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Environmental occurrence of phthalate and organophosphate esters in sediments across the Gulf of Lion (NW Mediterranean Sea)

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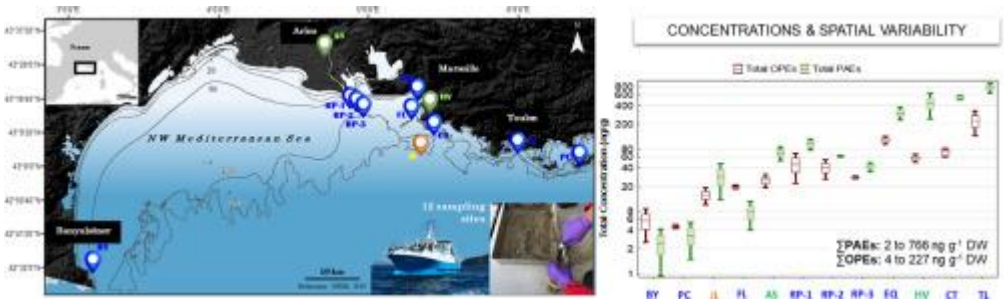
Abstract :

even phthalate (PAEs) and nine organophosphate esters (OPEs) were measured in surface sediments across the Gulf of Lion (NW Mediterranean Sea) at twelve stations characterized by different anthropogenic signatures. ∑PAEs and ∑OPEs concentrations ranged from 2 to 766 ng/g DW (av. 196 ng/g DW) and from 4 to 227 ng/g DW (av. 54 ng/g DW), respectively. Our analysis of the potential sources of these organic plastic additives in sediments of the Gulf of Lion suggests that the dominant factors affecting their occurrence and environmental distribution are port-based industrial activities and urban pressures. Indeed, the highest ∑PAEs and ∑OPEs concentrations were found close to the ports of Toulon and Marseille (Estaque) and at the sites impacted by the Marseille metropolitan area (i.e. at the outlets of the waste water treatment plant at Cortiou and at the mouth of the Huveaune River). The lowest levels were generally found in protected areas (e.g. Port-Cros) and at sites relatively far from the coast. DEHP was seen to be the most abundant PAE while TDCP, TEHP and TiBP were the most abundant OPEs in the area. Our results also expose the contribution of additives entering the Gulf of Lion via sedimentary material from the Rhône River, with positive correlations between the total organic carbon (TOC) content in the sediment and the ∑PAEs and ∑OPEs concentrations. However, additive concentrations decreased from shore to offshore in the Rhône River discharge area, indicating an efficient dilution of the contaminants accumulated at the river mouth area.

Graphical abstract



Highlights

► First study of the PAEs and OPEs occurrence in sediments of the Gulf of Lion ► DEHP and DnBP being identified as predominant PAEs ► TDCP and TiBP are predominant OPEs in the area. ► Port-based industrial activities and urban pressures are dominant sources. ► Additive concentration decreases from shore to offshore at Rhône River discharge area.

Keywords : Plastic additive, s Phthalates, Organophosphate esters, Sediment, Gulf of Lion

1. Introduction

The increasing worldwide demand in recent years for plastics and commonly used plastic additives has resulted in global awareness regarding the presence of organic pollutants such as phthalate and organophosphate esters (PAEs and OPEs, respectively) in all environments and their associated living organisms (Net al al., 2015; Wei et al., 2015). In 2016 global plastic production reached 355 million tons (PlasticsEurope, 2015), and plastic fragments can now be found in the marine environment in unprecedented amounts (Barnes et al., 2009). Since the beginning of the 20th century, PAEs have been used as plasticizers to facilitate processing and to increase the flexibility and toughness of manufactured plastic products: they are today in the class of synthetic chemicals with high production volumes and toxicological properties (Schecter et al., 2013; Wang et al., 2006). These chemicals are also added to paints, adhesives, cosmetics and personal care products (Guo & Kannan, 2012; Cao, 2010). In 2009, global PAE production stood at 6.2 million tons, of which 1.3 million tons were produced in China, mainly di- (2-ethylhexyl) phthalate (DEHP) and di-n-butyl phthalate (DnBP) (He et al., 2019). OPEs are listed among the most highly produced chemicals due to their high worldwide consumption (Yang et al., 2019) and their widespread used in numerous applications such as flame retardants, plasticizers and lubricants (Wei et al., 2015).

