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Andrea Paluselli, Vincent Fauvelle, Natascha Schmidt, François Galgani, Sopheak Net, et al.. Distribution of phthalates in Marseille Bay (NW Mediterranean Sea). *Science of the Total Environment*, 2018, 621, pp.578 - 587. 10.1016/j.scitotenv.2017.11.306 . hal-01769518v1

HAL Id: hal-01769518

<https://hal.science/hal-01769518v1>

Submitted on 18 Apr 2018 (v1), last revised 26 Feb 2019 (v2)

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Distribution of phthalates in Marseille Bay (NW Mediterranean Sea)

Andrea Paluselli¹, Vincent Fauvelle¹, Natascha Schmidt¹, François Galgani², Sopheak Net³ and Richard Sempéré^{1,*}

¹Aix-Marseille Univ., Université de Toulon, CNRS, IRD, M I O, Marseille, France

²IFREMER, Laboratoire Environnement Ressources, Provence Azur Corse (LER/PAC), Ifremer Centre de Méditerranée, ZP de Bregaillon, La Seyne sur Mer, France

³Université de Lille, Laboratoire LASIR, Villeneuve d'Ascq, France

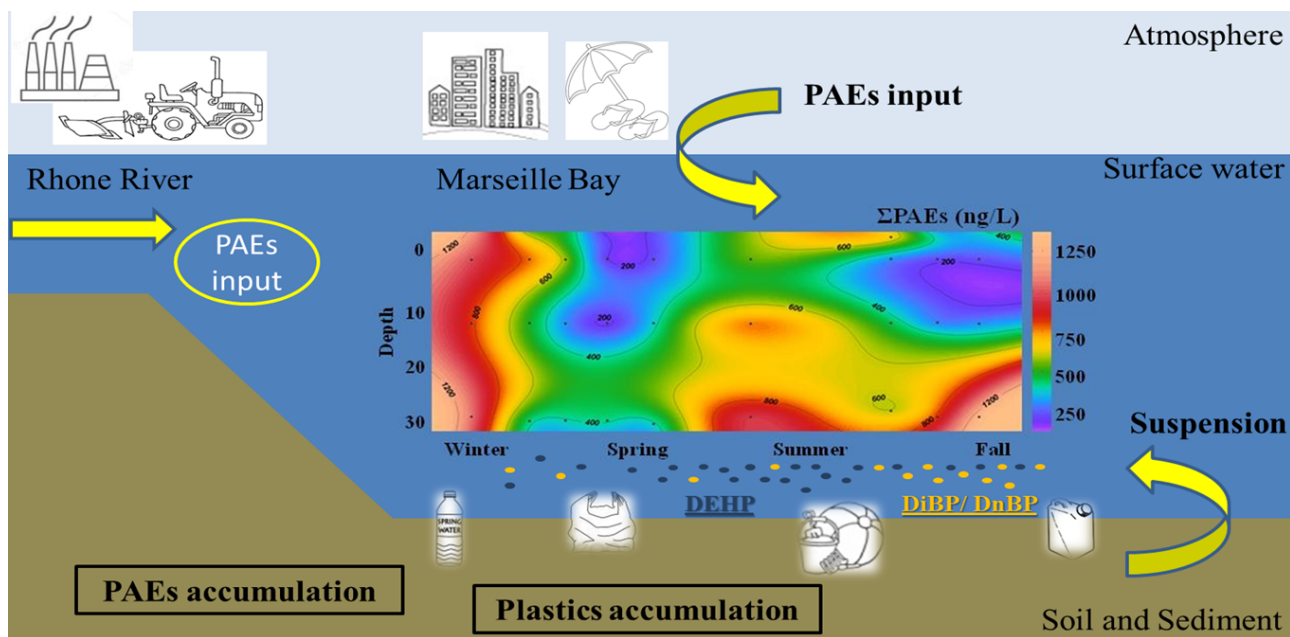
* Author to whom correspondence should be addressed; E-Mail: richard.sempere@mio.osupytheas.fr;

Keywords: Phthalates, DEHP, DMP, seawater, dissolved organic matter, endocrine disruptors

Science of The Total Environment, Volume 621, 15 April 2018, Pages 578-587

<https://doi.org/10.1016/j.scitotenv.2017.11.306>

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.

