
Distribution of phthalates in Marseille Bay (NW Mediterranean Sea)

Paluselli Andrea ¹, Fauvelle Vincent ¹, Schmidt Natascha ^{1,*}, Galgani Francois ², Net Sopheak ³, Sempéré Richard ^{1,*}

¹ Aix-Marseille Univ., Université de Toulon, CNRS, IRD, MIO, Marseille, France

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

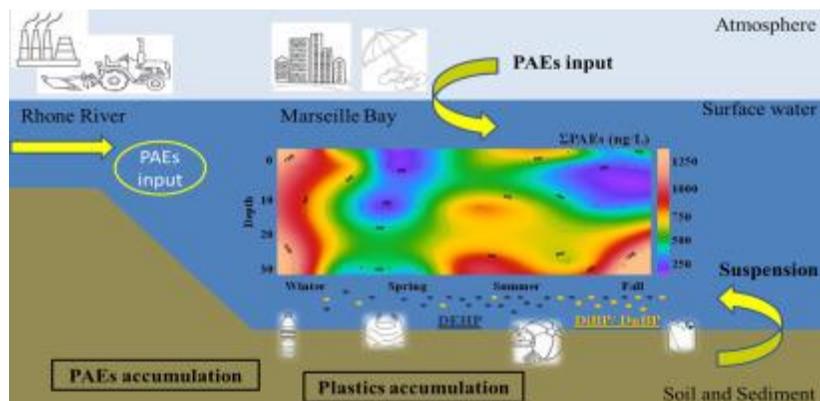
³ Université de Lille, Laboratoire LASIR, Villeneuve d'Ascq, France

* Corresponding author : Richard Sempéré, email address : richard.sempere@mio.osupytheas.fr

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.

Graphical abstract



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.

Keywords : Phthalates, DEHP, DMP, Seawater, Dissolved organic matter, Endocrine disruptors

44 **1 Introduction**

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

56 Previous studies have shown that PAEs are endocrine-disrupting chemicals with the capability of
57 inducing significant effects on the reproduction of various organisms, including protozoans, mollusks,
58 crustaceans, fishes and invertebrates,¹² on the ecosystem functioning¹³ and on human obesity and cancer
59 development.¹⁴⁻¹⁷ Therefore, PAEs have become a matter of concern for their potential risk to health and the
60 environment. Six PAEs (dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP),
61 benzylbutyl phthalate (BzBP), diethylhexyl phthalate (DEHP) and di-n-octyl phthalate (DnOP)) have been
62 included as priority pollutants of the US-EPA¹⁸, the European Union (EU)¹⁹ and the Chinese water list.²⁰
63 Accordingly, monitoring PAEs in the major environmental matrices has become a priority. After their
64 introduction in the environment, they can reach marine water by wastewater and riverine inputs, and end up
65 in the sediment via association with humic acid and adsorption onto particles and finally end up in the
66 sediment.²¹ Due to the physiochemical properties and biogeochemical cycling of PAEs, they have been
67 detected in food, air, water, soil and sediment^{6,22-32}. However, there is a lack of data related to their sources,
68 distribution in the whole water column as well as their transfer mechanisms from the molecular state to
69 different living species.

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

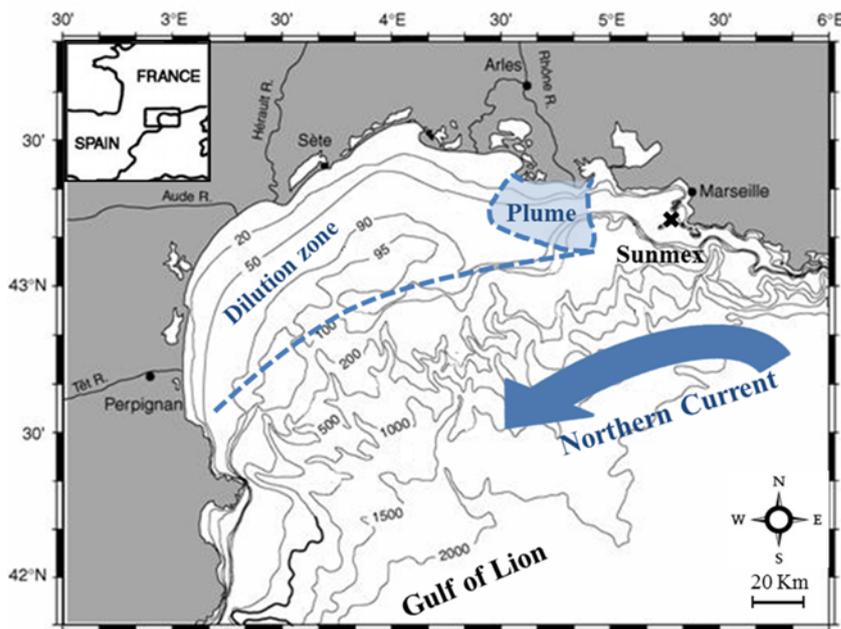
84 **2. Materials and Methods**

85 **2.1 Study area, sampling, and dissolved organic carbon analyses**

86 Seawater samples (n=72) were collected with R/V Antedon from the SUNMEX station (Fig. 1) in
87 the northwestern Mediterranean Sea in Marseille Bay (43°18'N, 05°22'E) from December 2013 to November
88 2014 at 1.5, 5, 15 and 30 m (with a bottom depth of 32-33 m) with a 12-L GO-FLO© (GENERAL
89 OCEANICS) bottle previously rinsed with 1% hydrochloric acid and ultrapure water to avoid contamination.
90 Immediately after sampling, the seawater samples were directly transferred from the GO-FLO© into 5-L
91 precombusted (450°C for 6 h) glass bottles closed with PTFE (polytetrafluoroethylene) lined screw caps,
92 wrapped with aluminum foil and brought back to the laboratory within 4 hours for processing. Four samples
93 collected in October 2014 at Marseille Bay were already published.⁵³ The samples were filtrated through
94 precombusted (450°C for 6 h) GFF filters (47-mm filter diameter, rinsed with 2 L of Milli-Q water and 150
95 mL of sample prior to filtration) in a glass apparatus directly and transferred into 1-L glass bottles. After
96 filtration, duplicate subsamples (10 mL) were collected for dissolved organic carbon (DOC) analyses with

97 precombusted Pasteur pipettes, transferred into precombusted glass vials, poisoned with sulfuric acid to pH ~
 98 2 to avoid any biological activity, closed with PTFE-lined screw caps and stored in the dark at 4°C. DOC
 99 concentrations were measured using a Shimadzu TOC-5000 carbon analyzer.⁵⁴ The nominal analytical
 100 precision of the procedure was within 2%. The accuracy of the instrument and the system blank were
 101 determined by analyzing reference materials (D. Hansell, Rosenstiel School of Marine and Atmospheric
 102 Science, Miami, USA), including the Deep Seawater reference (DSR) and low carbon water (LCW)
 103 reference materials. The average DOC concentrations in the DSR and LCW reference standards were 45 ± 2
 104 $\mu\text{M C}$, $n = 24$ and $1 \pm 0.3 \mu\text{M C}$, $n = 24$, respectively.

105 All glassware including Pasteur pipettes, glass bottles and glass filtration apparatus was previously
 106 cleaned in 1% hydrochloric acid bath, rinsed with ultrapure water and combusted at 450 °C for 6 h. All the
 107 GC/MS and DOC seawater analyses were conducted in duplicate in the MIO laboratory in Marseille within 6
 108 months. Filtration of samples was conducted in the MIO ISO class 6 chemistry cleanroom (temperature: 22
 109 °C; SAS pressure: +15 Pa; SAS brewing rate: 30 vol/h; lab pressure: +30 Pa; brewing rate: 50 vol/h).