PAEs and OPEs are among the most abundant organic plastic additives to be released into the environment during polymer degradation/aging (Meng et al.,

2014; Net et al., 2015; Paluselli et al., 2019). The assimilation and subsequent bioaccumulation of certain PAE and OPEs by living organisms may cause serious risks due to their carcinogenic and estrogenic effects on human and animal health, with potential impacts similar to those provoked by persistent organic pollutants (POPs) (Wei et al., 2015). More specifically, PAEs may induce endocrine disruption in both wild fish and mammals, as well as in humans, and may thus affect reproduction, fertility and development (Net et al., 2015). Neurotoxic, carcinogenic, mutagenic and hormone disturbance effects linked to some OPEs have been observed in extensive studies on humans and animals (Andresen & Bester, 2004; Lai et al., 2015; Zeng et al., 2014). Several phthalates are listed as priority pollutants by diverse national and international regulatory organizations including the United States Environmental Protection Agency (EPA) (Pan & Xing, 2008; Bernaldo de Quirós et al., 2019).

Due to their physico-chemical properties, most PAEs and OPEs exhibit a strong tendency to bind with carbon-rich suspended particulate matter, and then to accumulate in sediments (van der Veen & de Boer, 2012, Net et al., 2015). Determining their concentration and distribution in sediments thus becomes crucial to better understand current environmental levels, subsequent potential implications of their transfer to benthic communities, and the possible resulting impacts on the global functioning of marine ecosystems. However, most previous studies have focused on the presence of PAEs in the aquatic or atmospheric compartments, and to a lesser extent on OPEs in seawater and sediment (see compilation of studies presented in Table S1). Few data are available for coastal

sediments, particularly in highly impacted and sensitive marine environments, such as the Mediterranean Sea. This semi-enclosed basin is subject to strong anthropogenic pressure due to relatively large atmospheric and terrestrial inputs, overpopulation and coastal industrialization (MERMEX Group, 2011). Moreover, the awareness of impacts related to the presence of organic pollutants associated to plastics in the marine environment is increasing, in great part due to the overwhelming accumulation of plastic waste in both the Mediterranean water column (Cozar et al., 2015) and on the sea floor (Kane et al., 2020).

Here, we provide the first investigation of the spatial occurrence of PAEs and OPEs in sediment samples across the Gulf of Lion in the NW Mediterranean Sea. The Gulf of Lion receives to large inputs of sedimentary material and organic carbon and water-soluble organic compounds delivered by the major river in the NW Mediterranean (i.e. the Rhône) (Sempéré et al., 2000; Sempéré et al., 2018). In addition, both atmospheric (Castro-Jiménez et al., 2017) and riverine inputs of organic contaminants (Schmidt et al., 2019; 2020; Castro-Jiménez et al., 2019) have been reported in the area. Indeed, a recent study showed that PAEs and OPEs are transported by the Rhône River surface waters (Schmidt et al., 2020).

The main objectives are; i) to determine the environmental concentrations of PAEs and OPEs in sediments affected by different anthropogenic signatures; ii) to discuss their spatial distribution in the Gulf of Lion; iii) to explore the role of the Rhône River in delivering PAEs and OPEs associated with its sedimentary inputs in the area.