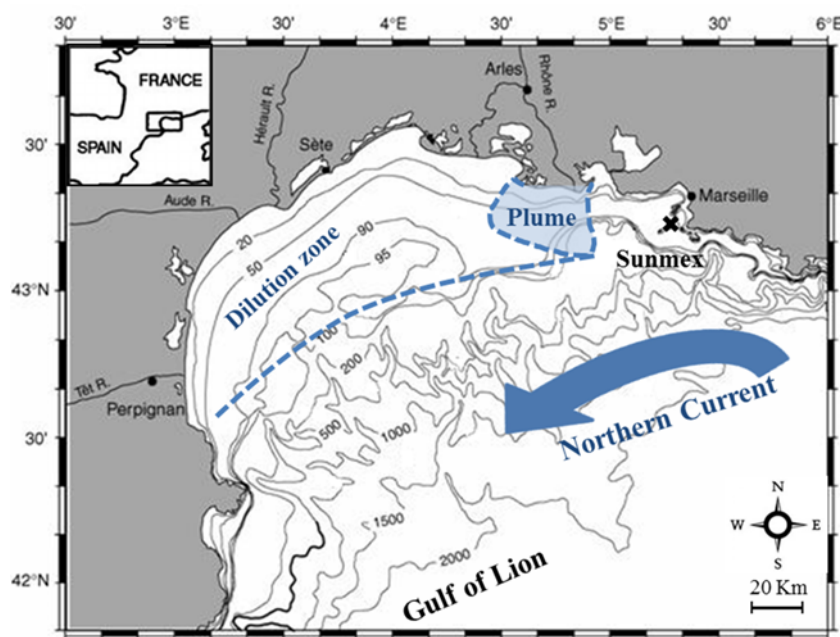
2. Materials and Methods

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°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 hours for processing. Four samples collected in October 2014 at Marseille Bay were already published.⁵³ 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

96 precombusted Pasteur pipettes, transferred into precombusted glass vials, poisoned with sulfuric acid to pH ~
 97 2 to avoid any biological activity, closed with PTFE-lined screw caps and stored in the dark at 4°C. DOC
 98 concentrations were measured using a Shimadzu TOC-5000 carbon analyzer.⁵⁴ The nominal analytical
 99 precision of the procedure was within 2%. The accuracy of the instrument and the system blank were
 100 determined by analyzing reference materials (D. Hansell, Rosenstiel School of Marine and Atmospheric
 101 Science, Miami, USA), including the Deep Seawater reference (DSR) and low carbon water (LCW)
 102 reference materials. The average DOC concentrations in the DSR and LCW reference standards were 45 ± 2
 103 $\mu\text{M C}$, $n = 24$ and $1 \pm 0.3 \mu\text{M C}$, $n = 24$, respectively.

104 All glassware including Pasteur pipettes, glass bottles and glass filtration apparatus was previously
 105 cleaned in 1% hydrochloric acid bath, rinsed with ultrapure water and combusted at 450 °C for 6 h. All the
 106 GC/MS and DOC seawater analyses were conducted in duplicate in the MIO laboratory in Marseille within 6
 107 months. Filtration of samples was conducted in the MIO ISO class 6 chemistry cleanroom (temperature: 22
 108 °C; SAS pressure: +15 Pa; SAS brewing rate: 30 vol/h; lab pressure: +30 Pa; brewing rate: 50 vol/h).



109

110 Figure 1. Area of study. The map (adapted from Frayssé et al.⁵⁵) shows the sampling stations in the Gulf of
 111 Lyon: SUNMEX (43°18'N, 05°22'E; depth 32 m) in the Bay of Marseille (December 2013–November 2014).
 112 Northern current is the main general circulation feature influencing the Gulf of Lyon with a geostrophic flux
 113 (calculated to 700 dbar) that varies throughout the year in a range of 0.9–1.8 Sv with its maximum in
 114 November or December³⁷. The Rhone River is the main fresh water supplier of the Mediterranean Sea with
 115 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,
 116 the Rhone River flux ranged from 1300 to 2800 $\text{m}^3 \text{ s}^{-1}$.

117

2.2 Phthalates analyses

Seven phthalates were studied including dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl 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.

