methods for organic chemical analysis of municipal and industrial wastewater. Method 625–Base/neutrals and acids, Appendix A to part 136.
- Espadaler, I., Caixach, J., Om, J., Ventura, F., Cortina, M., Pauné, F., Rivera, J., 1997. Identification of organic pollutants in Ter River and its system of reservoirs supplying water to Barcelona (Catalonia, Spain): a study by GC/MS and FAB/MS. *Water Res.* 31 (8), 1996–2004.
- Fankhauser-Noti, A., Grob, K., 2007. Blank problems in trace analysis of diethylhexyl and dibutyl phthalate: investigation of the sources, tips and tricks. *Anal. Chim. Acta* 582, 353–360.
- Farahani, H., Norouzi, P., Dinarvand, R., Ganjali, M.R., 2007. Development of dispersive liquid–liquid microextraction combined with gas chromatography–mass spectrometry as a simple, rapid and highly sensitive method for the determination of phthalate esters in water samples. *J. Chromatogr. A* 1172, 105–112.
- Farahani, H., Ganjali, M.R., Dinarvand, R., Norouzi, P., 2008. Screening method for phthalate esters in water using liquid-phase microextraction based on the solidification of a floating organic microdrop combined with gas chromatography–mass spectrometry. *Talanta* 76, 718–723.
- Fatoki, O.S., Bornman, M., Ravandhalala, L., Chimuka, L., Genthe, B., Adeniyi, A., 2010. Phthalate ester plasticizers in freshwater systems of Venda, South Africa and potential health effects. ISSN 1816–7950 (On-line). *Water SA* 36 (1), 117–125.
- Félix-Cafredo, T.E., Durán-Alvarez, J.C., Jiménez-Cisneros, B., 2013. The occurrence and distribution of a group of organic micropollutants in Mexico City's water sources. *Sci. Total Environ.* 454–455, 109–118.
- Fromme, H., Küchler, T., Otto, T., Pilz, K., Müller, J., Wenzel, A., 2002. Occurrence of phthalates and bisphenol A and F in the environment. *Water Res.* 36 (6), 1429–1438.
- Fu, P., Kawamura, K., Barrie, L.A., 2009. Photochemical and other sources of organic compounds in the Canadian high Arctic aerosol pollution during Winter–Spring. *Environ. Sci. Technol.* 43, 286–292.
- Fu, P.Q., Kawamura, K., Chen, J., Charrière, B., Sempéré, R., 2013. Organic molecular composition of marine aerosols over the Arctic Ocean in summer: contributions of primary emission and secondary aerosol formation. *Biogeosciences* 10, 653–667.
- Furtmann, K., 1994. Phthalates in surface water—a method for routine trace level analysis. *Fresenius J. Anal. Chem.* 348, 291–296.
- Gao, D., Li, Z., Wen, Z., Ren, N., 2014. Occurrence and fate of phthalate esters in full-scale domestic wastewater treatment plants and their impact on receiving waters along the Songhua River in China. *Chemosphere* 95, 24–32.
- Guo, Y., Kannan, K., 2012. Challenges encountered in the analysis of phthalate esters in foodstuffs and other biological matrices. *Anal. Bioanal. Chem.* 404, 2539–2554.
- Guo, L., Lee, H.K., 2013. Vortex-assisted micro-solid-phase extraction followed by low-density solvent based dispersive liquid–liquid microextraction for the fast and efficient determination of phthalate esters in river water samples. *J. Chromatogr. A* 1300, 24–30.
- Guo, B.Y., Wen, B., Shan, X.Q., Zhang, S.Z., Lin, J.M., 2005. Separation and determination of phthalates by micellar electrokinetic chromatographic. *J. Chromatogr. A* 1095 (1–2), 189–192.
- Hashizume, K., Nanya, J., Toda, C., Yasui, T., Nagano, H., Kojima, N., 2002. Phthalate esters detected in various water samples and biodegradation of the phthalates by microbes isolated from river water. *Biol. Pharm. Bull.* 25 (2), 209–214.
- He, W., Qin, N., Kong, X., Liu, W., He, Q., Ouyang, H., Yang, C., Jiang, Y., Wang, Q., Yang, B., Xu, F., 2013. Spatio-temporal distributions and the ecological and health risks of phthalate esters (PAEs) in the surface water of a large, shallow Chinese lake. *Sci. Total Environ.* 461–462, 672–680.
- Higgins, F., 2013. Rapid and Reliable Phthalate Screening in Plastics by Portable FTIR Spectroscopy. Agilent Technologies (Application note 59913649EN).
- Holádová, K., Prokúpková, G., Hajšlová, J., Poušťka, J., 2007. Headspace solid-phase microextraction of phthalic acid esters from vegetable oil employing solvent based matrix modification. *Anal. Chim. Acta* 582, 24–33.
- Howdeshell, K.L., Rider, C.V., Wilson, V.S., Gray Jr., L.E., 2008. Mechanisms of action of phthalate esters, individually and in combination, to induce abnormal reproductive development in male laboratory rats. *Environ. Res.* 108 (2), 168–176.
- Huang, P.C., Tien, C.J., Sun, Y.M., Hsieh, C.Y., Lee, C.C., 2008. Occurrence of phthalates in sediment and biota: relationship to aquatic factors and the biota-sediment accumulation factor. *Chemosphere* 73 (4), 539–544.
- Huang, D.Y., Zhou, S.G., Hong, W., Feng, W.F., Tao, L., 2013. Pollution characteristics of volatile organic compounds, polycyclic aromatic hydrocarbons and phthalate esters emitted from plastic wastes recycling granulation plants in Xingtian Town, South China. *Atmos. Environ.* 71, 327–334.
- Hubert, A., Wenzel, K.D., Engewald, W., Schüürmann, G., 2001. Accelerated solvent extraction—more efficient extraction of POPs and PAHs from real contaminated plant and soil samples. *Rev. Anal. Chem.* 20 (2), 101–144.
- Huckins, J.N., Petty, J.D., Boor, J.K., 2006. Monitors of organic chemicals in the environment. *Semipermeable Membrane Devices*. Springer Science + Business Media, LLC, New York.
- INERIS (Institut National de l'Environnement Industriel et des Risques), 2009. Report on the French interlaboratory exercise on the Water Framework Directive priority substances—Phthalates. INERIS Report No. DRC-09-95687-06768B (June, 48 pp.).
- INERIS (Institut National de l'Environnement Industriel et des Risques), 2011. Journée technique Phtalates, Aquaref, présentation, 69 diapositives, 24 mars.
- Isobe, T., Nishiyama, H., Nakashima, A., Takada, H., 2001. Distribution and behavior of nonylphenol, octylphenol and nonylphenol monoethoxylate in okyo metropolitan area: their association with aquatic particles and sedimentary distributions. *Environ. Sci. Technol.* 35 (6), 1041–1049.
- Isoo, K., Otsuka, K., Terabe, S., 2001. Application of sweeping to micellar electrokinetic chromatography-atmospheric pressure chemical ionization-mass spectrometric analysis of environmental pollutants. *Electrophoresis* 22 (16), 3426–3432.
- Jara, S., Lysebo, C., Greibrok, T., Lundanes, E., 2000. Determination of phthalates in water samples using polystyrene solid-phase extraction and liquid chromatography quantification. *Anal. Chim. Acta* 407 (1–2), 165–171.
- Jaworek, K., Czaplicka, M., 2013. Determination of phthalates in polymeric materials—comparison of GC/MS and GC/ECD methods. *Polímeros* 23 (6), 718–724.
- JOUE (Journal Officiel de l'Union Européenne), 2013. Directive 2013/39/UE du parlement Européen et du Conseil du 12 août 2013.
- Kawaguchi, M., Inoue, K., Yoshimura, M., Sakui, N., Okanouchi, N., Ito, R., Yoshimura, Y., Nakazawa, H., 2004. Trace analysis of phenolic xenoestrogens in water samples by stir bar sorptive extraction with in situ derivatization and thermal desorption–gas chromatography–mass spectrometry. *J. Chromatogr. A* 1041, 19–26.
- Kawaguchi, M., Sakai, N., Okanouchi, N., Ito, R., Saito, K., Izumi, S., Makino, T., Nakazawa, H., 2005. Stir bar sorptive extraction with in situ derivatization and thermal desorption–gas chromatography–mass spectrometry for measurement of phenolic xenoestrogens in human urine samples. *J. Chromatogr. B* 820, 49–57.
- Kerienė, I., Maruška, A., Sitonytė, J., 2011. Solid phase extraction and gas chromatographic–mass spectrometric analysis of phthalates in surface water: method development and validation. *Chemija* 22 (4), 204–209.

- Khedr, A., 2013. Optimized extraction method for LC-MS determination of bisphenol A, melamine and di(2-ethylhexyl) phthalate in selected soft drinks, syringes, and milk powder. *J. Chromatogr. B* 930, 98–103.
- Kim, M., Li, D., Shim, W.J., Oh, J.R., Park, J., 2007. Simultaneous gas chromatography-mass spectrometric determination of total and individual phthalic esters utilizing alkaline hydrolysis and silyl derivatization technique. *Bull. Korean Chem. Soc.* 28 (3), 432–438.
- Kolena, B., Petrovickova, I., Pilka, T., Pucherova, Z., Munk, M., Matula, B., Vankova, V., Petlus, P., Jenisova, Z., Rozova, Z., Wimmerova, S., Trnovec, T., 2014. Phthalate exposure and health-related outcomes in specific types of work environment. *Int. J. Environ. Res. Public Health* 11 (6), 5628–5639.
- Kong, S., Ji, Y., Liu, L., Chen, L., Zhao, X., Wang, J., Bai, Z., Sun, Z., 2013. Spatial and temporal variation of phthalic acid esters (PAEs) in atmospheric PM10 and PM2.5 and the influence of ambient temperature in Tianjin, China. *Atmos. Environ.* 74, 199–208.
- Leon, V.M., Alvarez, B., Cobollo, M.A., Munoz, S., Valor, I., 2003. Analysis of 35 priority semivolatile compounds in water by stir bar sorptive extraction-thermal desorption gas chromatography-mass spectrometry: I. Method optimization. *J. Chromatogr. A* 999 (1–2), 91–101.
- Li, F., Xie, Z., Schmidt, H., Sielemann, S., Baumbach, J.I., 2002. Ion mobility spectrometer for online of trace compounds. *Spectrochim. Acta B* 57, 1563–1574.
- Li, X.H., Ma, L.L., Liu, X.F., Fu, S., Cheng, H.X., Xu, X.B., 2006a. Phthalate ester pollution in urban soil of Beijing, People's Republic of China. *Bull. Environ. Contam. Toxicol.* 77 (2), 252–259.
- Li, H.Y., Qu, J.H., Liu, H.J., 2006b. Removal of a type of endocrine disruptors di-n-butyl phthalate from water by ozonation. *J. Environ. Sci.* 18 (5), 845–851.
- Li, X., Zhong, M., Xu, S., Sun, C., 2006c. Determination of phthalates in water samples using polyaniiline-based solid-phase microextraction coupled with gas chromatography. *J. Chromatogr. A* 1135 (1), 101–108.
- Lin, Z.P., Ikonomou, M.G., Jing, H., Mackintosh, C., Gobas, F.A.P.C., 2003. Determination of phthalate ester congeners and mixtures by LC/ESI-MS in sediments and biota of an urbanized marine inlet. *Environ. Sci. Technol.* 37 (10), 2100–2108.
- Lin, Z., Zhang, J., Cui, H., Zhang, L., Chen, G., 2010. Determination of phthalate esters in soil by microemulsion electrokinetic chromatography coupled with accelerated solvent extraction. *J. Sep. Sci.* 33, 3717–3725.
- Liou, S.H., Yang, G.C.C., Wang, C.L., Chiu, Y.H., 2014. Monitoring of PAEMs and beta-agonists in urine for a small group of experimental subjects and PAEs and beta-agonists in drinking water consumed by the same subjects. *J. Hazard. Mater.* 277, 169–179.
- Litz, N., Heise, S., Heinrich, C., 2007. Final report on the Project "Phthalate" in the Framework of the EU-Project Horizontal-Org. Federal Environment Agency Germany, Berlin. Department of Drinking Water Resources and Water Treatment, Schichauweg 58, D 12307 Berlin.
- Liu, W.I., 2008. Determination of sub-ppb level of phthalates in water by auto-SPME and GC-MS. Agilent Technologies (Application 5989-7726EN).
- Liu, Y., Chen, Z., Shen, J., 2013. Occurrence and removal characteristics of phthalate esters from typical water sources in Northeast China. *J. Anal. Methods Chem.* <http://dx.doi.org/10.1155/2013/419349> (ID 419349).
- Loos, R., Wollgast, J., Castro-Jiménez, J., Mariani, G., Huber, T., Locoro, G., Hanke, G., Umlauf, G., Bidoglio, G., 2008. Laboratory intercomparison study for the analysis of nonylphenol and octylphenol in river water. *TrAC 27* (1), 89–95.
- Luo, Y.B., Yu, Q.W., Yuan, B.F., Feng, Y.Q., 2012. Fast microextraction of phthalate acid esters from beverage, environmental water and perfume samples by magnetic multi-walled carbon nanotubes. *Talanta* 90, 123–131.
- Lv, X., Hao, Y., Jia, Q., 2013. Preconcentration procedures for phthalate esters combined with chromatographic analysis. *J. Chromatogr. Sci.* 51 (7), 1–13.
- Ma, T.T., Christie, P., Luo, Y.M., Teng, Y., 2014. Physiological and antioxidant responses of germinating mung bean seedlings to phthalate esters in soil. *Pedosphere* 24 (1), 107–115.
- Marega, M., Grob, K., Moret, S., Conte, L., 2013. Phthalate analysis by gas chromatography-mass spectrometry: blank problems related to the syringe needle. *J. Chromatogr. A* 1273, 105–110.
- Masia, A., Moliner-Martinez, Y., Munoz-Ortuno, M., Pico, Y., Campins-Falco, P., 2013. Multiresidue analysis of organic pollutants by in-tube solid phase microextraction coupled to ultra-high pressure liquid chromatography-electrospray-tandem mass spectrometry. *J. Chromatogr. A* 1306, 1–11.
- Maycock, D., Fawell, J., Merrington, G., Watts, C., 2008. Review of England and Wales monitoring data for which a national or international standard has been set. *Guidel. Drinking Water Qual.* 1–148.
- McDowell, D.C., Metcalfe, C.D., 2001. Phthalate esters in sediments near a sewage treatment plant outflow in Hamilton Harbour, Ontario: SFE extraction and environmental distribution. *J. Great Lakes Res.* 27, 3–9.
- Meng, X.Z., Wang, Y., Xiang, N., Chen, L., Liu, Z., Wu, B., Dai, X., Zhang, Y.H., Xie, Z., Ebinghaus, R., 2014. Flow of sewage sludge-borne phthalate esters (PAEs) from human release to human intake: implication for risk assessment of sludge applied to soil. *Sci. Total Environ.* 476–477, 242–249.
- Mousa, A., Basheer, C., Al-Arfaj, A.R., 2013. Application of electro-enhanced solid-phase microextraction for determination of phthalate esters and bisphenol A in blood and seawater samples. *Talanta* 115, 308–313.
- Muñoz-Ortuno, M., Argente-García, A., Moliner-Martinez, Y., Verdú-Andrés, J., Hernández-Hernández, R., Picher, M.T., Campins-Falcó, P., 2014. A cost-effective method for estimating di(2-ethylhexyl)phthalate in coastal sediments. *J. Chromatogr. A* 1324, 57–62.
- Net, S., Dumoulin, D., El-Osmani, R., Rabodonirina, S., Ouddane, B., 2014. Case study of PAHs, Me-PAHs, PCBs, phthalates and pesticides contamination in the Somme River water, France. *Int. J. Environ. Res. & Public Health* 8 (4), 1159–1170.
- Net, S., Sempéré, R., Delmont, A., Paluselli, A., Ouddane, B., 2015. Occurrence, fate and behavior and ecotoxicological state of phthalates in different environmental matrices. *Environ. Sci. Technol.* (submitted for publication).
- NIOSH (Institute for Occupational Safety and Health), 1994. Diethyl phthalate and di(2-ethylhexyl) phthalate: Method 5020.2, In *Diethyl phthalate and di(2-ethylhexyl) phthalate: Method 5020.2*. In: Cassinelli, M., O'Connor, P.F. (Eds.), NIOSH manual of analytical methods (NMAM), 4th ed.
- Peng, X., Feng, L., Li, X., 2013. Pathway of diethyl phthalate photolysis in sea-water determined by gas chromatography-mass spectrometry and compound-specific isotope analysis. *Chemosphere* 90 (2), 220–226.
- Prokúpková, G., Holodová, K., Poušta, J., Hajšlová, J., 2002. Development of a solid-phase microextraction method for the determination of phthalic acid esters in water. *Anal. Chim. Acta* 457, 211–223.
- Qiao, J., Wang, M., Yan, H., Yang, G., 2014. Dispersive solid-phase extraction based on magnetic dummy molecularly imprinted microspheres for selective screening of phthalates in plastic bottled beverages. *J. Agric. Food Chem.* 62 (13), 2782–2789.
- Reid, A.M., Brougham, C.A., Fogarty, A.M., Roche, J.J., 2009. Accelerated solvent-based extraction and enrichment of selected plasticizers and 4-nonylphenol, and extraction of tin from organotin sources in sediments, sludges and leachate soils. *Anal. Chim. Acta* 634 (2), 197–204.
- Rhind, S.M., Kyle, C.E., Kerr, C., Osprey, M., Zhang, Z.L., Duff, E.I., Lilly, A., Nolan, A., Hudson, G., Towers, W., Bell, J., Coull, M., McKenzie, C., 2013. Concentrations and geographic distribution of selected organic pollutants in Scottish surface soils. *Environ. Pollut.* 182, 15–27.
- Schantz, M., 2006. Pressurized liquid extraction in environmental analysis. *Anal. Bioanal. Chem.* 386, 1043–1047.
- Schiedek, T., 1995. Impact of plasticizers (phthalic acid esters) on soil and groundwater quality. *Groundw. Qual. Remediat. Prot.* 255, 149–156.
- Schreiber, A., Fu, F., Yang, O., Wan, E., Gu, E., Le Blanc, Y., 2011. Increasing Selectivity and Confidence in Detection When Analyzing Phthalates by LC-MS/MS. AB Sciex (AN 369041 1–01).
- Segura, P.A., Yargeau, V., Gagnon, C., 2012. On the application of high-resolution mass spectrometry to environmental analysis. *Int. J. Environ. Pollut. Remediat.* 1, 82–89.
- Serôdio, P., Nogueira, J.M.F., 2006. Considerations on ultra-trace analysis of phthalates in drinking water. *Water Res.* 40, 2572–2582.
- Staples, C.A., Adams, W.J., Parkerton, T.F., Gorsuch, W., 1997. Aquatic toxicity of eighteen phthalate esters. *Environ. Toxicol. Chem.* 16, 875–891.
- Steele, H.L., Hardy, J.K., 2009a. Solventless sampling of phthalate esters. *J. Environ. Sci. Health Part A Toxic/Hazard. Subst. Environ. Eng.* 44 (12), 1233–1236.
- Steele, H.L., Hardy, J.K., 2009b. Permeation sampling of phthalate esters in water. *J. Environ. Sci. Health Part A Toxic/Hazard. Subst. Environ. Eng.* 44 (4), 340–345.
- Sun, J., Huang, J., Zhang, A., Liu, W., Cheng, W., 2013a. Occurrence of phthalate esters in sediments in Qiantang River, China and inference with urbanization and river flow regime. *J. Hazard. Mater.* 248–249, 142–149.
- Sun, H., Jiang, F., Chen, L., Zheng, J., Wu, Y., Liu, M., 2013b. Determination of three phthalate esters in environmental samples by coal cinder extraction and cyclo-dextrin modified micellar electrokinetic chromatography. *J. Chromatogr. Sci.* 1–6.
- Takeda, S., Wakida, S.-I., Yamane, M., Kawahara, A., Higashi, K., 1993. Migration behavior of phthalate esters in micellar electrokinetic chromatography with or without added methanol. *Anal. Chem.* 65 (18), 2489–2492.
- Tan, B.L.L., Hawker, D.W., Müller, J.F., Leush, F.D.L., Tremblay, L.A., Chapman, H.F., 2008. Stir bar sorptive extraction and trace analysis of selected endocrine disruptors in water, biosolids and sludge samples by thermal desorption with gas chromatography-mass spectrometry. *Water Res.* 42, 404–412.
- Teil, M.J., Blanchard, M., Dargnat, C., Larcher-Tiphagne, K., Chevreuil, M., 2007a. Occurrence of phthalate diesters in rivers of the Paris district (France). *Hydrol. Process.* 21, 2515–2525.
- Teil, M.J., Blanchard, M., Dargnat, C., Tiphagne, K., Desportes, A., Chevreuil, M., 2007b. Dynamique des apports et comportement de perturbateurs endocriniens et de médicamenteux dans les réseaux d'assainissement: exemple des phthalates et des antibiotiques - Caractérisation des phthalates dans les échantillons de station d'épuration. Rapport GDR PIREN-SEINE 2006, Axe Thématique IV (11 pp.).
- Thermo Scientific, 2013. Enhanced sensitivity to detect phthalates by FT-IR. Application Note 52157.
- Tienpont, B., 2004. Determination of Phthalates in Environmental, Food and Biomaterials—An Analytical Challenge (Thesis).
- Toda, H., Sako, K., Yamagoe, Y., Nakamura, T., 2004. Simultaneous determination of phosphate esters and phthalate esters in clean room air and indoor air by gas chromatography-mass spectrometry. *Anal. Chim. Acta* 519, 213–218.
- Vikelsøe, J., Thomsen, M., Johansen, E., Carlsen, L., 1999. Phthalates and nonylphenols in soils. NERI Technical report No. 268, p. 129.
- Vikelsøe, J., Thomsen, M., Carlsen, L., 2002. Phthalates and nonylphenols in profiles of differently dressed soils. *Sci. Total Environ.* 296, 105–116.
- Wang, P., Wang, S.-L., Fan, C.Q., 2008. Atmospheric distribution of particulate- and gas-phase phthalic ester (PAEs) in a Metropolitan City, Nanjing, East China. *Chemosphere* 72 (10), 1567–1572.
- Wang, J., Luo, Y., Teng, Y., Ma, W., Christie, P., Li, Z., 2013. Soil contamination by phthalate esters in Chinese intensive vegetable production systems with different modes of use of plastic film. *Environ. Pollut.* 180, 265–273.
- Wang, X., Tao, W., Xu, Y., Feng, J., Wang, F., 2014. Indoor phthalate concentration and exposure in residential and office buildings in Xi'an, China. *Atmos. Environ.* 87, 146–152.
- Warden, J., 2007. Comparison of different PTV injection modes for the detection of phthalates in drinking water. LC-GC Europe 20(3), pp. 14–16 (Applications book).
- WHO (World Health Organization), 2004. 3rd ed. Guidelines for Drinking-water Quality vol. 1 (Geneva).

- Wu, X., Hong, H., Liu, X., Guan, W., Meng, L., Ye, Y., Ma, Y., 2013a. Graphene-dispersive solid-phase extraction of phthalate acid esters from environmental water. *Sci. Total Environ.* 444, 224–230.
- Wu, M.-H., Shi, Q.-H., Xu, G., Qian, D.-Y., 2013b. Solid phase microextraction detection for phthalate esters in environmental water. *J. Shanghai Univ.* 19 (6), 611–614.
- Wurl, O., 2009. Practical Guidelines for the Analysis of Seawater, Book, Ed. CRC Press Inc., p. 408.
- Xie, Z., Ebinghaus, R., Temme, C., Caba, A., Ruck, W., 2005. Atmospheric concentrations and air-sea exchanges of phthalates in the North Sea (German Bight). *Atmos. Environ.* 39, 3209–3219.
- Xie, Z., Ebinghaus, R., Temme, C., Lohmann, R., Cara, A., Ruck, W., 2007. Occurrence and air-sea exchange of phthalates in the Arctic. *Environ. Sci. Technol.* 41 (13), 4555–4560.
- Xu, G., Li, F.S., Wang, Q.H., 2008. Occurrence and degradation characteristics of dibutyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DEHP) in typical agricultural soils of China. *Sci. Total Environ.* 393 (2), 333–340.
- Xue, L., Zhang, D., Wang, T., Wang, X.-M., Du, X., 2014. Dispersive liquid-liquid microextraction followed by high performance liquid chromatography for determination of phthalic esters in environmental water samples. *Anal. Methods* 6, 1121–1127.
- Yan, H., Liu, B., Du, J., Row, K.H., 2010. Simultaneous determination of four phthalate esters in bottled water using ultrasound-assisted dispersive liquid-liquid microextraction followed by GC-FID detection. *Analyst* 135, 2585–2590.
- Yang, G.C.C., Yen, C.H., Wang, C.L., 2014. Monitoring and removal of residual phthalate esters and pharmaceuticals in the drinking water of Kaohsiung City, Taiwan. *J. Hazard. Mater.* 277, 57–61.
- Zeng, F., Cui, K., Xie, Z., Liu, M., Li, Y., Lin, Y., Zeng, Z., Li, F., 2008a. Occurrence of phthalate esters in water and sediment of urban lakes in a subtropical city, Guangzhou, South China. *Environ. Int.* 34, 372–380.
- Zeng, F., Cui, K., Xie, Z., Wu, L., Liu, M., Sun, G., Lin, Y., Luo, D., Zeng, Z., 2008b. Phthalate esters (PAEs): emerging organic contaminants in agricultural soils in peri-urban areas around Guangzhou, China. *Environ. Pollut.* 156, 425–434.
- Zeng, F., Cui, K.Y., Xie, Z.Y., Wu, L.N., Luo, D.L., Chen, L.X., Lin, Y.J., Liu, M., Sun, G.X., 2009. Distribution of phthalate esters in urban soils of subtropical city, Guangzhou, China. *J. Hazard. Mater.* 164 (2), 1171–1178.
- Zeng, F., Lin, Y., Cui, K., Wen, J., Ma, Y., Chen, H., Zhu, F., Ma, Z., Zeng, Z., 2010. Atmospheric deposition of phthalate esters in a subtropical city. *Atmos. Environ.* 44 (6), 834–840.
- Zhang, X., Chen, Z., 2014. Observing phthalate leaching from plasticized polymer films at the molecular level. *Langmuir* 30 (17), 4933–4944.
- Zhang, A.J., Perati, P., Lopez, L., 2013. Automated Solid-phase Extraction of Phthalates for Drinking Water Samples. Thermo Fisher Scientific (Poster Note PN70733).
- Zheng, X., Zhang, B.T., Teng, Y., 2014. Distribution of phthalate acid esters in lakes of Beijing and its relationship with anthropogenic activities. *Sci. Total Environ.* 476–477, 107–113.

Occurrence, Fate, Behavior and Ecotoxicological State of Phthalates in Different Environmental Matrices

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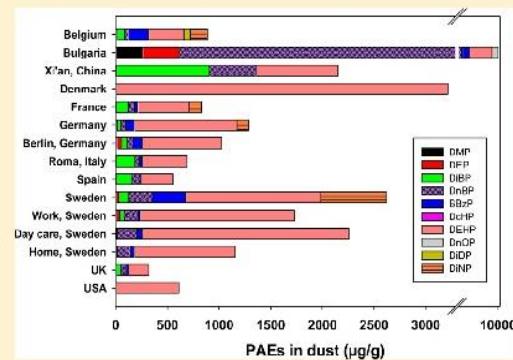
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Supporting Information

ABSTRACT: Because of their large and widespread application, phthalates or phthalic acid esters (PAEs) are ubiquitous in all the environmental compartments. They have been widely detected throughout the worldwide environment. Indoor air where people spend 65–90% of their time is also highly contaminated by various PAEs released from plastics, consumer products as well as ambient suspended particulate matter. Because of their widespread application, PAEs are the most common chemicals that humans are in contact with daily. Based on various exposure mechanisms, including the ingestion of food, drinking water, dust/soil, air inhalation and dermal exposure the daily intake of PAEs may reach values as high as 70 µg/kg/day. PAEs are involved in endocrine disrupting effects, namely, upon reproductive physiology in different species of fish and mammals. They also present a variety of additional toxic effects for many other species including terrestrial and aquatic fauna and flora. Therefore, their presence in the environment has attracted considerable attention due to their potential impacts on ecosystem functioning and on public health. This paper is a synthesis of the extensive literature data on behavior, transport, fate and ecotoxicological state of PAEs in environmental matrices: air, water, sediment, sludge, wastewater, soil, and biota. First, the origins and physicochemical properties of PAEs that control the behavior, transport and fate in the environment are reviewed. Second, the compilation of data on transport and fate, adverse environmental and human health effects, legislation, restrictions, and ecotoxicological state of the environment based on PAEs is presented.



INTRODUCTION

PAEs are widely used in the manufacture and processing of plastic products as plasticizers. Production of PAEs began in the 1920s and has intensified since 1950, when these compounds were used to impart flexibility to polyvinyl chloride (PVC) resins.¹ To date, plasticizers are used in a very broad range of industrial applications.^{2,3} Not chemically but only physically bound to the polymeric matrix, PAEs can easily be released into the environment directly and/or indirectly, during manufacture, use, and disposal.⁴ To date, PAEs are ubiquitous in the environment, including atmospheric aerosols,^{5,6} sludge from sewage and wastewater treatment,⁷ river and marine waters/⁸ sediments,^{5,8} drinking water,⁹ biota, and air.^{10,12}

Some PAEs are endocrine disrupting chemicals, and their environmental behavior has attracted considerable attention due to their potential impact on ecosystem functioning and on public health. Consequently, six of them have been placed on the priority pollutant list of the United States Environmental Protection Agency (U.S. EPA), the European Union (EU), and on the list of priority pollutants in Chinese waters,^{13,14} and the concentrations of PAEs have been regulated for water consumption. The use of PAEs is now subject to stricter

control and some have been prohibited or their reduction in numerous products has been recommended. A list of acronyms and abbreviations used in this review is provided in Table 1S in Supporting Information (SI).