2. Materials and methods

2.1. Study Area and Sampling

Surface sediment samples (n=12) were collected on board the R/V Antedon using a stainless-steel grab sampler at various stations across the Gulf of Lion (43°32′N, 06°36′E) in the NW Mediterranean Sea from January-July 2018 (Fig. 1, Table 1). Our strategy was to select sites subject to different anthropogenic pressures: “Banyuls” (BY) and “Port-Cros” (PC) are located in marine protected areas in the NW Mediterranean. The “Toulon” site (TL) is influenced by the enclosed military and domestic port areas of the city of Toulon, whereas “Estaque” (EQ) is subject to the influence of the commercial port/harbor of the city of Marseille. “Cortiou” (CT) is near the outlet of Marseille’s sewage treatment plant, and “Frioul” (FL), while located on the short passenger ferry crossing between Marseille and the Frioul archipelago, is less exposed to Rhône River or urban discharges. Additional sites are located offshore on the continental margin (“Julio” (JL)), and in the Rhône River dilution plume (RP1-3) with increasing salinities from RP1 to RP3. Two riverine sites were also investigated, the first in the Rhône River at “Arles” station (AS) and the second in the smaller “Huveaune” (HV) River, which discharges close to the Marseille beach area. Manual sampling was performed 3-4 m from the shore at these fluvial sites using a stainless-steel bucket. The content was poured onto a pre-cleaned stainless-steel tray, the first 2-5 cm of the sediment surface was

collected in a pre-cleaned glass bottle (0.5-1 kg of material) and was then stored at -20 °C. All use of plastic materials was avoided during sampling and storage.

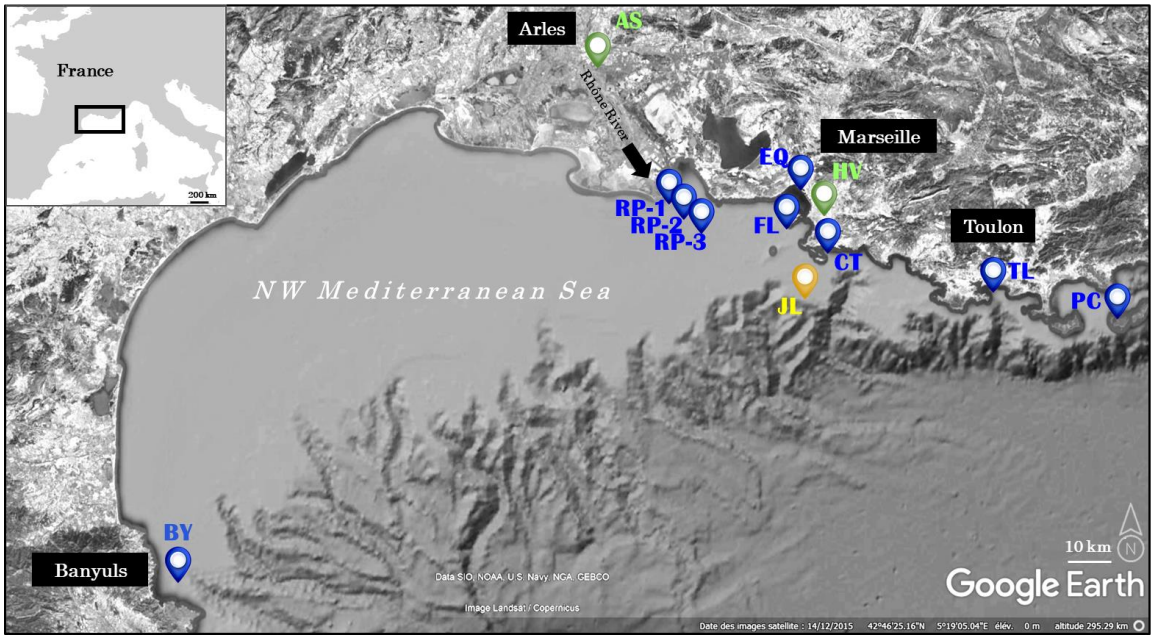


Fig 1. Research area and sampling stations. **BY**: Banyuls, **AS**: Arles (Rhône River), **RP-1**: Rhône plume-1, **RP-2**: Rhône plume-2, **RP-3**: Rhône plume-3, **HV**: Huveaune River, **JL**: Julio, **TL**: Toulon, **PC**: Port-Cros, **CT**: Cortiou, **FL**: Frioul, **EQ**: Estaque (AS and HV = riverine sites, JL = offshore site, others = coastal marine sites).