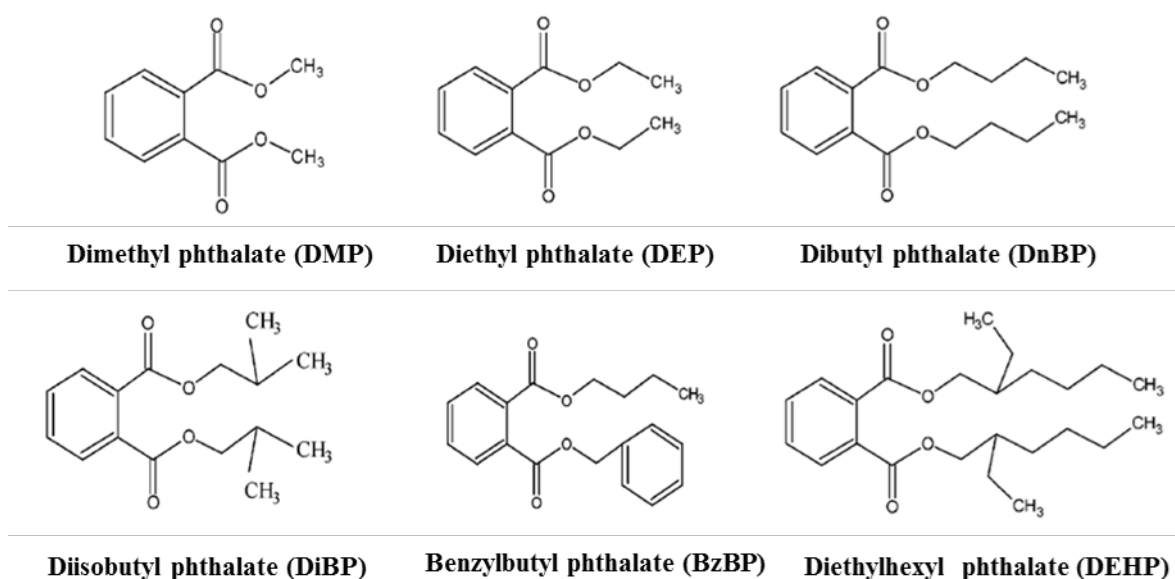


Figure 2. Chemical structure of the 6 detected PAEs. Dimethyl phthalate (DMP; MW = 194.18), Diethyl phthalate (DEP; MW = 222.24), Dibutyl phthalate (DnBP; MW = 278.34), Diisobutyl phthalate (DiBP; MW = 278.34), Benzylbutyl phthalate (BzBP; MW = 312.36) and Diethylhexyl phthalate (DEHP; MW = 390.56). 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% ± 3% for DEP to 110% ± 7% for DiBP. Internal standard recoveries were estimates as 94% ± 2% for DEP-d4, 77% ± 3% for DnBP-d4 and 14% ± 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