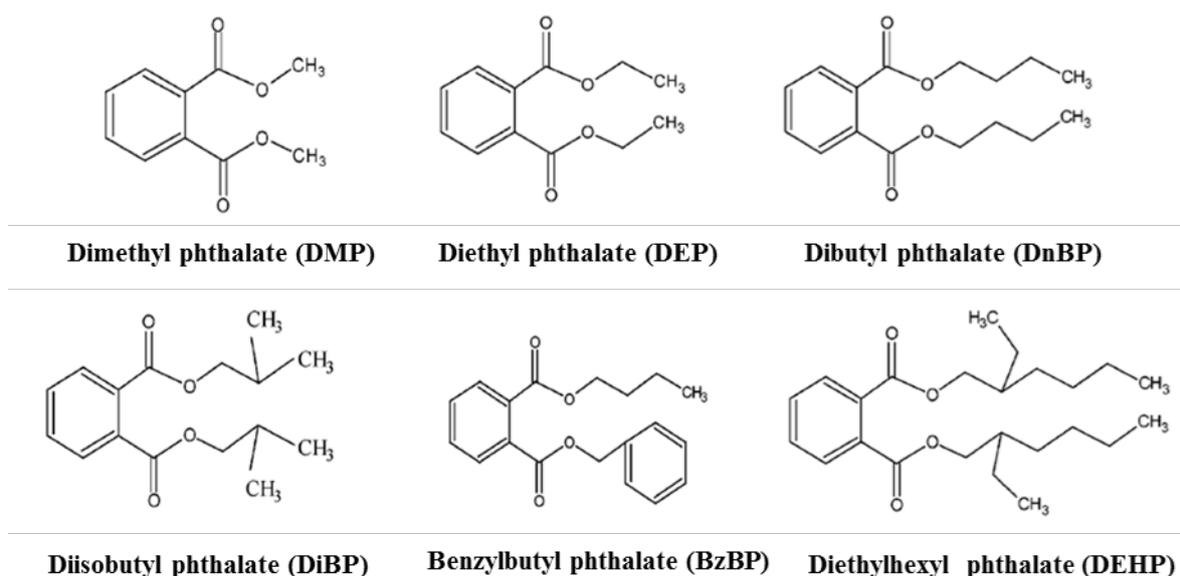
110

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

118

119 **2.2 Phthalates analyses**

120 Seven phthalates were studied including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-
 121 isobutyl phthalate (DiBP), di-n-butyl phthalate (DnBP), benzylbutyl phthalate (BzBP), diethylhexyl
 122 phthalate (DEHP) and di-n-octyl phthalate (DnOP) (Fig. 2). The deuterated internal standards were: DEP-d4,
 123 DnBP-d4, DEHP-d4. All native and labeled standards were of high purity grade (> 98%, 2000 $\mu\text{g mL}^{-1}$
 124 Supelco). Stock solutions were prepared in hexane and stored in the dark at 4°C. Working solutions
 125 (unlabeled and labeled standards) were prepared by dilution of these solutions at 20 mg L^{-1} . All solvents
 126 were glass-distilled grade and supplied by Rathburn Chemicals Ltd. (Walkerburn, UK). Milli-Q water was
 127 produced on-site on a Milli-Q system, Millipore (Molsheim, France) with resistivity higher than 18.2 $\text{M}\Omega\text{ cm}$
 128 (25°C) and Total Organic Carbon < 2 $\mu\text{g L}^{-1}$.



129

130 Figure 2. Chemical structure of the 6 detected PAEs. Dimethyl phthalate (DMP; MW = 194.18), Diethyl
 131 phthalate (DEP; MW = 222.24), Dibutyl phthalate (DnBP; MW = 278.34), Diisobutyl phthalate (DiBP; MW
 132 = 278.34), Benzylbutyl phthalate (BzBP; MW = 312.36) and Diethylhexyl phthalate (DEHP; MW = 390.56).
 133 Figure adapted from Xie et al.⁷

134

135 The extractions were performed following the method optimized for seawater PAE detection at trace
 136 levels.⁵³ PAEs were extracted by solid phase extraction (SPE) from seawater using a precombusted 6-mL
 137 glass reaction tube containing 200 mg of Oasis® HLB sorbent (Waters Corporation, 30 μm , 100 g). SPE was
 138 conducted on a Visiprep vacuum manifold from Sigma-Aldrich (Saint Quentin Fallavier, France). Before
 139 sample extraction, SPE cartridges were three times sequentially cleaned with 5 mL of acetone, 5 mL of

140 dichloromethane, conditioned with 5 mL of ethyl acetate, 5 mL of acetone and 5 mL of ultrapure water prior
141 sample processing. Seawater samples were spiked (for recovery estimate) with DEP-d4, DnBP-d4 and
142 DEHP-d4 at 50, 200 and 400 ng L⁻¹, respectively, prior to loading onto SPE cartridges under vacuum at a
143 flow rate of 5 to 10 mL min⁻¹. Then, 5 mL of ultrapure water was percolated to remove the remaining salt
144 and air-dried for around 1 h under vacuum. PAEs were eluted into precombusted 10 mL-vials by a 2-step
145 percolation of 3 mL of ethyl acetate. Ethyl acetate was gently evaporated to a final volume of 200 µL at
146 room temperature under a gentle stream of nitrogen (purity > 99,995 %). Then, samples were immediately
147 closed with PTFE lined screw caps rubbed with PTFE ribbon and stored before injection in the dark at -
148 20 °C.

149 Analysis was performed using an Agilent Technologies 6850 GC system coupled to an Agilent
150 Technologies 5975C mass spectrometer (GC/MS) operated with electron impact ionization (70 eV).
151 Chromatographic separation was achieved on an Agilent HP-5MS capillary column (30 m x 0.25 mm,
152 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
153 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
154 used as a carrier gas at a flow rate of 1.1 mL min⁻¹. Samples were manually injected (2 µL) on a splitless
155 mode injector with a temperature set at 250°C. The injector (Merlin Microseal system) was used as a low
156 carryover septum and a gas purifier (Charcoal, CP17972) to prevent contamination during the injection. Data
157 were acquired in single ion monitoring (SIM) mode for increased sensitivity with a dwell time of 100 ms.
158 Data were collected and analyzed with the Agilent ChemStation software.

159 **2.3 Quality control and quality assurance**

160 For each batch of 12 samples, a method blank, a spiked blank and a sample duplicate were
161 processed. The retention time and the response factors of GC/MS were assessed for each analytical sequence
162 from daily control standards to ensure the most appropriate quantification. The average recoveries of PAEs
163 spiked in seawater samples showed acceptable recovery for all phthalates, ranging from 97% ± 3% for DEP
164 to 110% ± 7% for DiBP. Internal standard recoveries were estimates as 94% ± 2% for DEP-d4, 77% ± 3%
165 for DnBP-d4 and 14% ± 2% for DEHP-d4. All material was produced in borosilicate glass previously kept in
166 an acidic bath overnight (10% hydrochloric acid), rinsed with ultrapure water, combusted at 450°C for

167 6 hours and rinsed with methanol and dichloromethane before use. Extractions were carried out in controlled
168 air conditions in an ISO class 6 chemistry cleanroom (temperature: 22°C; SAS pressure: +15 Pa; SAS
169 brewing rate: 30 vol/h; lab pressure: +30 Pa; brewing rate: 50 vol/h). Although precautions were considered
170 to prevent sample contamination during the protocol, DEP, DiBP and occasionally DnBP were detected in
171 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 $0.7 \pm 0.2 \text{ ng L}^{-1}$,
172 respectively. DEHP was occasionally detected in blanks between the MDL and the QDL. Limits of detection
173 (LOD) were derived from the blanks and quantified as mean blanks plus three times the standard deviation of
174 blanks, and they ranged from 0.11 ng L^{-1} for DMP to 1.67 ng L^{-1} for DEHP.