Table 1

Positions, ID codes and dates of the stations investigated in the NW Mediterranean

Station ID*	Sampling Date	Latitude (N)	Longitude (E)	Depth (m)	∑PAEs (ng/g DW)	∑OPEs (ng/g DW)

BY	02.07.18	42.48850	3.14330	27	2.4±2.5	5.7±5.3
PC	17.04.18	42.98333	6.36667	50	3.3±3.9	4.5±0.3
JL	24.01.18	43.13333	5.25000	95	29.5±23.5	14.6±4.3
FL	24.01.18	43.26667	5.30000	34	7.7±7.0	19.7±1.3
AS	21.06.18	43.68481	4.62620	1	69.0±17.4	24.9±6.0
RP-1	21.06.18	43.31667	4.85000	19	96.6±19.4	45.4±22.9
RP-2	21.06.18	43.31667	4.90000	42	61.2±1.8	40.1±13.8
RP-3	21.06.18	43.26667	4.05000	80	41.5±6.9	28.0±1.2
EQ	24.01.18	43.33333	5.30000	43	304.4±72.4	112.4±14.5
HV	06.02.18	43.26110	5.37730	1	435.4±192.9	57.1±8.6
CT	24.01.18	43.20000	5.40000	13	532.0±40.4	70.4±11.2
TL	17.04.18	43.10000	5.91667	11	766.3±136.3	227.5±154.7

* see legend Figure 1 for site identification; S=salinity

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2.2. Chemicals and Reagents

Dichloromethane (DCM), hexane, ethyl acetate (EtOAc), acetone, methanol, and toluene were purchased from Promochem (Picograde, LGC standard). Ultrapure water (MQ) was obtained from a Millipore (resistivity > 18.2 MΩ) Milli-Q system. Resprep activated copper granules (99.5%) were supplied by Restek (Bellefonte, PA, USA) and aluminum oxide 90 active neutral (alumina, 70-230 mesh ASTM) and sodium sulfate was purchased from Merck (Darmstadt,

Germany). Labelled and native PAEs were obtained from Supelco (Bellefonte, PA, USA). Labelled OPEs were purchased from C/D/N Isotopes Inc. (Pointe-Claire, Canada) (TBP-d_{27}, TPhP-d_{15}, TPrP- d_{21}) and from Cambridge Isotope Laboratories, Inc. (Tewksbury, MA, USA) (TCPP-d_{18}, TDCP-d_{15} and TCEP-d_{12}). Native OPEs were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). All details are presented in Table S2.

2.3. C, N, P determinations

Organic carbon of sediments was determined after removal of inorganic carbon by acidification with sulfuric acid (50 µl, 0.25 N) in tin sample cups. Acid additions were performed on given samples until no bubble reaction occurred, and then the samples were dried at 60°C. The organic carbon was then measured with a mass spectrometer (INTEGRA CN, Sercon) according to the method of Raimbault et al. (2008).