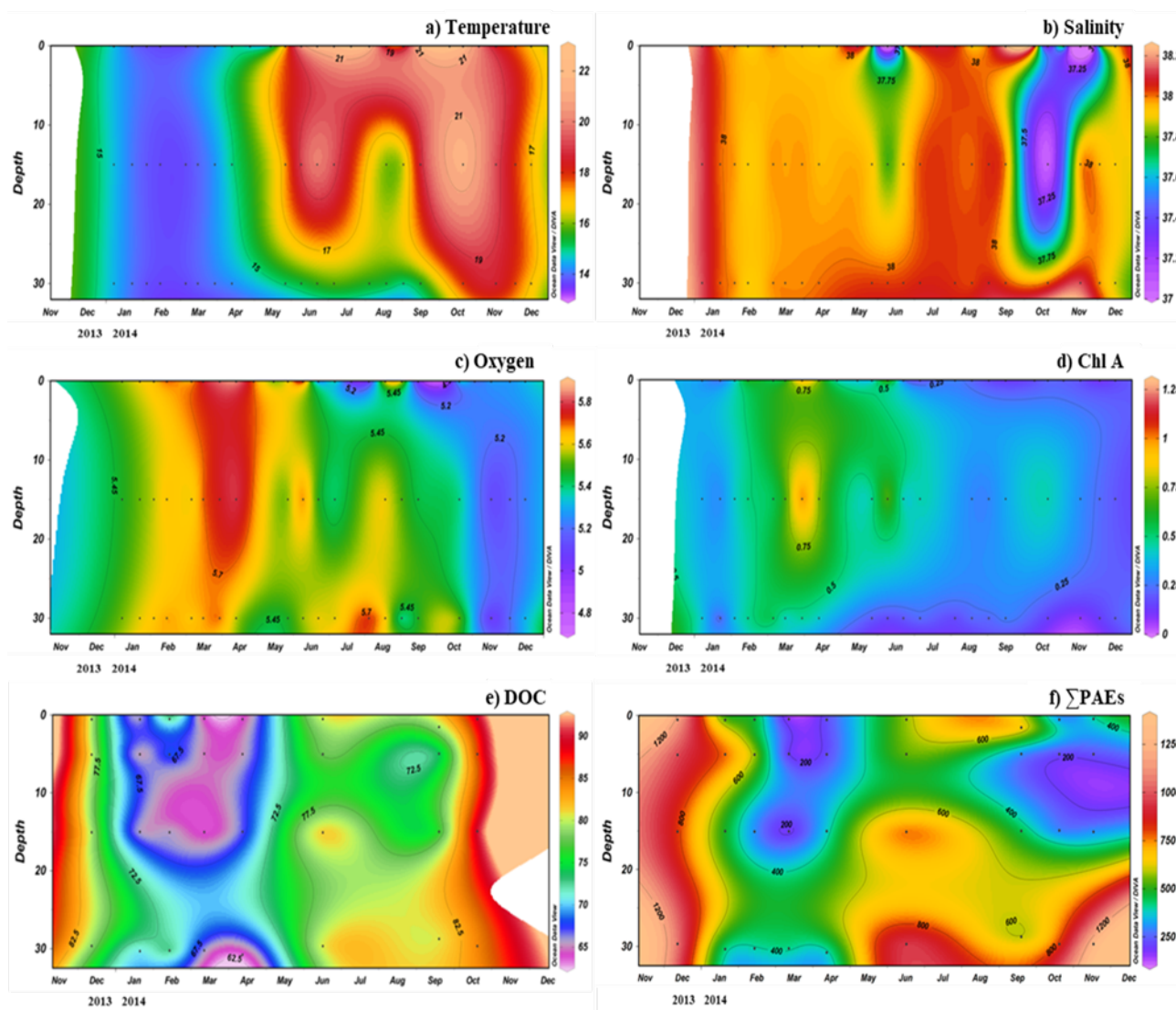
Principal component analysis (PCA) was applied to reduce the multidimensional nature of the dataset and to evaluate the interrelationships among the PAEs, sites and sampling periods. PCA was performed using the individual phthalate concentrations (i.e. DEHP, DiBP) as PCA parameters. This data set was 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

192 in winter. As a byproduct of primary production, the DOC distribution highlighted higher concentrations in
 193 spring-summer following phytoplankton growth (Fig. 3d). The high DOC concentrations near the bottom and
 194 in the whole water column during winter might instead be explained by resuspension of rich organic
 195 sediment and subsequent mixing under the action of wind as previously reported from CDOM (colored
 196 dissolved organic matter) and DOC time series studies.⁵⁸⁻⁵⁹ Such low DOC concentrations were comparable
 197 to those previously reported in open waters of the Mediterranean Sea,⁶⁰⁻⁶⁴ with a stable annual mean of $67 \pm$
 198 $7 \mu\text{MC}$ at 2 m and $63 \pm 6 \mu\text{MC}$ at 5 m.



199

200 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)
 201 and f) ΣPAEs (ng L^{-1}) time-series at SUNMEX station (Bay of Marseille) from December 2013 to
 202 November 2014. Samples were collected at 1.5, 5, 15 and 30 m.

203

204 Table 1. Concentration ranges, average concentrations and relative abundance of PAEs in Marseille Bay (n =
 205 72) from December 2013 to November 2014 (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
Bay of Marseilles (Dec 2013-Nov 2014)					
Dimethyl phthalate (DMP)	0.5	0.9-6.9	2.8 ± 2.2	0.2-1.4	0.6 ± 0.3
	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
Diethyl phthalate (DEP)	0.5	3.4-25.7	11.8 ± 7.6	1.1-4.9	2.6 ± 1.4
	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
Diisobutyl phthalate (DiBP)	0.5	34.2-215.7	89.5 ± 70.3	4.3-68.0	24.3 ± 21.9
	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
Dibutyl phthalate (DnBP)	0.5	12.0-314.6	76.7 ± 66.7	2.6-26.3	11.1 ± 7.9
	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
Benzylbutyl phthalates (BzBP)	0.5	2.7-4.9	3.7 ± 0.7	0.4-2.0	1.0 ± 0.6
	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
Diethylhexyl phthalate (DEHP)	0.5	42.3-802.0	331.4 ± 257.1	18.5-89.3	61.0 ± 23.8
	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		130.8- 1330.7	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⁻¹ ²⁶ 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.