I. Phthalates. I.1. Origin. Although di-*n*-butyl phthalate (DnBP) and di(2-ethylhexyl) phthalate (DEHP) can be synthesized by red algae¹⁵ their natural origins are negligible compared with PAEs produced by human activities. Industrial use of PAEs that began in the 1930s is very broad on the worldwide scale.¹⁶ To date, worldwide annual production of plastics has reached a level of 150 million tons, and 6–8 million tons of PAEs are consumed each year. European consumption of PAEs accounts for approximately 1 million tons.^{17,18} The production of PAEs increased from 1.8 million tons in 1975¹⁹ to more than 8 million tons in 2011.¹⁸ PAEs are used in a very broad range of applications,^{2,3} and their content can be up to 10–60% by weight.^{20,21} PAEs are present in many materials or

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Table 1. Physicochemical Properties of Some PAEs

PAEs	CAS N°	Mw (g/mol)	carbone atom per chain	Sw ²⁵ (mg/L)	V _P (Pa) ²⁵	logK _{OW} ²⁵	logK _{O_A} ²⁵	logB _{S_S} ²⁵	K _{AW}	H ²⁵ (Pa·m ³ / mol)	K _{oc} (L/kg) ^{10,24} (soil/ sediment)	K _{oc} (L/kg) ^{10,24} SSM
dimethyl phthalate	DMP	131–11–3	194.2	1	52.20	0.263	1.61	7.01	–5.40	9.78 × 10 ^{–3}	55–360	<5 × 10 ⁴
diethyl phthalate	DEP	84–66–2	222.2	2	59.1	6.48 × 10 ^{–2}	2.54	7.55	–5.01	2.44 × 10 ^{–2}	69–1726	79,400
dialyl phthalate	DAIP	131–17–9	246.3	3	165	2.71 × 10 ^{–2}	3.11	7.87	–4.76	4.28 × 10 ^{–2}		
di-n-propyl phthalate	DnPrP	131–16–8	250.3	3	77	1.74 × 10 ^{–2}	3.40	8.04	–4.64	5.69 × 10 ^{–2}		
di-n-butyl phthalate	DnBP	84–74–2	278.4	4	9.9	4.73 × 10 ^{–3}	4.27	8.54	–4.27	0.133	1375–14,900	1230–158,500
diisobutyl phthalate	DiBP	84–69–5	278.4	4	9.9	4.73 × 10 ^{–3}	4.27	8.54	–4.27	0.133		1020
di-n-pentyl phthalate	DnPeP	131–18–0	306.4	5	1.3	1.28 × 10 ^{–3}	5.12	9.03	–3.91	0.302		
butyl benzyl phthalate	BBzP	85–68–7	312.4	4, 6	3.8	2.49 × 10 ^{–3}	4.70	8.78	–4.08	0.205	9 × 10 ³ –17 × 10 ³	1 × 10 ⁵
di-n-hexyl phthalate	DnHxP	84–75–3	334.4	6	0.159	3.45 × 10 ^{–4}	6.00	9.53	–3.53	0.726	52,600	
butyl 2-ethylhexyl phthalate	BOP	85–69–8	334.4	4, 8	0.385	5.37 × 10 ^{–4}	5.64	9.37	–3.73	0.466		
di-n-heptyl phthalate	DiHppP	41451–28–9	362.5	7	2.00 × 10 ^{–2}	9.33 × 10 ^{–5}	6.87	10.04	–3.17	1.69		
di (<i>n</i> -hexyl, <i>n</i> -octyl, <i>n</i> -decyl) phthalate	610P	68–648–93–1	557	6, 8, 10	8.76 × 10 ^{–4}	1.31 × 10 ^{–5}	8.17	10.78	–2.61	6.05		
di(2-ethylhexyl) phthalate	DEHP	117–81–7	390.6	8	2.49 × 10 ^{–3}	2.52 × 10 ^{–5}	7.73	10.53	–2.80	3.95	87,420–51 × 10 ⁴	22 × 10 ³ –1 × 10 ⁶
di- <i>n</i> -octyl phthalate	DnOP	117–84–0	390.6	8	2.49 × 10 ^{–3}	2.52 × 10 ^{–5}	7.73	10.53	–2.80	3.95		2 × 10 ⁶
diisooctyl phthalate	DiOP	27554–26–3	390.6	8	2.49 × 10 ^{–3}	2.52 × 10 ^{–5}	7.73	10.53	–2.80	3.95		
diisooctyl phthalate	DiNP	28553–12–0	418.6	9	3.08 × 10 ^{–4}	6.81 × 10 ^{–6}	8.60	11.03	–2.43	9.26		
di- <i>n</i> -anonyl phthalate	DnNP	84–76–4	418.6	9	3.08 × 10 ^{–4}	6.81 × 10 ^{–6}	8.60	11.03	–2.43	9.26		
di- <i>n</i> -decyt phthalate	DnDP	84–75–5	446.7	10	3.08 × 10 ^{–4}	6.81 × 10 ^{–6}	8.60	11.03	–2.43	9.26		
diisodecyl phthalate	DiDP	26761–40–0	446.7	10	3.81 × 10 ^{–4}	1.84 × 10 ^{–6}	9.46	11.52	–2.06	21.6		
di (heptyl, nonyl, undecyl) phthalate	D711P	68515–42–4	557	7, 9, 11	3.08 × 10 ^{–4}	6.81 × 10 ^{–6}	8.60	11.03	–2.43	9.26		
diundecyl phthalate	DUP	3648–20–2	474.7	11	4.41 × 10 ^{–6}	4.97 × 10 ^{–7}	10.33	12.02	–1.69	50.5		
ditridecyl phthalate	DTDP	119–06–2	530.8	13	7.00 × 10 ^{–8}	3.63 × 10 ^{–8}	12.06	13.01	–0.95	275	1.2 × 10 ⁶	

products including PVC products, building materials (paint, adhesive, wall covering), personal-care products (perfume, eye shadow, moisturizer, nail polish, deodorizer, liquid soap, and hair spray), medical devices, detergents and surfactants, packaging, children's toys, printing inks and coatings, pharmaceuticals and food products, textiles, household applications such as shower curtains, floor tiles, food containers and wrappers, cleaning materials.

Low molecular weight PAEs such as dimethyl phthalate (DMP), diethyl phthalate (DEP), and DnBP are components of industrial solvents, solvents in perfumes, adhesives, waxes, inks, pharmaceutical products, insecticide materials, and cosmetics.²² DMP and DEP allow perfume fragrances to evaporate more slowly, lengthening the duration of the scent, and a small amount of DnBP gives nail polish a chip-resistant property. PAEs with longer alkyl chains are used as plasticizers in the polymer industry to improve flexibility, workability, and general handling properties, and 80% of PAEs are used for this purpose.²³ The dispersion of PAEs in the environment can occur at all stages of their use, from their synthesis to their transformation or degradation.

I.2. Physicochemical Properties. A few key physicochemical properties including water solubility (S_w), vapor pressure (Vp), Henry's constant (H), air–water partitioning (K_{AW}), octanol-air partition (K_{OA}), and octanol–water partitioning (K_{OW}), organic carbon partitioning (K_{OC}) control both the behavior, transport and fate in the environment and also the exchanges between the different reservoirs such as atmosphere, lithosphere, hydrosphere, and biosphere.^{10,24,25} S_w controls the distribution between water, soil/sediment, and atmosphere. Table 1 shows that S_w of PAEs are low and decrease with the increase in the carbon chain length. K_{OW} translates the affinity of an organic compound with the lipid molecules in living organisms. K_{OW} has been used to predict the tendency of a contaminant to concentrate in aquatic organisms.²⁶ Log K_{OW} increases with increasing alkyl chain length, indicating greater bioconcentration (Table 1). Vp declines more than 7 orders of magnitude with increasing alkyl chain length. Moreover, H indicates the tendency of a substance to escape from water into air. H can be calculated from Vp and S_w . Compounds with H values $\sim 1.01 \times 10^{-2}$ Pa·m³/mol are generally considered to have negligible volatility. For higher alkyl chains ranging from 4 to 13 carbon atoms, H values range from 0.133 to 275 Pa·m³/mol which indicates that transfer from the aqueous phase to the gas phase is important (Table 1). K_{OC} of PAEs range from 55 to 360 for DMP to 1.2×10^6 for ditridecyl phthalate (DTDP) in soil/sediment and from 1020 for diisobutyl phthalate (DiBP) to 2×10^6 for di-n-octyl phthalate (DnOP) in suspended solids matter (SSM) (Table 1). K_{AW} and K_{OA} partition coefficients are among the key factors controlling the distribution of PAEs in different matrices in the environment. Log K_{AW} and log K_{OA} increase with the increasing alkyl chain length. High values of log K_{OA} suggest that PAEs present in the atmosphere will be appreciably sorbed to aerosol particles and to soil and vegetation, whereas high values of log K_{AW} suggest that PAEs potentially evaporate more rapidly from water. However, rapid evaporation from water could be mitigated by sorption to SSM in the water.²⁵ The lower molecular weight PAEs are quite volatile and have very low log K_{AW} values, so they will volatilize rapidly from the pure state but only very slowly from aqueous solution.²⁵

II. Environmental Transport, Fate, Behavior. PAEs can be removed from environmental matrices by some processes

that include microbiological transformation and degradation, volatilization, photo-oxidation, photolysis, sorption and biological uptake.^{10,24,27,28} Field and laboratory studies have shown that aerobic or anaerobic microorganisms from various habitats (water, sediment, soil) are able to degrade PAEs. However, the half-lives of PAEs depend strongly on the condition of each habitat such as oxidant, microbial density, and sunlight irradiation.

Special attention should be focused on quality control/assurance (QC/QA) when quantifying PAEs concentration in environmental matrices. Literature data showed that one of the main problems for PAEs analysis is the risk of contamination, as PAEs are ubiquitous and could be present in water, organic solvents, air, glassware and in the plastic material used for the analysis. The primary issue for the quantification of PAEs is not the trace analysis itself but the risk of contaminating the environmental samples during the analytical procedure, which can often lead to false positive or overestimated result. Thus, special attention should be focused on the quality control and quality assurance when determined PAEs concentration. QC should be routinely implemented to minimize the risk of sample contamination. The blank should be free from any targeted PAEs to ensure that no significant contamination occurs during the whole procedure and ensure thus the reliable results. If PAEs are present at low concentrations, which account for less than a few % of those in the targeted sample, it is not necessary to subtract them from the sample measurement. However, if they are present at significant levels, they must be eliminated or subtracted from the sample measurement.²⁹

II.1. Air. PAEs are ubiquitous in the atmosphere, including air indoors where people spend 65–90% of their time.^{30,31} Indoor environments increase the lifetime of pollutants adsorbed to particles and dust by minimizing or eliminating the natural decomposition processes catalyzed by sunlight and rain.³² Indeed, direct photolysis and photodegradation are major reaction pathways of PAEs responsible for PAE decay in the atmosphere. DEP and butyl cyclohexane phthalate (BCP) react photochemically with OH[•] with an estimated half-life of 22.2 and 23 h, respectively.³³ For DMP and DEHP, photolysis is important in the atmosphere where the indirect process of OH[•] attack predominates. The half-lives of individual PAEs were estimated to be several days (see Supporting Information Table 4S)^{34,34}. Half-life of photo-oxidation of PAEs increases with the increasing alkyl chain length and OH[•] concentration. DnBP and DEHP have been used as softeners in water-based synthetic paintings,³⁵ so these compounds can be released into the atmosphere from painted surfaces³⁶ or photodegraded on mural painting surfaces under UV light irradiation in a dozen of hours (Supporting Information Table 4S).¹¹ On a mural painting, 68% of the total PAEs were degraded by irradiation only for a time period of 8 h.

PAEs can also be removed from the atmosphere by wet and dry deposition. PAEs with short carbon chains (<6) are present mainly in the gas phase, while PAEs with longer chains are mainly adsorbed on the particles.^{12,37} Wet deposition is an important source of removal of short alkyl chains while dry deposition is an important source of removal of PAEs with long alkyl chains. Depositional fluxes of Σ_{16} PAEs were estimated from 3.41 to 190 µg·m⁻²/day for strong anthropogenic activity zones. This deposition process is initiated preliminarily by the association of PAEs with atmospheric particles. Among the 16 PAEs, DiBP, DnBP, and DEHP were the dominant ones.³⁸

Atmospheric transport and deposition of PAEs can also be a significant process for their occurrence in soil and in the remote Atlantic and Arctic Oceans. The air–sea vapor exchange is an important process that intervenes in the mass balance of PAEs in the North Sea.^{36,39} The concentrations of PAEs were < n.d. to 3.4 ng/m³ in the atmosphere and < n.d. to 6.6 ng/L in the water phase. The average of the air–sea exchange fluxes was estimated at –338 ng/m²/day for DnBP and –13 ng/m²/day for BBzP, suggesting a net deposition. However, the air–sea exchange fluxes of DEHP ranged from –95 to 686 ng/m²/day with average of 53 ng/m²/day, indicating that DEHP can be both deposited and volatilized from the surface water but volatilization is dominant. Volatilization and deposition process of PAEs in air–sea interface depend on the *H*. PAEs with low *H* values such as DnBP and BBzP were preferentially deposited on sea surface, whereas DEHP with high *H* was dominated by volatilization. Air–sea exchanges of PAEs have also been estimated for the Norwegian, the Greenland, and the Arctic seas⁵ with total concentrations of 30–5030 pg/L and 1110–3090 pg/m³ in the aqueous dissolved phase and the atmospheric gas phase, respectively. For DEHP, deposition dominated the air–sea gas exchange, while volatilization from seawater took place in the near-coast environment. The estimated net gas deposition of DEHP was 5, 30, and 190 tons per year for the Norwegian, the Greenland and the Arctic Seas, respectively,⁵ suggesting that atmospheric transport and deposition of PAEs is a significant process for their occurrence in the remote Atlantic and Arctic Oceans.

II.2. Water. PAEs can be accumulated in the hydrosphere via numerous processes, namely, atmospheric deposition, leaching, and drainage.^{5,40–42} Hydrolysis of PAEs is negligible at neutral pH with aqueous hydrolysis half-lives in order of several years and up to more than 100 years for DnOP, DiOP and DEHP (see Supporting Information Table 4S).⁴³ UVB can penetrate surface water and induce photolysis of PAEs either directly by direct absorption of radiation or indirectly by the oxidation reactions of reactive chemical species such as OH[•], CO₃²⁻, ¹O₂, O₂²⁻, and chromophoric dissolved organic matter (CDOM) triplet states produced in surface waters by sunlight illumination of photoactive molecules (photosensitizers) such as nitrate, nitrite, and CDOM.^{44,45} Under these conditions, aqueous half-lives of PAEs decrease considerably and ranging between 2.4 and 12 years and 0.12–1.5 years for DEP and DEHP, respectively.⁴⁶ Under light irradiation, PAEs react with photogenerated OH[•] to form 4-hydroxy phthalate esters that present potential toxicity.²⁷

Biodegradation can be the most important process for the removal of PAEs from water. Indeed, PAEs can be accumulated and degraded rapidly by microorganism under both aerobic and anaerobic conditions. In surface waters (seawater or freshwater) under aerobic conditions excluding low temperatures (<5 °C) and poor nutritional conditions, the half-lives of primary degradation vary from less than 1 day to 2 weeks, and the half-lives for complete mineralization are approximately 10 times longer.¹⁰ However, Cousins and Palm⁴⁷ have reported the water half-life of DEHP and DiNP at 360 and 900 h, respectively (Supporting Information Table 4S). The biodegradation of PAEs varies depending on the density and type of species. DEP was detected in aquatic organisms with a modest level,^{48,49} and it is unlikely to biomagnify up the food chain because it is degraded by organisms.⁵⁰ The order of biodegradation of PAEs was algae < cnidarians < molluscs < crustaceans < fish.⁵¹ The half-life of DEP in fish tissue is 1–

2 days.^{52,53} Although DEHP can be volatilized from seawater in the near-coast environment, global tendencies suggest that deposition dominates the air–sea exchange of PAEs.^{5,39}

II.3. Sediment. Few studies have focused on the biodegradability of PAEs in river and marine sediment. The kinetics of anaerobic degradation of PAEs in river sediment depends on various factors including pH, temperature, surfactants, pollutants, or microbial inhibitors. Microbial action is thought to be the principal mechanism for PAEs degradation in both aquatic and terrestrial systems (e.g., sewage, soils, sediments, water).^{10,24} In mangrove sediments, under aerobic condition, the degradation half-lives of DnBP and DEHP were estimated to be only fews days (SI Table 4S). Similar half-lives of DEP, DnBP, and DEHP were found for river sediment under anaerobic conditions (30 °C with pH 7)⁵⁶ (Supporting Information Table 4S). For river sediment under anaerobic conditions, DnBP, DPhP, and BBzP might be degraded rapidly whereas DEP and DEHP degradation rates were very low.^{54,55} Primary biodegradation rates in sediments were estimated at 3–4 weeks and 3 months, respectively, for DnBP and DEHP.^{57,58} Sediment half-life of DEHP and DiNP were estimated at less than 1 year⁴⁷ (Supporting Information Table 4S). Otton et al.⁵⁹ measured the biodegradation kinetics of eight monoalkyl phthalate esters (MPEs) in marine and freshwater sediments collected from three locations in the Greater Vancouver area. The studied MPEs were degraded in both marine and freshwater sediments at 22 °C with half-lives ranging between 16 and 39 h. In marine sediments, half-lives of these eight MPEs were found in the ranges of 18 ± 4–35 ± 10 h, which is similar to the range of half-lives found in freshwater sediment (16 ± 2–39 ± 6 h).⁵⁹ These results suggest that the half-life of PAEs increased strongly (ca. 8-fold) with temperatures in the range of 5–22 °C and did not depend on alkyl chain length.

II.4. Soil. Atmospheric deposition and sewage sludge used as soil amendment are the important sources of PAEs in soil, especially in agricultural areas. The most abundant PAEs in soil are DiBP, DnBP and DEHP, which represent 74.2–99.8% of \sum_{16} PAEs.⁴¹ In soil, the half-lives of PAEs vary from 1 to 75 days, much lower than the half-life found for polychlorobiphenyls (7–25 years) under the same conditions.¹⁷ DEP was not expected to persist in the environment with a degradation half-life in soil of approximately 0.75 days at 20 °C, whereas only 10% of DEHP was removed from the same soil after 70 days incubation.⁶⁰ However, more recently, Cousins and Palm⁴⁷ have reported the soil half-life of DEHP and DiNP at 30 and 75 days, respectively.

Depending on meteorological conditions, PAEs in soil can also contribute to water or atmospheric pollution by evaporation, leaching, deposition and drainage,^{40–42} consequently modifying their concentration and fate. Abiotic degradation experiments of DnBP and DEHP indicated that only 0.60–2.91% were degraded during 30 days which is much slower than their biodegradation,⁴⁰ depending on the type of soil. Half-lives of DnBP and DEHP were estimated at 7.8 ± 0.1 and 26.3 ± 0.7 days in black soil versus 8.3 ± 0.2 and 30.8 ± 0.7 days in fluvo-aquic soil likely due to the higher density of microorganisms in the former case.⁴⁰

III. Impact on Biosphere and Regulation. The toxicity of PAEs remains under debate because the debate is characterized by tension between the commercial importance of PAEs and their impact on human health and on the environment. However, a large variety of field and laboratory studies reveals

high exposure and evident toxicity of PAEs affecting human health and other biospheres.

III.1. Human Exposure and Health Impact. For humans, the potential pathways for exposure to PAEs are inhalation, contaminated foodstuffs, drinking water or dermal contact with cosmetics containing PAEs.^{22,61,62} Thus, the study of PAEs in air, foodstuffs, drink and other products in human life has been paid more attention.^{63–65} Concentration levels of some individual PAE in milk, drink and food are presented in Table 2S in Supporting Information. The concentrations of individual PAE were detected from not detected level to few thousands ng/g dw and can be up to 24 µg/g dw in foods (DEHP in olive oil) and 215 µg/L in milk (Supporting Information Table 2S). The low molecular weight PAEs (DMP, DEP) were found at much lower levels compared to the high molecular weight PAEs and the highest was detected for DEHP (Supporting Information Table 2S). Total PAEs were detected in the range 0.133–3.804 µg/L in drinking water^{64,66} whereas $\sum_{17}^{} \text{PAEs}$ ranged from 0.29 to 23.77 µg/m³ in indoor air and within 123–9504 µg/g in the dust phase.¹² High levels of PAEs were detected in indoor air where people spent 65–90% of their time.^{30,31,67} The daily intake of six PAEs through air inhalation in indoor air has been estimated for infants, toddlers, children, teenagers and adults.⁶⁵ The total exposure doses were within the median daily intake of 155.850–664.332 ng/kg/day for $\sum_6^{} \text{PAEs}$, and the highest level was detected in infants. The daily exposure to indoor PAEs in indoor air and dust was estimated to range from 2.6 µg/kg/day (for adults) to 7.4 µg/kg/day (for toddlers).¹²

Overall, from various exposure pathways based on ingestion of food, drinking water, dust/soil, air inhalation, oral and dermal exposure pathways, daily intake of DMP, DEP, DnBP, DiBP, BBzP, and DEHP has been estimated in the range of 0.08–69.58 µg/kg/day.^{64,68} Food as the major contributor represents more than 67% of human exposure.⁶⁴ Consequently, PAEs and their metabolites have been detected in the human body (i.e., breast milk, blood, urine).^{69,70} In urine, metabolites of DnBP and DEHP were the main PAEs metabolites (PAEMs) detected.⁶⁹ Urinary PAEMs concentrations did not depend on sexes but they depend significantly on age.⁶⁹ The most frequently detected PAEs were reported to be DnBP and DEHP, found at highest levels in venous blood followed by breast milk, umbilical cord blood and urine; this order depends on metabolic factors.⁷⁰ When ingested through contaminated food, PAEs are converted by intestinal lipases to MPE, suggesting that DEHP was converted to mono-2-ethylhexyl phthalate (MEHP), while DnBP and BBzP were converted to the toxic metabolite monobenzyl phthalate (MBzP).^{71,72} High levels of four urinary phthalate metabolites have been reported.⁷³ Blood, serum and urine are the general choice of biological matrixes to assess the level of PAEs and their metabolites exposure in human. However, hair is an alternative biological specimen. In urine, MnBP was found to be the highest, followed by the metabolites MEP, MEHP and MiNP with, respectively, 71.42 ± 90.19 , 68.32 ± 43.74 , 15.37 ± 20.09 , and 1.47 ± 4.47 ng/mL. In epidemiological studies, DEHP has been associated with the development of wheezing and allergic airway diseases.^{74,75} Some PAEs are known to be toxic to the developing male reproductive system, and low-molecular-weight PAEs have been found to cause irritation of eyes, nose and throat.⁷⁶ Some PAEs (DnBP, DEHP) and their metabolite (MBP) can cause serious to human health. Given the high contributor of food (>67%) on human exposure,

stricter controls should be adopted for food to minimize the effect of PAEs on human health.

However, despite the cited adverse effects, DEHP could be beneficial for the patients with glioblastoma multiforme. Exposure of glioblastoma cells to DEHP revealed a significant inhibition of cell migration and invasion and led to a significant reduction in cell proliferation.⁷⁷

The main concerns related to exposure to PAEs in humans are the effects on reproduction, including fertility problems (effect of endocrine disruption), the development of newborns and carcinogenic character.³⁴ Howdeshell et al.⁷⁸ have reported that when PAEs were mixed with other antiandrogenic compounds, the effect cumulative on male reproductive tract development when administered during sexual differentiation in utero, potentially affecting human reproductive development were observed.

III.2. Potential Environmental Risk. Numerous studies have focused on the ecotoxicology of PAEs in biota including aquatic organisms and rodents. The latter is useful to estimate the toxicity to humans. Compilation data of DnBP and DEHP showed that aquatic organisms can accumulate high levels of PAEs.¹⁰ More recently, Vethak et al.⁷⁹ reported contamination of DEP and DEHP in freshwater species such as the bream at 1900–3120 µg/kg dw of DEHP and 720–800 µg/kg dw of DEP and for such marine species as the flounder, at 40–70 µg/kg dw of DEHP and 100–200 µg/kg dw of DEP.

PAEs are involved in endocrine disrupting effects, namely, upon reproductive physiology in different species of fish and mammals.⁸⁰ They are also toxic for many other species: for DEP, LC50/EC50 values ranged from 3 mg/L (marine alga) to 132 mg/L (protozoan), with the lowest NOECs for algae, invertebrates, and fish in the range of 1.7–4 mg/L.²⁴ PAEs acquire unequivocal estrogenic activity under light irradiation that leads to the formation of 4-hydroxy PAEs.²⁷ A recent study reported that exposure to DEHP from hatching to adulthood accelerated the start of spawning and decreased the egg production of exposed marine madaka females whereas exposure to both DEHP and MEHP resulted in a reduction of the fertilization rate of oocytes spawned by untreated females paired with treated males.⁸¹ DEHP induced histological changes in the testes and ovaries: the testes displayed a reduced number of spermatozoa, and the ovaries displayed an increased number of atretic follicles. The toxic effects of DEHP may be induced by both DEHP itself and DEHP metabolites, including MEHP.⁸¹ Using a 72 h zebrafish embryo toxicity test, LC50 values of BBzP, DnBP and a mixture of six PAEs were 0.72, 0.63, and 0.50 mg/L, respectively.⁸² DEHP, DiDP, DiNP, and DnOP did not cause more than 50% exposed embryo mortality even at high concentrations. The symptoms caused by PAEs in aquatic organisms were death, tail curvature, necrosis, cardio edema, and no touch response. This work highlighted the developmental toxicity of BBzP and DnBP and the estrogenic endocrine disrupting activity of BBzP, DnBP, DEHP, and DiNP on intact organisms.^{82,83} The effects of PAEs on wildlife are multiples. The estrogenic effect is one of the important biological impacts of PAEs on wildlife.^{80,83} They appear to act by interfering with the functioning of various hormone systems.⁸³ DMP, BBzP, DnBP, and DEHP have been shown to affect reproduction in annelids (both aquatic and terrestrial), molluscs, crustaceans, insects, fish and amphibians, to impair development in crustaceans and amphibians and to induce genetic aberrations.⁸³

Table 2. Regulations and Guidelines Applicable to Some PAEs Are Listed in Priority List^a

	soil (mg/kg dw)					
	DMP	DEP	DnBP	BBzP	DEHP	DnOP
ERLs (fresh wt) ²¹			0.7		1	
PER ⁹⁵	200	100	0.014		239	0.91
PGW ⁹⁵	27	7.1	8.1	122	435	
	water ($\mu\text{g}/\text{L}$)					
	DEP	DMP	DEHP	BBzP	DiBP	DnBP
drinking water standard			8, ⁸⁶ 6 ⁹⁶			
PEC			3.2 ⁹⁷			
EQS			0.17 ⁹⁸			
EQS (Max.) ⁹¹	200 (1000)	800 (4000)	20 (40)	20 (100)	8 (DiBP+ DnBP) (40)	
trigger values for freshwater (level of protection of species in %)*	3000 (99%) 3700 (95%) 4300 (90%) 5100 (80%)	900 (99%) 1000 (95%) 1100 (90%) 1300 (80%)	ID			9.9 (99%) 26 (95%) 40.2 (90%) 64.6 (80%)
Trigger values for marine water *	ID	ID	ID			ID
NQE for fresh, marine water			1.3 ⁹²			
ERLs			0.19 ²¹		10 ^{21,99}	
PGW						100 ¹⁰⁰
NOEC				77 ⁹⁷		22.8 ¹⁰¹
						500 ¹⁰²
	sediment (mg/kg dw)					
	DMP	DEP	BBzP	DnBP	DnOP	DEHP
ERLs ²¹				1.82		1
PNEC				3.1 ⁹⁰		
PEC						33.7 ¹⁰³
NOEC	0.53 ¹⁰⁵		0.049 ¹⁰⁴	2.2 ¹⁰⁵	0.58 ¹⁰⁵	0.47 ¹⁰⁵
MAEC (marine)		0.61 ¹⁰⁵	0.64 ¹⁰⁴	17 ¹⁰⁵	45 ¹⁰⁵	0.78 ¹⁰⁵
	sludge (mg/kg dw)					
land application					100 for DEHP ⁹³	

^aERLs: Environmental risk limit; EQS: environmental quality standards; PER: protection of ecological resources; PGW: protection of groundwater; PEC: predicted environmental concentration; NOEC: No observed effect concentration; MAEC: minor adverse effect concentration; ID: Insufficient data to derive a reliable trigger value. *Australian and New Zealand Guidelines for Fresh and Marine Water Quality. PAPER No. 4, Volume 1, The Guidelines (Chapters 1–7), October 2000.

Soil contaminated by PAEs also has a strong effect on the fauna and flora.⁶⁰ Some PAEs (DEHP, DnBP, BBzP) and their metabolites are estrogenic and exhibit adverse reproductive effects.⁸⁴ For rodents, PAEs can effect on testicular atrophy, liver damage, decreased fertility, decreased fetal weight, increased kidney weights and antiandrogenic activity. The LC50 of DEHP is estimated at 40 g/kg and for DEP at 9.4 g/kg.^{76,85} The effect of DEHP and its metabolites is notably important in young animals and prenatal exposure during pregnancy. DEHP also affects the female fertility. Oral exposure to DEHP in rodents induced fetal death and malformations. DEHP is categorized as Group-2B agent by International Agency for Research on Cancer (IARC) and confirmed to have 2.4 times higher risk causing female breast cancer.²³

III.3. Regulations and Restrictions. Due to their potential health and environmental risks, PAEs have become a matter of worldwide concern. The WHO recommends the concentration of DEHP in drinking water below 8 $\mu\text{g}/\text{L}$.⁸⁶ U.S., Australia, Japan, and New Zealand have recommended a DEHP maximum value in drinking water to be 6 $\mu\text{g}/\text{L}$, 9, 100, and 10 $\mu\text{g}/\text{L}$ respectively.⁸⁷ Serious questions have been raised about toy and childcare applications, especially if the toys are susceptible to being chewed or sucked by children.⁸⁸ The use of PAEs in toys or objects that can be placed in the mouth of

children is now restricted or prohibited in many countries such as UE, U.S., Canada, Argentina, Brazil, and Japan.^{89,90}

Due to the possible endocrine disrupting effects of PAEs, environmental quality standards (EQSs) based on the annual average concentrations in aquatic environments have been calculated,⁹¹ ranging from 20 $\mu\text{g}/\text{L}$ for DEHP to 800 $\mu\text{g}/\text{L}$ for DMP. However, EU proposed a guideline for environmental quality (NQE or Norme de qualité environnementale) of 1.3 $\mu\text{g}/\text{L}$ for DEHP in fresh and marine waters.⁹² While Australian and New Zealand guidelines proposed trigger values of 5100, 1300, and 64.6 $\mu\text{g}/\text{L}$ respectively for DMP, DEP, and BnBP as threshold values for the protections of 80% of species in freshwater (Table 2). However, for DEHP, there is insufficient data to derive a reliable trigger value neither in fresh and marine water (Table 2). The limit values established for DEHP in sludge for disposal onto farmland is proposed at 100 mg/kg dw,⁹³ while Danish Ministerial fixed the value at 50 mg/kg dw.⁹⁴ For natural sediment, Working Guidelines have been set for some PAEs (Table 2). The EU has included DnBP and DEHP in the list of substances suspected to cause endocrine disruption.¹³ DEHP has been classified by the EU as a substance causing toxic effects on fertility and development in humans. To minimize the health and environmental risk, DEHP has been replaced by DiNP and DiDP, which are

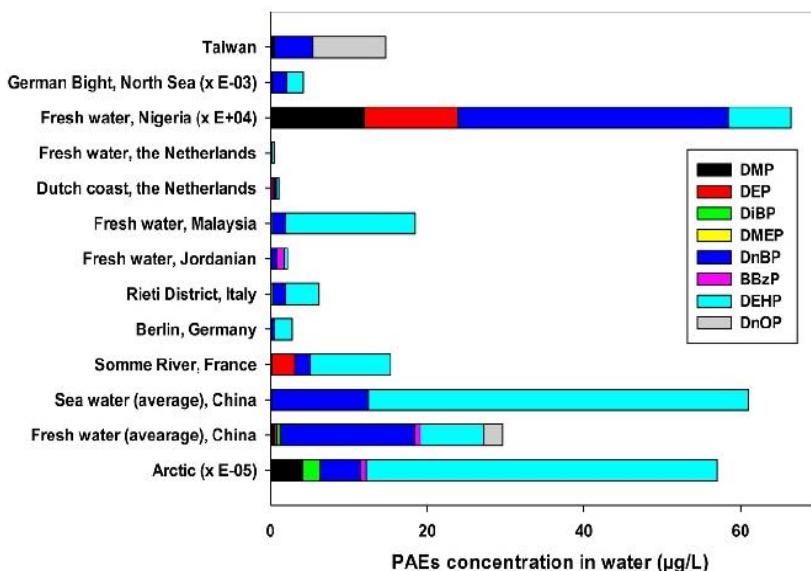


Figure 1. Composition of PAEs in different types of fresh and marine water for worldwide scale; detail values and references are given on Supporting Information Table 2S.

