Distribution of phthalates in Marseille Bay (NW Mediterranean Sea)

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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
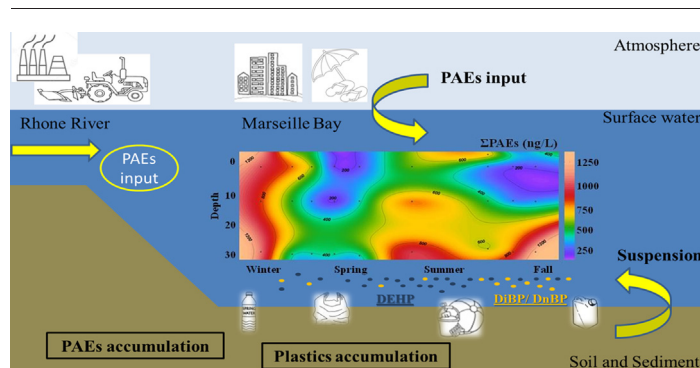
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ABSTRACT

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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et al., 2015a). PAEs account for approximately 92% of produced plasticizers and represent the most produced and consumed plasticizers worldwide (Rahman and Brazel, 2004; He et al., 2013) since these compounds are used to improve the flexibility of polyvinyl chloride (PVC) resins (Kimber and Dearman, 2010; Net et al., 2015b). Other industrial applications include the manufacturing of cosmetics, insect repellents, insecticide carriers and propellants (Net et al., 2015a; Net et al., 2015b; Xie et al., 2007). 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 (Holahan and Smith, 2015; IARC, 2000; Halden, 2010). 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 materials (Staples et al., 1997) as well as from plastic polymer migration (Andrady, 2011).

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 (Andrady, 2011), on the ecosystem functioning (Kolena et al., 2014) and on human obesity and cancer development (Okamoto et al., 2011; Howdeshell et al., 2008; Buckley et al., 2016; Wang et al., 2016). 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-EPA (United States Environmental Protection Agency, 2014), the European Union (EU) (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, 2007) and the Chinese water list (National Standard of the People's Republic of China, 2006). 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 (Bauer et al., 1998). Due to the physiochemical properties and biogeochemical cycling of PAEs, they have been detected in food, air, water, soil and sediment (Net et al., 2015b; Turner and Rawling, 2000; Fromme et al., 2002; Horn et al., 2004; Brossa et al., 2005; Teil et al., 2007; Xie et al., 2005; Xie et al., 2006; Zeng et al., 2008; Ferreira and Morita, 2012; Fu et al., 2009; Fu et al., 2013). 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 (The Mermex Group, 2011). Mediterranean rivers and primarily the Rhone River supply large amounts of freshwater, particles and organic carbon to the Mediterranean Sea (Sempéré et al., 2000; Panagiotopoulos et al., 2012). 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 (The Mermex Group, 2011; UNEP Chemicals, 2002) generate a large volume of wastewater, which provides marine litter, microplastics (Deudero and Alomar, 2015; Collignon et al., 2012; Cozar et al., 2015; Faure et al., 2015; Pedrotti et al., 2016; Suaria et al., 2016; Ruiz-Orejon et al., 2016; Schmidt et al., submitted), anthropogenic molecules (Sicre et al., 2008; Sempéré et al., in press), persistent organic pollutants (POPs) and related contaminants such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) (The

Mermex Group, 2011; Berrojalbiz et al., 2011; Castro-Jimenez et al., 2010) 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 (Brossa et al., 2005; Sanchez-Avila et al., 2012), and there is only one study dealing with the distribution of a series of PAEs in the Mediterranean basin (Paluselli et al., in press). 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°18′N, 05°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 °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 h for processing. Four samples collected in October 2014 at Marseille Bay were already published (Paluselli et al., in press). The samples were filtrated 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 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 °C. DOC concentrations were measured using a Shimadzu TOC-5000 carbon analyzer (Sempéré et al., 2008). 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 ± 2 μM C, $n = 24$ and 1 ± 0.3 μM 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).

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