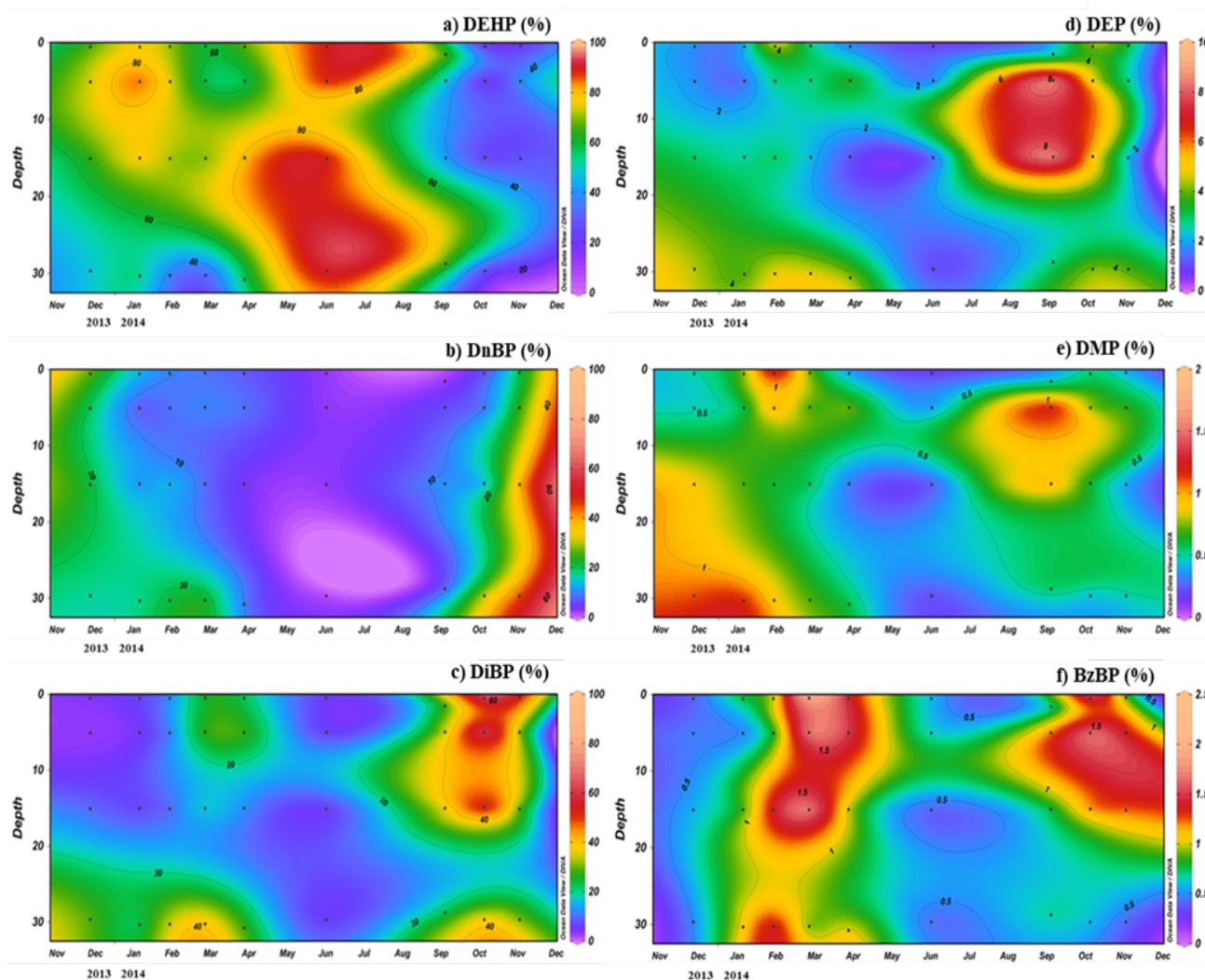
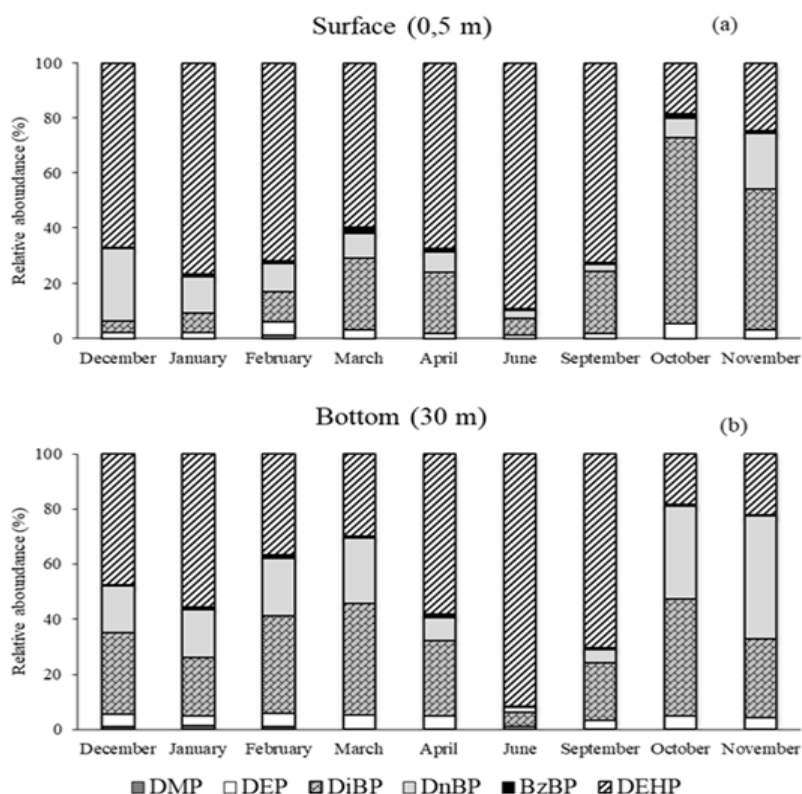