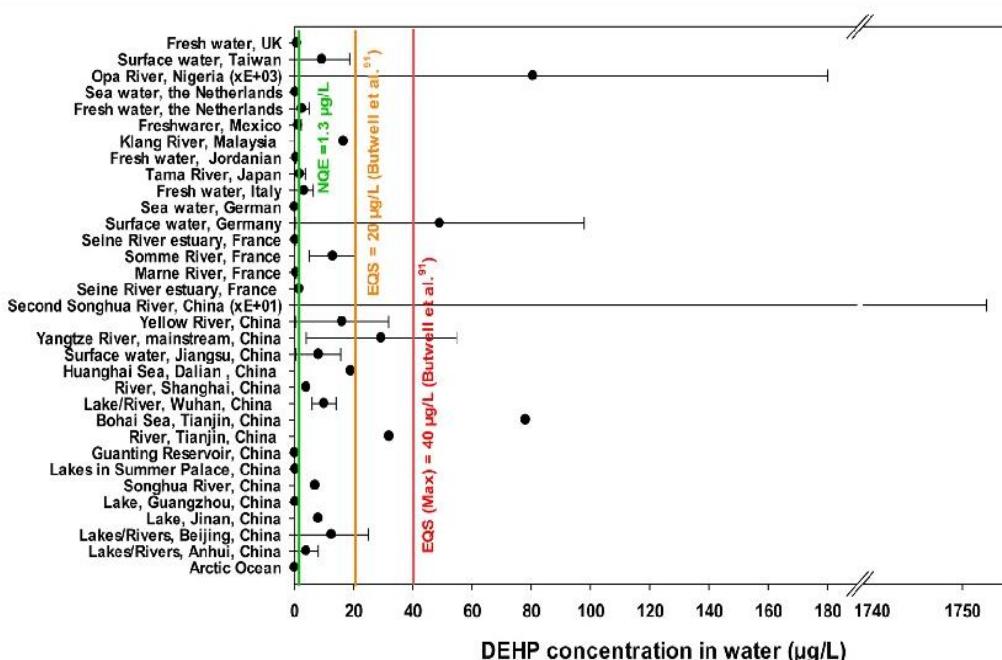


Figure 2. Worldwide contamination levels of DEHP in fresh and marine water compared to the NQE and EQS values (Detailed values and references are given in Supporting Information Table 2S).

considered not hazardous. Six PAEs (DMP, DEP, DnBP, BBzP, DEHP, and DnOP) have been included in the list of priority pollutants compiled by both the U.S. EPA and the EU and on the list of priority pollutants in Chinese waters.¹⁴ Table 2 presents different limited or recommended values available in different environmental matrices.

IV. Occurrence and Ecotoxicological State of PAEs. Even if PAEs can be eliminated from different environmental matrices via various processes as reported in previous sections, their extensive use and permanent emissions have resulted in their ubiquitous presence in the environment. PAEs have been widely detected in air, surface water, sediments, and soil on a worldwide scale. Indoor air is also highly contaminated by PAEs released from plastics and consumer products in homes, in

suspended particulate matter and house dust.^{62,106} Concentration of PAEs in different environmental matrices has been reported in numerous papers and the compiled data are presented in Table 2S in Supporting Information.

The ubiquity of PAEs in the environment today has given rise to a heightened awareness of the biochemical and toxicological roles of these compounds in the biosphere. As reported previously, some PAEs have been added to the priority list and limited or recommended values have been set for the most abundant and toxic PAEs. The main objectives are the protection of ecological resources and human health. For a better representation of contamination level and ecotoxicological status of the environment, the composition of PAEs in different matrices and their contamination levels as listed in SI

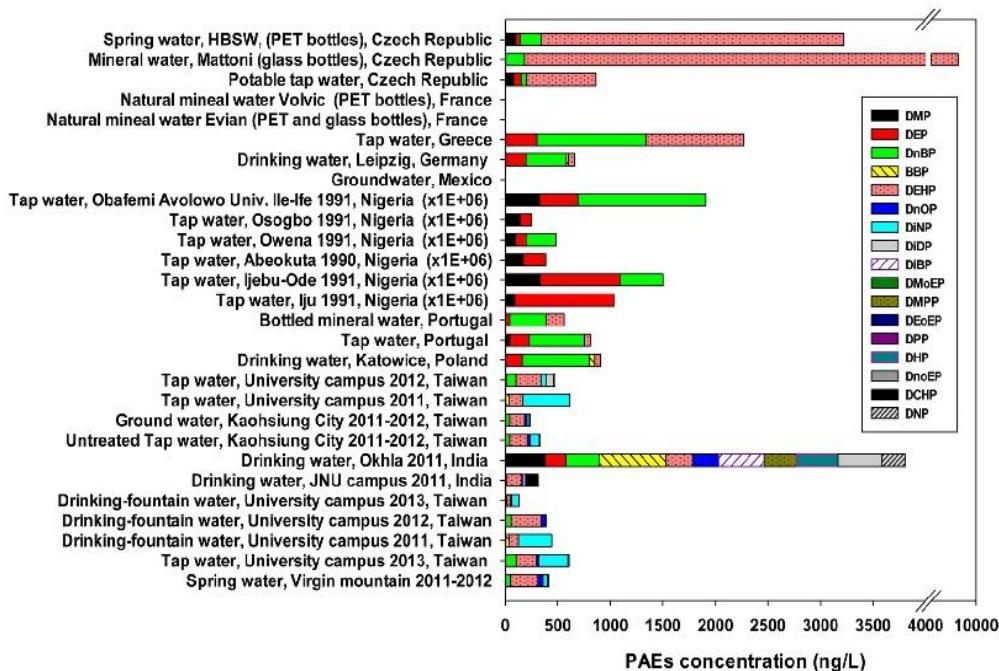


Figure 3. Composition of PAEs drinking water for worldwide scale; detailed values and references are given on Supporting Information Table 2S.

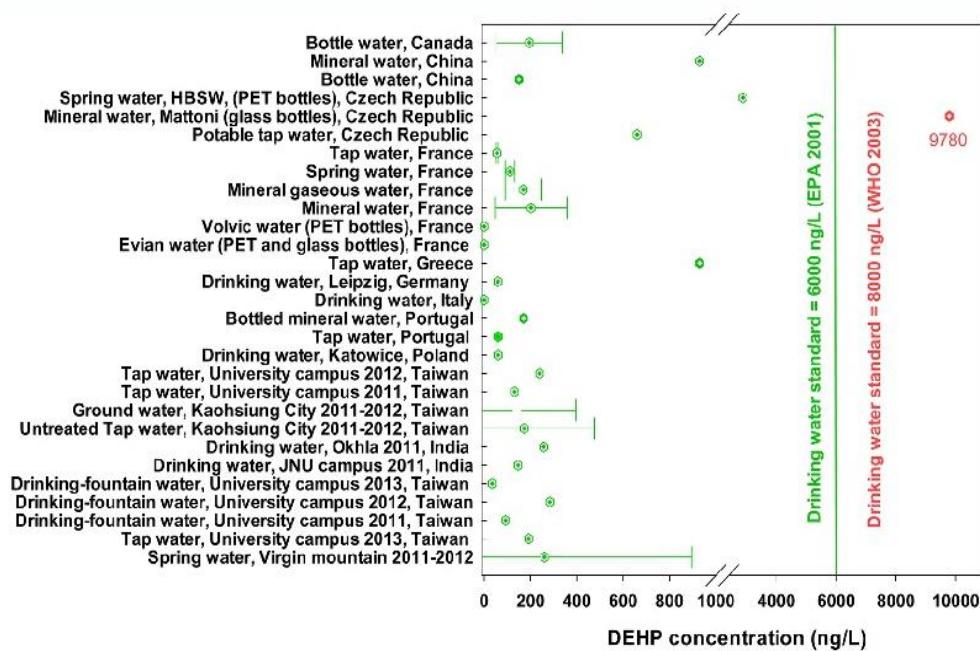


Figure 4. Worldwide contamination levels of DEHP in drinking water compared to the drinking water standard (Detailed values and references are given in Supporting Information Table 2S).

Table 2S are presented in graph form and compared to the limits or recommended values.

IV.1. Fresh and Marine Surface Water. Numerous processes such as WWTP output, leaching, drainage, and atmospheric deposition are the major sources of PAEs in aquatic system. Among the large variety of PAEs, DMP, DEP, DiBP, DMEP, DnBP, BBP, DEHP, and DnOP are among the most frequently detected in surface water (Supporting Information Table 2S). Figure 1 showed the composition of PAEs in fresh and marine water. Generally, studies focused on the six PAEs listed as priority substances which are the most toxic and also the predominant PAEs in the environment. Zheng et al.¹⁰⁷

measured the concentration of 15 PAEs in water both in dissolved phase and associated with SSM. The \sum_6 PAEs represents 64.8 and 66.9% of the \sum_{15} PAEs respectively in dissolved phase and associated with SSM. DEHP and DnBP were predominant PAEs following by DiBP and BBP.¹⁰⁷ Figure 1 confirms the predominant of DnBP and DEHP in fresh and marine water.

Marine and coastal environment present low level of PAEs compared to freshwater (Supporting Information Table 2S, Figure 1). For better evaluation the ecotoxicological state of aquatic system based on PAEs, the data were compared with the guidelines or recommend values. Figure 2 showed the

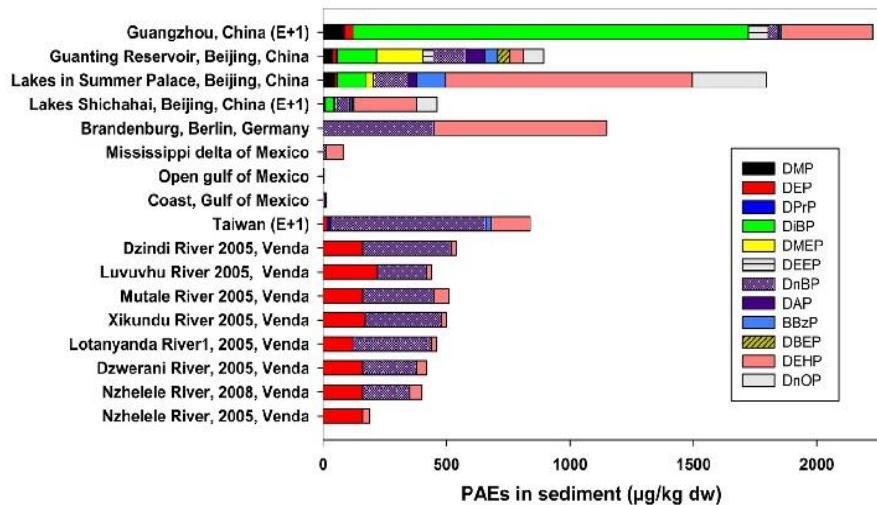


Figure 5. Worldwide composition of PAEs in sediment (Detailed values are given in Supporting Information Table 2S).

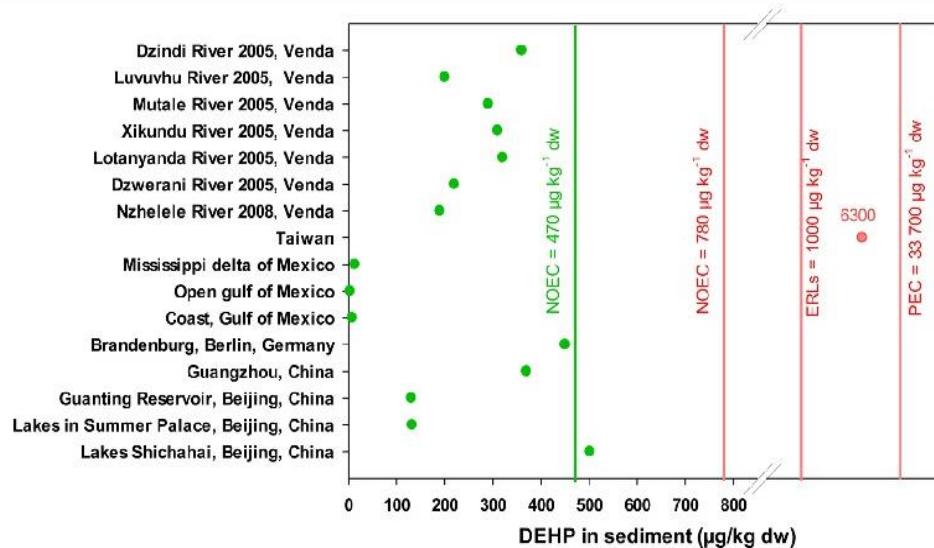


Figure 6. Contamination levels of DEHP in sediment compared to the NOEC, MAEC, ERLs, PEC and values (Detailed values and references are given on Supporting Information Table 2S).

contamination level of DEHP in fresh and marine water for worldwide scale compared to NQE valued fixed by EU. Based on NQE ($1.3 \mu\text{g/L}$) in fresh and marine water, majority of measured point exceeded the guideline value. The value is much higher than the eqs ($0.17 \mu\text{g/L}$)⁹⁸ and ERLs ($0.19 \mu\text{g/L}$)²¹ (Figure 2). Some values were much higher than maximum allowance value of EQS reported by Butwell et al.⁹¹ at $40 \mu\text{g/L}$ for DEHP. It is difficult to evaluate the effects of PAEs on the aquatic environment because several parameters should be taken into consideration. Some values have been proposed by many research groups as reported previously. Predicted effect concentration (PEC) which identifies the concentration above which harmful effects on organisms were expected to occur frequently has been proposed at $3.2 \mu\text{g/L}$.⁹⁷ Above all, it is clear that the majority of concentrations shown in Figure 2 are considerably higher than all the limit values (PEC, NQE, ERLs) previously reported.

The contamination levels of DnBP, DMP, DEP and BBzP in fresh and marine water is presented in Supporting Information Figures 2S to 4S. For DnBP, notably few samples are present at the level below the lowest observed effect concentration

(LOEC) and ERLs values set at 2 and $10 \mu\text{g/L}$, respectively. In some cases, the concentrations were higher than the PGW value fixed at $100 \mu\text{g/L}$ (Supporting Information Figure 2S). Thus, DnBP may affect not only aquatic organisms but also the groundwater resources. DMP and DEP were present under the EQS level except for the concentration reported by Fatoki and Ogunfowoka¹⁰⁸ from Nigeria (Supporting Information Table 2S; Figure 3S). Their concentrations were reported at very high levels, sometimes exceeding $500 \mu\text{g/L}$. The EQS of BBzP has been set at $20 \mu\text{g/L}$, with the maximum value set at $100 \mu\text{g/L}$.⁹¹ Based on these EQS values, fresh and marine water possess acceptable levels for this compound. Only one value detected at Al-Khobar, Saudi Arabia was present at a high level ($36.48 \mu\text{g/L}$) and exceeded the EQS.

IV.2. Drinking Water. PAEs present in drinking water can generally reach several $\mu\text{g/L}$, and in some cases, their levels can reach on the order of mg/L .¹⁰⁸ Figure 3 presents worldwide distribution of each PAE currently detected in drinking water. There is no predominant PAE notable among the large variety of PAEs detected in drinking water (i.e., mineral water, tap water, fountain water). Actually, it is difficult to determine the

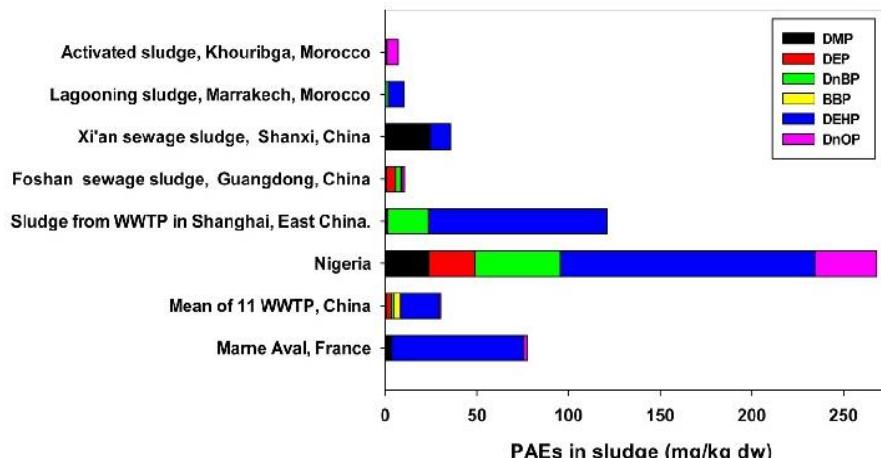


Figure 7. Composition of PAEs in sludge (Detailed values and references are given in Supporting Information Table 2S).

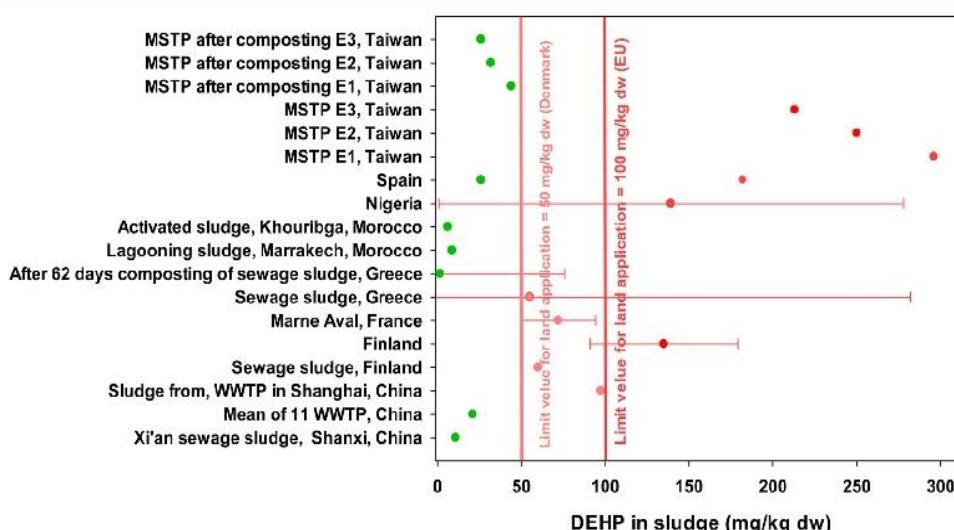


Figure 8. Worldwide contamination levels of DEHP in sludge compared to the limiting value (Detailed values and references are given in Supporting Information Table 2S).

predominant PAE because targeted compounds change from one study to another. Based in Figure 3, DMP, DEP, DnBP, and DEHP were the PAEs most often detected in drinking water. Nevertheless, even if six PAEs were added onto the priority list of the U.S. EPA, the drinking water standard for DEHP has been the only one established.

Figure 4 presents the contamination levels of drinking water by DEHP compared to the drinking water standards. The concentrations of DEHP most often detected in drinking water were in the range of a few hundred ng/L. Compared to the drinking water standard, the DEHP concentration does not exceed the guideline value, with the exception of mineral water (Mattoni) commercialized in the Czech Republic, where the concentration exceeded 9 µg/L.¹⁰⁹ Moreover, PAEs in drinking water can be removed by some novel technology such as the simultaneous electrocoagulation and electrofiltration process).⁶⁶ This process coupled with the tubular carbon nanofiber/carbon/alumina com-pposite membrane has been used to PAEs in drinking water with satisfactory removal yield. The removal efficiencies ranged from 42 to 78%.⁶⁶

IV.3. Sediment. In sediments, DnBP and DEHP were found in abundance (Supporting Information Table 2S; Figure 5). We note that DnBP can be used as a predictive indicator for the

sediment \sum_{16} PAEs concentration.¹¹⁰ DEHP concentrations have been compared to the ERLs, NOEC and PEC values. All measured levels are below the ERLs, NOEC, MAEC, and PEC values with the exception of the data reported for Lakes water from Beijing and Taiwan (Figure 6).

IV.4. Sludge. Presently, six PAEs were detected in wastewater, sewage sludge and compost samples. Their sum can exceed 250 mg/kg (Supporting Information Table 2S; Figure 7). In general, DEP, DnBP, and DEHP were the predominant PAEs in sludge and compost. However, composting can reduce the concentrations of PAEs initially present in sewage sludge,^{111,112} with removal rates of up to 77.3–100%.^{112,113} Figure 7 shows the composition of PAEs in various types of sludge. In sludge, the removal rates of PAEs with short alkyl chains length were higher than those with long alkyl chains length.^{10,114} PAEs with short alkyl chains are more easily biodegraded and mineralized than those with long alkyl chains, of which some are considered resistant to degradation. However, during the composting, long alkyl chain length compounds could be transformed to compounds with shorter alkyl chain length compounds.^{60,114} Amir et al.¹¹⁴ has previously reported the transformation mechanism for the conversion of long alkyl chain length to DnBP, DEP, and DMP.

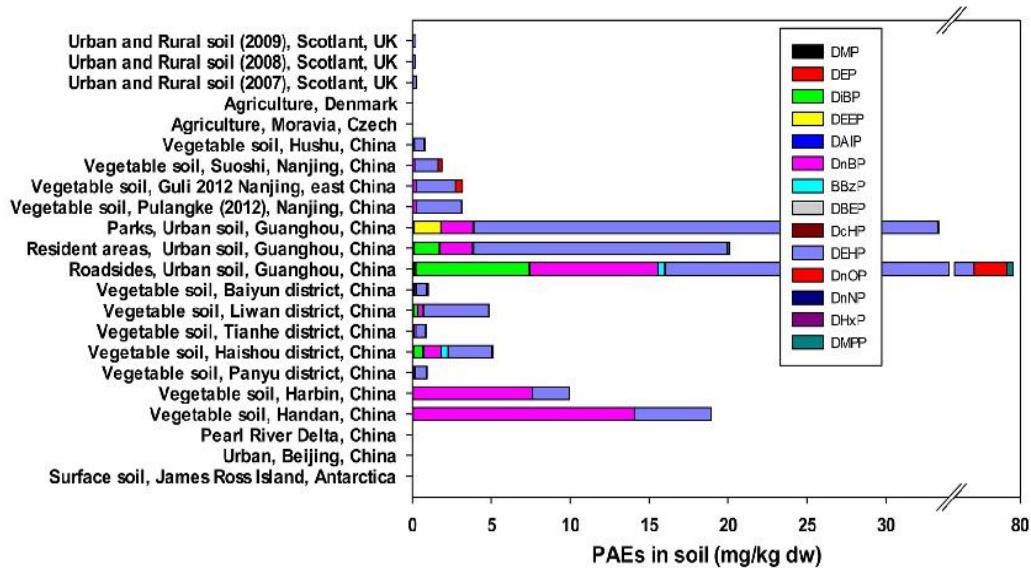


Figure 9. Worldwide composition of PAEs in soil (Detailed values and references are given in Supporting Information Table 2S).

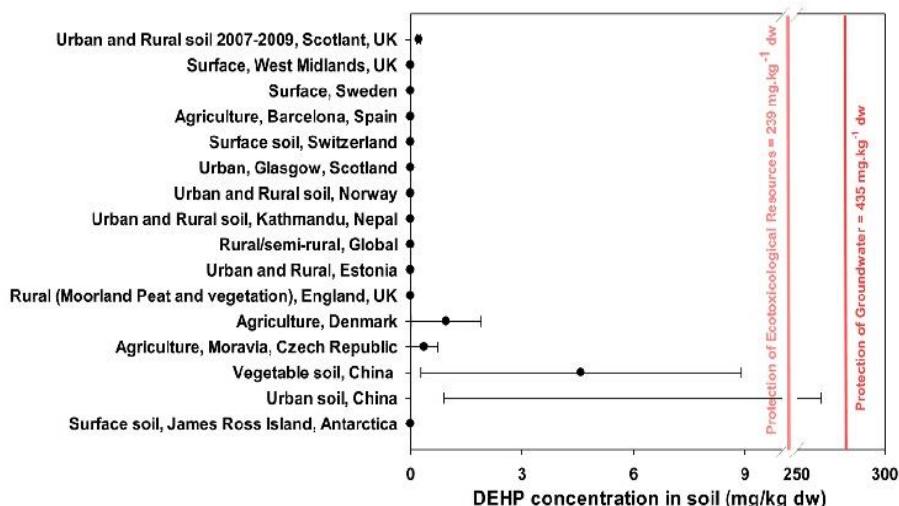


Figure 10. Worldwide contamination levels of DEHP in soil compared to the limiting values for PER and PGW (Detailed values and references are given in Supporting Information Table 2S).

The half-lives of DEHP were calculated at 45.4 days for lagooning sludge and 28.9 days for activated sludge.¹¹⁴ The degradation rates of the four PAEs were DBP > BBzP > DEP > DEHP.¹²⁵ Generally, PAEs can be eliminated by WWTP with satisfactory removal yields from wastewater.^{7,115–118} However, PAEs can accumulate in sludge which can be recycled for application on agricultural soil, which could then be a source of soil and water pollution by leaching or draining. Moreover, during a heavy rain period, WWTP can be overflowed, thus leading to the contamination of the surrounding environment. Figure 8 shows the worldwide contamination levels of DEHP in sludge.

Most of different types of sludge contain high levels of DEHP that can exceed the limit value set by the EU and Danish Ministerial for land application (Figure 8). However, it is noteworthy that composting can be an effective approach to remove PAEs from sludge before land application because it reduces the PAEs initially present in sludge.^{111,112} Given the high half-life of PAEs in soil, stricter controls should be adopted before using sludge as a soil amendment. As reported in a

previous section, the half-life of DEHP was estimated to be anywhere from 30 days⁴⁷ to a few hundred days.⁶⁰

IV.5. Soil. Atmospheric deposition and sewage sludge used as a soil amendment are the major sources of PAEs in soil. Vikelsøe et al.¹¹⁸ have demonstrated the correlation between PAEs concentration in soils and the level of sludge amended. In soil, DnBP and DEHP were the most abundant PAEs (Figure 9). DnOP and DiBP were also frequently detected, but their concentrations were much lower than the concentrations of DnBP and DEHP. Generally, noncultivated soils contain the lowest contents of PAEs, suggesting that these types of pollutants are largely derived from human agricultural activities. To better evaluate the ecological risk, DEHP concentrations have been compared to Protection of Ecological Resources (PER) and PGW values (Figure 10). The concentration of DEHP is below the PGW level. In general, the DEHP concentrations in soil were below the levels of PER, with the exception of the urban soil measured at Guangzhou in China (Figure 10). However, the DEHP concentrations often exceed the ERL values (1 mg/kg wt).²¹

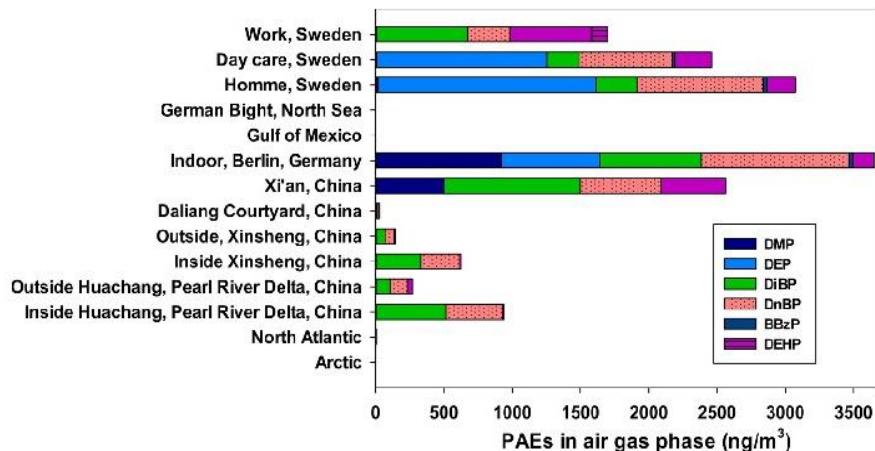


Figure 11. Worldwide contamination levels of PAEs in air (gas phase) (detailed values and references are given in Supporting Information Table 2S).

The contamination levels of DMP, DEP, DnBP, and DnOP are presented in Supporting Information Figures 5S and 6S. The DMP and DEP contamination levels were very low and did not exceed 0.4 mg/kg dw. Moreover, their values were much lower than the PGW and PER values set by the New York State Department of Environmental Conservation in 2010. The DnOP contamination was also detected at lower levels than the PER value set at 0.91 mg/kg dw. However, in a few cases DnBP was detected at levels higher than the PER and PGW values (Figure 12).

IV.6. Indoor and Outdoor Air. DnBP and DEHP were detected as the predominant PAEs in air.^{12,19,37,119,120} The total atmospheric levels of \sum_6 PAEs (DMP, DEP, DnBP, BBzP, DEHP, and DnOP) was 57.4 ng/m³ in Paris.³⁷ As PAEs are released from anthropogenic activities, their concentrations are present at higher levels in a urban center than in suburban areas. \sum_6 PAEs were detected at 97 ng/m³ in the urban center versus 27.8 ng/m³ in the suburban areas.¹¹⁹ In the remote Arctic, the total concentration of atmospheric PAEs (i.e., \sum_6 PAEs) was detected at 2.14 ng/m³. Worldwide, \sum_6 PAEs were detected at higher levels in indoor air than outdoor air: 1014–1828 ng/m³ in China,^{62,65} 1289–2386 ng/m³ in Sweden,¹⁰⁶ 545–2160 ng/m³ in the U.S.^{121,122}

DMP, DEP, DiBP, DnBP, and DEHP were detected in marine aerosols. Their total concentrations were 0.79–12.4 ng/m³, with an average of 2.6 ng/m³, which were higher than those reported in the North Sea to the high Arctic atmosphere (0.38–1.02 ng/m³) during the summer of 2004.³⁹ A possible source of PAEs in the Arctic troposphere may be associated with long-range transport from midlatitudes and the subsequent deposition on the snow/ice sheet. The deposited PAEs onto snow and ice can also be released into the atmosphere with the increase of the ambient temperature during the spring and summer months.¹²³ PAEs have been suggested to contribute to secondary oxidation products in organic aerosol fractions.^{124,125} Phthalic acid dominated the isomeric composition, which is consistent with those reported in continental aerosols.¹¹⁹ We note that a limiting value for this compound in ambient air has not been established.

Figures 11 and 12 show the composition of PAEs in air in both the gas phase and dust phase. In the gas phase, DiBP and DnBP were present in the highest frequency, which led to these compounds possessing the highest concentrations of the PAEs investigated. DEHP was also frequently detected in the gas

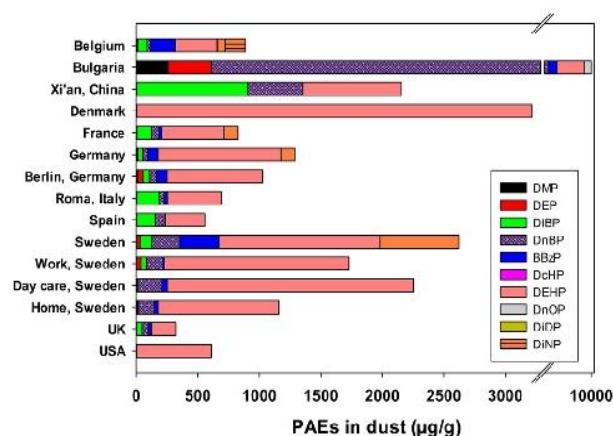


Figure 12. Worldwide contamination levels of PAEs in air (dust phase) (detailed values and references are given in Supporting Information Table 2S).

phase air, but its concentration was much lower than the concentrations detected for DiBP and DnBP (Figure 11). In the dust phase, DEHP was the predominant PAE identified, followed by DnBP and DiBP (Figure 12).