175 **2.4 Statistics**

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

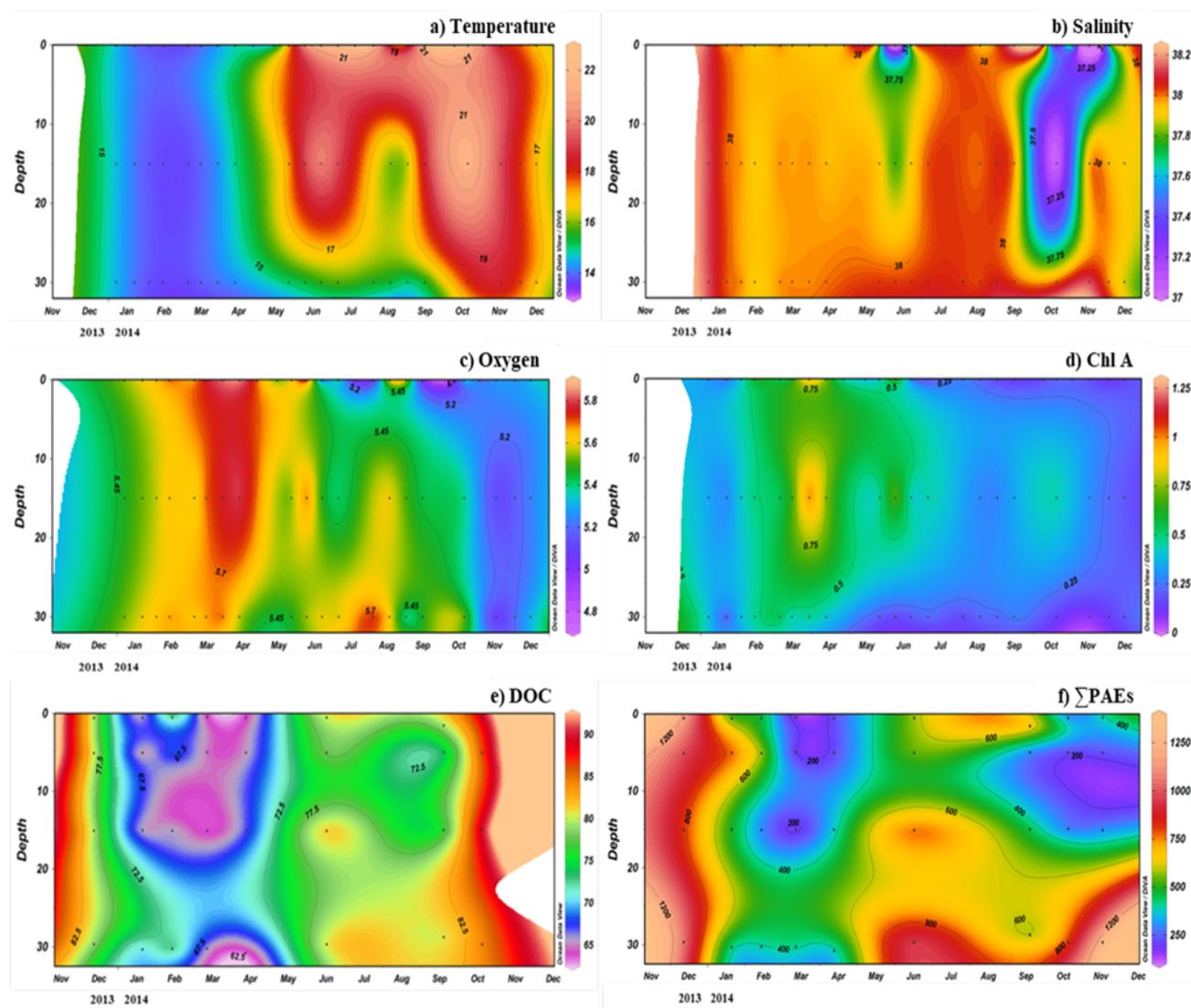
183

184 **3 Results and discussion**

185 **3.1 General characteristics of the water column**

186 The hydrological data (Fig. 3) are in line with previous well-known features in Marseille Bay and
187 the local coastal area indicating that (1) the water column was well mixed during winter and fall periods,
188 most of the time under the action of wind,⁵⁵⁻⁵⁷ whereas (2) the water began warming in May (16–17°C)
189 causing water stratification. It is noteworthy that lower salinity was observed in October-November 2014
190 probably in association with freshwater intrusion (Fig. 3b). The DOC distribution (Fig. 3e) showed a clear
191 seasonal trend with a concentration range of 62.5-72.5 μM in winter-spring and 72.5-90 μM during summer-
192 fall. Higher DOC values (79-81 μM) were observed in the spring water column as well as above the bottom

193 in winter. As a byproduct of primary production, the DOC distribution highlighted higher concentrations in
 194 spring-summer following phytoplankton growth (Fig. 3d). The high DOC concentrations near the bottom and
 195 in the whole water column during winter might instead be explained by resuspension of rich organic
 196 sediment and subsequent mixing under the action of wind as previously reported from CDOM (colored
 197 dissolved organic matter) and DOC time series studies.⁵⁸⁻⁵⁹ Such low DOC concentrations were comparable
 198 to those previously reported in open waters of the Mediterranean Sea,⁶⁰⁻⁶⁴ with a stable annual mean of $67 \pm$
 199 $7 \mu\text{MC}$ at 2 m and $63 \pm 6 \mu\text{MC}$ at 5 m.



200

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

204

205 Table 1. Concentration ranges, average concentrations and relative abundance of PAEs in Marseille Bay (n =
 206 72) from December 2013 to November 2014 (samples were collected at 0.5, 5, 15 and 30 m depth).