Figure 4. Relative abundances for DEHP (a), DnBP (b), DiBP (c), DEP (d), DMP (e) and BzBP (f) at SUNMEX station in Marseille Bay from December 2013 to November 2014.

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 ($3-120 \text{ ng L}^{-1}$; 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 ($0.07-4.55 \text{ ng L}^{-1}$; ^{52,66}) in NW Mediterranean Sea, PCB ($2.2-82.4 \text{ pg L}^{-1}$; 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 $4-6 \text{ pg L}^{-1}$.⁶⁷ PCDD/Fs was reported with two orders of magnitude lower than PAEs concentration ($42.5-64.0 \text{ fg L}^{-1}$).⁶⁸ However, PAE concentrations are nevertheless two orders of magnitude lower than the sum of

246 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
 247 or in the Rhone River close to the Marseille Bay.⁴⁹



248

249 Figure 5. Relative abundance of PAEs in surface (0.5 m; a) and bottom (30 m; b) seawater samples collected
 250 at SUNMEX station in Marseille Bay from December 2013 to November 2014.
 251

252 3.3 PCA analysis

253

254

255 several clusters (samples scores, Fig. 6a) over PC1 and PC2 that represent 79.7% of the total information.
 256 Samples collected at Marseille Bay formed five well-identified clusters (Fig. 6a) including the fall samples in
 257 the lower left quadrant, the spring in the central left, the summer in the upper left, winter samples in the
 258 upper right quadrant and the bottom samples in the right quadrant. Of the biomarkers plotted, DMP, DEP
 259 and DnBP being positive on PC1 and most negative on PC2 form a compact cluster on the central-right
 260 quadrant and separated from DEHP located in the upper quadrant (positive on PC1 and PC2 factors) and
 261 from DiBP in the lower quadrant (positive on PC1 and negative on PC2). DEHP is a plasticizer used in the
 262 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.