IV.7. PAEs in Wildlife. PAEs are hydrophobic compounds with logK_{OW} can be up to 12.06 (Table 1) which indicate that they have strong ability to accumulate into organisms. Hydrophobicity of PAEs increase with increase of carbon length chain. The contamination levels of some PAEs in biota including fishes, mammals, algae and others species are listed in Table 3S in SI. Fish species were reported to accumulate large variety of PAEs both parent and metabolite products including MPEs. PAEs and their metabolites were detected from the top of food chain (plankton, algae) to predator organisms (fish, marine mammals).^{10,126–131} Plankton and shellfish can accumulate individual PAE from not detected (nd) level to few hundreds ng/g.^{130,131} For freshwater ecosystem, the concentrations of individual PAE detected in fish species were in the range of nd to few hundreds µg/g.^{127,128} Two orders of magnitude lower were reported for marine fish^{127,129} (detailed values are given in Supporting Information Table 3S). In marine mammal, individual PAE was detected in the range of <LOQ to few µg/g.^{130,131} The highest was detected in liver of Beluga whale *Delphinapterus leucas* which the

concentration can be up to $4.15 \mu\text{g/g}$ of DEHP in wet weight animal.¹³⁰

Bioaccumulation/Bioconcentration factors (BAF or BCF) have been calculated for PAEs. A BCF or BAF >1000 indicates a high capacity for the species to accumulate or concentrate the pollutant.¹³² BAF and BCF of individual PAEs in wildlife are compiled in Supporting Information Table S5. Few study was focused on BAF of PAEs in wildlife. The BAF of individual PAE (DEP, DnBP, BBzP, DEHP, and DnOP) in three mammals and five invertebrates <0.25 excepted for DnOP in invertebrates that can be up to 2400 (Supporting Information Table S5).¹³³ Fishes have been reported to concentrate PAEs at significant level with total BCF of 57, 117, 45–663, 11–900, 207, and 2668–2125 mL/g/wet respectively for DMP, DEP, BBzP, DEHP, DiOP, and DnDP. Staples et al.¹⁰ have compiled literature data on the total BCF for aquatic organisms. They reported that crustacea and insect can accumulate DnBP with total BCF of 185–1485 and 458–714 mL/g/wet, respectively. Total BCF of 100 mL/g/wet has been reported for BBzP for Mollusca.¹⁰ Total BCF of DHxP has been reported to be 999–5269 mL/g/wet for crustacea. DnOP can bioconcentrate various aquatic species including in algae, mollusca, crustacean and insecta with total BCF of 8412, 699, 1429, and 1338 mL/g/wet, respectively.¹⁰ Similarly, DEHP were measured at high level of total BCF at 987, 264–2627, 83–3916, and 315–1892 mL/g/wet respectively for algae, mollusca, crustacean and insect.¹⁰ Total BCF of DiNP in mollusca was reported at 1844 mL/g/wet. Total BCF of DiDP were measured at 2998–3977 and 90–147 mL/g/wet for mollusca and crustacean.¹⁰ DnBP, DnOP, and DEHP were the three PAEs that can be bioconcentrated at high level in fish, shellfish and green algae (Supporting Information Table S5). Low molecular weight PAEs (DMP and DEP) were detected to accumulate at low level in aquatic species. The low values of BAF and BCF for some PAEs may be due to the fact that PAEs can be degraded or metabolized by species. Indeed, microbes from diverse habitats have been shown to degrade PAEs.¹⁰ High metabolite product of DEHP (MEHP) has been detected in plankton¹³⁰ which indicate that plankton can biodegrade DEHP by converting to MEHP. Thus, BCF can be an important factor of PAEs fate in the environment because it leads to biodegradation. Primary biodegradation half-lives of PAEs range from <1 day to ~ 2 weeks and clear trends between different PAEs or between fresh water and marine waters are not apparent.¹⁰ Ultimate degradation half-lives of DEHP (averaged about 12–67 days depend on temperature) are about an order of magnitude higher compared to primary biodegradation half-lives.

CONCLUSIONS

PAEs can be degraded by different biotic and abiotic pathways, as such they are not expected to be highly persistent in aquatic and terrestrial environments (air, water, sediment, and soil). Global half-lives of PAEs in air vary from few hours to few days. PAEs in water can be eliminated by hydrolysis, photolysis, photooxidation, and biodegradation. However, there is a paucity of data dealing with accurate description of degradation processes for the complete set of PAEs. Current knowledge shows that degradation half-lives of individual PAE ranges from a few days to months in soils and sediments according to the environmental conditions. Biodegradation activity appears to be greater than abiotic degradation in surface waters, sediments and soils. PAEs with low molecular weight are more easily

biodegraded than those with higher molecular weights. In natural environments, large variations of degradation of PAEs are caused by their physicochemical properties, the type of bacterial strains, temperature variations and nutritional conditions. Primary degradation half-life in water is expected to be on the order of less than 1 week, whereas the half-lives in soils can be up to several months. Longer half-lives are more likely under anaerobic conditions and in cold, nutrient poor environments.

PAEs can be eliminated from different environmental matrices via various processes. However, their extensive use and permanent emissions have resulted in their ubiquitous presence in the environment. These products can cause toxic effects on fertility and the development of humans as well as on many aquatic and terrestrial species. Consequently, the chronic exposure of PAEs to aquatic organisms and humans raises many questions. This study contributes in establishing the geochemical cycle of PAEs in the environment according to anthropogenic, hydrological and climatic factors.

ASSOCIATED CONTENT

Supporting Information

Additional information as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

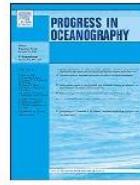
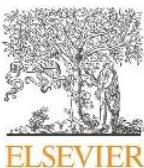
- (1) Kimber, I.; Dearman, R. J. An assessment of the ability of phthalates to influence immune and allergic responses. *Toxicology* **2010**, *271* (3), 73–82.
- (2) Simoneit, B. R. T.; Medeiros, P. M.; Didyk, B. M. Combustion products of plastics as indicators for refuse burning in the atmosphere. *Environ. Sci. Technol.* **2005**, *39*, 6961–6970.
- (3) Serôdio, P.; Nogueira, J. M. F. Considerations on ultra-trace analysis of phthalates in drinking water. *Water Res.* **2006**, *40* (13), 2572–2582.
- (4) Cadogan, D. F.; Papez, M.; Poppé, A. C.; Scheubel, J. An assessment of the release, occurrence and possible effect of plasticizers in the environment. *Prog. Rubber Plast. Technol.* **1993**, *10* (1), 1–19.
- (5) Xie, Z.; Ebinghaus, R.; Temme, C.; Lohmann, R.; Cara, A.; Ruck, W. Occurrence and air-sea exchange of phthalates in the Arctic. *Environ. Sci. Technol.* **2007**, *41* (13), 4555–4560.
- (6) Fu, P.; Kawamura, K.; Barrie, L. A. Photochemical and other sources of organic compounds in the Canadian high Arctic aerosol pollution during winter–spring. *Environ. Sci. Technol.* **2009**, *43*, 286–292.
- (7) Dargnat, C.; Teil, M. J.; Chevreuil, M.; Blanchard, M. Phthalate removal throughout wastewater treatment plant: case study of Marne Aval station (France). *Review. Sci. Total Environ.* **2009**, *407* (4), 1235–1244.

- (8) Net, S.; Dumoulin, D.; El-Osmani, R.; Rabodonirina, S.; Ouddane, B. Case study of PAHs, Me-PAHs, PCBs, phthalates and pesticides contamination in the Somme River water, France. *Int. J. Environ. Res. Public Health* **2014**, *8* (4), 1159–1170.
- (9) Gao, D.; Li, Z.; Wen, Z.; Ren, N. Occurrence and fate of phthalate esters in full-scale domestic wastewater treatment plants and their impact on receiving waters along the Songhua River in China. *Chemosphere* **2014**, *95*, 24–32.
- (10) Staples, C. A.; Peterson, D. R.; Parkerton, T. F.; Adams, W. J. The environmental fate of phthalates esters: A literature review. *Chemosphere* **1997**, *35*, 667–749.
- (11) Barreca, S.; Indelicato, R.; Orecchio, S.; Pace, A. Photo-degradation of selected phthalates on mural painting surfaces under UV light irradiation. *Microchemical J.* **2014**, *114*, 192–196.
- (12) Wang, X.; Tao, W.; Xu, Y.; Feng, J.; Wang, F. Indoor phthalate concentration and exposure in residential and office buildings in Xi'an, China. *Atmos. Environ.* **2014**, *87*, 146–152.
- (13) Commission Staff Working Document on the Implementation of the Community Strategy for Endocrine Disruptors—A Range of Substances Suspected of Interfering with the Hormone Systems of Humans and Wildlife; CEC (Commission of the European Communities): Brussels, 2007.
- (14) Yuan, B.; Li, X.; Graham, N. Aqueous oxidation of dimethyl phthalate in a Fe(IV)/TiO₂/UV reaction system. *Water Res.* **2008**, *42*, 1413–1420.
- (15) Chen, C. Y. Biosynthesis of di-(2-ethylhexyl) phthalate (DEHP) and di-n-butyl phthalate (DBP) from red alga-Bangia atropurpurea. *Water Res.* **2004**, *38* (4), 1014–1018.
- (16) Schiedek, T. Impact of plasticizers (phthalic acid esters) on soil and groundwater quality. *Groundwater Qual.: Rem. Protect.* **1995**, *22*, 149–156.
- (17) Mackintosh, C. E.; Maldonado, J. A.; Ikonomou, M. G.; Gobas, F. A. P. C. Sorption of phthalate esters and PCBs in a marine ecosystem. *Environ. Sci. Technol.* **2006**, *40* (11), 3481–3488.
- (18) Schreiber, A.; Fu, F.; Yang, O.; Wan, E.; Gu, E.; Le Blanc, Y. Increasing and Confidence in Detection When Analyzing Phthalates by LC-MS/MS, AB Sciex, AN 3690411-01, 2011.
- (19) Peijnenburg, W. J. G. M.; Struijs, J. Occurrence of phthalate esters in the environment of the Netherlands. *Ecotoxicol. Environ. Saf.* **2006**, *63*, 204–215.
- (20) Earls, A. O.; Axford, I. P.; Braybrook, J. H. Gas chromatography-mass spectrometry determination of the migration of phthalate plasticisers from polyvinyl chloride toys and childcare articles. *J. Chromatogr. A* **2003**, *983* (1–2), 237–246.
- (21) Van Wezel, A. P.; Van Vlaardingen, P.; Posthumus, R.; Crommentuijn, G. H.; Sijm, D. T. H. M. Environmental risk limits for two phthalates, with special emphasis on endocrine disruptive properties. *Ecotoxicol. Environ. Saf.* **2000**, *46*, 305–321.
- (22) Koniecki, D.; Wang, R.; Moody, R. P.; Zhu, J. Phthalates in cosmetic and personal care products: concentrations and possible dermal exposure. *Environ. Res.* **2011**, *111* (3), 329–336.
- (23) IARC. *Monographs on the Evaluation of Carcinogenic Risks to Humans. Some Industrial Chemicals*; International Agency for Research on Cancer: Lyon, France, 2000, p. 77.
- (24) Staples, C. A.; Adams, W. J.; Parkerton, T. F.; Gorsuch, W. Aquatic toxicity of eighteen phthalate esters. *Environ. Toxicol. Chem.* **1997b**, *16*, 875–891.
- (25) Cousins, I.; Mackay, D. Correlating the physical-chemical properties of phthalate esters using the 'three solubility' approach. *Chemosphere* **2000**, *41* (9), 1389–1399.
- (26) Lyman, W. J.; Reehl, W. F.; Rosenblatt, D. H. *Handbook of Chemical Property Estimation Methods-Environmental Behavior of Organic Compounds*; American Chemical Society: Washington, DC, 1990; Vol. 960.
- (27) Okamoto, Y.; Hayashi, T.; Toda, C.; Ueda, K.; Hashizume, K.; Itoh, K.; Nishikawa, J.; Nishihara, T.; Kojima, N. Formation of estrogenic products from environmental phthalate esters under light exposure. *Chemosphere* **2006**, *64* (10), 1785–1792.
- (28) Abdel-Daiem, M. M.; Rivera-Utrilla, J.; Ocampo-Pérez, R.; Méndez-Díaz, J. D.; Sánchez-Polo, M. Environmental impact of phthalic acid esters and their removal from water and sediment by different technologies—A review. *J. Environ. Manage.* **2012**, *109*, 164–178.
- (29) Net, S.; Delmont, A.; Sempéré, R.; Paluselli, A.; Ouddane, B. Reliable quantification of phthalates in environmental matrices (air, water, sediment, sludge and soil): A review. *Sci. Total. Environ.* **2015**, *515–516*, 162–180.
- (30) Brasche, S.; Bischof, W. Daily time spent indoors in German homes—Baseline data for the assessment of indoor exposure of German occupants. *Int. J. Hyg Environ. Health* **2005**, *208* (4), 247–253.
- (31) Hwang, H. M.; Park, E. K.; Young, T. M.; Hammock, B. D. Occurrence of endocrine-disrupting chemicals in indoor dust. *Sci. Total Environ.* **2008**, *404* (1), 26–35.
- (32) Cizdziel, J. V.; Hodge, V. F. Attics as archives for house infiltrating pollutants: trace elements and pesticides in attic dust and soil from southern Nevada and Utah. *Microchem. J.* **2000**, *64* (1), 85–92.
- (33) HSDB, 1994. Hazardous Substances Data Bank. Bethesda, MD, National Library of Medicine, National Toxicology Information Program, 11 September 1994.
- (34) Behnke, W.; Nolting, F.; Zetzs, C. An aerosol smog chamber for testing abiotic degradation. In *Pesticide Science and Biotechnology, Proceedings of the International Congress of Pesticide Chemistry*; Greenhalgh, R., Roberts, T.R. Eds. ; Blackwell Publishers: Oxford, UK, 1987; pp 401–404.
- (35) Orecchio, S.; Indelicato, R.; Barreca, S. Determination of selected phthalates by gas chromatography–mass spectrometry in mural paintings from Palermo (Italy). *Microchem. J.* **2014**, *114*, 187–191.
- (36) Maertens, R. M.; Bailey, J.; White, P. A. The mutagenic hazards of settled house dust: a review. *Mutat. Res.* **2004**, *567* (2–3), 401–425.
- (37) Teil, M.-J.; Blanchard, M.; Chevreuil, M. Atmospheric fate of phthalate esters in an urban area (Paris-France). *Sci. Total Environ.* **2006**, *354*, 212–223.
- (38) Zeng, F.; Lin, Y.; Cui, K.; Wen, J.; Ma, Y.; Chen, H.; Zhu, F.; Ma, Z.; Zeng, Z. Atmospheric deposition of phthalate esters in a subtropical city. *Atmos. Environ.* **2010**, *44* (6), 834–840.
- (39) Xie, Z.; Ebinghaus, R.; Temme, C.; Caba, A.; Ruck, W. Atmospheric concentrations and air-sea exchanges of phthalates in the North Sea (German Bight). *Atmos. Environ.* **2005**, *39*, 3209–3219.
- (40) Xu, G.; Li, F. S.; Wang, Q. H. Occurrence and degradation characteristics of dibutyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DEHP) in typical agricultural soils of China. *Sci. Total Environ.* **2008**, *393* (2), 333–340.
- (41) Zeng, F.; Cui, K. Y.; Xie, Z. Y.; Wu, L. N.; Luo, D. L.; Chen, L. X.; Lin, Y. J.; Liu, M.; Sun, G. X. Distribution of phthalate esters in urban soils of subtropical city, Guangzhou, China. *J. Hazard. Mater.* **2009**, *164* (2), 1171–1178.
- (42) Wang, W. X.; Zhang, Y. L.; Wang, S. L.; Fan, C. Q.; Xu, H. Distributions of phthalic esters carried by total suspended particulates in Nanjing, China. *Environ. Monit. Assess.* **2012**, *184* (11), 6789–6798.
- (43) Wolfe, N. L.; Steen, W. C.; Burns, L. A. Phthalate ester hydrolysis: Linear free energy relationships. *Chemosphere* **1980**, *9* (7–8), 403–408.
- (44) Tedetti, M.; Kawamura, K.; Narukawa, M.; Joux, F.; Charrière, B.; Sempéré, R. Hydroxyl radical-induced photochemical formation of dicarboxylic acids from unsaturated fatty acid (oleic acid) in aqueous solution. *J. Photochem. Photobiol. A Chem.* **2007**, *188*, 135–139.
- (45) Vione, D.; Minella, M.; Maurino, V.; Minero, C. Indirect photochemistry in sunlit surface waters: Photoinduced production of reactive transient species. *Chem.—Eur. J.* **2014**, *20*, 10590–10606.
- (46) Wolfe, N. L.; Burns, L. A.; Steen, W. C. Use of linear free energy relationship and an evaluative model to assess the fate and transport of phthalate esters in the aquatic environment. *Chemosphere* **1980**, *9*, 393–402.

- (47) Cousins, I. T.; Palm, A. Physical-chemical properties and estimated environmental fate of brominated and iodinated organic compounds. In *The Handbook of Environmental Chemistry*. 3R; Neilson, A. H., Ed.; Springer-Verlag: Berlin/Heidelberg, 2003; pp 301–334.
- (48) Camanzo, J.; Rice, C. P.; Jude, D. J.; Rossmann, R. Organic priority pollutants in nearshore fish from 14 Lake Michigan tributaries and embayments, 1983. *J. Great Lakes Res.* **1987**, *13* (3), 296–309.
- (49) DeVault, D. S. Contaminants in fish from Great Lakes harbors and tributary mouths. *Arch. Environ. Contam. Toxicol.* **1985**, *14*, 587–594.
- (50) U.S. EPA. *Health and Environmental Effects Profile for Phthalic Acid Esters*; US Environmental Protection Agency, Office of Research and Development, Environmental Criteria and Assessment Office (EPA/600/22): Cincinnati, OH, 1989.
- (51) Wofford, H. W.; Wilsey, C. D.; Neff, G. S.; Giam, C. S.; Neff, J. M. Bioaccumulation and metabolism of phthalate esters by oysters, brown shrimp and sheepshead minnows. *Ecotoxicol. Environ. Saf.* **1981**, *5*, 202–210.
- (52) Barrows, M. E.; Petrocelli, S. R.; Macek, K. J.; Carroll, J. J. Bioconcentration and elimination of selected water pollutants by bluegill sunfish (*Lepomis macrochirus*). In *Dynamics, Exposure and Hazard Assessment of Toxic Chemicals*; Haque R., Ed.; Ann Arbor Science: Ann Arbor, MI, 1980; pp 379–392.
- (53) Veith, G. D.; Macek, K. J.; Petrocelli, S. R.; Carroll, J. An Evaluation of Using Partition Coefficients and Water Solubility to Estimate Bioconcentration Factors for Organic Chemicals in Fish, Aquatic Toxicology. In Eaton, J. G., Parrish, P. R., Hendricks, A. C., Eds.; American Society for Testing and Materials: Philadelphia, PA 1980; pp 116–129 (ASTM Special Technical Publication 707).
- (54) Yuan, S.-Y.; Huang, I.-C.; Chang, B.-V. Biodegradation of dibutyl phthalate and di-(2-ethylhexyl) phthalate and microbial community changes in mangrove sediment. *J. Hazard. Mater.* **2010**, *184*, 826–831.
- (55) Yuan, S. Y.; Liu, C.; Liao, C. S.; Chang, B. V. Occurrence and microbial degradation of phthalate esters in Taiwan river sediments. *Chemosphere* **2002**, *49*, 1295–1299.
- (56) Chang, B. V.; Liao, C. S.; Yuan, S. Y. Anaerobic degradation of diethyl phthalate, di-n-butylphthalate, and di-(2-ethylhexyl) phthalate from river sediment in Taiwan. *Chemosphere* **2005**, *58* (11), 1601–1607.
- (57) Fish, T. D.; Jones, J. R.; Johnson, T. Characteristics of various hydrosoils and their relative importance in the biodegradation of DEHP. In *77th Annual Meeting Abstracts Am. Soc. Microbiol.*: New Orleans, 1977.
- (58) Tegatz, M. E.; Plaia, G. R.; Deans, C. H. Toxicity of dibutyl phthalate-contaminated sediment of laboratory-and field-colonized estuarine benthic communities. *Bull. Environ. Contain. Toxicol.* **1986**, *37*, 141–150.
- (59) Otton, S. V.; Sura, S.; Blair, J.; Ikonomou, M. G.; Gobas, F. A. P. C. Biodegradation of mono-alkyl phthalate esters in natural sediments. *Chemosphere* **2008**, *71* (11), 2011–2016.
- (60) Cartwright, C. D.; Thompson, I. P.; Burns, R. G. Degradation and impact of phthalate plasticizers on soil microbial communities. *Environ. Toxicol. Chem.* **2000**, *19* (5), 1253–1261.
- (61) Heudorf, U.; Mersch-Sundermann, V.; Angerer, J. Phthalates: Toxicology and exposure. *Int. J. Hyg. Environ. Health* **2007**, *210* (5), 623–634.
- (62) Guo, Y.; Kannan, K. Comparative assessment of human exposure to phthalate esters from house dust in China and the United States. *Environ. Sci. Technol.* **2011**, *45* (8), 3788–3794.
- (63) Weschler, C. J. Indoor/outdoor connections exemplified by processes that depend on an organic compound's saturation vapour pressure. *Atmos. Environ.* **2003**, *37*, 5455–5465.
- (64) Das, M. T.; Ghosh, P.; Thakur, I. S. Intake estimates of phthalate esters for South Delhi population based on exposure media assessment. *Environ. Pollut.* **2014**, *189*, 118–125.
- (65) Zhang, L.; Wang, F.; Ji, Y.; Jiao, J.; Zou, D.; Liu, L.; Shan, C.; Bai, Z.; Sun, Z. Phthalate esters (PAEs) in indoor PM₁₀/PM_{2.5} and human exposure to PAEs via inhalation of indoor air in Tianjin, China. *Atmos. Environ.* **2014**, *85*, 139–146.
- (66) Yang, G. C. C.; Yen, C. H.; Wang, C. L. Monitoring and removal of residual phthalate esters and pharmaceuticals in the drinking water of Kaohsiung City, Taiwan. *J. Hazard. Mater.* **2014**, *277*, 53–61.
- (67) Cousins, A. P.; Holmgren, T.; Remberger, M. Emissions of two phthalate esters and BDE 209 to indoor air and their impact on urban air quality. *Sci. Total Environ.* **2014**, *470–471*, 527–535.
- (68) Clark, K. E.; David, R. M.; Quinn, R.; Kramarz, K. W.; Lampi, M. A.; Staples, C. A. Modeling human exposure to phthalate esters: A comparison of indirect and biomonitoring estimation methods. *Hum. Ecol. Risk Assess.* **2011**, *17* (4), 923–965.
- (69) Liou, S.-H.; Yang, G. C. C.; Wang, C.-L.; Chiu, Y.-H. Monitoring of PAEs and beta-agonists in urine for a small group of experimental subjects and PAEs and beta-agonists in drinking water consumed by the same subjects. *J. Hazard. Mater.* **2014**, *277*, 169–179.
- (70) Chen, J. A.; Liu, H.; Qiu, Z.; Shu, W. Analysis of di-n-butyl phthalate and other organic pollutants in Chongqing women undergoing parturition. *Environ. Pollut.* **2008**, *156* (3), 849–853.
- (71) Main, K. M.; Mortensen, G. K.; Kaleva, M. M.; Boisen, K. A.; Damgaard, I. N.; Chellakooty, M.; Schmidt, I. M.; Suomi, A. M.; Virtanen, H. E.; Petersen, J. H.; Andersson, A. M.; Toppari, J.; Skakkebæk, N. E. Human breast milk contamination with phthalates and alterations of endogenous reproductive hormones in infants three months of age. *Environ. Health Perspect.* **2006**, *114* (2), 270–276.
- (72) Singh, S.; Li, S. S.-L. Epigenetic effects of environmental chemicals bisphenol A and phthalates. *Int. J. Mol. Sci.* **2012**, *13*, 10143–10153.
- (73) Kolena, B.; Petrovicova, I.; Pilka, T.; Pucherova, Z.; Munk, M.; Matula, B.; Vankova, V.; Petlus, P.; Jenisova, Z.; Rozova, Z.; Wimmerova, S.; Trnovec, T. Phthalate exposure and health-related outcomes in specific types of work environment. *Int. J. Environ. Res. Public Health* **2014**, *11* (6), 5628–5639.
- (74) Oie, L.; Hersoug, L. G.; Madsen, J. O. Residential exposure to plasticizers and its possible role in the pathogenesis of asthma. *Environ. Health Perspect.* **1997**, *105* (9), 972–978.
- (75) Blanc, P. D.; Toren, K. How much adult asthma can be attributed to occupational factors? *Am. J. Med.* **1999**, *107* (6), 580–587.
- (76) Benson, R. Hazard to the developing male reproductive system from cumulative exposure to phthalate esters-dibutyl phthalate, diisobutyl phthalate, butylbenzyl phthalate, diethylhexyl phthalate, dipentyl phthalate, and diisononyl phthalate. *Regul. Toxicol. Pharmacol.* **2009**, *53* (2), 90–101.
- (77) Sims, J. N.; Graham, B.; Pacurari, M.; Leggett, S. S.; Tchounwou, P. B. Ndebele, K. Di-ethylhexylphthalate (DEHP) modulates cell invasion, migration and anchorage independent growth through targeting S100P in LN-229 glioblastoma cells. *Int. J. Environ. Res. Public Health* **2014**, *11*, 5006–5019.
- (78) Howdeshell, K. L.; Rider, C. V.; Wilson, V. S.; Gray, L. E., Jr. Mechanisms of action of phthalate esters, individually and in combination, to induce abnormal reproductive development in male laboratory rats. *Environ. Res.* **2008**, *108* (2), 168–176.
- (79) Vethaak, A. D.; Rijs, G. B. J.; Schrap, S. M.; Ruiter, H.; Gerritsen, A.; Lahr, J. *Oestrogens and Xeno-Estrogens in the Aquatic Environment of the Netherlands*, Occurrence, potency and biological effects RIZA/RIKS-report no. 2002-001, 2002.
- (80) Harris, C. A.; Henttu, P.; Parker, M. G.; Sumpter, J. P. The estrogenic potential of phthalate esters in vitro. *Environ. Health Perspect.* **1997**, *105* (8), 802–811.
- (81) Ye, T.; Kang, M.; Huang, Q.; Fang, C.; Chen, Y.; Shen, H.; Dong, S. Exposure to DEHP and MEHP from hatching to adulthood causes reproductive dysfunction and endocrine disruption in marine medaka (*Oryzias melastigma*). *Aquat. Toxicol.* **2014**, *146*, 115–126.
- (82) Chen, X.; Xu, S.; Tan, T.; Lee, S. T.; Cheng, S. H.; Lee, F. W. F.; Xu, S. J. L.; Ho, K. C. Toxicity and estrogenic endocrine disrupting

- activity of phthalates and their mixtures. *Int. J. Environ. Res. Public Health* **2014**, *11* (3), 3156–3168.
- (83) Oehlmann, J.; Schulte-Oehlmann, U.; Kloas, W.; Jagnytsch, O.; Lutz, I.; Kusk, K. O.; Wollenberger, L.; Santos, E. M.; Paull, G. C.; Van Look, K. J. W.; Tyler, C. R. A critical analysis of the biological impacts of plasticizers on wildlife. *Philos. Trans. R. Soc., B* **2009**, *364* (1526), 2047–2062.
- (84) Scholz, N. Ecotoxicity and biodegradation of phthalate monoesters. *Chemosphere* **2003**, *53* (8), 921–926.
- (85) AESN (Agence de l'Eau Seine Normandie). *Guide Pratique Des Substances Toxiques Dans les Eaux Douces et Littorales du Bassin Seine-Normandie*, 2008.
- (86) Guidelines for Drinking Water Quality, 3rd ed.; WHO (World Health Organization): Geneva, 2004; Vol. 1.
- (87) Maycock, D.; Fawell, J.; Merrington, G.; Watts, C. Review of England and Wales monitoring data for which a national or international standard has been set. Guidel. *Drinking Water Qual.* **2008**, *1*–148.
- (88) Marcilla, A.; García, S.; García-Quesada, J. C. Study of the migration of PVC plasticizers. *J. Anal. Appl. Pyrolysis* **2004**, *71* (2), 457–463.
- (89) Chemical Inspection and Regulation Service (CIRS). http://www.cirs-reach.com/Testing/Phthalates_Testing.html.
- (90) Bette, H. California bans phthalates in toys for children. Chemical and Engineering News, 12. 2007. <http://pubs.acs.org/cen/news/85/i43/8543news4.html>.
- (91) Butwell, A. J.; Hetheridge, M.; James, H. A.; Johnson, A. C.; Young, W. F. *Endocrine Disrupting Chemicals in Wastewater—A Review of Occurrence and Removal*, Report No. 02/TX/04/S; Water Industry Research Limited (UKWIR): London, 2001.
- (92) Journal officiel de l'Union européenne. Directive 2013/39/UE du parlement Européen et du Conseil du 12 août 2013.
- (93) CEC (Commission of the European Communities), 2000. Working document on sludge 3rd draft Report No.ENV.E.3/LM. DG. Environment, Brussels. Retrieved 31 July 2003 from The European Water Association. http://www.ewaonline.de/pages/sludge_en.pdf.
- (94) Danish Ministerial Order. No. 823, 1996. Application of Waste Products for Agricultural Purposes, September 16, 1996.
- (95) New York State Department of Environmental Conservation, 2010. Soil Cleanup Guidance. http://www.dec.ny.gov/docs/remediation_hudson_pdf/cpsoil.pdf.
- (96) U.S. EPA. Methods for organic chemical analysis of municipal and industrial wastewater, Method 606: Phthalate esters. *Code Fed. Regul.* **40**. 2001.
- (97) Naito, W.; Gamo, Y.; Yoshida, K. Screening-level risk assessment of di(2-ethylhexyl)phthalate for aquatic organisms using monitoring data in Japan. *Environ. Monit. Assess.* **2006**, *115*, 451–471.
- (98) Marchand, M.; Tissier, C.; Tixier, C.; Troncynski, J. Les contaminants chimiques dans le Directive Cadre sur l'Eau. Septembre 2004-R.INT.DIR/DEL-PC/2004.11, 2004. <http://www.ifremer.fr/envlit/documentation/documents.htm>.
- (99) EU. *European Union Risk Assessment Report for Dibutyl Phthalate with Addendum to the Environmental Section 2004*; Office for Official Publications of the European Communities: Luxembourg, 2004.
- (100) Ward, T. J.; Boerie, R. L. *Early Life Stage Toxicity of Di-n-Butylphthalate (DnBP) to the Rainbow Trout (Oncorhynchus mykiss) under Flow-through Conditions*; Resource Analysts, Inc., Environ. Systems Division: Hampton, NH, 1991; unpublished.
- (101) Ohtani, H.; Miura, I.; Ichikawa, Y. Effects of dibutyl phthalate as an environmental endocrine disrupter on gonadal sex differentiation of genetic males of the frog *Rana rugosa*. *Environ. Health Perspect.* **2000**, *108* (12), 1189–1193.
- (102) Lee, S. K.; Veeramachaneni, D. N. R. Subchronic exposure to low concentrations of di-n-butyl phthalate disrupts spermatogenesis in *Xenopus laevis* frogs. *Toxicol. Sci.* **2005**, *84* (2), 394–407.
- (103) EU. *European Union Risk Assessment Report for Bis(2-Ethylhexyl) Phthalate*. Draft of March 2006; Office for Official Publications of the European Communities: Luxembourg, 2006.
- (104) Barrick, R.; Becker, S.; Brown, L.; Beller, H.; Pastorok, R. *Sediment Quality Values Refinement: 1988 Update and Evaluation of Puget Sound AET*, Vol. 1 Prepared for the Puget Sound Estuary Program. PTI Environmental Services: Bellevue, Washington, 1988; (Cited from: D. D. MacDonald, S. L. Smith, M. P. Wong and P. Murdoch. 1992. The development of Canadian Marine Environmental Quality Guidelines. Marine).
- (105) *Sediment Management Standards*; Washington State Department of Ecology, April 1991.
- (106) Bergh, C.; Torgrip, R.; Emenius, G.; Ostman, C. Organophosphate and phthalate esters in air and settled dust—A multi-location indoor study. *Indoor Air* **2011**, *21* (1), 67–76.
- (107) Zheng X.; Zhang, B. T.; Teng, Y. Distribution of phthalate acid esters in lakes of Beijing and its relationship with anthropogenic activities. *Sci. Total Environ.* **2014**, *476–77*, 107–113.
- (108) Fatoki, O. S.; Ogunfowokan, A. O. Determination of phthalate ester plasticizers in the aquatic environment of southwestern Nigeria. *Environ. Int.* **1993**, *19*, 619–623.
- (109) Prokůpková, G.; Holadová, K.; Poustka, J.; Hajšlová, J. Development of a solid-phase microextraction method for the determination of phthalic acid esters in water. *Anal. Chim. Acta* **2002**, *457* (2), 211–223.
- (110) Zeng, F.; Cui, K.; Xie, Z.; Liu, M.; Li, Y.; Lin, Y.; Zeng, Z.; Li, F. Occurrence of phthalate esters in water and sediment of urban lakes in a subtropical city, Guangzhou, South China. *Environ. Int.* **2008**, *34*, 372–380.
- (111) Pakou, C.; Kormaros, M.; Stamatelatou, K.; Lyberatos, G. On the fate of LAS, NPEOs and DEHP in municipal sewage sludge during composting. *Bioresour. Technol.* **2009**, *100*, 1634–1642.
- (112) Cai, Q. Y.; Mo, C. H.; Lu, H.; Zeng, Q. Y.; Wu, Q. T.; Li, Y. W. Effect of composting on the removal of semivolatile organic chemicals (SVOCs) from sewage sludge. *Bioresour. Technol.* **2012**, *126*, 453–457.
- (113) Cheng, H.-F.; Kumar, M.; Lin, J.-G. Degradation kinetics of di(2-ethylhexyl) phthalate (DEHP) and organic matter of sewage sludge during composting. *J. Hazard. Mater.* **2008**, *154*, 55–62.
- (114) Amir, S.; Hafidi, M.; Merlini, G.; Hamdi, H.; Jouraiphy, A.; El Gharous, M.; Revel, J. C. Fate of phthalic acid esters during composting of both lagooning and activated sludges. *Process. Biochem.* **2005**, *40* (6), 2183–2190.
- (115) Marttinen, S.; Kettunen, R.; Sormunen, K. M.; Rintala, J. Removal of bis(2-ethylhexyl) phthalate at a sewage treatment plant. *Water Res.* **2003**, *37* (6), 1385–1393.
- (116) Marttinen, S. K.; Kettunen, R. H.; Rintala, J. A. Occurrence and removal of organic pollutants in sewages and landfill leachates. *Sci. Total Environ.* **2003**, *301* (1–3), 1–12.
- (117) Tran, B. C.; Teil, M. J.; Blanchard, M.; Alliot, F.; Chevreuil, M. BPA and phthalate fate in a sewage network and an elementary river of France. Influence of hydroclimatic conditions. *Chemosphere* **2015**, *119*, 43–51.
- (118) Vikelsøe, J.; Thomsen, M.; Carlsen, L. Phthalates and nonylphenols in profiles of differently dressed soils. *Sci. Total Environ.* **2002**, *296*, 105–116.
- (119) Wang, Z.; Jing, M.; Lee, F. S.; Wang, X. Synthesis of 8-hydroxyquinoline Bonded Silica (SHQ) and its application in flow injection-inductively coupled plasma mass spectrometry analysis of trace metals in seawater. *Chin. J. Anal. Chem.* **2006**, *34* (4), 459–462.
- (120) Wang, P.; Wang, S. L.; Fan, C. Q. Atmospheric distribution of particulate- and gas-phase phthalic ester (PAEs) in a Metropolitan City, Nanjing, East China. *Chemosphere* **2008**, *72* (10), 1567–1572.
- (121) Adibi, J. J.; Whyatt, R. M.; Williams, P. L.; Calafat, A. M.; Camann, D.; Herrick, R.; Nelson, H.; Bhat, H. K.; Perera, F. P.; Silva, M. J.; Hauser, R. Characterization of phthalate exposure among pregnant women assessed by repeat air and urine samples. *Environ. Health Perspect.* **2008**, *116* (4), 467–473.
- (122) Rudel, R. A.; Dodson, R. E.; Perovich, L. J.; Morello-Frosch, R.; Camann, D. E.; Zuniga, M. M.; Yau, A. Y.; Just, A. C.; Brody, J. G. Semivolatile endocrine-disrupting compounds in paired indoor and outdoor air in two Northern California communities. *Environ. Sci. Technol.* **2010**, *44* (17), 6583–6590.