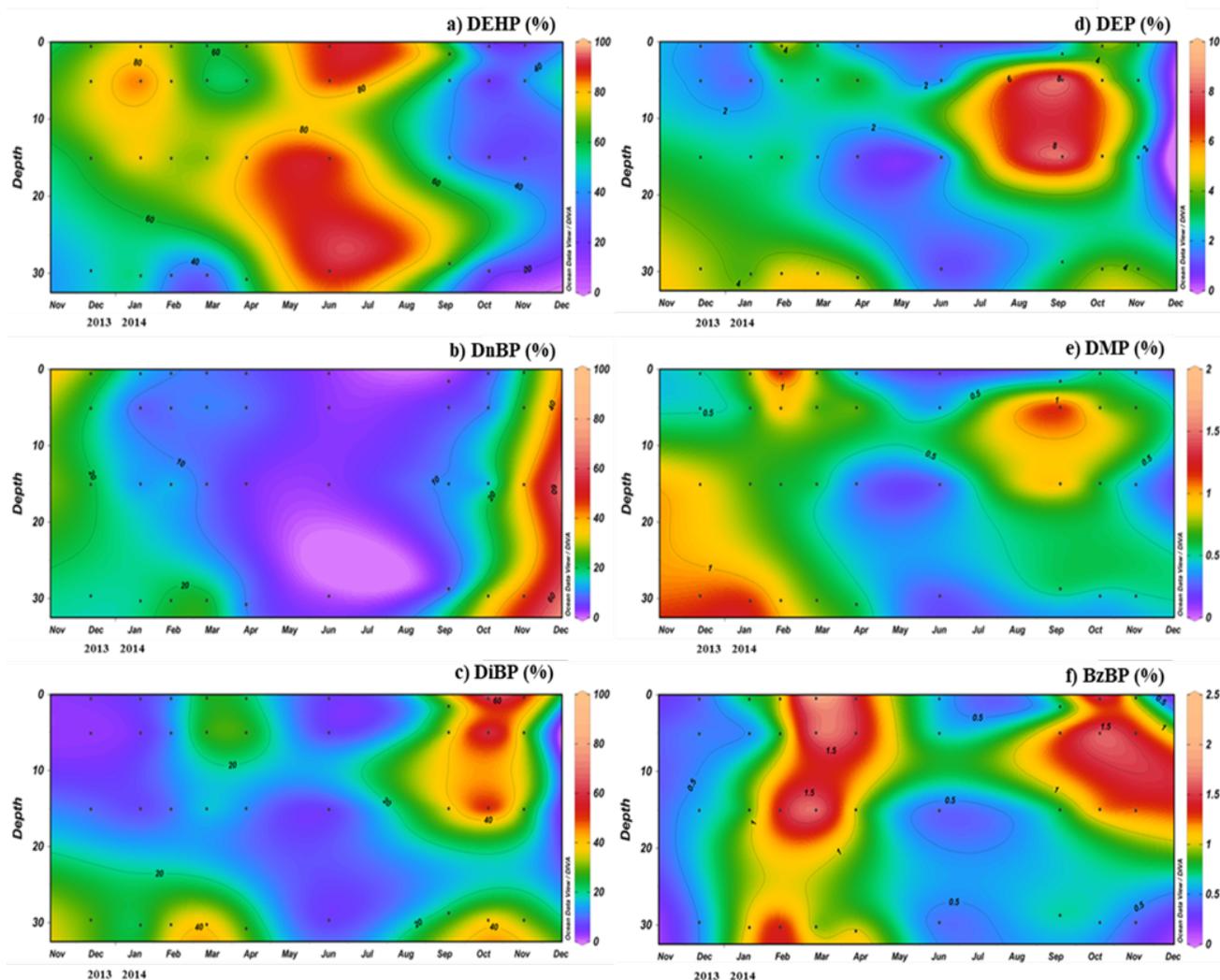
	Depth (m)	Concentrations (ng L ⁻¹)		Relative abundance (%)	
		Range	Av. ± SD	Range	Av. ± SD
<i>Bay of Marseilles (Dec 2013-Nov 2014)</i>					
Dimethyl phthalate (DMP)	0.5	0.9-6.9	2.8 ± 2.2	0.2-1.4	0.6 ± 0.3
	5	0.8-6.8	2.9 ± 2.0	0.3-1.1	0.7 ± 0.4
	15	0.8-7.7	2.7 ± 2.3	0.2-0.9	0.6 ± 0.3
	30	2.1-11.9	4.5 ± 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	

207 3.2 Concentration and relative abundance of PAEs in Marseille Bay

208 All targeted PAEs were detected in all samples collected at SUNMEX station except DnOP. During
209 the studied period, the sum of the 6 PAEs' concentrations in the water column (Σ PAEs) ranged from 130 to
210 1330 ng L⁻¹ (av. 520 ng L⁻¹; Table 1; Fig. 3f) in Marseille Bay. The highest Σ PAEs concentrations were
211 observed all along the well mixed water column in winter 2013 as well as near the bottom in the May-August
212 and September-December 2014 periods (Figs. 3). By contrast, the lowest Σ PAEs concentrations were found
213 in shallower waters between 0.5 and 15 m by the end of winter and in October-November 2014 where low
214 salinities were observed (Fig. 3b). Note that the October-November 2014 period corresponds to possible
215 freshwater intrusion into Marseille Bay⁵⁶ as suggested by lower salinity values (Fig. 3b). In Marseille Bay,
216 for 62 out of 72 samples, DEHP (9.3-91.6%) was the most abundant PAE, followed by DiBP (3.8-78%) and
217 DnBP (2.1-44.8%) (Fig. 4-5; Tab. 1). By contrast, DMP, DEP and BzBP were the least abundant (0.2-2%)
218 and can be considered minor species here.

219 Very limited data are available for the occurrence and fate of PAEs as a simultaneous series in
220 marine waters and more specifically in both the Mediterranean Sea and river waters, making any comparison
221 of Σ PAEs data with existing studies difficult. However we found that our data are consistent with literature.
222 Indeed, examination of already published individual PAEs, indicated that our DEHP concentrations (20-920
223 ng L⁻¹; Tab. 1) were in the same range as values reported for NW Spanish coastal seawater (30-620 ng L⁻¹;⁵²)
224 and the southern coast of the UK (100-2200 ng L⁻¹;²²) but one order of magnitude lower than that for the
225 Northern Mediterranean Spanish coast.²⁵ Noteworthy lower values were also reported in the North Sea for
226 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
227 and 323-779 ng L⁻¹, were found in the Seine River whereas DMP concentrations were reported in the range
228 of 2.5–5.5 ng L⁻¹ in six Spanish rivers including Ebro River.⁵² DEP was detected in different studies in the
229 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
230 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
231 L⁻¹.^{52,65} Limited data are available for the distribution of PAEs in coastal seawater.

232



233

234 Figure 4. Relative abundances for DEHP (a), DnBP (b), DiBP (c), DEP (d), DMP (e) and BzBP (f) at
 235 SUNMEX station in Marseille Bay from December 2013 to November 2014.
 236

237

238

239

240

241

242

243

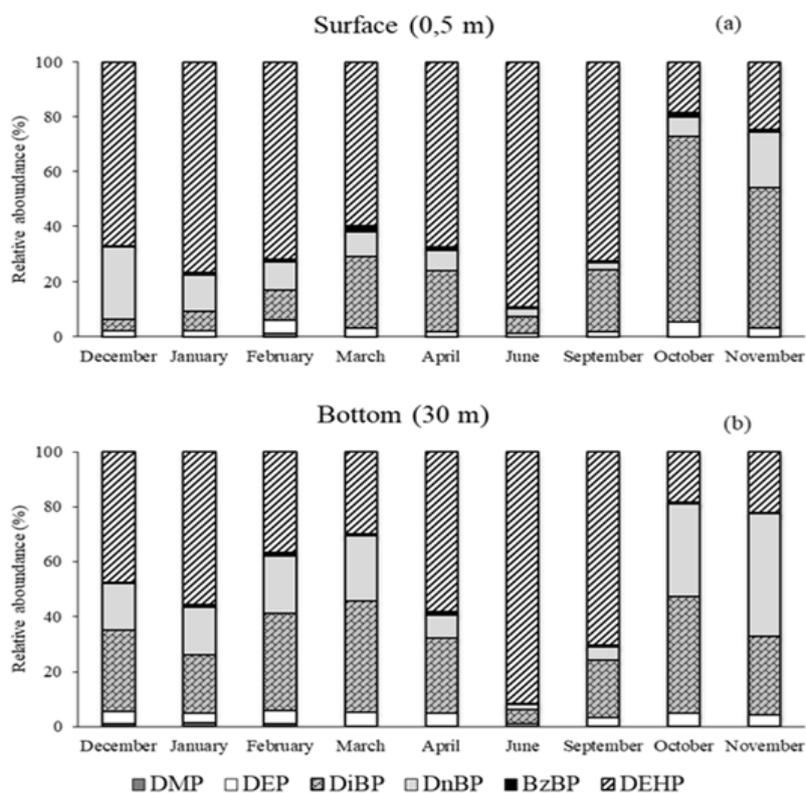
244

245

246

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

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



249

250 Figure 5. Relative abundance of PAEs in surface (0.5 m; a) and bottom (30 m; b) seawater samples collected
 251 at SUNMEX station in Marseille Bay from December 2013 to November 2014.
 252