2.4. Pretreatment and extraction

Sediment samples were freeze-dried using a Christ Beta 2-4 LO Plus LT then sieved through a pre-cleaned stainless-steel sieve (500 µm diameter) before extraction. Sediment samples (3.000 ± 0.005 g DW were placed into pre-cleaned glass centrifuge tubes, mixed with about 0.5-1 g of active copper, then spiked (100 ng/sample) with labeled surrogate standards (TBP-d_{27}, TCPP-d_{18}, TDCP-

d_{15}, DnBP-d_4) to monitor the overall extraction efficiency of the target compounds and left to equilibrate for about 15 min. Four replicates (i.e. separated extractions) were carried out for each sampling site. For each extraction, after the addition of 5 mL DCM, the samples were vortexed (10-15s), sonicated without heating and centrifuged at 4000 rpm for 10 minutes. All the supernatants were then transferred to EtOAc and DCM pre-cleaned/conditioned glass columns containing 250 ± 2.5 mg of Oasis MAX (Waters) sandwiched between two PFTE frits and mounted in a 12-port SPE vacuum Manifold (Supelco, Sigma-Aldrich). Each extraction batch contained two blanks. The extracts were allowed to pass through the clean-up phase by gravity. A second extraction step was performed by adding 5 mL DCM/EtOAc (50/50) prior to following the procedure indicated above. The combined extracts were evaporated to ~1 mL under gentle flow using a 12-port Visidry Drying Attachment (Supelco, Sigma-Aldrich). An additional clean-up step was performed by passing the extracts through 1.5 g of 3% deactivated alumina packed in a pre-cleaned Pasteur pipette topped with 0.5 g of sodium sulfate. The micro-column was first conditioned by a few mL of hexane, then the 1mL extract was added to the column and allowed to pass through it by gravity. A final elution was performed with 10 mL of DCM and the new extract was evaporated as indicated above, then transferred to a GC vial and further evaporated to ~ 50 µL. Labelled OPE (TPrP- d_{21}, TCEP- d_{12}, TPhP-d_{15}) and PAE (DEP-d_4, DEHP-d_4) syringe standards (used for quantification of target compounds) were added (100 ng/sample) and the extracts were preserved at -20 °C until Gas Chromatography–Mass Spectrometry (GC-MS) analysis.

2.5. Instrumental analysis

Samples were analyzed by gas chromatography coupled with mass spectrometry (GC-MS) for nine OPEs and seven PAEs (Text S1), as well as the corresponding surrogate labeled standards (Table S2), in selected ion monitoring (SIM) and electron impact (EI, 70 eV) modes using a 30 m x 0.25 mm i.d. x 0.25 µm HP-5MS capillary column (Agilent J&W) (Fauvelle et al., 2018).

2.6. Quality assurance/quality control (QA/QC)

Strict measures were taken to prevent potential cross-contamination during OPE and PAE analysis. First, the use of plastic material was avoided at all times and all glassware was cleaned overnight with detergent, rinsed with tap water + MQ water and then baked at 450 °C for 6 h before use. Alumina and sodium sulfate were also baked overnight at 450 ºC before use. Sample pre-treatment (except freeze-drying) and extraction/clean-up steps were performed entirely in an International Standards Organization (ISO) 6 cleanroom (22 °C, SAS +15 Pa cleanroom pressure, 50 vol h^{-1} brewing rate) (Paluselli et al., 2018). Four replicates of sediment samples were extracted for each site except for CT (due to limited available material), and method blanks relating to all steps were made for each batch of extractions. The retention time and the response factors of GC-MS were evaluated for each analytical sequence by regularly injecting

different calibration levels. One hexane injection was performed every 4-5 samples to check and monitor potential cross contamination along the sequence.