- (123) Fu, P. Q.; Kawamura, K.; Chen, J.; Charrière, B.; Sempéré, R. Organic molecular composition of marine aerosols over the Arctic Ocean in summer: Contributions of primary emission and secondary aerosol formation. *Biogeosciences* **2013**, *10*, 653–667.
- (124) Kawamura, K.; Yasui, O. Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere. *Atmos. Environ.* **2005**, *39*, 1945–1960.
- (125) Kundu, S.; Kawamura, K.; Andreae, T. W.; Hoffer, A.; Andreae, M. O. Molecular distributions of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in biomass burning aerosols: Implications for photochemical production and degradation in smoke layers. *Atmos. Chem. Phys.* **2010**, *10*, 2209–2225.
- (126) Brown, D.; Thompson, R. S. Phthalates and the aquatic environment: Part II The bioconcentration and depuration of di-2-ethylhexyl phthalate (DEHP) and di-isodecyl phthalate (DIDP) in mussels (*Mytilus edulis*). *Chemosphere* **1982**, *11*, 427–435.
- (127) Cheng, Z.; Nie, X. P.; Wang, H. S.; Wong, M. H. Risk assessments of human exposure to bioaccessible phthalate esters through market fish consumption. *Environ. Int.* **2013**, *54–58*, 75–80.
- (128) Huang, P. C.; Tien, C. J.; Sun, Y. M.; Hsieh, C. Y.; Lee, C. C. Occurrence of phthalates in sediment and biota: Relationship to aquatic factors and the biota-sediment accumulation factor. *Chemosphere* **2008**, *73*, 539–544.
- (129) Güven, K. C.; Coban, B. Phthalate pollution in fish *Sarda sarda*, *Engraulis encrasicolus*, *Mullus surmuletus*, *Merlangius merlangus* and shrimp *Parapenaeus longirostris*. *J. Black Sea/Mediterr. Environ.* **2013**, *19* (2), 185–189.
- (130) Morin, A. *Distribution of phthalate esters in a marine mammal food chain from Canada's Eastern Arctic*, 2003.
- (131) Fossi, M. C.; Panti, C.; Guerranti, C.; Coppola, D.; Giannetti, M.; Marsili, L.; Minutoli, R. Are baleen whales exposed to the threat of microplastics? A case of study of the Mediterranean fin whale (*Balaenoptera physalus*). *Mar. Pollut. Bull.* **2012**, *64*, 2374–2379.
- (132) Porter, A.; Hayden, N. *Nonylphenol in the Environment: A Critical Review*; Department of Civil and Environmental Engineering, University of Vermont: Burlington, VT, 2002.
- (133) HAZWRAP. *Loring Air Force Base Ecological Risk Methodology*; Martin Marietta Energy Systems, 1994.



Occurrence of microplastics in surface waters of the Gulf of Lion (NW Mediterranean Sea)

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Gulf of Lion
Marseille Bay

Between 2014 and 2016 a total of 43 microplastic samples were collected at six sampling stations in the eastern section of the Gulf of Lion (located in the northwestern Mediterranean Sea), as well as upstream of the Rhône River. Microplastics were found in every sample with highly variable concentrations and masses. Concentrations ranged from $6 \cdot 10^3$ items km^{-2} to $1 \cdot 10^6$ items km^{-2} (with an average of $112 \cdot 10^3$ items km^{-2}), and mass ranged from 0.30 g km^{-2} to 1018 g km^{-2} DW (mean $61.92 \pm 178.03 \text{ g km}^{-2}$). The samples with the highest and lowest microplastic count originate both from the Bay of Marseille. For the Bay of Marseille, it is estimated that the total microplastic load consist of $519 \cdot 10^3 - 101 \cdot 10^6$ items weighing $0.07 - 118 \text{ kg}$. Estimations for daily microplastic transport by the Northern Current and the Rhône River, two important hydrologic features of the northwestern Mediterranean Sea, range from 0.18 to 86.46 t and from 0.20 to 21.32 kg , respectively. Particles $< 1 \text{ mm}^2$ clearly dominated sampling stations in the Northern Current, the Rhône River and its plume (52, 53 and 61%, respectively), suggesting a long exposure time in the environment. Items between 1 mm^2 and 5 mm^2 in size were the most abundant microplastics in Marseille Bay (55%), which suggests coastal pollution sources or the removal of smaller particles from surface waters e.g. by ballasting owing to the presence of epibionts.

1. Introduction

Plastic and its chemical compounds have played an important role in the Anthropocene and might threaten human health (Kobrosly et al., 2014; Tranfo et al., 2012; Sathyarayana 2008; Heudorf et al., 2007) and both terrestrial (Zhao et al., 2016; Lwanga et al., 2016; Oehlmann et al., 2009) and marine environments (Przybylinska and Wyszkowski, 2016; Van Franeker and Law, 2015; Sigler, 2014). In 2014, 311 million tons of plastic were produced worldwide, 15% of which were consumed in Europe (PlasticsEurope, 2015). The degradation of large plastic items into microplastics ($\leq 5 \text{ mm}$) in the ocean is a slow and heterogeneous process, varying with respect to the quality, shape and size of the plastic. This process is driven by mechanical forcing (e.g., waves), salt water, and UV radiation (Ter Halle et al., 2016). Because of its small size, micro debris can easily be ingested (e.g., Desforges et al., 2015; Neves et al., 2015). Approximately $270 \cdot 10^3$ tons of plastic are suspected to float in the world's oceans (Eriksen et al., 2014). Estimates for floating microplastic loads range from $7 \cdot 10^3$ to $35 \cdot 10^3$ tons for global

open-ocean surface waters (Cózar et al., 2014) or from $93 \cdot 10^3$ to $236 \cdot 10^3$ tons depending on the model used (Van Sebille et al., 2015). Plastic accounts for 60 to 80% of all marine litter, followed in quantity by glass and metal (UNEP, 2009). About $370 \cdot 10^9$ plastic particles or 1455 tons have been estimated to be floating on the surface of the Mediterranean Sea (Ruiz-Orejón et al., 2016). Other estimates range from 756 to 2969 tons (Cózar et al., 2015) and from 874 to 2576 tons (Suaria et al., 2016).

The Mediterranean Sea is a semi-enclosed basin subject to significant anthropogenic pressures (e.g., The MerMex group, 2011; Blanfumé et al., 2016; Hassoun et al., 2015; Casale et al., 2015). Marine debris, including microplastics, are a particularly important concern in this region (Deudero and Alomar, 2015; Cózar et al., 2015; Ioakeimidis et al., 2014; Faure et al., 2015; Pedrotti et al., 2016). Concerns about marine litter in the Mediterranean Sea were first expressed in 1976 when the Barcelona Convention was signed with the goal of preventing and abating marine and coastal pollution (UNEP, 2009). In subsequent years, studies have been undertaken to better understand pollution

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sources and trajectories, through approaches as modeling the transport of floating marine debris (Mansui et al., 2014). However, knowledges on the spatial and temporal microplastic distribution remain limited (Ruiz-Orejón et al., 2016; Suaria et al., 2016; Cázar et al., 2015). Their contents are highly variable, although the sea surface circulation seems to be the main driver on the distribution of floating marine litter whatever their sizes. Currents affect time-dependent movements that remain difficult to predict, and cause several non-trivial Lagrangian mechanisms (Zambianchi et al., 2014). In semi-enclosed seas, such as the Mediterranean Sea, aggregation patterns are not permanent and high variability is observed at a small scale (Suaria et al., 2016). Wind-induced effects on floating material and Stokes drift velocities require further investigation, such as refinement of regional models. Nevertheless, some available scenarios could be hypothesized with possible retention areas in the northwestern Mediterranean and the Tyrrhenian sub-basins (Poullain et al., 2012; Mansui et al., 2014). The Gulf of Lion is in the northwestern sector of the Mediterranean Sea, and its hydrodynamics are influenced by shallow water depths of the shelf, wind regimes (Mistral and Marin), the Northern Current (NC), and freshwater inputs from the Rhône River (Gatti et al., 2006; Fraysse et al., 2014). The NC has a high seasonal variability: while a decrease in intensity is observed in summer, it becomes faster, deeper and narrower in winter (Millot, 1991). Intrusion of the NC onto the shelf of the Gulf of Lion has been observed (Ross et al., 2016; Barrier et al., 2016 and references therein). This productive shelf is also highly exploited for commercial fishing (Báñaru et al., 2013) and the coastal area is strongly influenced by tourism activities. Given this areas great economic, touristic and environmental significance, monitoring threats, such as pollution sources, is essential. Therefore, the primary goal of this study was to provide insight into the temporal and spatial distribution of microplastics in the eastern sector of the Gulf of Lion. Furthermore, we wanted to examine relationships between microplastic size distributions and possible pollution sources and transportation routes.

2. Materials and methods

Following the framework of the Particule-MERMEX and PLASTOX projects, microplastic debris were collected at different times between February 2014 and April 2016 (Table S1) in three distinct areas with specific hydrodynamic characteristics (Fig. 1) within the eastern sector of the Gulf of Lion (northwestern Mediterranean Sea). The first area is located 40 km offshore at the eastern part (station #1, also called 'Antares site') and is within the direct influence of the Northern Current, which runs east to west along the shelf break over 2475 m of water (Martini et al., 2016). The second area includes the Bay of Marseille (stations #2, 3 and 4), which is significantly influenced by a population of approximately 1 million inhabitants and by the daily volume of about $250 \cdot 10^3 \text{ m}^3$ of waste waters released from the Marseille-Cortiou

wastewater treatment plant (WWTP) (Savriama et al., 2015; Tedetti et al., 2012). To the west, the third study area is the downstream part of the Rhône River (station #6, Arles, 48 km from the river mouth) and within the dilution plume (station #5, about 2.5 km from the mouth) (Sempéré et al., 2000). Sampling dates, GPS coordinates, microplastic concentration, mean wind speed and wind direction are provided in the supplementary data (Table S1) along with information on precipitation. Surface current speeds and directions were extracted from the Mars 3D model (<http://marc.ifremer.fr>).

Microplastic samples were collected using a Manta net (0.50 m x 0.15 m opening) mounted with a 780 μm mesh size and towed horizontally at the surface. Ten samples from March and April 2016 were collected (in Marseille at stations 3 and 4) with a 330 μm mesh size (Suppl. Table 1). Sampling was only conducted under low swell conditions (< 1 m). The net was towed for 20 minutes at an average speed of 2.5 knots approximately 50 m behind the research vessel. It was towed at a slight angle to avoid disturbances caused by the boat's wake. Samples from the Rhône River (station #6) were collected from a fixed location on the dock of the river. Sampled superficies at this station were calculated by comparing the flow rate during sampling with reference flow rates and river speeds. Lower-limit river speeds were used for estimates, since river speeds tend to be slower near the dock.

The net was carefully rinsed and the content of the cod-end was poured into a 1 L glass bottle, preserved with a buffered seawater formalin solution (final concentration 5%), and kept in cold and dark conditions until further analysis. Samples were then sieved (mesh size 125 μm), and rinsed with ultrapure water (ISO 3696). Plastic debris were picked out with tweezers under a dissecting microscope. Fibers were not taken into account due to the high risk of contamination. No Fourier Transform Infrared Spectroscopy (FTIR) Analysis was performed to verify the nature of the items, so despite all efforts to maximize result reliability, it cannot be excluded that some non-plastic items were estimated to be microplastics.

The number, size and shape of each item was identified using a ZooScan© (HYDROPTIC SARL). Each item was placed on the screen of the ZooScan without any water. Surface area measurements in pixels were obtained using the ImageJ software and then converted into mm^2 and the Equivalent Spherical Diameter (ESD). Plastic items $\leq 5 \text{ mm}$ were considered. All microplastics from each sample were then weighed (Mettler AE 240, reliability $\pm 0.1 \text{ mg}$). Microplastic abundance ($\text{items } \text{km}^{-2}$) and dry weight ($\text{g } \text{km}^{-2}$) were calculated for each sample using the towing distance and the net opening surface. Analysis of variance (one-way and two-way ANOVA) with a 0.05 level of significance was performed to assess whether the microplastic abundance and size distribution varied with space (stations) and time. The Tukey test was used whenever significant differences were detected. All statistical analyses were performed using R version 3.3.2.

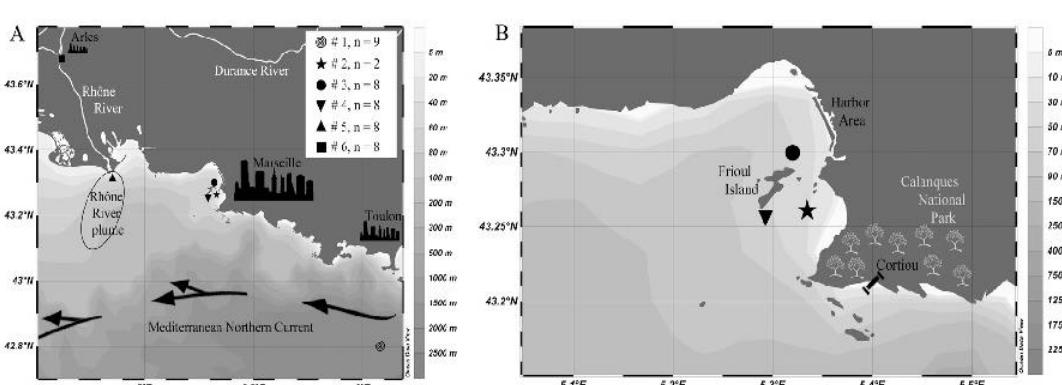


Fig. 1. The sampling stations situated in the eastern Gulf of Lion (A) including Antares site (station 1), Marseille Bay site (stations 2–4) and Rhône River site (stations 5–6). The Rhône River plume as observed during north/northwest wind conditions and the Northern Current (NC) are also indicated. Zoom of the Bay of Marseille (B) with the local WWTP (Cortiou). Map modified after Schlitzer, 2009.

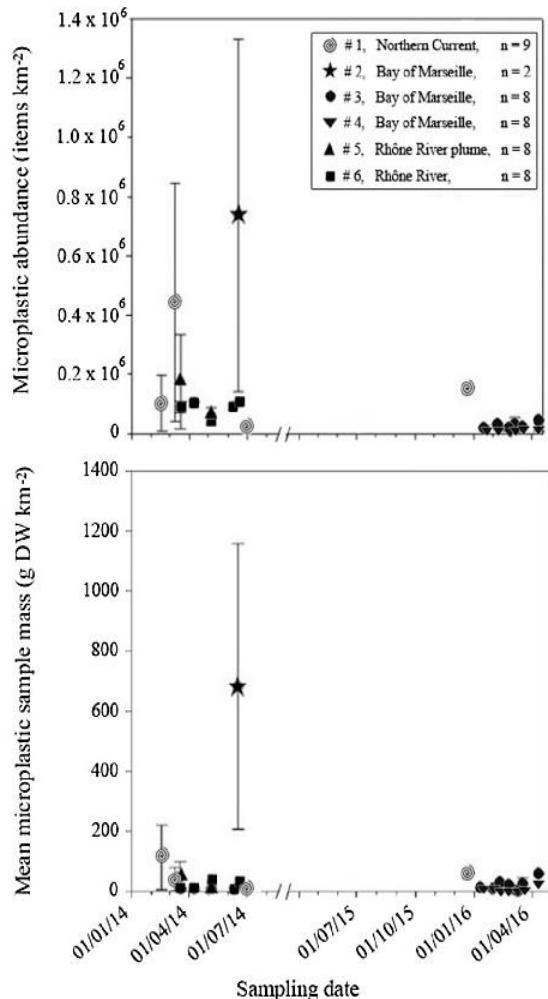


Fig. 2. Microplastic abundance (top; particles km^{-2}) and weight (bottom; g dry weight km^{-2}) for the six stations studied at the three sites. For samples collected the same day at the same station, points represent the averaged values and error bars the standard deviation. n = overall number of samples taken at this station. Note: the weight of one sample collected on 10/03/14 was not available and the data point hence only represents the weight of the two other samples collected this day at station #1.

3. Results and discussion

3.1. Microplastic abundance

Microplastic abundance ranged from $6 \cdot 10^3$ to $1 \cdot 10^6$ (mean $96 \cdot 10^3$) items km^{-2} in the Marseille Bay area, from $33 \cdot 10^3$ to $400 \cdot 10^3$ (mean $113 \cdot 10^3$) items km^{-2} in the Rhône River plume, from $7 \cdot 10^3$ to $69 \cdot 10^3$ (mean $34 \cdot 10^3$) items km^{-2} in the river itself and from $9 \cdot 10^3$ to $916 \cdot 10^3$ (mean $212 \cdot 10^3$) items km^{-2} off-shore (Fig. 2, top). The highest microplastic concentration ($1 \cdot 10^6$ items km^{-2}) was observed at station #2 (Marseille Bay area). The day this sample was collected was characterized by calm conditions with no noteworthy surface currents near the station. In contrast, the other two stations on the coast of Marseille, stations #3 and #4, showed very low particle concentrations (averages $20 \cdot 10^3$ and $10 \cdot 10^3$ items km^{-2} , respectively). While a comparison between these both stations and the station #2 is difficult, because the samples were collected in different years (2016 vs. 2014), some assumptions can still be considered. Goldstein et al. (2013) reported that a high spatial heterogeneity for microplastic concentrations could be found not only at a large scale but also on a smaller scale for samples taken at distances of 10 km from one another. Heterogeneous spatial debris distribution can be the result of currents, wave- and wind-driven turbulences, river inputs or hydrodynamic features such as

upwelling, downwelling, gyres or fronts (e.g., Kukulka et al., 2012; Suaria and Aliani, 2014; Collignon et al., 2012). More generally, high concentrations of microplastics, especially small fragments, are found in coastal waters because of the proximity of densely populated areas, (Pedrotti et al., 2016) and continental inputs from the atmosphere or rivers (Collignon et al., 2012). Point pollutions could also play an important role in the Bay of Marseille, where the fierce northwestern Mistral wind can transport litter from city streets into coastal waters. Another possible source of microplastics in the Bay of Marseille is the local sewage facility (Cortiou) where treated wastewater enters the sea in the southeastern part of the city. On March 17, 2016 a slight surface current coming from Cortiou at a speed of approximately 0.5 m s^{-1} entered the area of stations #3 and 4. The microplastic concentrations observed that day were the highest ever found at station #4 ($15 \cdot 10^3$ items km^{-2}) and the second highest for station #3 ($27 \cdot 10^3$ items km^{-2}). Interestingly, microplastic abundance was always higher at station #3 compared to station #4, in spite of their geographical proximity ($p < .05$).

Our median concentration ($31 \cdot 10^3$ items km^{-2}) was about one third of the mean value, highlighting potential surges in microplastic presence, possibly linked to climatic and hydrodynamic events. Hydrodynamic processes influencing microplastic distribution are e.g. vertical mixing or eddies and anticyclonic gyres. The latter of which are unsteady formations in the Mediterranean Sea (Pedrotti et al., 2016), but could lead to punctual increases in regional microplastic abundances. Additionally, in our study area, there is the Northern Current, which varies greatly in intensity, depth, and position (Millot, 1991). Data collected at station #1 showed temporal variability, with concentrations of microplastics being significantly higher on March 10, 2014 ($p < .05$) when the Northern Current was fast and narrow with maximum speeds of approximately 0.9 m s^{-1} . However, triplicated trawls exhibited a range of microplastic abundances from $103 \cdot 10^3$ to $916 \cdot 10^3$ items km^{-2} at this sampling date, implying that a nine fold difference in abundances can be observed in the same sampling area within two hours. This further highlights the strong temporal variability observed for microplastic concentrations. Overall no seasonal differences were detected ($p > .05$), but the low number of observations limits the strength of any comparison. Goldstein et al. (2013) observed seasonal heterogeneity at much larger scale in the northeastern Pacific Ocean between summer 2009 and fall 2010.

Floating debris transported by the NC could be transported to the Balearic Islands, where models calculated high beaching probabilities (Mansui et al., 2014), or to the seafloor which is known to be a (micro-) plastic sink (Claessens et al., 2011; Ioakeimidis et al., 2014; Woodall et al., 2014). Reasons of microplastic sedimentation can be the nature of the plastic material, (if its density is higher than the one of seawater, Tekman et al., 2017), the biofouling accumulation on microplastic surfaces (Woodall et al., 2014), the incorporation of free microplastics into marine aggregates or the incorporation of microplastics into fast-sinking faecal pellets after ingestion by zooplanktons and fishes (Cole et al., 2013).

The overall average microplastic abundance for our samples was $112 \cdot 10^3$ items km^{-2} , which is in the same range as other areas in the northwestern basin, where mean densities have been estimated to $115 \cdot 10^3$ items km^{-2} (Collignon et al., 2012), $130 \cdot 10^3$ items km^{-2} (Faure et al., 2015) and $150 \cdot 10^3$ items km^{-2} (De Lucia et al., 2014). Higher amounts were measured for the entire Mediterranean basin ($243 \cdot 10^3$ items km^{-2} , Cázár et al., 2015), due to high concentrations in some Mediterranean areas. Densely populated areas as the semi-enclosed Adriatic Sea and the Levantine Basin were characterized by high densities of $1,050 \cdot 10^3$ (max: $4,600 \cdot 10^3$; Suaria et al., 2015) and $1,518 \cdot 10^3$ (max: $65 \cdot 10^6$; Van der Hal et al., 2017) items km^{-2} , respectively. Our results are consistent with previous studies and indicate that the northwestern Mediterranean Sea contains similar mean microplastic concentrations as the Atlantic and Pacific Oceans (mean: $134 \cdot 10^3$ items km^{-2} and $124 \cdot 10^3$ items km^{-2} , respectively, Eriksen

et al., 2014). Hereby it needs to be considered that the Atlantic and Pacific Oceans are also known to be highly heterogeneous, with microplastic accumulation and non-accumulation zones. Examples for a heavily contaminated area are the East Asian Seas, where a mean microplastic abundance of $1720 \cdot 10^3$ items km^{-2} was measured (Isobe et al., 2015).

Microplastic abundances in the Rhône River at Arles (station #6; $34 \cdot 10^3 \pm 19 \cdot 10^3$ items km^{-2} ; net size $0.50 \text{ m} \times 0.15 \text{ m}$, mesh size $780 \mu\text{m}$) were relatively low, but were similar to values reported by De Alencastro (2014) upstream at Chancy ($\sim 52 \cdot 10^3$ items km^{-2} ; net size $0.60 \text{ m} \times 0.18 \text{ m}$, mesh size $300 \mu\text{m}$). In comparison, a mean microplastic abundance of $893 \cdot 10^3$ items km^{-2} was found in the Rhine River, a watercourse flowing through highly industrialized areas, such as North-Rhine Westphalia (Germany), where many plastic factories are located (Mani et al., 2015). Concentrations observed in the Rhône River plume (station #5, up to $400 \cdot 10^3$ items km^{-2}) were higher than in the river itself, suggesting that the Rhône River – sea interface may generate a temporal accumulation zone for debris. In general, however, the area covered by our six sampling stations is not considered to be a retention area, but can better be described as a “transit area”. The size of the Mediterranean basin reduces the potential for formation of permanent gyres as in the Atlantic, Pacific and Indian Oceans, where plastic often concentrates (Cózar et al., 2015).

At the river mouth, microplastic concentrations were either significantly greater ($p < .05$) or similar to those observed upstream in the Rhône River. Concerning the river plume, we should highlight the similitude in zooplankton composition of two samples collected with the same Manta trawl, first, on the 10/03/14 at the station #1 (NC) and then (18/03/14), at the Rhône River Plume station (station #5). High abundances (> 1000 individuals per sample) of *Velella velella*, a free-floating hydrozoan, were observed at both dates (Thibault D. pers. com.), implying a potential intrusion of water masses from the NC onto the shelf. Such intrusions have already been observed before (Barrier et al., 2016). Salinity data from the Mars 3D model support the hypothesis: while the Rhône River plume was extended in all directions on 10/03/14 and the following days, saltier surface waters pushed from the eastern direction into the area from 16/03/14 on and thus, reduced the extension area of the river plume. During the period examined, the velocity of the NC flowing through station #1 was about 0.4 m s^{-1} (Suppl. Table 1), but currents leaving the main branch in northwestern directions flowed at reduced speeds of about 0.2 m s^{-1} . At this speed range ($0.2\text{--}0.4 \text{ m s}^{-1}$), water masses could have travelled about $140\text{--}275 \text{ km}$ in eight days, which is consistent with the straight line distance (120 km) between both stations. However, we would like to point out that these are only indications, since an accurate model would be needed to simulate the exact trajectory of the water masses and microplastics in question.

3.2. Microplastic weight

Microplastic dry weight showed a similar variability, ranging from $0.30 \text{ g DW km}^{-2}$ to $1018 \text{ g DW km}^{-2}$, with the maximum observed in Marseille Bay (Fig. 2, bottom). An average of $61.92 \text{ g DW km}^{-2}$ ($\pm 178.03 \text{ g DW km}^{-2}$) was found in the study area. This value is similar to averages of 60 and 63 g DW km^{-2} reported for the western part of the northwestern Mediterranean Sea (Collignon et al., 2012) and the upstream part of the Rhône River (De Alencastro, 2014), respectively.

An estimated surface area of 87 km^2 of the Bay of Marseille would provide a total microplastic load of 0.07 to 118 kg (mean 9.94 kg), representing a range of concentrations from $0.5 \cdot 10^6$ to $101 \cdot 10^6$ (mean $8 \cdot 10^6$) microplastic pieces in surface waters. For the Rhône River, the flow rate used for calculations varied between $1150 \text{ m}^3 \text{ s}^{-1}$ and $1600 \text{ m}^3 \text{ s}^{-1}$ during the sampling period. Using minimum and maximum concentration and weight values, we calculated a daily microplastic spill of $0.20\text{--}21.32 \text{ kg}$ (dry weight), representing $10 \cdot 10^6\text{--}40 \cdot 10^6$ items discharged by the Rhône River into the

Mediterranean Sea. Similarly, microplastic loads for the Northern Current were calculated using volumetric transport rates of 0.7 Sv (Conan and Millot, 1995) and 2 Sv (Petrenko, 2003) and the minimum and maximum concentration and weight values. This method provided an estimate of daily transport ranging from 0.18 to 86.46 tons (dry weight) of microplastic, representing $4 \cdot 10^9$ to $1 \cdot 10^{12}$ items. These calculations give minimum ranges, since they are based on the assumption that microplastics concentrate within 15 cm under the surface. Turbulences, especially in rivers, may however transfer microplastics through several meters of the water column. As interesting as they are, these extrapolations should be considered with caution, since microplastic abundances show a high amount of variability and are difficult to predict.

3.3. Microplastic size distribution

The mean size of microplastic was $1.48 \pm 0.88 \text{ mm}$, however significant differences ($p < .01$) were observed between samples from the Bay of Marseille (stations # 2–4) and all other sampling stations. For better visualization of the size distribution of our samples, we calculated the equivalent spherical diameter (ESD) of each microplastic particle (Fig. 3). A general exponential distribution curve was observed with the smallest items being the most important, except in the Bay of Marseille, where microplastics were more evenly distributed over the size range. The overall size distribution observed in this study closely resembles those observed for the Mediterranean Sea (Ruiz-Orejón et al., 2016; Cózar et al., 2015), open ocean waters (Cózar et al., 2014) and the Northeast Pacific Ocean (Goldstein et al., 2013). Manta nets are the most commonly used sampling device for microplastic sampling in aquatic ecosystems and were also used in this study. The mesh size of the net can influence the size distribution as well as the speed of the tow, as smaller particles avoiding the net can be forced aside from the net opening or large particles can squeeze out through the mesh. This study used mainly a $780 \mu\text{m}$ mesh sized net and a $330 \mu\text{m}$ mesh sized net only for ten sampling events at stations # 3 and #4 (Suppl. Table 1). We expected to collect more $0.0\text{--}0.4 \text{ mm}$ items at both concerned stations (#3 and #4) by using the $330 \mu\text{m}$ mesh sized net, but microplastics of this size class were observed neither in samples from the $330 \mu\text{m}$ mesh size, nor in samples from the $780 \mu\text{m}$ mesh size. No influence on the microplastic size distribution caused by the use of these different mesh sizes was hence observed. This was statistically confirmed by removing all samples collected with the $330 \mu\text{m}$ net from the dataset and repeating the one-way ANOVA with the following post-hoc test and obtaining the same significant results.