253 3.3 PCA analysis

254

255

256

257

258

259

260

261

262

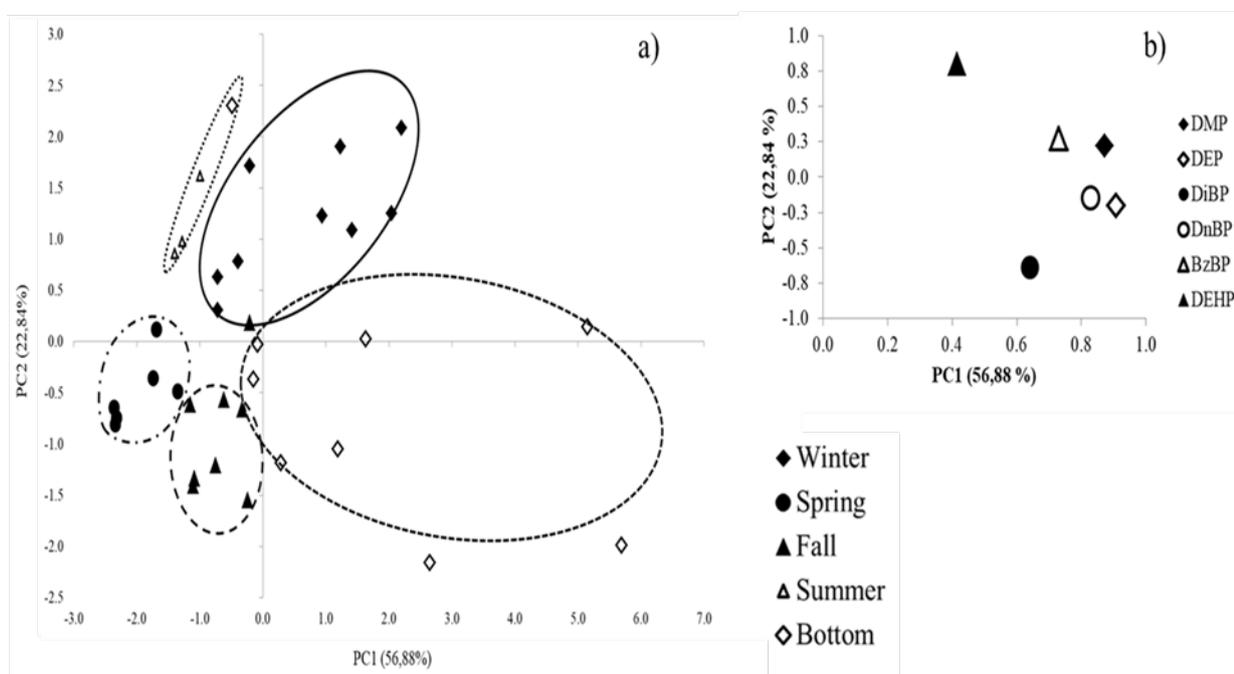
263

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

264 group is related to their common use as components of solvents, adhesives, pharmaceutical products,
 265 insecticide materials and cosmetics.

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

272



273

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

279

280 3.4 Potential sources and sinks of PAEs in the water column

281 The averaged concentrations of PAEs found in Marseille Bay ($522.7 \pm 313.3 \text{ ng L}^{-1}$) samples are
 282 significantly higher than that previously found offshore (maximum depth 2500 m) ($135 \pm 74 \text{ ng L}^{-1}$,⁵³)
 283 suggesting that the freshwater input and urban area provide a significant amount of PAEs to Marseille Bay.

284 Our results also indicated i) significant seasonal variations of ΣPAEs in Marseille Bay suggesting variability
285 in sources, degradation processes of PAEs occurring in coastal seawaters, and/or partitioning of PAEs onto
286 particulate matter; ii) heterogeneous vertical distribution by the end of winter/spring and homogenous
287 concentration in the whole water column in the winter period with a large ΣPAEs increase of concentration
288 above the sea floor at different periods of the year.

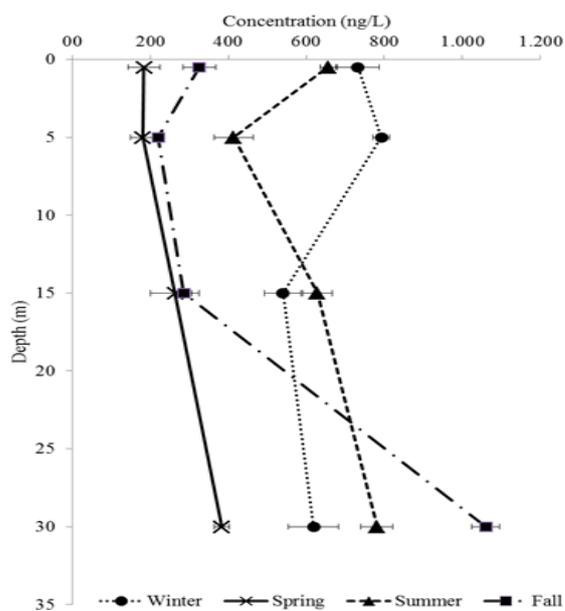
289 *Seasonal variation*

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

305 *Higher concentration near the bottom*

306 Interestingly, we found that PAE concentrations are quite elevated above the bottom being, in most
307 cases, higher than the corresponding concentration on the sea surface (Fig. 3f), with the exclusion of winter
308 2013 and September for which PAE concentrations are similar in the whole water column probably because
309 of winter mixing under the action of Mistral wind.⁵⁵ Such an accumulation of ΣPAEs near the bottom has
310 already been reported in a previous study in offshore Mediterranean seawater at 2000 m depth.⁵³ A gradient

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



315

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

317

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

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

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

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

352 Surprisingly, a significant decrease of DEHP concentration and relative abundance was observed
353 after the summer (October/November 2014) (Figs. 4-5). The change in relative abundance during fall, even
354 on the surface, was due to an increase of DiBP and to a lesser extent DnBP and could be associated with
355 potential resuspension as we observed only high PAE concentration in bottom samples. Note that the
356 variable intensity of the resuspension processes might be favored by the Northern Current entering into the
357 Gulf of Lyon and being particularly high from October to May⁷⁶ intensifying the inputs and shelf/slope

358 exchange processes including turbulent mixing and vertical flux on the continental slope.^{76,79} In these
359 circumstances exchange with the deep bottom, already observed to be rich in plastic debris, could represent a
360 seasonal source of PAEs for the Bay of Marseille at the end of the stratification season, especially in the
361 eastern canyons close to Marseille. This area was already noticed to accumulate most of the debris in the
362 Gulf of Lyon, especially plastic bags.⁷²⁻⁷³ Our data together with others studies, suggest sediment
363 resuspension as an important process explaining the heterogeneous vertical distribution. However, additional
364 specific experiments are needed to confirm such hypothesis.