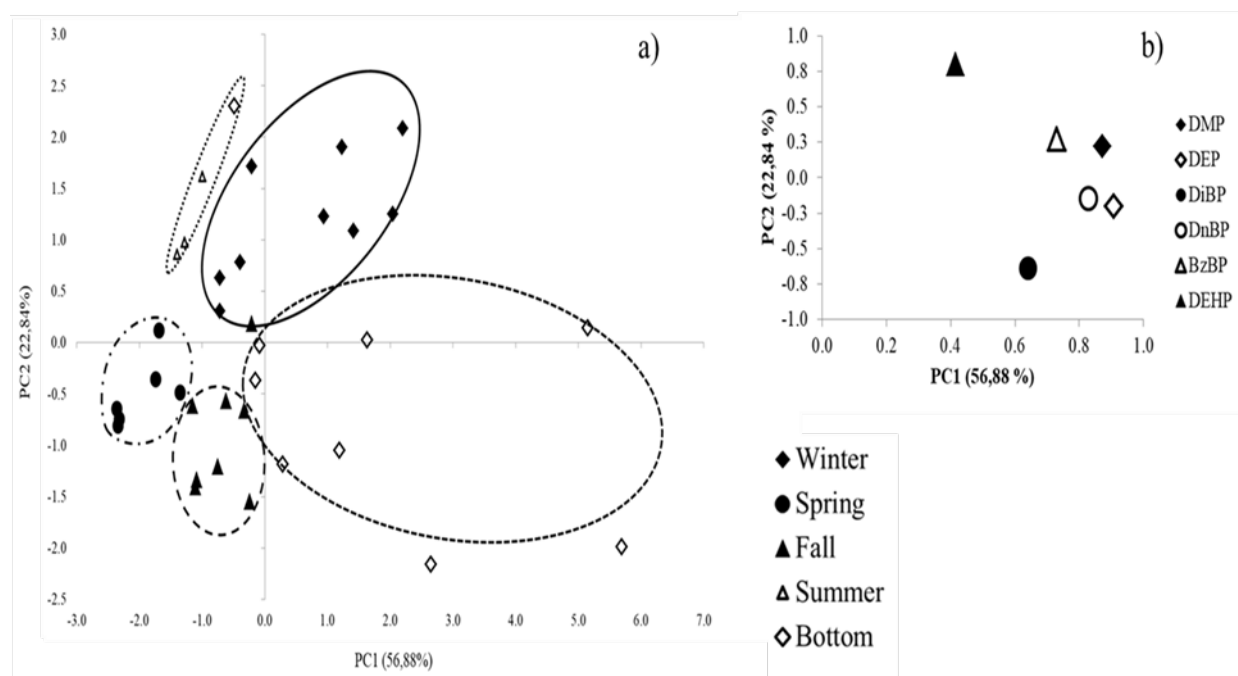


Figure 6. Principal components analysis (PCA) for PAEs in the study area was applied to reduce the multidimensional nature of the dataset and to evaluate the interrelationships among the PAEs, sites and sampling periods. The PCA statistics were performed using the statistical package XLSTAT 2010.2 (Addinsoft). 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 Σ PAEs 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 Σ PAEs increase of concentration above the sea floor at different periods of the year.

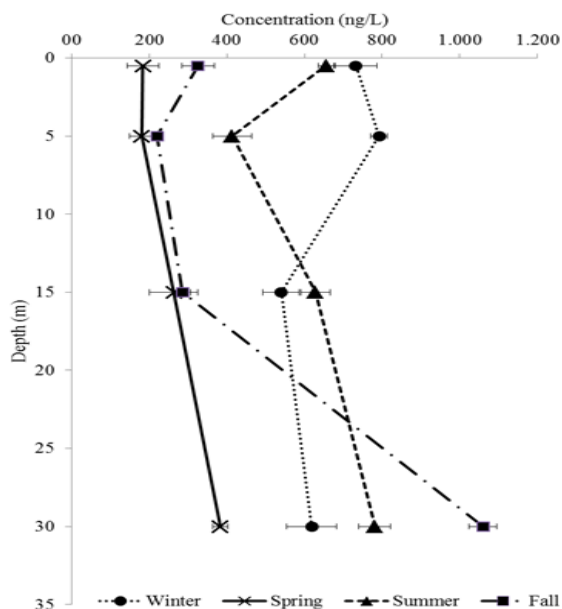
Seasonal variation

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 Σ PAEs near the bottom has already been reported in a previous study in offshore Mediterranean seawater at 2000 m depth.⁵³ A gradient