Size distribution can be an indicator of the source of marine debris and of its distance to the shoreline. While Pedrotti et al. (2016) observed that small sized microplastics were more abundant within the first kilometre adjacent to the coastline, Isobe et al. (2015) found that the percentage of larger plastic particles is typically greater in areas close to the pollution source.

The surface area distributions of stations #1 (NC) and #6 (Rhône River) clearly resemble each other. Both are dominated by small particles ($< 1 \text{ mm}^2$: 52 and 53%, respectively, Fig. 4). This size class only represented 27% for stations in the Bay of Marseille, but represented 61% of microplastic particles at the Rhône River plume. The second size class ($1\text{--}5 \text{ mm}^2$) was the most abundant in Marseille Bay (55%). The largest pieces ($> 10 \text{ mm}^2$) were poorly represented ($< 5\%$) at all stations. The size class distributions are likely related to the distance of the collected particles from pollution sources. In the case of station #1 (NC), it is likely that microplastics were transported by the Northern Current and may have originated in regions farther east, such as the Italian coast. At station #6 (Rhône River), the size distribution suggests that the collected microplastics were in the Rhône River watershed for some time and certainly originated from highly industrialized and/or populated regions higher upstream (e.g., Lyon with $\sim 500,000$ inhabitants). The position of the Rhône River plume varies based on wind

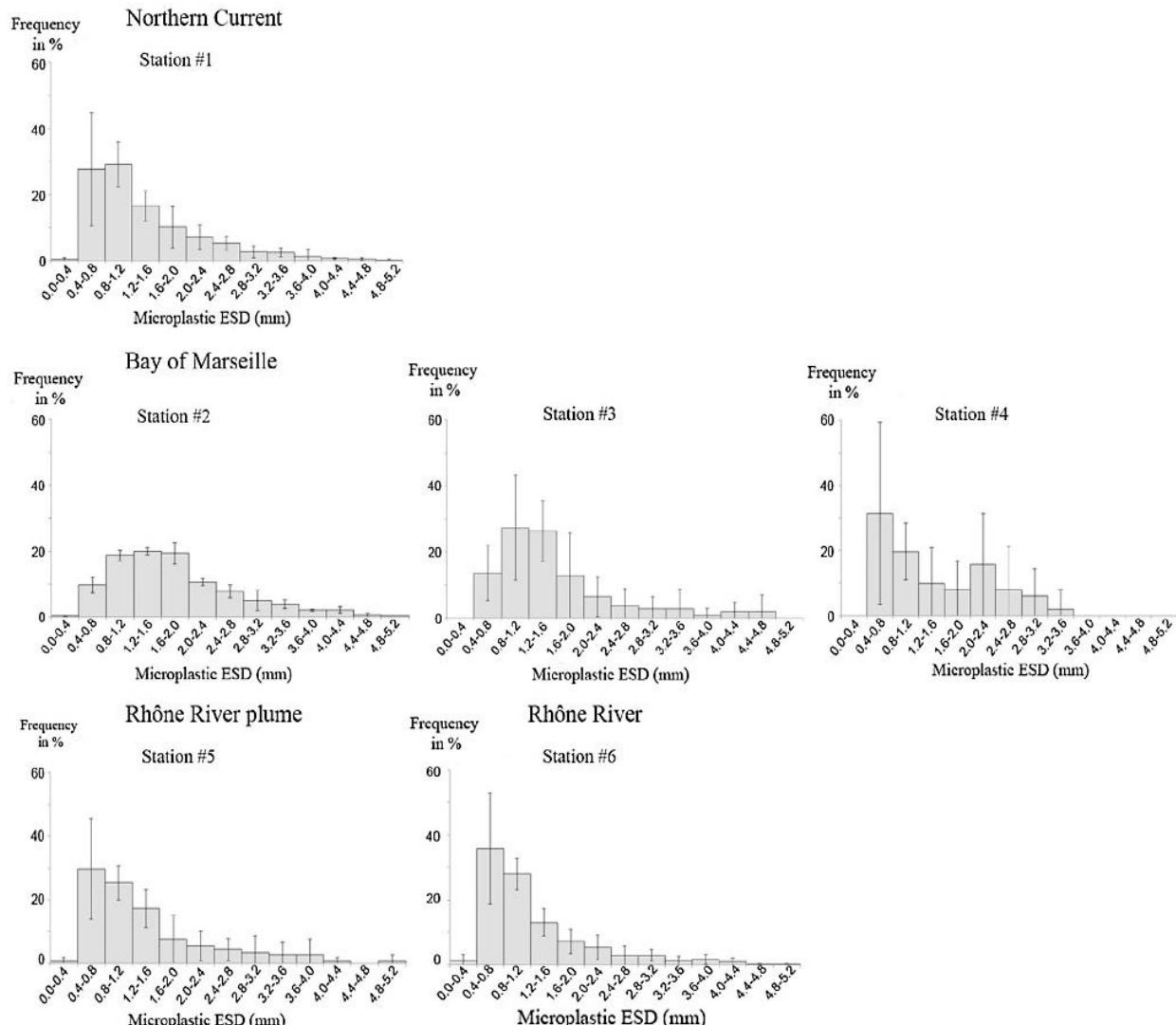


Fig. 3. Microplastic size distributions (ESD in mm) measured at six sampling stations with a ZooScan apparatus. Error bars represent the standard deviation.

and river flow; therefore, debris will be contributed from both the river itself and surrounding coastal areas in variable amounts. Since the smallest particles are most abundant here, it is probable that these microplastics, have also been transported by water masses for some time before collection. In the Bay of Marseille (stations #2–4) the dominance of larger particles (1–5 mm²) suggests that the microplastics collected in this area were closer to their source and mainly originate from the urban area. A more efficient removal of the smallest floating particles in this region, via ballasting due to epiphytic growth, could also be a possible explanation (Ryan, 2015).

4. Conclusions

This study provides additional data on microplastic occurrence in the eastern Gulf of Lion. Our results revealed that surface water microplastic concentrations and size distributions in this area affected by anthropogenic impacts are consistent with those already published for the western Mediterranean Sea. Significant temporal and spatial heterogeneity was observed for microplastic abundances. Our results confirm that the Rhône River, large cities, such as Marseille, and the Northern Current act as sources and/or transportation routes of microplastics collected in the northwestern basin of the Mediterranean Sea. As our microplastics are floating, it was shown that it can be

pertinent to study the zooplankton composition of samples additionally to currentology data, in order to improve our knowledge on microplastic transport in the sea.

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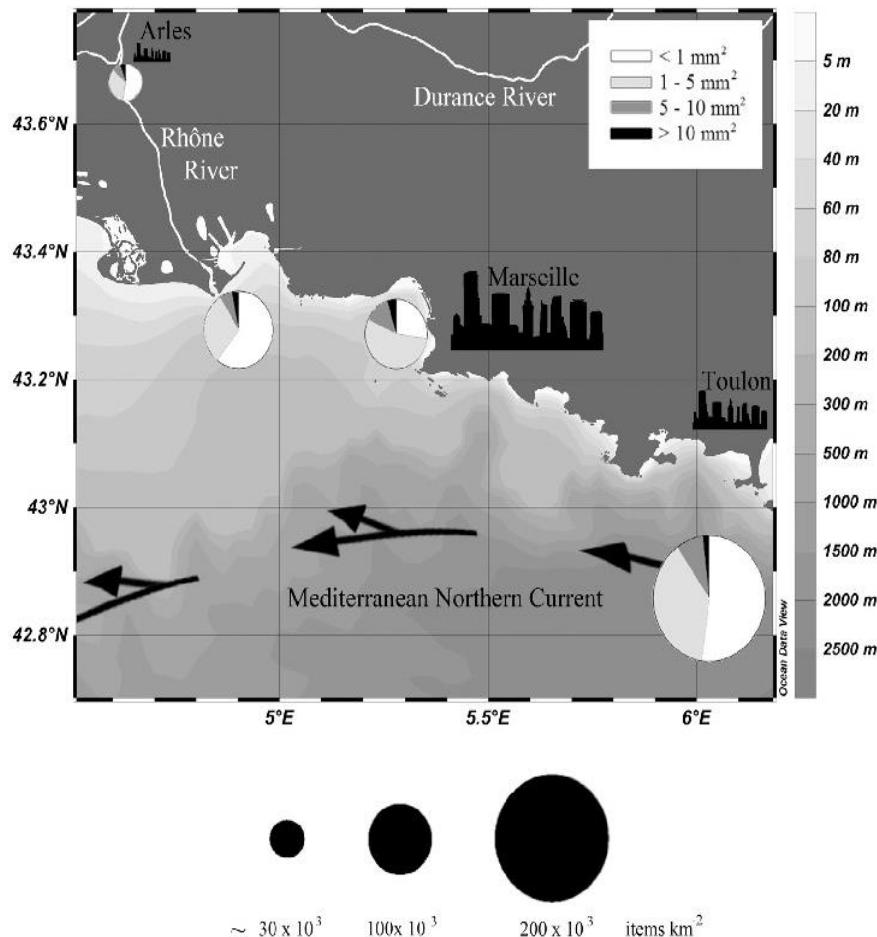


Fig. 4. Spatial occurrence of microplastics and surface area distribution in the Northern Current (station #1), the Bay of Marseille (stations #2-4), the Rhône River plume (station #5) and the Rhône River (station #6). The size of the pie charts is hereby proportional to overall particle concentrations. Map modified after Schlitzer, 2009.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.pocean.2017.11.010>.

References

- Banaru, D., Mellon-Duval, C., Roos, D., Bigot, J.-L., Souplet, A., Jadaud, A., Beaubrun, P., Fromentin, J.-M., 2013. Trophic structure in the Gulf of Lions marine ecosystem (north-western Mediterranean Sea) and fishing impacts. *J. Mar. Syst.* 111–112, 45–68.
- Barrier, N., Petrenko, A.A., Oummières, Y., 2016. Strong intrusions of the Northern Mediterranean Current on the eastern Gulf of Lion: insights from in-situ observations and high resolution numerical modelling. *Ocean Dyn.* 66, 313–327.
- Blanfuné, A., Boudouresque, C.F., Verlaque, M., Bejjaj, S., Kashta, L., Nasto, I., Ruci, S., Thibaut, T., 2016. Response of rocky shore communities to anthropogenic pressures in Albania (Mediterranean Sea): ecological status assessment through the CARIT method. *Mar. Pollut. Bull.* 109, 409–418.
- Casale, P., Freggi, D., Furii, G., Vallini, C., Salvemini, P., Deflorio, M., Totaro, G., Raimondi, S., Fortuna, C., Godley, B.J., 2015. Annual survival probabilities of juvenile loggerhead sea turtles indicate high anthropogenic impact on Mediterranean populations. *Aquat. Conserv. Mar. Freshwater Ecosyst.* 25, 690–700.
- Claessens, M., De Meester, S., Van Landuyt, L., De Clerck, K., Janssen, C.R., 2011. Occurrence and distribution of microplastics in marine sediments along the Belgian coast. *Mar. Pollut. Bull.* 62, 2199–2204.
- Cole, M., Lindeque, P., Fileman, E., Halsband, C., Goodhead, R., Moger, J., Galloway, T.S., 2013. Microplastic ingestion by zooplankton. *Environ. Sci. Technol.* 47 (12), 6646–6655.
- Collignon, A., Hecq, J.-H., Glagani, F., Voisin, P., Collard, F., Goffart, A., 2012. Neustonic microplastic and zooplankton in the North Western Mediterranean Sea. *Mar. Pollut. Bull.* 64, 861–864.
- Conan, P., Millot, C., 1995. Variability of the Northern Current off Marseilles, western Mediterranean Sea, from February to June 1992. *Oceanol. Acta* 18 (2), 193–205.
- Cózar, A., Echevarría, F., González-Gordillo, J.I., Irigoien, X., Úbeda, B., Hernández-León, S., Palma, A.T., Navarro, S., García-de-Lomas, J., Ruiz, A., Fernández-de-Puelles, M.L., Duarte, C.M., 2014. Plastic debris in the open ocean. *PNAS* 111 (28), 10239–10244.
- Cózar, A., Sanz-Martín, M., Martí, E., González-Gordillo, J.I., Úbeda, B., Gálvez, J.Á., Irigoien, X., Duarte, C.M., 2015. Plastic accumulation in the mediterranean sea. *PLoS ONE* 10 (4), 1–12.
- De Alencastro, L.F., 2014. Evaluation de la pollution par les plastiques dans les eaux de surface en Suisse. Rapport final. Sur mandat de l'Office fédéral de l'environnement (OFEV), pp. 22–23.
- De Lucia, G.A., Caliani, I., Marra, S., Camedda, A., Coppa, S., Alcaro, L., et al., 2014. Amount and distribution of neustonic micro-plastic off the Western Sardinian coast (Central-Western Mediterranean Sea). *Mar. Environ. Res.* 100, 10–16.
- Desforges, J.-P.W., Galbraith, M., Ross, P.S., 2015. Ingestion of microplastics by zooplankton in the northeast Pacific Ocean. *Arch. Environ. Contam. Toxicol.* 69, 320–330.
- Deudero, S., Alomar, C., 2015. Mediterranean marine biodiversity under threat: re-viewing influence of marine litter on species. *Mar. Pollut. Bull.* 98, 58–68.
- Eriksen, M., Lebreton, L.C.M., Carson, H.S., Thiel, M., Moore, C.J., Borerro, J.C., Galgani, F., Ryan, P.G., Reisser, J., 2014. Plastic pollution in the world's oceans: more than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea. *PLoS ONE* 9 (12), 1–15.
- Faure, F., Saini, C., Potter, G., Galgani, F., De Alencastro, L.F., Hagmann, P., 2015. An evaluation of surface micro- and mesoplastic pollution in pelagic ecosystems of the Western Mediterranean Sea. *Environ. Sci. Pollut. Res.* 22 (16), 12190–12197.
- Fraysse, M., Piaraud, I., Ross, O.N., Faure, V.M., Pinazo, C., 2014. Intrusion of Rhone river diluted water into the bay of marseille: generation processes and impacts on ecosystem functioning. *J. Geophys. Res. Oceans* 119, 6535–6556.
- Gatti, J., Petrenko, A., Leredde, Y., Devenon, J.-L., Ulises, C., 2006. The Rhone river dilution zone present in the northeastern shelf of the Gulf of Lion in December 2003. *Cont. Shelf Res.* 26 (15), 1794–1805.
- Goldstein, M.C., Titmus, A.M., Ford, M., 2013. Scales of spatial heterogeneity of plastic marine debris in the Northeast Pacific Ocean. *PLoS ONE* 8 (11), 1–11.
- Hassoun, A.E.R., Gemayel, E., Krasakopoulou, E., Goyet, C., Saab, M.A.-A., Guglielmi, V., Touratier, F., Falco, C., 2015. Acidification of the Mediterranean Sea from anthropogenic carbon penetration. *Deep-Sea Res. I* 102, 1–15.
- Heudorf, U., Mersch-Sundermann, V., Angerer, J., 2007. Phthalates: toxicology and exposure. *Int. J. Hyg. Environ. Health* 210 (5), 623–634.
- Ioakeimidis, C., Zeri, C., Kaberi, H., Galatzi, M., Antoniadis, K., Streftaris, N., Galgani, F., Papathanassiou, E., Papatheodorou, G., 2014. A comparative study of marine litter on the seafloor of coastal areas in the Eastern Mediterranean and Black Seas. *Mar. Pollut. Bull.* 89, 296–304.
- Isobe, A., Uchida, K., Tokai, T., Iwasaki, S., 2015. East Asian seas: a hot spot of pelagic microplastics. *Mar. Pollut. Bull.* 101, 618–623.
- Kobrosly, R.W., Evans, S., Miodovník, A., Barrett, E.S., Thurston, S.W., Calafat, A.M.,

- Swan, S.H., 2014. Prenatal phthalate exposures and neurobehavioral development scores in boys and girls at 6–10 years of age. *Environ. Health Perspect.* 122 (5), 521–528.
- Kukulka, T., Proskurowski, G., Morét-Ferguson, S., Meyer, D.W., Law, K.L., 2012. The effect of wind mixing on the vertical distribution of buoyant plastic debris. *Geophys. Res. Lett.* 39, 1–6.
- Lwanga, E.H., Gersten, H., Gooren, H., Peters, P., Salánki, T., van der Ploeg, M., Besseling, E., Koelmans, A.A., Geissen, V., 2016. Microplastics in the Terrestrial Ecosystem: Implications for *Lumbricus terrestris* (Oligochaeta, Lumbricidae). *Environ. Sci. Technol.* 50, 2685–2691.
- Mani, T., Hauk, A., Walter, U., Burkhardt-Holm, P., 2015. Microplastics profile along the Rhine River. *Nature Sci. Rep.* 5, 17988. <http://dx.doi.org/10.1038/srep17988>.
- Mansui, J., Molcard, A., Ourmières, Y., 2014. Modelling the transport and accumulation of floating marine debris in the Mediterranean basin. *Mar. Pollut. Bull.* 91, 249–257.
- Martini, S., Michotey, V., Casalot, L., Bonin, P., Guasco, S., Garel, M., Tamburini, C., 2016. Bacteria as part of bioluminescence emission at the deep ANTARES station (North-Western Mediterranean Sea) during a one-year survey. *Deep-Sea Res. I* 116, 33–40.
- Millot, C., 1991. Mesoscale and seasonal variabilities of the circulation in the western Mediterranean. *Dyn. Atmos. Oceans* 15, 179–214.
- Neves, D., Sobral, P., Ferreira, J.L., Pereira, T., 2015. Ingestion of microplastics by commercial fish off the Portuguese coast. *Mar. Pollut. Bull.* 101, 119–126.
- Oehlmann, J., Schulte-Oehlmann, U., Kloas, W., Jagnytsch, O., Lutz, I., Kusk, K.O., Wollenberger, L., Santos, E.M., Paull, G.C., Van Look, K.J.W., Tyler, C.R., 2009. A critical analysis of the biological impacts of plasticizers on wildlife. *Philos. Trans. R. Soc. B* 364, 2047–2062.
- Pedrotti, M., Petit, S., Elineau, A., Bruzaud, S., Crebassa, J., Dumontet, B., Marti, E., Gorsky, G., Cozar, A., 2016. Changes in the floating plastic pollution of the Mediterranean Sea in relation to the distance to land. *PLoS ONE* 11 (8), e0161581.
- Petrenko, A.A., 2003. Variability of circulation features in the Gulf of Lion NW Mediterranean Sea. Importance of inertial currents. *Oceanol. Acta* 26, 323–338.
- Pouain, P., Menna, M., Mauri, E., 2012. Surface geostrophic circulation of the Mediterranean Sea derived from drifter and satellite altimeter data. *J. Phys. Oceanogr.* 42 (6), 973–990.
- Przybylinska, P.A., Wyszkowski, M., 2016. Environmental contamination with phthalates and its impact on living organisms. *Ecol. Chem. Eng. Soc.* 23 (2), 347–356.
- PlasticsEurope, 2015. Plastics – The Facts 2015: An analysis of European plastics production, demand and waste data. <<http://www.plasticseurope.org/Document/plastics-the-facts-2015.aspx>> (accessed 11.01.2016).
- Ruiz-Orejón, L.F., Sardá, R., Ramis-Pujol, J., 2016. Floating plastic debris in the Central and Western Mediterranean Sea. *Mar. Environ. Res.* 120, 136–144.
- Ross, O.N., Fraysse, M., Pinazo, C., Pairaud, I., 2016. Impact of an intrusion by the Northern Current on the biogeochemistry in the eastern Gulf of Lion, NW Mediterranean. *Estuar. Continent. Shelf Res.* 170, 1–9.
- Ryan, P.G., 2015. Does size and buoyancy affect the long-distance transport of floating debris? *Environ. Res. Lett.* 10, 084019.
- Sathyarayana, S., 2008. Phthalates and children's health. *Curr. Problems Pediatr. Adolesc. Health Care* 38 (2), 34–49.
- Savriama, Y., Stige, L.C., Gerber, S., Pérez, T., Alibert, P., David, B., 2015. Impact of sewage pollution on two species of sea urchins in the Mediterranean Sea (Cortiou, France): radial asymmetry as a bioindicator of stress. *Ecol. Ind.* 54, 39–47.
- Schlitzer, R., 2009. *Ocean Data View*, <<http://odv.awi.de>> .
- Sempéré, R., Charrière, B., Cauwet, G., Van Wambeke, F., 2000. Carbon inputs of the Rhône River to the Mediterranean Sea: biogeochemical implications. *Global Biogeochem. Cycles* 14, 669–681.
- Sigler, M., 2014. The effects of plastic pollution on aquatic wildlife: current situations and future solutions. *Water Air Soil Pollut.* 225, 2184.
- Suaria, G., Aliani, S., 2014. Floating debris in the Mediterranean Sea. *Mar. Pollut. Bull.* 86, 494–504.
- Suaria, G., Avio, C.G., Lattin, G.L., Regoli, F., Aliani, S., 2015. Neustonic microplastics in the Southern Adriatic Sea. Preliminary results. *Micro* 2015. In: Seminar of the Fishgear Project, Abstract Book (Piran), 42.
- Suaria, G., Avio, C.G., Mineo, A., Lattin, G.L., Magaldi, M.G., Belmonte, G., Moore, C.J., Regoli, F., Aliani, S., 2016. The Mediterranean Plastic Soup: synthetic polymers in Mediterranean surface waters. *Nature Sci. Rep.* 6, 37551. <http://dx.doi.org/10.1038/srep37551>.
- Tedetti, M., Longhitano, R., Garcia, N., Guigue, C., Ferretto, N., Goutx, M., 2012. Fluorescence properties of dissolved organic matter in coastal Mediterranean waters influenced by a municipal sewage effluent (Bay of Marseilles, France). *Environ. Chem.* 9 (5), 438–449.
- Tekman, M.B., Krumpen, T., Bergmann, M., 2017. Marine litter on deep Arctic seafloor continues to increase and spreads to the North at the HAUSGARTEN observatory. *Deep Sea Res. Part I* 120, 88–99.
- Ter Halle, A., Ladirat, L., Gendre, X., Goudouneche, D., Pusineri, C., Routaboul, C., Tenailleau, C., Dupoyer, B., Perez, E., 2016. Understanding the fragmentation pattern of marine plastic debris. *Environ. Sci. Technol.* 50, 5668–5675.
- The MerMex Group, 2011. Marine ecosystems' responses to climatic and anthropogenic forcings in the Mediterranean. *Prog. Oceanogr.* 91, 97–166.
- Tranfo, G., Caporossi, L., Paci, E., Aragona, C., Romanzi, D., de Carolis, C., de Rosa, M., Capanna, S., Papaleo, B., Pera, A., 2012. Urinary phthalate monoesters concentration in couples with infertility problems. *Toxicol. Lett.* 213, 15–20.
- UNEP, 2009. *Marine Litter: A Global Challenge*, 232.
- Van der Hal, N., Asaf, A., Dror, A., 2017. Exceptionally high abundances of microplastics in the oligotrophic Israeli Mediterranean coastal waters. *Mar. Pollut. Bull.* 116, 151–155.
- Van Franeker, J.A., Law, K.L., 2015. Seabirds, gyres and global trends in plastic pollution. *Environ. Pollut.* 203, 89–96.
- Van Sebille, E., Wilcox, C., Lebreton, L., Maximenko, N., Hardesty, B.D., van Franeker, J.A., Eriksen, M., Siegel, D., Galgani, F., Law, K.L., 2015. A global inventory of small floating plastic debris. *Environ. Res. Lett.* 10, 124006.
- Woodall, L.C., Sanchez-Vidal, A., Canals, M., Paterson, G.L.J., Coppock, R., Sleight, V., Calafat, A., Rogers, A.D., Narayanaswamy, B.E., Thompson, R.C., 2014. The deep sea is a major sink for microplastic debris. *R. Soc. Open Sci.* 1, 140317.
- Zambianchi, E., Iermano, I., Aliani, S., 2014. Marine litter in the Mediterranean Sea, An Oceanographic perspective. In: Ciesn Workshop N 46 (Coordination F Galgani), Tirana, 18–21 June 2014, 172 pages.
- Zhao, S., Zhu, L., Li, D., 2016. Microscopic anthropogenic litter in terrestrial birds in Shanghai, China: not only plastics but also natural fibers. *Sci. Total Environ.* 550, 1110–1115.

Occurrence, Loading, and Exposure of Atmospheric Particle-Bound POPs at the African and European Edges of the Western Mediterranean Sea

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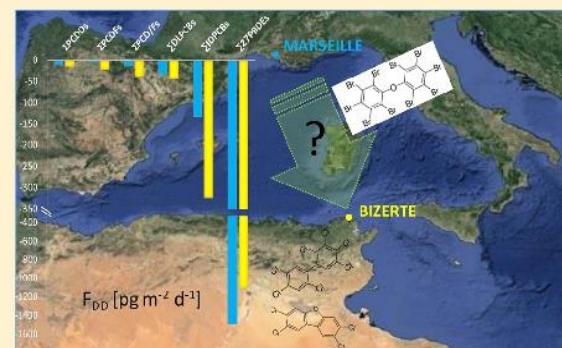
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Supporting Information

ABSTRACT: A comparative study for 62 toxic chemicals based on the monthly collection of aerosol samples during 2015–2016 in two coastal cities at both the African (Bizerte, Tunisia) and European (Marseille, France) edges of the Western Mediterranean basin is presented. Legacy polychlorinated biphenyls (\sum_{18} PCBs) and polychlorinated dibenz-p-dioxins and dibenzofurans (\sum_{17} PCDD/Fs) show generally higher median levels at the African edge (2.1 and 0.2 pg m^{-3} , respectively) compared to the European coastal site (1.0 and 0.08 pg m^{-3} , respectively). Contrarily, the “emerging” polybrominated diphenyl ethers’ (\sum_{27} PBDEs) median concentrations were higher in Marseille (~9.0 pg m^{-3}) compared to Bizerte (~6.0 pg m^{-3}). Different past usages and current emission patterns were found at both edges of the Western Mediterranean, most probably linked to the respective different regulatory frameworks for toxic chemicals. Our results indicate that the total organic carbon (TOC) and/or the elemental carbon (EC) contents in the atmospheric aerosol may have a stronger effect than the total suspended particle (TSP) content as a whole on the spatial-temporal variability and the long-range atmospheric transport potential of the studied POPs. A “jumping” of the PBDE local atmospheric stocks from the Northwestern European Mediterranean edge to the Northwestern African coast seems to be possible under favorable conditions at present. While a higher PBDE median loading is estimated for the Marseille area (~550 $\text{ng m}^{-2} \text{y}^{-1}$) compared to Bizerte (~400 $\text{ng m}^{-2} \text{y}^{-1}$), the median PCB and PCDD/F dry deposition fluxes were higher at the African site, resulting in a 3-fold higher toxic equivalent (TEQ) loading of dioxin-like pollutants (400 $\text{pg TEQ m}^{-2} \text{y}^{-1}$) compared to Marseille (~140 $\text{pg TEQ m}^{-2} \text{y}^{-1}$), with potential implications for aquatic organisms. However, the inhalation exposure assessment points to a minimum risk for human health at both sites.



INTRODUCTION

Atmospheric particulate matter has been recognized as a major environmental airborne pollutant impacting human health and ecosystems.¹ A recent study performed in the Mediterranean Sea supports the hypothesis that atmospheric aerosols can elicit a number of toxic effects in marine organisms due to the presence of hydrophobic contaminants intimately associated with the atmospheric particle phase.² High molecular weight (HMW) polycyclic aromatic hydrocarbons (PAHs) and generally persistent organic pollutants (POPs) such as polychlorinated dibenz-p-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are among the contaminants suspected to produce these hazardous effects.² In addition, POPs associated with the atmospheric

particle phase can be more resistant to atmospheric degradation processes (e.g., photodegradation), increasing therefore their atmospheric residence times, subsequent long-range atmospheric transport (LRAT), and potential exposure.² A first step in order to elucidate the potential role of particle-bound POPs in toxic pathways and to estimate their atmospheric dry deposition, considered as the main vector for the introduction of the most hydrophobic contaminants in aquatic ecosystems, is their accurate qualitative (congener specific distribution) and

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quantitative (environmental concentration) determinations in the atmospheric aerosol. The legacy PCDD/Fs and PCBs may lead to complex mixtures in the environment. However, the 17 2,3,7,8-chlorine substituted PCDD/Fs (i.e., seven PCDDs or “dioxins” + 10 PCDFs or “furans”) and the 12 dioxin-like PCBs (_{DL}PCBs) named CBs-81, -77, -105, -114, -118, -123, -126, -156, -157, -167, -169, -189, jointly considered as dioxin-like pollutants, have received most of the attention due to their accumulation and toxic effects in biota and humans.^{3–6} In addition, a set of nondioxin-like PCBs, commonly referred to as indicator PCBs (_{ID}PCBs), containing CBs-28, -52, -101, -138, -153, and -180 are often monitored due to their higher environmental concentrations and potential toxic effects by different mechanisms of action.^{7–9} Other POPs with recognized toxicity too, such as polybrominated diphenyl ethers (PBDEs), can add up to the “contaminant-aerosol cocktail.”^{10,11} These pollutants have different sources in the environment. PCDD/Fs can occur as unintentional byproducts in a number of industrial processes and domestic heating,^{12,13} while current emissions of PCBs are urban/industrial centers, open burning of products containing PCBs, waste incinerations, accidental fires and revolatilization from environmental reservoirs.^{14,15} PBDEs were mostly used (and still used in some regions) as flame retardants and, contrary to PCDD/Fs and PCBs, are considered as a first generation of “emerging contaminants” (only recently restricted). Three PBDE commercial formulations were extensively used worldwide: the penta-formulation (with predominance of BDE-47 and -99), the octa-BDE (with PBDE-183 as one of the major components), and the deca-BDE (with BDE-209 predominating).¹⁶

These contaminants are globally banned by the Stockholm Convention of POPs (including all PBDE formulations) and regulated by the Water and Marine Strategy Framework Directives at the European level (except for the octa- and deca-PBDE formulations). However, still very little or no information exists on current baseline levels and stocks for many marine areas, even in environments under important anthropogenic pressure like the Mediterranean Sea. This semienclosed environment of high ecological and socio-economic relevance is largely impacted by POPs and related contaminants.^{17–19} PCDD/Fs, PCBs, and PBDEs are among the POPs found in the atmospheric compartment from various Northwestern Mediterranean coastal environments (from rural to large cities)^{20–26} and the central/Eastern basin,^{27–33} but also farther from the coast in the entire Mediterranean Sea.^{34–36} The European Mediterranean coast is by far the most studied, and only a few measurements (focusing in the Southeastern Mediterranean) have been carried out in the African Mediterranean edge.^{37,38} The atmospheric occurrence of POPs over the Northwestern Mediterranean African coast is still largely unknown. In addition, parallel observations at both the African and European margins of the Mediterranean Sea have never been attempted to the best of our knowledge.

We report here results from 22 aerosol samples (total suspended particles, TSP) simultaneously collected (once per month) in two urban coastal sites at both the African and European edges of the Western Mediterranean. The samples have been analyzed for 62 toxic chemicals associated with the atmospheric aerosol. The main objectives of this study are (1) to establish baseline atmospheric levels of three of the most toxic POPs families (i.e., PCDD/Fs, PCBs, and PBDEs) in two reference urban coastal sites in the European and African

Western Mediterranean and (2) to compare the status of pollution, to estimate the atmospheric loading and potential exposure of those chemicals at both edges of the Western Mediterranean coast.