365 **5. Conclusion**

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

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

380

381 **Acknowledgments**

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

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

389

390

391

References

392

- 393 (1) Serôdio, P.; Nogueira, J.M.F. Considerations on ultra-trace analysis of phthalates in drinking water.
394 *Water Res.* **2006**, 40 (13), 2572–2582.
- 395 (2) Net, S.; Delmont, A.; Sempéré, R.; Paluselli, A.; Ouddane, B. Reliable quantification of phthalates in
396 environmental matrices (air, water, sludge, sediment and soil): A review. *Sci. Total Environ.* **2015 a**,
397 515–516 , 162–180. <http://dx.doi.org/10.1016/j.scitotenv.2015.02.013>.
- 398 (3) Rahman, M.; Brazel, C.S. The plasticizer market: an assessment of traditional plasticizers and
399 research trends to meet new challenges. *Prog. Polym. Sci.* **2004**, 29, 1223-1248.
- 400 (4) He, W.; Qin, N.; Kong, X.; Liu, W.; He, Q.; Ouyang, H.; Yang, C.; Jiang, Y.; Wang, Q.; Yang, B.;
401 Xu, F. Spatio-temporal distributions and the ecological and health risks of phthalate esters (PAEs) in
402 the surface water of a large, shallow Chinese lake. *Sci. Total Environ.* **2013**, 461–462, 672–680.
- 403 (5) Kimber, I.; Dearman, R.J. An assessment of the ability of phthalates to influence immune and
404 allergic responses. *Toxicol.* **2010**, 271 (3), 73–82.
- 405 (6) Net, S.; Sempéré, R.; Delmont, A.; Paluselli, A.; Ouddane, B. Occurrence, Fate, Behavior and
406 Ecotoxicological State of Phthalates in Different Environmental Matrices. *Environ. Sci. Technol.*
407 **2015 b**, 49 (7), 4019–4035.
- 408 (7) Xie, Z.; Ebinghaus, R.; Temme, C.; Lohmann, R.; Caba, A.; Ruck, W. Occurrence and Air-Sea
409 Exchange of Phthalates in the Arctic. *Environ. Sci. Technol.* **2007**, 41, 4555-4560.
- 410 (8) Holahan, M.R.; Smith, C.A. Phthalates and neurotoxic effects on hippocampal network plasticity.
411 *NeuroToxicology* **2015**, 48, 21–34.
- 412 (9) IARC. Some industrial chemicals, di(2-ethylhexyl) phthalate. *IARC Monogr. Eval. Carcinog. Risks*
413 *Hum.* **2000**, 77, 41-148.
- 414 (10) Halden, R.U. Plastics and Health Risks. *Annu. Rev. Public Health* **2010**, 31, 179-194.
- 415 (11) Staples, C.A.; Peterson, D.R.; Parkerton, T.F.; Adams, W.J. The environmental fate of phthalate
416 esters: a literature review. *Chemosphere* **1997**, 35 (4), 667-749.
- 417 (12) Andrady, A.L. Microplastics in the marine environment. *Mar. Pollut. Bull.* **2011**, 62 (8), 1596–1605.
- 418 (13) Kolena, B.; Petrovívova, I.; Pilka, T.; Pucherova, Z.; Munk, M.; Matula, B.; Vankova, V.; Petlus, P.;
419 Jenisova, Z.; Rozova, Z.; Wimmerova, S.; Trnovec, T. Phthalate exposure and health-related
420 outcomes in specific types of work environment. *Int. J. Environ. Res. Publ. Health* **2014**, 11(6),
421 5628-5639.
- 422 (14) Okamoto, Y.; Ueda, K.; Kojima, N. Potential risks of phthalates esters: acquisition of endocrine-
423 disrupting activity during environmental and metabolic processing. *J. Health Sci.* **2011**, 57, 497-503.
- 424 (15) Howdeshell, K.I.; Rider, C.V.; Wilson, V.S.; Gray Jr, L.E. Mechanisms of action of phthalate esters,
425 individually and in combination, to induce abnormal reproductive development in male laboratory
426 rats. *Environ. Res.* **2008**, 108 (2), 168-176.
- 427 (16) Buckley, J.P.; Engel, S.M.; Mendez, M.A.; Richardson, D.B.; Daniels, J.L.; Calafat, A.M.; Wolff,
428 M.S.; Herring, A.H. Prenatal phthalate exposures and childhood fat mass in a New York City cohort.

- 429 *Environ. Health Perspect.* **2016**, 124 (4), 507-513.
- 430 (17) Wang, Y.; Zeng, Q.; Sun, Y.; You, L.; Wang, P.; Li, M.; Yang, P.; Li, J.; Huang, Z.; Wang, C.; Li,
431 S.; Dan, Y.; Li, Y. Phthalate exposure in association with serum hormone levels, sperm DNA
432 damage and spermatozoa apoptosis: A cross-sectional study in China. *Environ. Res.* **2016**, 150, 557-
433 565.
- 434 (18) United States Environmental Protection Agency, 40 CFR Part 423, Appendix A, December 2014.
435 <https://www.epa.gov/sites/production/files/2015-09/documents/priority-pollutant-list-epa.pdf>.
- 436 (19) *Commission staff working document on the implementation of the community strategy for endocrine*
437 *disruptors-A range of substances suspected of interfering with the hormone system of humans and*
438 *wildlife*; CEC (Commission of the European Communities): Brussels, **2007**.
- 439 (20) National Standard of the People's Republic of China, *Standard for drinking water quality* GB 5749-
440 2006.
- 441 (21) Bauer, M.J.; Herrmann, R.; Martin, A.; Zellmann, H. Chemodynamics, transport behavior and
442 treatment of phthalic acid esters in municipal landfill leachates. *Water Sci. Technol.* **1998**, 38 (2),
443 185-192.
- 444 (22) Turner, A.; Rawling, M.C. The behaviour of di-(2-ethylhexyl) phthalate in estuaries. *Mar. Chem.*
445 **2000**, 68 (3), 203–217.
- 446 (23) Fromme, H.; Kuchler, T.; Otto, T.; Pilz, K.; Muller, L.; Wenzel, A. Occurrence of phthalates and
447 bisphenol A and F in the environment. *Water Res.* **2002**, 36, 1429-1438.
- 448 (24) Horn, O.; Nalli, S.; Cooper, D.; Nicell, J. Plasticizer metabolites in the environment. *Water Res.*
449 **2004**, 38, 3693–3698.
- 450 (25) Brossa, L.; Marcé, R.; Borrull, F.; Pocurull, E. Occurrence of twenty-six endocrine-disrupting
451 compounds in environmental water samples from Catalogna, Spain. *Environ. Toxicol. Chem.* **2005**,
452 24, 261-267.
- 453 (26) Teil, M.; Blanchard, M.; Dagnat, C.; Larcher-Tiphagne, K.; Chevreuil, M. Occurrence of phthalates
454 diesters in river of the Paris district (France). *Hydrol. Process.* **2007**, 21, 2515-2525.
- 455 (27) Xie, Z.; Ebinghaus, R.; Temme, C.; Caba, A.; Ruck, W. Atmospheric concentrations and air–sea
456 exchanges of phthalates in the North Sea (German Bight). *Atmos. Environ.* **2005**, 39, 3209–3219.
- 457 (28) Xie, Z.; Selzer, J.; Ebinghaus, R.; Caba, A.; Ruck, W. Development and validation of a method for
458 the determination of trace alkylphenols and phthalates in the atmosphere. *Anal. Chim. Acta* **2006**,
459 565, 198–207.
- 460 (29) Zeng, F.; Cui, K.; Xie, Z.; Liu, M.; Li, Y.; Lin, Y.; Zeng, Z.; Li, F. Occurrence of phthalate
461 esters in water and sediment of urban lakes in a subtropical city, Guangzhou, South China. *Environ.*
462 *Int.* **2008**, 34, 372–380.
- 463 (30) Ferreira, I.D.; Morita, D.M. Ex-situ bioremediation of Brazilian soil contaminated with plasticizers
464 process wastes. *Braz. J. Chem. Eng.* **2012**, 29 (1), 77-86.