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



314
 315 Figure 7. Σ PAEs vertical profile at Bay of Marseille in 4 seasons (average values) of 2014.
 316

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

322 This vertical gradient might also be connected to a concentration of plastic debris above the sea floor
 323 that may releases various chemical additives including phthalates into surrounding waters during their
 324 degradation as stated before. Indeed, accumulation of debris with a large proportion of plastic material has
 325 been observed several times, by trawling sampling and by video quantification based on recordings at the sea
 326 floor of the French Mediterranean coast including Marseille Bay,⁷²⁻⁷⁴ the Rhone River plume area as well as
 327 canyons and continental slopes in the northwestern Mediterranean.⁷⁵ In most cases, plastic bags accounted
 328 for more than 90% of the total debris⁷² and in particular in the eastern canyons of the Gulf of Lion⁷⁴ close to

329 Marseille. Such debris are likely PAE-producer candidates. Chemical diffusion from sediment, or sediment
 330 resuspension/bioturbation could though explain higher PAE concentration close to the sediment.
 331 Resuspension episodes of PAE-rich sediment in the water column (originating from wind-driven turbulence
 332 and hydrodynamic features⁷⁶ such as upwelling above the seafloor as previously reported for CDOM and
 333 DOC in Marseille Bay⁵⁸) are possible. However, higher DOC concentrations were not observed close to the
 334 sediment (Fig. 3e), supporting poor physical transport from the sediment toward the water column. Transport
 335 by chemical diffusion would therefore be predominant, in case PAEs input came from the sediment.

336 Interestingly, in Marseille Bay bottom samples, DiBP and DnBP relative abundance values were
 337 predominant over DEHP or higher (compared to surface waters) and match the period of high concentration
 338 of total PAEs. Indeed, in surface water samples, the relative abundance of DEHP, DnBP and DiBP averaged
 339 $66 \pm 18\%$, $11 \pm 6\%$ and $21 \pm 15\%$, respectively, whereas these values averaged $48 \pm 21\%$, $21 \pm 12\%$ and 32
 340 $\pm 14\%$, respectively, in bottom samples during the year (Fig. 5). A possible explanation would be a higher
 341 degradation rate of LMW-PAEs close to the atmosphere/water interface due to higher organisms' density, as
 342 suggested by Yuan et al.⁷⁷ The predominance (or higher relative abundance) of DnBP and DiBP *versus*
 343 DEHP in deepwater samples is in line with previous observations at a deep offshore station ($z = 2400$ m).⁵³
 344 The variation of PAE relative abundance near the bottom could also be explained considering the higher
 345 hydrophobicity of DEHP ($\log K_{ow} = 7.54$, SPARC) compared with DnBP and DEP ($\log K_{ow} = 4.63$ and 2.51 ,
 346 respectively, SPARC), which could determine different grades of PAE repartition between sediment and
 347 water, making available a smaller dissolved fraction of DEHP and suggesting that DEP and even DnBP
 348 mainly exist under freely dissolved phase compared with DEHP. The higher desorption rate of these
 349 phthalate, with the exception of DEHP and DMP, in the interface sediment/water was already observed in a
 350 previous study⁷⁸

351 Surprisingly, a significant decrease of DEHP concentration and relative abundance was observed
 352 after the summer (October/November 2014) (Figs. 4-5). The change in relative abundance during fall, even
 353 on the surface, was due to an increase of DiBP and to a lesser extent DnBP and could be associated with
 354 potential resuspension as we observed only high PAE concentration in bottom samples. Note that the
 355 variable intensity of the resuspension processes might be favored by the Northern Current entering into the
 356 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.

5. 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.

Acknowledgments

This study was conducted as part of the project PLASTOX-JPI-Ocean, PlasticMicro-EC2CO and MERMEX/MISTRALS LABex-OTMed projects and supported by 'Pole Mer Méditerranée'. This study is a contribution to the international SOLAS and LOICZ projects. We acknowledge the financial support from the PACA region, which provided a PhD scholarship for A. Paluselli. The authors are grateful to the crews of the R/V *Antedon II* and SAM-M I O platform for operation at sea as well as Patrick Raimbault, Nagib

386 Bhairy for hydrological data and sampling and Anne Delmont for help in sampling and DOC analyses.
387 Reviewers are kindly acknowledged for improving the revised version of the MS.

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