MATERIALS AND METHODS

Sampling and Study Areas. Atmospheric aerosol samples (TSP) were simultaneously collected from March 2015 to January 2016 in two representative coastal locations under strong anthropogenic pressure at both the African and European Western Mediterranean Sea edges: the cities of Bizerte (Tunisia) and Marseille (France; Figure S1). The air was drawn through precombusted quartz fiber filters (QFFs) placed in high volume air samplers (Tisch Environmental, Inc., USA). The sampling volume ranged from ~1800 to ~5000 m³ depending on the site and sampling event (Table S1).

Marseille. Samples were collected on the roof (~10 m AGL) of the Endoume Marine Research Station (43°16'49.90" N, 5°20'57.32" E) located at the water front and around 4 km from the city center and the Marseille maritime terminal. Marseille can be considered as a northwestern large coastal city of the Mediterranean basin (~1 million inhabitants), inducing important car traffic and biomass burning. A detailed area description has been reported elsewhere.^{39–41} Briefly, Marseille hosts one of the most important ports of the Mediterranean Sea (~88 million tonnes of goods handled per year) and stands in the vicinity (40 km southeast) of the large petrochemical and industrial complex of the Fos-Berre area (e.g., petroleum refining, cement factory, waste combustion units, metallurgical industries). The region is well-known for its intense photo-oxidative pollution episode^{42,43} and several characteristic wind patterns, generally below 5 m s⁻¹, except during the mistral events (northwestern strong wind, 20–30 m s⁻¹), which are frequent in the area (100 days/year; Figure S1)

Bizerte. Sampling was conducted on the roof top (~8 m AGL) of the Faculty of Science of Bizerte (37°16'0.5802" N, 9°52'49.875" E) around 1 km far from the city center, close to the Gulf of Bizerte shoreline and Bizerte lagoon water front (Figure S1). A detailed sampling description is offered elsewhere.⁴⁴ Briefly, Bizerte is a medium-size city (~127 000 inhabitants), located in the north of Tunisia, between the Mediterranean Sea and the Bizerte lagoon. Even if agriculture and fishery activities are important in the area, a considerable number of light and heavy industries (i.e., cement, plastic, textile, mechanic and electronic, iron and steel metallurgy, petroleum refining, and lubricants) are present in the area.⁴⁴ An average temperature of 22 °C, with a hot summer and mild spring, frequent (200 days per year) northwestern winds (average speed of 6–8 m s⁻¹), and precipitation episodes mostly in fall and winter months, characterized the climate of Bizerte area.⁴⁴

Sample Processing. QFFs were lyophilized, weighed, and spiked with a suit of PCDD/F, PCB, and PBDE ¹³C-labeled standards prior to Soxhlet extraction (24 h) with an *n*-hexane/DCM (9:1) mixture. Extracts were rota-evaporated and cleaned up by using the “Dioxin Prep System-Florisil Version” (Supelco, Bellefonte, PA, USA). PCBs and PBDEs were collected in a first fraction by elution (100 mL of *n*-hexane) of the multilayer silica gel column coupled to a florisil column and a subsequent elution (40 mL of DCM) of only the multilayer silica gel column (prior removal of the florisil column). PCDD/Fs were obtained in a second fraction by elution of the florisil column with 50 mL of DCM. Final

extracts were rota-evaporated to ~1 mL, transferred to vials, and dried under a gentle nitrogen steam. Fractions were reconstituted in a few microliters of the respective PCDD/F, PCB, and PBDE ^{13}C -labeled injection standards prior to instrumental analysis (Text S1).

Instrumental Analysis. Samples were analyzed for 17 PCDD/Fs (congeners 2,3,7,8-susbtituted), 18 PCBs (12 DL-PCBs+6_{ID}-PCBs), and 27 PBDEs (Text S1). Quantification was carried out by isotopic dilution according to U.S. EPA method 1613⁴⁵ on a gas chromatograph (Trace GC ultra, Thermo Fisher Scientific, Milan, Italy) coupled to a high resolution mass spectrometer (DFS, Thermo Fisher Scientific, Bremen, Germany). The injection temperature was 260 °C, and 1 μL of extract was injected (splitless mode). GC separation of PCBs and PCDD/Fs was achieved using a 60 m \times 0.25 mm \times 0.25 μm DB-5MS column (Agilent J&W, USA), while a 15 m \times 0.25 mm \times 0.10 μm Rxi-5Sil MS column (Restek, USA) was used for PBDEs. Different oven temperature programs were used for each family of analytes (Table S2). Positive electron ionization (EI+) was used operating in selected ion monitoring (SIM) mode at a 10 000 resolving power.

Quality Assurance/Quality Control (QA/QC). Clean QFFs were individually wrapped in aluminum foil, baked at 450 °C overnight, weighted, and then stored at -20 °C in double sealed plastic bags until used. Field blanks, consisting of baked QFFs transported to the sampling area, mounted in the sampler, and dismounted, were collected at both sites, stored, and analyzed concurrently with the samples. After sampling, QFFs were wrapped in aluminum foil again and stored in the dark at -20 °C. Blank levels were generally low for the three POP classes compared to their concentrations in the samples, ranging from 0.02 to 3.5 pg (PCDD/Fs), from not detected (n.d.) to 150 pg (PCBs), and from n.d. to 530 pg (PBDEs) depending on the congener and sample (Table S3). Laboratory blanks (one blank per five-sample batch) showed lower or similar levels to field blanks, so no contamination during sampling, storage, and analysis occurred. Results were blank corrected. Chromatographic peaks were only considered when the ratio between the two monitored ions was within $\pm 15\%$ of the theoretical value, and the signal-to-noise (S/N) ratio was >3 (instrumental limit of detection, LOD). Limits of quantification (LOQs) corresponded to S/N ≥ 10 . Calibration curves were daily checked. Median LODs ranged from ~0.3 to ~1.1 pg (PCDD/Fs), from 2.1 to ~8.3 pg (PCBs), and from ~1.1 to 32.5 pg (PBDEs) depending on the compound and sample (Table S4). Median method recoveries (extraction-clean-up-analysis) varied from 70 to 97% (PCDD/Fs), from 83 to 110% (PCBs) and from 60 to 120% (PBDEs; Table S5). Results were corrected by recoveries.

TOC, EC Determinations, and Statistical Analysis. Total organic carbon (TOC) content was determined in filter subsamples by high temperature combustion (CHN analyzer).⁴⁶ For the elemental carbon (EC) determination, additional filter subsamples were precombusted at 340 °C over 2 h under oxygen flow⁴⁷ and then analyzed as indicated above. STATA/SE 12.1 software was employed for the statistical data analysis.

RESULTS AND DISCUSSION

Concentrations in the Atmospheric Aerosol. Dioxin-like POPs. $\Sigma 2,3,7,8\text{-PCDD/F}$ concentrations in the aerosols over the Bizerte area (Tunisia) ranged from 32 to 1100 fg m^{-3} (222 fg m^{-3} , median) along the sampling period and were

generally higher than those over the Marseille coastal area (France), varying from 31 to 1280 fg m^{-3} (83 fg m^{-3} , median; Figure 1A). The highest differences were found for the months

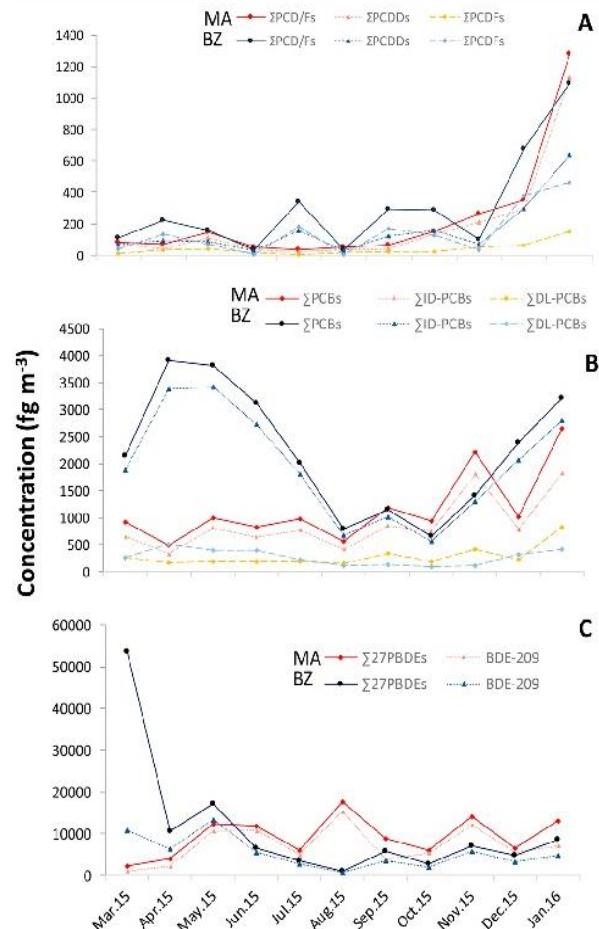


Figure 1. Temporal variability of PCDD/F (A), PCB (B), and PBDE (C) concentrations in atmospheric aerosols over Marseille (MA) and Bizerte (BZ) coastal areas from March 2015 to January 2016.

of April, July, and September 2015 (3-, 11-, ~5-fold higher levels in Bizerte, respectively). However, these values were not significantly different (Mann–Whitney test, $p = 0.28$) for the sum of 2,3,7,8-PCDD/Fs, most probably due to the high annual variability, in particular in the Bizerte site, and the limited number of samples analyzed. Significant differences were only found for two furan congeners (i.e., 2,3,4,6,7,8-HxCDF and 1,2,3,4,6,7,8-HpCDF; Mann–Whitney test, $p = 0.04$; Figure S2, Table S6). A general trend showing higher PCDD/F levels in the coldest months of the year was observed at both sites. This effect has been previously reported in other Mediterranean coastal areas and has been attributed to the combined effect of the increase of diffusive combustion sources (e.g., domestic heating and road traffic) and a less efficient dispersion of the local emissions during cold conditions.²³

The $\Sigma 2,3,7,8\text{-PCDD/F}$ was clearly dominated by the contribution of PCDDs in Marseille, whereas a more even contribution of PCDDs and PCDFs was found for the aerosols of the Bizerte area (Figure 1A), pointing to different PCDD/F sources at both sites.

This is the first time that PCDD/Fs have been measured in atmospheric aerosols from the Marseille area and in a coastal

site at the African Mediterranean edge. The concentrations found at both sites are within the range of those previously reported for a coastal area in the Gulf of Lion (50–1500 fg m⁻³),²³ urban/industrial sites from the Barcelona area (570–1162 fg m⁻³),²⁴ and in the open Northwestern Mediterranean (94–990 fg m⁻³).³⁵ Reported values from a cruise transect close to the Northwestern Mediterranean African coast (38 fg m⁻³) are lower than those measured in the Bizerte coastal area.³⁵ Concentrations measured in a background site in the Barcelona area (230 fg m⁻³) are lower, too, than those in Marseille.²⁴ No data for comparison was found in the central/eastern Mediterranean Sea. Recent PCDD/F measurements carried out in the atmospheric aerosol over remote areas from the Atlantic, Pacific, and Indian oceans revealed 6- to 11-fold lower background levels (5 to 113 fg m⁻³).⁴⁸

The \sum_{18} PCB concentrations measured in the aerosols from Bizerte, ranging from 0.7 to ~4.0 pg m⁻³ (2.1 pg m⁻³, median), were significantly higher (Mann–Whitney test, $p = 0.03$) than those measured in the aerosols over Marseille, which varied from 0.5 to 2.7 pg m⁻³ (1.0 pg m⁻³, median). \sum_{ID} PCBs dominated the total levels at both sites with \sum_{ID} PCB concentrations significantly higher, too, in Bizerte (0.6 to 3.4 pg m⁻³, median value of ~2.0 pg m⁻³) than in Marseille (0.3 to 1.8 pg m⁻³, median value of 0.8 pg m⁻³; Mann–Whitney test, $p = 0.01$; Figure 1B). \sum_{DL} PCB concentrations, which represented a minor contribution to the total PCB atmospheric stock at both sites, were not statistically different (0.1–0.5 pg m⁻³ in Bizerte compared to 0.1–0.8 pg m⁻³ in Marseille). However, the concentrations of some of the most toxic $_{DL}$ PCBs (i.e., CB-81, -126, -169) as well as CBs-167 and -189 were significantly higher in Bizerte than in the Marseille coastal area (2–4 fold-higher median values depending on the congener; Figure S3, Table S7).

\sum_{18} PCB (and \sum_{ID} PCB) concentrations exhibited different annual trends in both sites. While a general increase of concentrations was observed in winter months compared to spring and summer in Marseille, a more pronounced seasonality was observed for Bizerte, showing clearly higher concentrations in spring–early summer and late autumn–winter months, with minimum levels in August, September, and October (Figure 1B). As a result, 2- to 8-fold higher \sum_{18} PCB levels were measured in Bizerte than in Marseille from March to July, while the concentration differences between the two sites in winter months were less important, and in some months (e.g., November) higher for Marseille. Interestingly, higher \sum_{DL} PCB concentrations were generally measured from August 2015 to January (except in December) in Marseille. These facts highlight the differential environmental behavior, seasonality, and related exposure of individual PCBs at both sites.

PCB data comparability may be tricky since different numbers and types of PCBs may be considered. Therefore, for comparative purposes we focus only on $_{ID}$ PCBs. \sum_{ID} PCB concentrations measured at both edges of the Northwestern Mediterranean Sea were generally lower than previous coastal measurements performed in the Northwestern Mediterranean in the Gulf of Lion (0.5 to 7.2 pg m⁻³)^{23,26} and those carried out close to the Barcelona area (9–26 pg m⁻³).²⁶ Cruise measurements encompassing the Mediterranean Sea and the Southwestern Black Sea in 2006 and 2007 revealed higher concentrations, too, for \sum_{ID} PCB (0.4–18 pg m⁻³), but PCB-118 was included in the sums.³⁶ However, concentrations measured in Bizerte and Marseille were generally higher than

those reported for a coastal site (considered as a background location) in the Eastern Mediterranean,²⁷ consistent with previous studies indicating higher PCB levels in the Western Mediterranean.³⁶ Most of the previous studies correspond to measurements performed more than a decade ago (as for PCDD/Fs), so comparison must be done carefully. Particle-bound PCBs have received little attention since then in the Mediterranean basin compared to gas phase PCBs, most probably due to the dominant role of vapor PCBs driving total PCB ambient levels (especially for low MW congeners) and the increasing applications of passive sampling techniques to POP atmospheric measurements. Thus, recent studies in the Mediterranean Sea considered only the gas phase or the assemble gas+particle phases.^{32,33} \sum_{DL} PCB background measurements in the atmospheric aerosol over remote areas from the Atlantic, Pacific, and Indian oceans revealed up to 500-fold lower levels (1–2675 fg m⁻³).⁴⁸

These figures confirmed that the Northwestern Mediterranean Sea is considerably exposed to dioxin-like POPs and might act in turn as a potential secondary source, in particular of PCBs, for other Mediterranean regions (less exposed) and for the most pristine areas of the major oceans of the Earth. It has been reported that the principal control on the levels of legacy POPs in active circulation in the global environment is currently in a state of transition (from primary to secondary source control).¹⁴ The role of the Northwestern Mediterranean Sea (and other similar impacted marine areas) as potential secondary sources at present remains uncertain and requires further investigation.

PBDEs. \sum_{27} PBDE concentrations were generally higher than dioxin-like POPs (in particular compared to PCDD/Fs) at both sites. Levels in the aerosol from Bizerte ranged from 1.0 to 54.0 pg m⁻³ (~6.0 pg m⁻³, median), while in Marseille they varied from 2.2 to 17.6 pg m⁻³ (~9.0 pg m⁻³, median; Figure 1C). A general trend of higher levels in the Marseille area was found, with the exception of the samples collected in spring in Bizerte, in particular the one of March 2015 (which exhibited 3 to ~50-fold higher PBDE levels than the rest of samples collected in Bizerte). This concentration peak can be attributed to an unusual higher concentration of medium-high MW PBDEs in that sample compared to the others, in particular BDE-183 (Table S8), likely due to the combined effect of the air mass back trajectories (BTs) and potential local sources during this sampling event (see discussion below). However, the concentrations at both sites did not show a statistical difference (Mann–Whitney test, $p > 0.05$). Still, some individual congeners exhibited statistical differences but with contrasting trends, like BDE-47 with 3-fold higher median concentrations in Marseille than Bizerte (Mann–Whitney test, $p = 0.01$), while BDE-3, -7, -71, -77, -126, and -156 showing higher levels in the aerosols from Bizerte ($p < 0.01$ –0.04; Figure S4, Table S8). PBDE-209 was the major contributor to the total \sum_{27} PBDE for most of the samples at both sites (Figure 1C).

\sum_{27} PBDE concentrations measured in Marseille and Bizerte were generally within the range of those reported for a coastal site in the Northwestern Mediterranean (2–18 pg m⁻³, \sum_8 PBDE),²³ higher than levels in a coastal background site in the Central/Eastern Mediterranean (0.5–2 pg m⁻³, \sum_{15} PBDE)³⁰ but in the lower end of values reported for aerosols collected over large cities in the Eastern Mediterranean like Athens (Greece; 15–23 pg m⁻³, \sum_{12} PBDE)²⁹ and Izmir (Turkey; 27–62 pg m⁻³, \sum_7 PBDE).³⁸

POPs Patterns in the Atmospheric Aerosol. The PCDD/F atmospheric pattern (congener relative contribution) for most of the Bizerte samples showed an important contribution of furans, with $1,2,3,4,6,7,8\text{-HpCDF}$ and OCDF accounting for $16.3 \pm 3.7\%$ and $12.2 \pm 7.3\%$ of the $\sum_{2,3,7,8}\text{PCDD/F}$, values almost reaching the relative contribution of $1,2,3,4,6,7,8\text{-HpcDD}$ ($17.0 \pm 4.0\%$) and OCDD ($25.5 \pm 4.5\%$), which are the two most abundant PCDDs (Figure 2A-2).

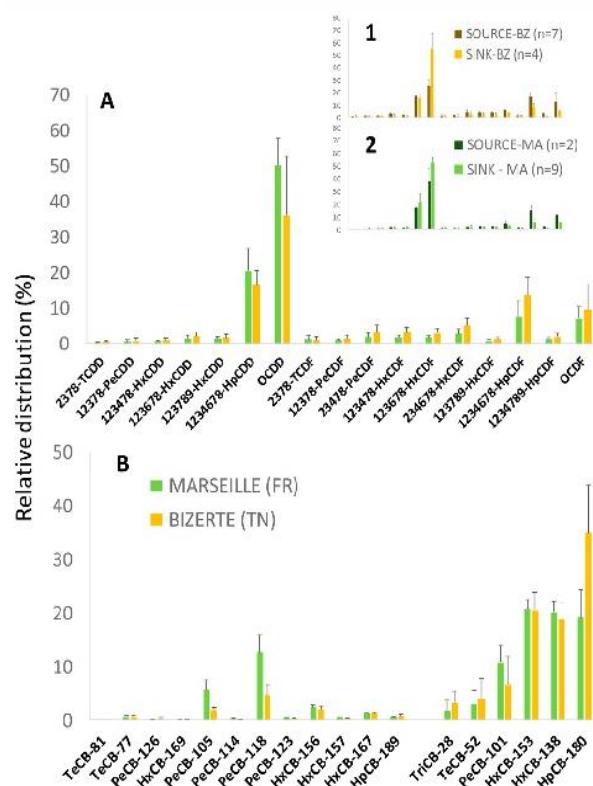


Figure 2. Average atmospheric pattern ($n = 11$) of PCDD/F (A) and PCBs (B) in Marseille (MA) and Bizerte (BZ) coastal areas. The small figures 1 and 2 show a focus on the differences in the atmospheric pattern found in Bizerte (dominated by a characteristic “source pattern,” $n = 7$) and in Marseille (dominated by a characteristic “sink” pattern, $n = 9$).

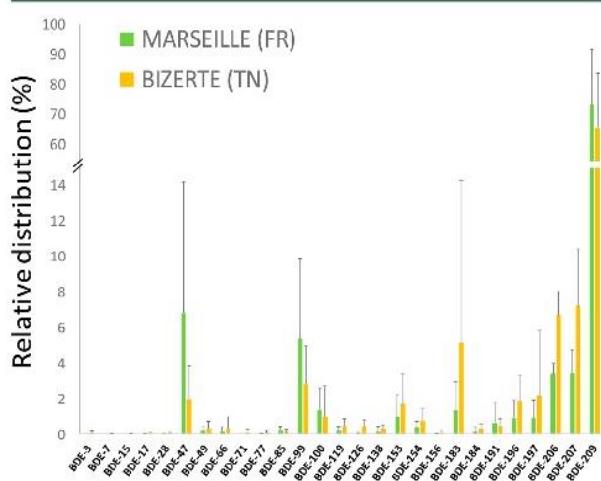
1). However, the PCDD/F pattern in samples from Marseille was dominated by a higher contribution of $1,2,3,4,6,7,8\text{-HpCDD}$ ($21.2 \pm 6.8\%$) and OCDD ($53.0 \pm 4.0\%$) and lower contribution of $1,2,3,4,6,7,8\text{-HpCDF}$ and OCDF accounting for $5.8 \pm 3.0\%$ and $6.0 \pm 2.8\%$ of the $\sum_{2,3,7,8}\text{PCDD/F}$, respectively (Figure 2A-2). A higher contribution of PCDFs in the PCDD/F atmospheric pattern compared to PCDDs has been associated in previous studies with “fresh” emissions (sources), a situation in which the lower chlorinated congeners, in particular PCDFs, have insufficient time to experience significant atmospheric degradation/depletion processes.^{23,35,49,50} Contrarily, a predominance of higher chlorinated PCDDs and little contribution of PCDFs is considered as a “sink” signal where the lighter congeners were “weathered” in their travel from the source to the sampling sites due to atmospheric processes (e.g., photodegradation).

These patterns suggest current local PCDD/F emission in Bizerte in combination with a minor contribution of long/medium-range atmospheric transport of PCDD/Fs to the area. Contrarily, the long/medium range atmospheric transport

seems to drive the atmospheric occurrence of PCDD/Fs in the Marseille area with a minor contribution of local sources. The possibility of short-range atmospheric transport from the adjacent industrial areas (Fos-Berre) to Marseille with known sources of PCDD/Fs (e.g., from incinerators, metallurgical and petrochemical facilities) is not excluded. Nevertheless, because of the surrounding topography of Marseille, bordered by the Mediterranean from the southwest and enclosed from the north, east, and south by mountain ranges up to ~ 700 m ASL, direct transport from the Fos-Berre area to Marseille is rarely observed. Such transport could occur when the wind is a composition of a land/sea breeze and light mistral, but the air mass will go toward the sea before coming back to Marseille, which corresponds to a half-range atmospheric transport. Furthermore, these wind conditions correspond generally to a sunny period inducing strong photochemical processes.^{39–41,43}

The PCB atmospheric pattern was dominated in general by the HMW _DPCBs at both sites. A clear predominance of PCB-180 in Bizerte (accounting for the $35.0 \pm 8.7\%$ of the $\sum_{18}\text{PCBs}$) was observed compared to the Marseille area ($19.2 \pm 5.1\%$ of the $\sum_{18}\text{PCBs}$). A similar pattern was observed in the two sites for _DPCB, but PCB-118 and -105 predominated in Marseille ($12.6 \pm 3.2\%$ and $5.7 \pm 1.8\%$, respectively) compared to Bizerte ($4.6 \pm 2.0\%$ and $1.9 \pm 0.5\%$, respectively). The different abundance of these three major PCBs may be either a reflection of different past usage of PCB commercial mixtures at both sites or a reflection of distinct emissions rates to the environment at present. For example, PCB-180 is one of the major constituents of Aroclor 1260 and 1262, while CB-105 and -118 were relatively more abundant in the Aroclor 1254 formulation. One of the major uses of these Aroclor formulations was as industrial oils destined for transformers.⁵¹ It has been very recently reported that a large number of transformers containing PCBs are still used or stored in unsatisfactory conditions in the Bizerte area with a high probability of oil leaks.⁴⁴ This could explain the higher contribution of PCB-180 in Bizerte compared to Marseille.

The predominance of BDE209 was reflected also in the atmospheric congener pattern (Figure 3) accounting for $72.3 \pm 18.6\%$ and $65.5 \pm 18.0\%$ of the $\sum_{27}\text{PBDE}$ in Marseille and Bizerte, respectively. The important abundance of this BDE denotes the past and maybe current usage of deca-PBDE.



formulations at both edges of the Northwestern Mediterranean Sea.¹⁶ In addition, the predominance of BDE-47 and BDE-99 in the pattern from Marseille samples, too, together with their higher abundance ($6.8 \pm 7.3\%$ and $5.3 \pm 4.5\%$ for BDE-47 and -99, respectively) compared to the pattern in Bizerte ($2.0 \pm 1.9\%$ and $2.8 \pm 2.5\%$ for BDE-47 and -99, respectively), point first to a major usage of penta-PBDE compared to the octa-PBDE formulations in Marseille and, second, to a different emission and usage pattern compared to Bizerte, where a major usage of octa-PBDE formulations may be the most likely scenario represented by a higher BDE-183, -206, and -207 predominance in Bizerte, reaching up to 31.6, 9.1, and 13.8% of the $\sum_{27}\text{PBDE}$, respectively.

Factors Affecting Temporal and Spatial Variability. The finest fractions of the atmospheric TSP, like TOC and EC, have been reported to efficiently sorb POPs-like contaminants.^{29,52,53} Generally higher median concentrations of TSP ($66.0 \mu\text{g m}^{-3}$), TOC ($7.5 \mu\text{g m}^{-3}$), and EC ($2.0 \mu\text{g m}^{-3}$) were measured in the aerosols over Bizerte compared to the Marseille area, exhibiting 48.0 , 6.4 , and $0.9 \mu\text{g m}^{-3}$ of TSP, TOC, and EC, respectively. However, only significant differences (Mann–Whitney test, $p = 0.03$ – 0.006) were found for the TSP and EC (Figure S5). No correlations were found for PCDD/F concentrations and TSP levels in any of the sites, and only $\sum_{18}\text{PCB}$, $\sum_{10}\text{PCBs}$, and one PCB congener correlated ($p = 0.01$ – 0.04) with TSP concentration in Bizerte (Figure S6). $\sum\text{PCDD/F}$ and $\sum_{DL}\text{PCB}$ (as well as most of PCDD/Fs and a certain number of $_{DL}\text{PCBs}$) concentrations positively correlated with TOC concentration ($p = 0.004$ – 0.03) but not with EC levels in Marseille. Only 2,3,7,4-TCDD positively correlated with TOC concentrations in Bizerte, and no correlations were observed for $_{DL}\text{PCBs}$ and TOC in Bizerte. Interestingly, PCDD/F concentrations were not correlated with EC levels in any of the sites, while $\sum_{DL}\text{PCBs}$, $\sum_{18}\text{PCB}$, and $\sum_{10}\text{PCBs}$ were correlated with EC mostly in Bizerte ($p = 0.002$ – 0.01), most probably due to the higher EC levels in this site. $\sum_{27}\text{PBDE}$ concentrations did not significantly correlate with TSP, TOC, or EC in any of the sites. However, while only two individual PBDEs correlated with TSP levels (Bizerte), a considerable number of PBDE congeners were correlated with TOC concentrations in Marseille and with EC levels in Bizerte (Figure S7). The fact that PCDD/Fs did not correlate with EC is somehow unexpected since this correlation has been suggested in other atmospheric studies.^{54,55} The narrow range of variation of EC concentrations in the samples analyzed could have resulted in this lack of correlation. Regarding TOC, the correlations mostly observed for Marseille could be the result of different TOC sources (different sorption properties) in both sites (e.g., more related to urban activities in Marseille and predominantly industrial activities in Bizerte).

Our results indicate that the TOC and/or EC contents in the atmospheric aerosol may have a stronger effect than the TSP as a whole on the spatial-temporal variability of the studied POPs. Concentrations normalized by TOC slightly decreased the $\sum_{2,3,7,8}\text{PCDD/F}$, $\sum_{18}\text{PCB}$, $\sum_{10}\text{PCBs}$, and $\sum_{27}\text{PBDE}$ annual variability at both sites (except for the month of January 2016) and confirmed the similar spatial variability with no significant differences for PCDD/Fs ($p = 0.67$) and PBDEs ($p = 0.66$) and higher levels of $\sum_{18}\text{PCB}$ (although not significant, $p = 0.07$) and $\sum_{10}\text{PCBs}$ ($p = 0.03$) in Bizerte (Figure S8). The higher concentrations in January 2016 resulted in 4- to 9-fold higher levels in Bizerte (412, 1050, 154, and $3210 \text{ ng g}_{TOC}^{-1}$) compared to Marseille (80, 113, 51, and $811 \text{ ng g}_{TOC}^{-1}$) for

$\sum_{2,3,7,8}\text{PCDD/F}$, $\sum_{10}\text{PCB}$, $_{DL}\text{PCBs}$, and $\sum_{27}\text{PBDE}$, respectively. In addition, an increase of the concentration differences (normalized by TOC) compared to their respective volumetric concentrations was found for $_{DL}\text{PCBs}$ in March 2015.

Concentrations normalized by EC (Figure S9) showed predominant levels of $\sum_{2,3,7,8}\text{PCDD/F}$ for Marseille in March 2015 and January 2016 (where the lowest concentrations of EC were measured) and confirmed the $\sum_{18}\text{PCB}$ and $\sum_{10}\text{PCB}$ higher levels in Bizerte during spring–early summer compared to Marseille but pointed to generally higher concentrations in Marseille from September to winter. Interestingly, a statistically significant ($p < 0.01$) predominance of $_{DL}\text{PCB}$ levels in Marseille resulted from the normalization by EC, which was not verified as volumetric or TOC normalized concentrations. The same effect ($p < 0.001$) was observed for the $\sum_{27}\text{PBDE}$, exhibiting higher levels in Marseille for all months ($7.4 \mu\text{g g}_{EC}^{-1}$, median value) than in Bizerte ($3.0 \mu\text{g g}_{EC}^{-1}$, median value) with clear peak differences in August and September.

Four-day BTs were calculated (50, 500, and 1000 m AGL) by using the HYSPLIT model⁵⁶ (Figure S10). The lowest $\sum_{2,3,7,8}\text{PCDD/F}$ levels were registered in the months of June, July, and August 2015 in Marseille, where air masses had a clear Atlantic influence, while the highest level was measured in the month of January 2016 with air masses showing continental influence (Figure S9). A similar min–max temporal pattern was observed in Bizerte, with lower levels in summer months (except for July) than in January. However, the BTs in July revealed a more important continental influence for Bizerte compared to Marseille. $\sum_{18}\text{PCB}$ concentrations had a minimum level in April 2015 over Marseille, with air masses mostly circulating over the Western Mediterranean waters, and peaked also in January 2016. The lowest $\sum_{18}\text{PCB}$ concentrations were measured in October in Bizerte, whereas the higher levels correspond to April 2015 (with air masses circulating over the Bizerte area and the African continent) consistent with suspected current local PCB emissions.