- 465 (31) Fu, P.; Kawamura, K.; Barrie, L.A.. Photochemical and other source of organic compounds in the
466 Canadian high Arctic aerosol pollution during winter-spring. *Environ. Sci. Technol.* **2009**, 43, 286-
467 292.
- 468 (32) Fu, P.; Kawamura, K.; Chen, J.; Charrière, B.; Sempéré, R. Organic molecular composition of
469 marine aerosols over the Arctic Ocean in summer: contributions of primary emission and secondary
470 aerosol formation. *Biogeosciences* **2013**, 10, 653–667.
- 471 (33) Ye, T.; Kang, M.; Huang, Q.; Fang, C.; Chen, Y.; Shen, H.; Dong, S. Exposure to DEHP and MEHP
472 from hatching to adulthood causes reproductive dysfunction and endocrine disruption in marine
473 medaka (*Oryzias melastigma*). *Aquat. Toxicol.* **2014**, 149, 115-126.
- 474 (34) Gao, J.; Chi, J. Biodegradation of phthalate acid esters by different marine microalgal species. *Mar.*
475 *Pollut. Bull.* **2015**, 99, 70–75.
- 476 (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
477 estrogenic disrupting activity of phthalates and their mixtures. *Int. J. Environ. Res. Publ. Health*
478 **2014**, 11 (3), 3156-3168.
- 479 (36) The Mermex Group. Marine ecosystems responses to climatic and anthropogenic forcings in the
480 Mediterranean. *Progr. Oceanogr.* **2011**, 91, 97–166.
- 481 (37) Sempéré, R.; Charrière, B.; Van Wambeke, F.; Cauwet, G. Carbon inputs of the Rhône River to the
482 Mediterranean Sea: Biogeochemical implications. *Global Biogeochem. Cycles* **2000**, 14 (2), 669-
483 681.
- 484 (38) Panagiotopoulos, C.; Sempéré, R.; Para, J.; Raimbault, P.; Rabouille, C.; Charrière, B. The
485 composition and flux of particulate and dissolved carbohydrates from the Rhone River into the
486 Mediterranean Sea. *Biogeosciences* **2012**, 9, 1827-1844.
- 487 (39) UNEP Chemicals. Regionally based assessment of persistent toxic substances. Mediterranean
488 Regional Report, *UNEP* **2002**, Geneve.
- 489 (40) Deudero, S.; Alomar, C. Mediterranean marine biodiversity under threat: Reviewing influence of
490 marine litter on species. *Mar. Pollut. Bull.* **2015**, 98 (1-2), 58-68.
- 491 (41) Collignon, A.; Hecq, J.-H.; Galgani, F.; Voisin, P.; Collard, F.; Goffart, A. Neustonic microplastic
492 and zooplankton in the North Western Mediterranean Sea. *Mar. Pollut. Bull.* **2012**, 64, 861-864.
- 493 (42) Cozar, A.; Sanz-Martin, M.; Marti, E.; Gonzalez-Gordillo, J.I.; Ubeda, B.; Galvez, J.A.; Irigoien, X.;
494 Duarte, C.M. Plastic accumulation in the Mediterranean Sea. *PLoS ONE* **2015**, 10 (4).
- 495 (43) Faure, F.; Demars, C.; Wieser, O.; Kunz, M.; De Alencastro, L.F. Plastic pollution in Swiss surface
496 waters: nature and concentrations, interaction with pollutants. *Environ. Chem.* **2015**, 12 (5), 582-591.
- 497 (44) Pedrotti, M.L.; Petit, S.; Elineau, A.; Bruzard, S.; Crebassa, J.C.; Dumontet, B.; Marti, E.; Gorsky,
498 G.; Cozar, A. Changes in the floating plastic pollution of the Mediterranean Sea in relation to the
499 distance to land. *PLoS ONE* **2016**, 11 (8).

- 500 (45) Suaria, G.; Avio, C. G.; Mineo, A.; Lattin, G. L.; Magaldi, M.G.; Belmonte, G.; Moore, C. J.;
501 Regoli, F.; Aliani, S. The Mediterranean Plastic Soup: synthetic polymers in Mediterranean surface
502 waters. *Nat. Scient. Rep.* **2016**, 6, 37551.
- 503 (46) Ruiz-Orejon, L.F.; Sarda, R.; Ramis-Pujol, J. Floating plastic debris in the Central and Western
504 Mediterranean Sea. *Mar. Environ. Res.* **2016**, 120, 136-144.
- 505 (47) Schmidt, N.; Thibault, D.; Galgani, F.; Paluselli, A.; Sempéré, R. Occurrence of microplastics and
506 potential contribution of phthalates in the surface waters of the Gulf of Lion (NW Mediterranean
507 Sea). *Progr. Oceanogr.* Submitted.
- 508 (48) Sicre, M.A.; Fernandes, M.B.; Pont, D. Poly-aromatic hydrocarbon (PAH) inputs from the Rhone
509 River to the Mediterranean Sea in relation with the hydrological cycle: Impact of floods. *Mar.*
510 *Pollut. Bull.* **2008**, 56 (11), 1935-1942.
- 511 (49) Sempéré, R.; Charrière, B.; Castro-Jimenez, J.; Kawamura, K.; Panagiotopoulos, C. Occurrence of α ,
512 ω -dicarboxylic acids and ω -oxoacids in the surface waters of the Rhone River and fluxes into the
513 Mediterranean Sea. *Progr. Oceanogr.* **2017**, in press. <https://doi.org/10.1016/j.pocean.2017.07.002>.
- 514 (50) Berrojalbiz, N.; Dachs, J.; Ojeda, M.J.; Valle, M.C.; Castro-Jimenez, J.; Wollgast, J.; Ghiani, M.;
515 Hanke, G.; Zaldivar, J.M. Biogeochemical and physical controls on concentrations of polycyclic
516 aromatic hydrocarbons in water and plankton of the Mediterranean and Black Sea. *Global*
517 *Biogeochem. Cycles* **2011**, 25 (4).
- 518 (51) Castro-Jimenez, J.; Eisenreich, S.J.; Ghiani, M.; Mariani, G.; Skejo, H.; Umlauf, G.; Wollgast, J.;
519 Zaldivar, J.M.; Berrojalbiz, N.; Reuter, H.I.; Dachs, J. Atmospheric occurrence and deposition of
520 polychlorinated dibenzo-p-dioxins and dibenofurans (PCDD/Fs) in the open Mediterranean Sea.
521 *Environ. Sci. Technol.* **2010**, 44 (14), 5456-5463.
- 522 (52) Sanchez-Avila, J.; Tauler, R.; Lacorte, S. Organic micropollutants in coastal waters from NW
523 Mediterranean Sea: Sources distribution and potential risk. *Environ. Int.* **2012**, 46, 50–62.
- 524 (53) Paluselli, A.; Aminot, Y.; Galgani, F.; Net, S.; Sempéré, R. Occurrence of phthalate acid esters
525 (PAEs) in the northwestern Mediterranean Sea and the Rhone River. *Progr. Oceanogr.* **2017**, in
526 press. DOI: 10.1016/j.pocean.2017.06.002.
- 527 (54) Sempéré, R.; Tedetti, M.; Panagiotopoulos, C.; Charrière, B.; Van Wambeke, F. Distribution and
528 bacterial availability of dissolved neutral sugars in the South East Pacific. *Biogeosciences* **2008**, 5,
529 1165–1173.
- 530 (55) Fraysse, M.; Pairaud, I.; Ross, O.N.; Faure, V.M.; Pinazo, C. Intrusion of Rhone River diluted water
531 into the Bay of Marseille: Generation processes and impacts on ecosystem functioning. *J. Geophys.*
532 *Res.* **2014**, 119 (10), 6535-6556.
- 533 (56) Gatti, J.; Petrenko, A.; Devenon, J.L.; Leredde, Y.; Ulses, C. The Rhone River dilution zone present
534 in the northeastern shelf of the Gulf of Lion in December 2003. *Cont. Shelf Res.* **2006**, 26 (15), 1794-
535 1805.