Interestingly, $\sum_{27}\text{PBDE}$ exhibited the lowest concentrations in the months of March 2015 over Marseille, with air masses showing an important component coming from the North African coast, while the highest concentrations were measured in the same month in Bizerte, with air masses showing the 50 m height component coming from the Gulf of Lion area. Recent reports have shown evidence of the North to South atmospheric particle transport over some regions in the Northwestern and Eastern Mediterranean Sea.^{57,58} In addition, PBDEs have been described to be mostly associated with the finest particles of the atmospheric aerosol,²⁹ consistent with the correlations found with the TOC and/or EC contents (more abundant and stronger) compared to the TSP as discussed above. This will result in higher atmospheric residence times and a higher potential of LRAT. These facts may support the hypothesis of the potential “jumping” of PBDE local atmospheric stocks from the Northwestern European Mediterranean edge to the Northwestern African coast (where lower PBDE ambient levels have been generally measured) under favorable conditions. Indeed, the two sites are relatively close (around 780 km straight line). However, this hypothesis requires further confirmation with more sites at both edges of the Northwestern Mediterranean. In addition, a better characterization of PBDE local sources (emission inventory) at the African edge is needed. The BT analysis reveals, too, other potential hot spots farther west in the North African

coast, which find their way to the Bizerte area passing through the Gibraltar strait and along the African coast, as observed in the month of May 2015. The three POP families exhibited higher levels in the Bizerte area compared to Marseille (with a different air mass circulation pattern) in this month. This situation has been previously described for PCDD/Fs³⁵ and PAHs¹⁸ in the same region. BTs could only explain part of the annual and spatial variability for the studied POPs, most probably due to their different environmental sources and current local emissions patterns (mostly for legacy POPs) at the studied sites as discussed above, which may prevail over the BT influence on a local/regional scale in different seasons of the year. In addition, other parameters affecting the atmospheric gas-particle partitioning of POPs (e.g., temperature, relative humidity) may have an important influence on the local scale.

Atmospheric Dry Deposition and Exposure. Dry deposition fluxes (F_{DD} , pg m⁻² d⁻¹) of PCDD/Fs, PCBs, and PBDEs were calculated as

$$F_{DD} = v_d C_A \quad (1)$$

where C_A is the POP volumetric concentration in the aerosol (pg m⁻³) and v_d (cm s⁻¹) is the particle deposition velocity. A reference value of 0.2 cm s⁻¹ for v_d was adopted for both sites. This value is within the range of v_d 's experimentally measured⁵⁹ or previously used in the coastal Northwestern Mediterranean Sea^{23,35,36} for the estimation of dry deposition fluxes of POPs. However, a degree of uncertainty is associated with this calculation due to the lack of v_d measurements during the sampling events.

Overall, the atmospheric loading at both coastal areas is dominated by PBDEs, ranging from 70 to ~3400 ng m⁻² y⁻¹, followed by PCBs (30 to ~250 ng m⁻² y⁻¹) and PCDD/Fs (2 to 80 ng m⁻² y⁻¹) as expected from their relative atmospheric concentrations and the assumptions considered in these calculations (Tables 1, S9–S11). These fluxes were generally within the range of previously reported dry deposition estimations in the Mediterranean and Southwestern Black Sea for the same POPs.^{23,28,35} However, some differences were found in the atmospheric loading at both edges of the Mediterranean Sea. While a higher PBDE median loading is estimated for Marseille area (~550 ng m⁻² y⁻¹) compared to Bizerte (~400 ng m⁻² y⁻¹), the median dry deposition fluxes of PCBs (135 ng m⁻² y⁻¹) and PCDD/Fs (14 ng m⁻² y⁻¹) in Bizerte were higher than those of Marseille, ~60 and 5 ng m⁻² y⁻¹, respectively. Indeed, a 3-fold higher loading of dioxin-like pollutants was estimated for Bizerte as toxic equivalents (TEQ;⁶⁰ 400 pg TEQ m⁻² y⁻¹, median) compared to Marseille (137 pg TEQ m⁻² y⁻¹, median) due to a higher contribution of PCDFs and _{DL}PCBs in Bizerte (Table 1). These figures indicate a higher potential exposure to these toxic chemicals at the African edge of the Western Mediterranean.

Considering 1.6×10^{10} m² as the surface of the Gulf of Lion⁶¹ and an equivalent surface in the surroundings of Bizerte in the African coast, from 9 to 10 kg of POPs can be annually loaded (median value) to surface waters at both edges of the Mediterranean associated with the atmospheric aerosol. The sensitive environment of a Bizerte coastal lagoon (1.28×10^8 m²)⁶² could receive up to 0.5 kg of POPs yearly. This loading of toxic chemicals may have implications for the aquatic organisms, but this evaluation cannot be performed with the present data. However, it should be further investigated.

Table 1. Atmospheric Dry Deposition Fluxes of PCDD/Fs, PCBs, and PBDEs in Marseille and Bizerte Coastal Areas

	Marseille (FR)				Bizerte (TN)				Marseille (FR)				Bizerte (TN)						
	median	mean	range	median	mean	range	median	mean	range	median	mean	range	median	mean	range				
													TEQ (pg m ⁻² y ⁻¹)						
$\sum_{i=1}^4$ PCDDs	4.4	12.1	1.5–71.2	5.8	10.0	1.7–40.1	60.9	179.7	9.7–941.0	122.5	421.2	28.2–1955.8	$\sum_{i=1}^4$ PCDFs	1.5	2.5	0.5–9.6			
$\sum_{i=1}^4$ PCDFs	1.5	2.5	0.5–9.6	8.0	9.2	0.3–29.0	84.0	139.9	16.9–507.8	214.2	602.9	16.5–2473.1	$\sum_{i=1}^7$ PCD/Fs	5.2	14.6	2.0–80.8			
$\sum_{i=1}^7$ PCD/Fs	5.2	14.6	2.0–80.8	14	19.2	2.0–69.2	128.6	319.7	26.5–1448.8	375.3	1024.1	45.0–4428.9	$\sum_{i=1}^{12}$ PCBs	12.1	17.7	8.7–52.2			
$\sum_{i=1}^{12}$ PCBs	12.1	17.7	8.7–52.2	16.1	16.9	5.4–32.2	8.40	10.10	2.0–21.6	23.7	37.8	4.1–136.7	$\sum_{i=1}^{12}$ PCBs	49.0	55.3	20.81–115.2			
$\sum_{i=1}^{12}$ PCBs	49.0	55.3	20.81–115.2	118.7	124.1	35.9–216.1	$\sum_{i=1}^{18}$ PCBs	61.1	73.0	30.8–167.4	134.8	141.0	41.3–246.2	$\sum_{i=1}^{18}$ PCBs	547.90	586.90	141.0–1110.3		
$\sum_{i=1}^{18}$ PCBs	547.90	586.90	141.0–1110.3	405.00	695.80	69.4–3386.0	$\sum_{i=1}^{27}$ PBDEs	674.5 ^b	173.8–1358.5 ^b	533.9 ^b	855.9 ^b	112.7–371.4 ^b	137.1 ^c	329.8 ^c	28.5–1470.4 ^c	$\sum_{i=1}^{27}$ PBDEs	614.2 ^b	674.5 ^b	173.8–1358.5 ^b
$\sum_{i=1}^{27}$ PBDEs	614.2 ^b	674.5 ^b	173.8–1358.5 ^b	674.5 ^b	173.8–1358.5 ^b	674.5 ^b	$\sum_{i=1}^{62}$ POPs	1061.9 ^c	399.0 ^c	1061.9 ^c	399.0 ^c	1061.9 ^c	49.2–4565.4 ^c	$\sum_{i=1}^{62}$ POPs	1061.9 ^c	399.0 ^c	1061.9 ^c		

^aTEQ values are calculated using WHO-TEF 2005. ^b $\sum_{i=1}^{29}$ POPs. ^c $\sum_{i=1}^{29}$ POPs (dioxin-like POPs).

A human health risk assessment for the whole set of dioxin-like POPs was performed based on inhalation exposure. We follow here a similar approach to a very recent assessment based on only two dioxin-like PCBs performed in the Bizerte area.⁴⁴ Briefly, concentrations expressed as WHO₀₅ TEQ were calculated using the latest available toxic equivalency factors (TEFs).⁵⁰ A daily air inhalation volume of 15 m³ for an adult of 60 kg was assumed.⁶³ The $\Sigma_{2,3,7,8}$ -PCDD/F and Σ_{DL} PCB concentrations in the aerosols over the Bizerte area, ranged from 0.7 to 70.2 and 0.07 to 2.2 WHO₀₅ TEQ fg m⁻³, respectively, whereas in Marseille levels they varied from 0.4 to 23.0 and 0.03 to 0.3 WHO₀₆ TEQ fg m⁻³, respectively. Median TEQ values (for all dioxin-like congeners) of 6.3 and 2.2 WHO₀₅ TEQ fg m⁻³ (Bizerte and Marseille) would result in potential intakes of 0.002 and 0.001 pg TEQ kg⁻¹ day⁻¹, respectively. Both levels are 3 orders of magnitude lower than the daily intake threshold of 1–4 pg TEQ kg⁻¹ day⁻¹ proposed by the WHO.⁶⁴ The atmospheric particle phase PCDD/F concentration can be considered as a good descriptor of the total atmospheric concentration due to their general predominance in this compartment after their emissions to the environment.^{22,23,35,49} Contrarily, PCBs show a general preferential partitioning (mostly low MW congeners) to the vapor phase.^{36,48} However, according to field measurements performed in various urban, coastal, and remote Mediterranean environments and inland aquatic ecosystems, the Σ_{DL} PCB gas phase concentrations are not expected to exceed more than 100 fold the measured particulate phase concentrations.^{23,27,36,63,65} Therefore, the worst case Σ_{DL} PCB TEQ concentration could be estimated as 100-fold the TEQ calculated considering only the particle-bound PCB concentrations, resulting in a corrected daily intake (for all dioxin-like congeners) of 0.01 and 0.004 pg TEQ kg⁻¹ day⁻¹ in Bizerte and Marseille areas, respectively. This new value still is far below the daily intake threshold proposed by the WHO, and therefore a risk by the inhalation route is excluded at present in the studied areas. It should be noted though that the daily intake threshold proposed by the WHO is based on toxicity studies evaluating dose-response through oral exposure. However, absorption and tissue partitioning could be different via the inhalation route, and the local toxicity effect to lungs is not considered, so there is still an uncertainty degree in this assessment.

There are no TEFs associated with PBDEs, and according to the European Chemicals Agency, the risks of deca-BDE and lower brominated transformation products to the humans via the environment cannot be adequately addressed in a quantitative way due to the high uncertainties regarding long-term exposure and effects.⁶⁶ Similarly to PCDD/Fs, PBDE particle-bound atmospheric concentrations can be a good indicator of the total atmospheric levels, particularly considering that one of the most abundant PBDEs is the HMW PBDE-209 (almost exclusively in the particle phase). For example, the PBDE particle-bound fraction in a large Mediterranean city (Athens, Greece) exhibiting a similar atmospheric TSP concentration as Marseille and Bizerte accounted from more than the 70% of the total airborne PBDE concentrations.²⁹ Following the above calculations, median intakes of 1.6 and 2.2 pg kg⁻¹ day⁻¹ were estimated for Bizerte and Marseille, respectively. As a reference, 3 orders of magnitude higher (~7.0 ng kg⁻¹ day⁻¹) PBDE intakes have been reported for American adults.⁶⁷ However, the exposure to PBDE has been mostly associated with indoors environments (mainly dust ingestion

and dermal contact)⁶⁷ and inhalation is not considered as the main route of concern for these substances.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b04614.

Additional data on the sampling and analytical procedures, QA/QC, compound-by-compound atmospheric levels and spatial distribution (box-plots), and deposition fluxes (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Health Aspects of air Pollution. Results from the WHO Project “Systematic Review of Health Aspects of air Pollution in Europe.” World Health Organization: Geneva, 2004; p 30.
- (2) Mesquita, S. R.; Dachs, J.; van Drooge, B. L.; Castro-Jiménez, J.; Barata, C.; Vieira, N.; Guimarães, L.; Piña, B.; Navarro-Martín, L. Toxicity assessment of atmospheric particulate matter in the Mediterranean and Black Seas open waters. *Sci. Total Environ.* **2016**, *545–546*, 163–170.
- (3) Safe, S.; Hutzinger, O. Polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBBs): biochemistry, toxicology and mechanism of action. *Crit. Rev. Toxicol.* **1984**, *13*, 319–395.
- (4) Safe, S. Polychlorinated biphenyls (PCBs), dibenzofurans (PCDDs), dibenzofurans (PCDFs) and related compounds: environmental and mechanistic considerations which support the development of toxic equivalency factors (TEFs). *Crit. Rev. Toxicol.* **1990**, *21*, 51–88.
- (5) Van den Berg, M.; Birnbaum, L.; Bosveld, A. T. C.; Brunström, B.; Cook, P.; Feeley, M.; Giesy, J. P.; Hanberg, A.; Hasegawa, R.; Kennedy, S. W.; Kubiak, T.; Larsen, J. C.; van Leeuwen, R. F. X.; Liem, A. K.; Nolt, C.; Peterson, R. E.; Poellinger, L.; Safe, S.; Schrenk, D.; Tillitt, D.; Tysklind, M.; Younes, M.; Wærn, F.; Zacharewski, T. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environ. Health Perspec.* **1998**, *106*, 775–792.

- (6) Parzefall, W. Risk assessment of dioxin contamination in human food. Risk assessment of dioxin contamination in human food. *Food Chem. Toxicol.* **2002**, *40*, 1185–1189.
- (7) European Food Safety Authority.. Opinion of the scientific panel on contaminants in the food chain on a request from the Commission related to the presence of non-dioxin-like PCBs in feed and food. *EFSA J.* **2005**, *284*, 1–137.
- (8) Faroone, O.; Jones, D.; De Rosa, C. Effects of polychlorinated biphenyls on the nervous system. *Toxicol. Ind. Health* **2000**, *16*, 305–333.
- (9) Monosson, E. Reproductive and developmental effects of PCBs in fish: a synthesis of laboratory and field studies. *Rev. Toxicol.* **1999**, *3*, 25–75.
- (10) De Wit, C. An overview of brominated flame retardants in the environment. *Chemosphere* **2002**, *46*, 583–624.
- (11) Vonderheide, A. P.; Mueller, K. E.; Meija, M.; Welsh, G. L. Polybrominated diphenyl ethers: Causes for concern and knowledge gaps regarding environmental distribution, fate and toxicity. *Sci. Total Environ.* **2008**, *400*, 425–436.
- (12) Harrad, S. J.; Jones, K. C. A source inventory and budget for chlorinated dioxins and furans in the United Kingdom environment. *Sci. Total Environ.* **1992**, *126*, 89–107.
- (13) Brzuzy, L. P.; Hites, R. A. Global mass balance for polychlorinated dibenz-p-dioxins and dibenzofurans. *Environ. Sci. Technol.* **1996**, *30*, 1797–1804.
- (14) Nizzetto, L.; Macleod, M.; Borgå, K.; Cabrerizo, A.; Dachs, J.; Di Guardo, A.; Ghirardello, D.; Hansen, K. M.; Jarvis, A.; Lindroth, A.; Ludwig, B.; Monteith, D.; Perlinger, J. A.; Schererger, M.; Schwedenmann, L.; Semple, K. T.; Wick, L. Y.; Zhang, G.; Jones, K. C. Past, Present, and Future Controls on Levels of Persistent Organic Pollutants in the Global Environment. *Environ. Sci. Technol.* **2010**, *44*, 6526–6531.
- (15) Breivik, K.; Sweetman, A.; Pacyna, J. M.; Jones, K. C. Towards a global historical emission inventory for selected PCB congeners – a mass balance approach: 2. Emissions. *Sci. Total Environ.* **2002**, *290*, 199–224.
- (16) La Guardia, M. J.; Hale, C. R.; Harvey, E. Detailed Polybrominated Diphenyl Ether (PBDE) Congener Composition of the Widely Used Penta-, Octa-, and Deca-PBDE Technical Flame-retardant Mixtures. *Environ. Sci. Technol.* **2006**, *40*, 6247–6254.
- (17) Durrieu de Madron, X. et al. Marine ecosystems' responses to climatic and anthropogenic forcings in the Mediterranean. *Prog. Oceanogr.* **2011**, *91*, 97–16610.1016/j.pocean.2011.02.003.
- (18) Castro-Jiménez, J.; Berrojalbiz, N.; Wollgast, J.; Dachs, J. Polycyclic aromatic hydrocarbons (PAHs) in the Mediterranean Sea: atmospheric occurrence, deposition and decoupling with settling fluxes in the water column. *Environ. Pollut.* **2012**, *166*, 40–47.
- (19) Castro-Jiménez, J. et al., Sources, Transport and Deposition of Atmospheric Organic Pollutants in the Mediterranean Sea. In *Occurrence, Fate and Impact of Atmospheric Pollutants on Environmental and Human Health*; McConnell, L., Dachs, J., Hapeman, C. J., Eds.; ACS Symposium Series; American Chemical Society, Washington, DC, 2013; Vol. 1149, pp 231–260.
- (20) Dalla Valle, M.; Marcomini, A.; Sfriso, A.; Sweetman, A. J.; Jones, K. C. Estimation of PCDD/F distribution and fluxes in the Venice Lagoon, Italy: Combining measurement and modelling approaches. *Chemosphere* **2003**, *51*, 603–616.
- (21) Jaward, F. M.; Farrar, N. J.; Harner, T.; Sweetman, A. J.; Jones, K. C. Passive air sampling of PCBs, PBDEs and organochlorine pesticides across Europe. *Environ. Sci. Technol.* **2004**, *38*, 34–41.
- (22) Castro-Jiménez, J.; Deviller, G.; Ghiani, M.; Loos, R.; Mariani, G.; Skejo, H.; Umlauf, G.; Wollgast, J.; Laugier, T.; Héas-Moisan, K.; Léauté, F.; Munsch, C.; Tixier, C.; Troncynski, J. PCDD/F and PCB multi-media ambient concentrations, congener patterns and occurrence in a Mediterranean coastal lagoon (Etang de Thau, France). *Environ. Pollut.* **2008**, *156*, 123–135.
- (23) Castro-Jiménez, J.; Mariani, G.; Vives, I.; Skejo, H.; Umlauf, G.; Zaldívar, J. M.; Dueri, S.; Messiaen, G.; Laugier, T. Atmospheric concentrations, occurrence and deposition of persistent organic pollutants (POPs) in a Mediterranean coastal site (Etang de Thau, France). *Environ. Pollut.* **2011**, *159*, 1948–1956.
- (24) Mari, M.; Schuhmacher, M.; Feliubadal, J.; Domingo, J. L. Air concentrations of PCDD/Fs, PCBs and PCNs using active and passive air samplers. *Chemosphere* **2008**, *70*, 1637–1643.
- (25) Gambaro, A.; Radaelli, M.; Piazza, R.; Stortini, A. M.; Contini, D.; Belosi, F.; Zangrando, R.; Cescon, P. Organic micropollutants in wet and dry depositions in the Venice Lagoon. *Chemosphere* **2009**, *76*, 1017–1022.
- (26) Garcia-Flor, N.; Dachs, J.; Bayona, J. M.; Albaiges, J. Surface waters are a source of polychlorinated biphenyls to the coastal atmosphere of the North-Western Mediterranean Sea. *Chemosphere* **2009**, *75*, 1144–1152.
- (27) Mandalakis, M.; Stephanou, E. G. Study of atmospheric PCB concentrations over the eastern Mediterranean Sea. *J. Geophys. Res.* **2002**, *107*, ACH 18-1.
- (28) Mandalakis, M.; Apostolaki, M.; Stephanou, E. G.; Stavrakakis, S. Mass budget and dynamics of polychlorinated biphenyls in the eastern Mediterranean Sea. *Global biogeochem. Cy.* **2005**, *19*, 1–16.
- (29) Mandalakis, M.; Besis, A.; Stephanou, E. G. Particle-size distribution and gas/particle partitioning of atmospheric polybrominated diphenyl ethers in urban areas of Greece. *Environ. Pollut.* **2009**, *157*, 1227–1233.
- (30) Iacovidou, E.; Mandalakis, M.; Stephanou, E. G. Occurrence and diurnal variation of polychlorinated biphenyls and polybrominated diphenyl ethers in the background atmosphere of Eastern Mediterranean. *Chemosphere* **2009**, *77*, 1161–1167.
- (31) Mosca, S.; Torelli, N. G.; Guerriero, E.; Tramontana, G.; Pomponio, S.; Rossetti, G.; Rotatori, M. Evaluation of a simultaneous sampling method of PAHs, PCDD/Fs and dl-PCBs in ambient air. *J. Environ. Monit.* **2010**, *12*, 1092–1099.
- (32) Lammel, G.; Audy, O.; Besis, A.; Efstatiou, C.; Eleftheriadis, K.; Kohoutek, J.; Kukucka, P.; Mulder, M. D.; Přibylová, P.; Prokeš, R.; Rusina, T. P.; Samara, C.; Sofuoğlu, A.; Sofuoğlu, S. C.; Taşdemir, Y.; Vassilatou, V.; Voutsas, D.; Vrana, B. Air and seawater pollution and air-sea gas exchange of persistent toxic substances in the Aegean Sea: spatial trends of PAHs, PCBs, OCPs and PBDEs. *Environ. Sci. Pollut. Res.* **2015**, *22*, 11301–11313.
- (33) Pozo, K.; Palmeri, M.; Palmeri, V.; Estellano, V. H.; Mulder, M. D.; Efstatiou, C. I.; Sará, G. L.; Romeo, T.; Lammel, G.; Focardi, S. Assessing persistent organic pollutants (POPs) in the Sicily Island atmosphere, Mediterranean, using PUF disk passive air samplers. *Environ. Sci. Pollut. Res.* **2016**, *23*, 20796–20804.
- (34) Iwata, H.; Tanabe, S.; Sakai, N.; Tatsukawa, R. Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate. *Environ. Sci. Technol.* **1993**, *27*, 1080–1098.
- (35) Castro-Jiménez, J.; Eisenreich, S. J.; Ghiani, M.; Mariani, G.; Skejo, H.; Umlauf, G.; Wollgast, J.; Zaldívar, J. M.; Berrojalbiz, N.; Reuter, H. I.; Dachs, J. Atmospheric occurrence and deposition of polychlorinated dibenz-p-dioxins and dibenzofurans (PCDD/Fs) in the open Mediterranean Sea. *Environ. Sci. Technol.* **2010**, *44*, 5456–5463.
- (36) Berrojalbiz, N.; Castro-Jiménez, J.; Mariani, G.; Wollgast, J.; Hanke, G.; Dachs, J. Atmospheric occurrence, transport and deposition of polychlorinated biphenyls and hexachlorobenzene in the Mediterranean and Black seas. *Atmos. Chem. Phys.* **2014**, *14*, 8947–8959.
- (37) Cetin, B.; Yatkin, S.; Bayram, A.; Odabasi, M. Ambient concentrations and source apportionment of PCBs and trace elements around an industrial area in Izmir, Turkey. *Chemosphere* **2007**, *69*, 1267–1277.
- (38) Cetin, B.; Odabasi, M. Particle-Phase Dry Deposition and Air-Soil Gas-Exchange of Polybrominated Diphenyl Ethers (PBDEs) in Izmir, Turkey. *Environ. Sci. Technol.* **2007**, *41*, 4986–4992.
- (39) El Haddad, I.; Marchand, N.; Wortham, H.; Temime-Roussel, B.; Piot, C.; Besombes, J.-L.; Baduel, C.; Voisin, D.; Armengaud, A.; Jaffrezo, J.-L. Insights into the secondary fraction of the organic aerosol

- in a Mediterranean urban area: Marseille. *Atmos. Chem. Phys.* **2011**, *11* (5), 2059–2079.
- (40) El Haddad, I.; Marchand, N.; Wortham, H.; Piot, C.; Besombes, J.-L.; Cozic, J.; Chauvel, C.; Armengaud, A.; Robin, D.; Jaffrezo, J.-L. Primary sources of PM_{2.5} organic aerosol in an industrial Mediterranean city, Marseille. *Atmos. Chem. Phys.* **2011**, *11* (5), 2039–2058.
- (41) El Haddad, I.; D'Anna, B.; Temime Roussel, B.; Nicolas, M.; Boreave, A.; Favez, O.; Voisin, D.; Sciaire, J.; George, C.; Jaffrezo, J. L.; Wortham, H.; Marchand, N. Towards a better understanding of the origins, chemical composition and aging of oxygenated organic aerosols: case study of a Mediterranean industrialized environment, Marseille. *Atmos. Chem. Phys.* **2013**, *13*, 7875–7894.
- (42) Flaounas, E.; Coll, I.; Armengaud, A.; Schmechtig, C. The representation of dust transport and missing urban sources as major issues for the simulation of PM episodes in a Mediterranean area. *Atmos. Chem. Phys.* **2009**, *9*, 8091–8101.
- (43) Sempéré, R.; Para, J.; Tedetti, M.; Charrière, B.; Mallet, M. Variability of Solar Radiation and CDOM in Surface Coastal Waters of the Northwestern Mediterranean Sea. *Photochem. Photobiol.* **2015**, *91*, 851–861.
- (44) Barhoumi, B.; Castro-Jiménez, J.; Guigue, C.; Goutx, M.; Sempéré, R.; Derouiche, A.; Achouri, A.; Touil, S.; Driss, M. R.; Tedetti, M. Levels and risk assessment of hydrocarbons and organochlorines in atmospheric suspended particles from a north African coastal city (Bizerte, Tunisia). *J. Hazard. Mater.* Submitted.
- (45) US-EPA, Method 1613. Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS; U.S. Environmental Protection Agency: Washington, DC, October 1994.
- (46) Raimbault, P.; Garcia, N.; Cerutti, F. Distribution of inorganic and organic nutrients in the South Pacific Ocean. Evidence for long-term accumulation of organic matter in nitrogen-depleted waters. *Biogeosciences* **2008**, *5*, 281–298.
- (47) Cachier, H.; Bremond, P.-M.; Buat-Menard, P. Determination of atmospheric soot carbon with a simple thermal method. *Tellus, Ser. B* **1989**, *41B*, 379–390.
- (48) Morales, L.; Dachs, J.; González-Gaya, B.; Hernán, G.; Ábalos, M.; Abad, E. Background Concentrations of Polychlorinated Dibenz-p-Dioxins, Dibenzofurans, and Biphenyls in the Global Oceanic Atmosphere. *Environ. Sci. Technol.* **2014**, *48*, 10198–10207.
- (49) Lohmann, R.; Jones, K. C. Dioxins and furans in air and deposition: a review of levels, behaviour and processes. *Sci. Total Environ.* **1998**, *219*, 53–81.
- (50) Brubaker, W.W. JR.; Hites, R. A. Polychlorinated dibenzodioxins and dibenzofurans: gas-phase hydroxyl radical reactions and related atmospheric removal. *Environ. Sci. Technol.* **1997**, *31*, 1805–1810.
- (51) Takasuga, T.; Senthilkumar, K.; Matsumura, T.; Shiozaki, K.; Sakai, S.-I. Isotope dilution analysis of polychlorinated biphenyls (PCBs) in transformer oil and global commercial PCB formulations by high resolution gas chromatography–high resolution mass spectrometry. *Chemosphere* **2006**, *62*, 469–484.
- (52) Dachs, J.; Eisenreich, S. Adsorption onto Aerosol Soot Carbon Dominates Gas-Particle Partitioning of Polycyclic Aromatic Hydrocarbons. *Environ. Sci. Technol.* **2000**, *34*, 3690–3697.
- (53) Koelmans, A. A.; Jonker, M. T. O.; Cornelissen, G.; Bucheli, T. D.; Van Noort, P. C. M.; Gustafsson, O. Black carbon: The reverse of its dark side. *Chemosphere* **2006**, *63*, 365–377.
- (54) Yu, L.; Mai, B.; Meng, X.; Bi, X.; Sheng, G.; Fu, J.; Peng, P. Particle-bound polychlorinated dibenz-p-dioxins and dibenzofurans in the atmosphere of Guangzhou, China. *Atmos. Environ.* **2006**, *40*, 96–108.
- (55) Lohmann, R.; Gioia, R.; Eisenreich, S. J.; Jones, K. C. Assessing the importance of ab- and adsorption to the gas-particle partitioning of PCDD/Fs. *Atmos. Environ.* **2007**, *41*, 7767–7777.
- (56) Draxler, R. R.; Rolph, G. D. *HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model*; NOAA Air Resources Laboratory: Silver Spring, MD, 2011; access via NOAA ARL READY Website: <http://ready.arl.noaa.gov/HYSPLIT.php>.
- (57) Berland, K.; Rose, C.; Pey, J.; Culot, A.; Freney, E.; Kalivitis, N.; Kouvarakis, G.; Cerro, J. C.; Mallet, M.; Sartelet, K.; Beckmann, M.; Bourriane, T.; Roberts, G.; Marchand, N.; Mihalopoulos, N.; Sellegri, K. Spatial extent of new particle formation events over the Mediterranean Basin from multiple ground-based and airborne measurements. *Atmos. Chem. Phys.* **2017**, *17*, 9567–9583.
- (58) Kalivitis, N.; Birnili, W.; Stock, M.; Wehner, B.; Massling, A.; Wiedensohler, A.; Gerasopoulos, E.; Mihalopoulos, N. Particle size distributions in the Eastern Mediterranean troposphere. *Atmos. Chem. Phys.* **2008**, *8*, 6729–6738.
- (59) Del Vento, S.; Dachs, J. Influence of the surface microlayer on atmospheric deposition of aerosols and polycyclic aromatic hydrocarbons. *Atmos. Environ.* **2007**, *41*, 4920–4930.
- (60) Van den Berg, M.; Birnbaum, L. S.; Denison, M.; De Vito, M.; Farland, W.; Feeley, M.; Fiedler, H.; Hakansson, H.; Hanberg, H.; Haws, K. L.; Rose, M.; Safe, S.; Schrenk, D.; Tohyama, C.; Tritscher, A.; Tuomisto, J.; Tysklind, M.; Walker, N.; Peterson, R. E. The 2005 world health organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicol. Sci.* **2006**, *93*, 223–241.
- (61) Alekseenko, E.; Raybaud, V.; Espinasse, B.; Carlotti, F.; Queguiner, B.; Thouvenin, B.; Garreau, P.; Baklouti, M. Seasonal dynamics and stoichiometry of the planktonic community in the Northwestern Mediterranean Sea: a 3D modeling approach. *Ocean Dynamics* **2014**, *64*, 179–207.
- (62) Barhoumi, B.; El Megdiche, Y.; Clérandeau, C.; Ben Ameur, W.; Mekni, S.; Bouabdallah, S.; Derouiche, A.; Touil, S.; Cachot, J.; Driss, M. R. Occurrence of polycyclic aromatic hydrocarbons (PAHs) in mussel (*Mytilus galloprovincialis*) and eel (*Anguilla anguilla*) from Bizerte lagoon, Tunisia, and associated human health risk assessment. *Cont. Shelf Res.* **2016**, *124*, 104–116.
- (63) Gregoris, E.; Argiriadis, E.; Vecchiatto, M.; Zambon, S.; De Pieri, S.; Donateo, A.; Contini, D.; Piazza, R.; Barbante, C.; Gambaro, G. Gas-particle distributions, sources and health effects of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) in Venice aerosols. *Sci. Total Environ.* **2014**, *476–477*, 393–405.
- (64) Van Leeuwen, F. X. R.; Feeley, M.; Schrenk, D.; Larsen, J. C.; Farland, W.; Younes, M. Dioxins: WHO's tolerable daily intake (TDI) revisited. *Chemosphere* **2000**, *40*, 1095–1101.
- (65) Castro-Jiménez, J.; Eisenreich, S. J.; Mariani, G.; Skejo, H.; Umlauf, G. Monitoring atmospheric levels and deposition of dioxin-like pollutants in sub-alpine Northern Italy. *Atmos. Environ.* **2012**, *56*, 194–202.
- (66) Background document to the Opinion on the Annex XV dossier proposing restrictions on Bis(pentabromophenyl) ether. Committee for Risk Assessment (RAC)/ Committee for Socio-economic Analysis (SocietalAC). European Chemicals Agency (ECHA): Helsinki, 2015; p 365.
- (67) An Exposure Assessment of Polybrominated Diphenyl Ethers, EPA/600/R-08/086F; U.S. Environmental Protection Agency, National Center for Environmental Assessment: Washington, DC, 2010.