- 536 (57) Barrier, N.; Petrenko, A.A.; Ourmières, Y. Strong intrusions of the Northern Mediterranean Current
537 on the eastern Gulf of Lion: insights from in-situ observations and high resolution numerical
538 modeling. *Ocean Dyn.* **2016**, 66 (3), 313-327.
- 539 (58) Para, J.; Coble, P.G.; Charrière, B.; Tedetti, M.; Fontana, C.; Sempéré, R. Fluorescence and
540 absorption properties of chromophoric dissolved organic matter (CDOM) in coastal surface waters
541 of the northwestern Mediterranean Sea, influence of the Rhône Rive not completer. *Biogeosciences*
542 **2010**, 7, 4083-4103.
- 543 (59) Sempéré, R.; Para, J.; Tedetti, M.; Chattière, B.; Mallet, M. Variability of Solar radiation and CDOM
544 in Surface Coastal Waters of the Northwestern Mediterranean Sea. *Photochem. Photobiol.* **2015**, 91
545 (4), 851-861.
- 546 (60) Doval, M.D.; Perez, F.F.; Berdalet, E. Dissolved and particulate organic carbon and nitrogen in the
547 Northwestern Mediterranean. *Deep-Sea Res. Part I Oceanogr. Res. Pap.* **1999**, 46 (3), 511-537.
- 548 (61) Dafner, E.; Sempéré, R.; Bryden, H.L. Total organic carbon distribution and budget through the Strait
549 of Gibraltar in April 1998. *Mar. Chem.* **2001**, 73 (3-4), 233-252.
- 550 (62) Santinelli, C.; Sempéré, R.; Van-Wambeke, F.; Charriere, B.; Seritti, A. Organic carbon dynamics in
551 the Mediterranean Sea: an integrated study. *Global Biogeochem. Cycles* **2012**, 26.
- 552 (63) Sempéré, R.; Panagiotopoulos, C.; Lafont, R.; Marroni, B.; Van Wambeke, F. Total organic
553 dynamics in the Aegean Sea. *J. Mar. Syst.* **2002**, 33-34, 355-364.
- 554 (64) Sempéré, R.; Dafner, E.; Van Wambeke, F.; Lefevre, D.; Magen, C.; Allegre, S.; Bruyant, F.;
555 Bianchi, M.; Prieur, L. Distribution and cycling of total organic carbon across the Almeria-Oran
556 Front in the Mediterranean Sea: implications for carbon cycling in the western basin. *J. Geophys.*
557 *Res.* **2003**, 108.
- 558 (65) Dargnat, C.; Teil, M.J.; Chevreuil, M.; Blanchard, M. Phthalate removal throughout wastewater
559 treatment plant: Case study of Marne Aval station (France). *Sci. Total Environ.* **2009**, 407 (4), 1235–
560 1244.
- 561 (66) Ahrens, L.; Gerwinski, W.; Theobald, N.; Ebinghaus, R. Sources of polyfluoroalkyl compounds in
562 the North Sea, Baltic Sea and Norwegian Sea: evidence from their spatial distribution in surface
563 water. *Mar. Pollut. Bull.* **2010**, 60 (2), 255-260.
- 564 (67) Lammel, G.; Audy, O.; Basis, A.; Efstathiou, C.; Eleftheriasis, K.; Kohoutek, J.; Kukucka, P.;
565 Mulder, M.D.; Pribylova, P.; Prokes, R.; Rusina, T.P.; Samara, C.; Sofuoglu, A.; Sofuoglu, S.;
566 Tasdemir, Y.; Vassilatou, V.; Voutsas, D.; Vrana, B. Air and seawater pollution and air-sea gas
567 exchange of persistent toxic substances in the Aegean Sea: spatial trends of PAHs, PCBs, OCPs and
568 PBDEs. *Environ. Sci. Pollut. Res.* **2015**, 22(15), 11301-11313.
- 569 (68) Castro-Jimenez, J.; Deviller, G.; Ghiani, M.; Loos, R.; Mariani, G.; Skejo, H.; Umlauf, G.; Wollgast,
570 J.; Laugier, T.; Heas-Moisan, K.; Leaute, F.; Munsch, C.; Tixier, C.; Tronczynski, J. PCDD/F and
571 PCB multi-media ambient concentrations, congener patterns and occurrence in a Mediterranean
572 coastal lagoon (Etang de Thau, France). *Environ. Pollut.* 2008, 156 (1), 123-125.

- 573 (69) Tedetti, M.; Kawamura, K.; Charriere, B.; Chevalier, N.; Sempéré, R. Determination of low
574 molecular weight dicarboxylic and ketocarboxylic acids in seawater samples. *Anal. Chem.* **2006**, 78,
575 6012-6018.
- 576 (70) Gu, J.; Han, B.; Duan, S.; Zhao, Z.; Wang, Y. Degradation of the endocrine-disrupting dimethyl
577 phthalate carboxylic ester by *Sphingomonas yanoikuyae* DOS01 isolated from the South China Sea
578 and the biochemical pathway. *Int. Biodeterior. Biodegradation* **2009**, 63 (4), 450-455.
- 579 (71) Iwaki, H.; Nishimura, A.; Hasegawa, Y. Isolation and characterization of marine bacteria capable of
580 utilizing phthalate. *World J. Microbiol. Biotechnol.* **2012**, 28 (3), 1321-1325.
- 581 (72) Galgani, F.; Jaunet, S.; Campillo, A.; Guenegon, X.; His, E. Distribution and abundance of debris on
582 the continental shelf of the north-western Mediterranean Sea. *Mar. Pollut. Bull.* **1995**, 30 (11), 713-
583 717.
- 584 (73) Galgani F.; Souplet, A.; Cadiou, Y. Accumulation of debris on the deep sea floor off the French
585 Mediterranean coast. *Mar. Ecol. Prog. Ser.* **1996**, 142(1-3), 225-234.
- 586 (74) Galgani F.; Leaute, J.P.; Moguedet, P.; Souplet, A.; Verin, Y.; Carpentier, A.; Goraguer, H.;
587 Latrouite, D.; Andral, B.; Cadiou, Y.; Mahe, J.C.; Poulard, J.C.; Nerisson, P. Litter on the sea floor
588 along European coasts. *Mar. Pollut. Bull.* **2000**, 40 (6), 516-527.
- 589 (75) Fabri, M-C.; Pedel, L.; Beuck L.; Galgani, F.; Hebbeln D.; Freiwald A. Megafauna of vulnerable
590 marine ecosystems in French mediterranean submarine canyons: Spatial distribution and
591 anthropogenic impacts. *Deep Sea Res. Part 2 Top. Stud. Oceanogr.* **2014**, 104, 184-207.
- 592 (76) Lapouyade, A.; Durrieu de Madron, X. Seasonal variability of the advective transport of particulate
593 matter and organic carbon in the Gulf of Lion (NW Mediterranean). *Oceanol. Acta* **2001**, 24 (3),
594 295-312.
- 595 (77) Yuan, S.; Huang, I.; Chang, B. Biodegradation of dibutyl phthalate and di-(2-ethylhexyl) phthalate
596 and microbial community changes in mangrove sediment. *J Hazard Mater* **2010**, 184 (1-3), 826-831.
- 597 (78) Mackintosh, C.; Maldonado, J.; Ikonomou, M.A.; Gobas, P.C. Sorption of Phthalate Esters and
598 PCBs in a Marine Ecosystem. *Environ. Sci. Technol.* **2006**, 40,3481-3488.
- 599 (79) Monaco, A.; Durrieu de Madron, X.; Radakovitch, O.; Heussner, J.; Carbonne, J. Origin and
600 variability of downward biogeochemical fluxes on the Rhone continental margin (NW
601 Mediterranean). *Deep-Sea Res. Part I Oceanogr. Res. Pap.* **1999**, 46 (9), 1483-1511.