After correction by blanks and determination of the naturally occurring amounts of target compounds in the selected sediment (spiking experiment performed on sediment FL), recoveries ranged from 66 ± 3.2% - 109 ± 4.3% and 52 ± 15% - 131 ± 17% for native PAEs and OPEs, respectively (Table S3). In addition, all samples analyzed (n=46) were spiked with labelled surrogates, showing average recoveries varying from 77 ± 22% for TBP-d_{27}, 47 ± 18% for TCPP-d_{18}, 70 ± 13 % for TDCP-d_{15} and 97 ± 10 % for DnBP-d_4 (Table S3). Mean blank values (n=7) varied from 0.001 to 8.62 ng depending on the compound (Table S4). For the three compounds undetected in the blanks (i.e. DMP, TiBP and TEHP), the corresponding instrumental limits of quantification (LOQ) were used. For most compounds the values in the blanks represented $<$17% of the values in the real samples on average. Slightly higher average contributions were observed for two OPEs (i.e TPP and TnBP) representing between the 21-24% of values on the samples. This contribution approached the 50% for only 4 compounds (i.e=DEP, DiBP, DnBP and EHDPP) which exhibited general lower concentrations in the sediments, explaining this higher % with respect to the blanks. All results presented are blank corrected by subtracting the corresponding mean blank value. The LOQ were determined based on a signal-to-noise (S/N) ratio of ≥10 at the lowest calibration level, and varied from 0.0001 to 0.01ng depending on the compound (Table S4).

2.7. Statistical analysis

Principal component analysis (PCA) was carried out to decrease the multidimensional effect of the dataset and to assess the relationships between the OPEs, PAEs and sampling sites. The PCA analyses were performed using the Statsoft/Statistica10. Statistical significance was a p-value of <0.05. LOQ values were assigned for non-detected values and/or for values which, after blank correction, reverted to non-detected.

3. Results and discussion

3.1. Total carbon, nitrogen and phosphorus in the sediments

TC ranged from 1.8-12.7 %, while TOC varied between 0.3-5.4 %. Relatively high TOC values were detected at stations under the influence of the Rhône River (Table 2 and Fig. S1)., Our results show, however, that TOC values were higher in stations with high terrestrial inputs, namely TL, HV and EQ (Fig. S1). The highest N (%) values were measured at TL station, followed by those at EQ and RP stations. Our results also indicate that the N (%) level decreased from shore to offshore at the stations in the discharge area of the Rhône River. The highest organic phosphorus values were detected at TL and JL stations, and the highest inorganic phosphorus values were found at AS and EQ stations.

Levels of inorganic phosphorus were found to be 2-6 times higher than levels of organic phosphorus at AS, RP (1-3) and EQ stations.

Table 2

TC, TOC, TON, TOP and TIP variations in Gulf of Lion sediments

Parameters	Valid n	Mean	Minimum	Maximum	Std. Dev.
% Total Carbon	12	8.4	1.8	12.7	3.2
% Total Organic Carbon	18	1.7	0.3	5.4	1.5
% Total Nitrogen	35	0.12	0.02	0.31	0.07
% Inorganic Phosphorus	10	0.03	0.01	0.06	0.02
% Organic Phosphorus	12	0.02	0.01	0.03	0.01

3.2. Environmental levels and relative abundances

∑PAEs and ∑OPEs sediment concentrations in the Gulf of Lion ranged from 2 to 766 ng/g DW (av. 196 ng/g DW) and from 4 to 227 ng/g DW (av. 54 ng/g DW), respectively (Table 1, Fig. 2, Figs. S2a-S2b; Tables S5-S6). ΣPAE and ∑OPE showed higher concentrations in areas subject to substantial anthropogenic activities such as the military port of Toulon (TL), Marseille's Huveaune River mouth (HV) and the Cortiou Wastewater Treatment Plant (WWTP) discharge area (CT), as well as the harbor at Estaque (EQ), just next to Marseille (Figs. S3-S4). Lower concentrations were found in more remote areas including the Port-Cros (PC) Marine Protected Area, Banyuls Bay (BY), Frioul

Island (FL) off Marseille and at the offshore Julio (JL) station (Figs. S3-S4). It should be noted that sediment concentrations of ∑PAE and ∑OPEs decreased from shore to offshore at all stations near the Rhône River mouth (RP stations), highlighting the inputs of additives associated with the sedimentary material transported by this river. Furthermore, this dilution gradient suggests the efficient dispersal of additives in the sediments across the Rhône's discharge area.

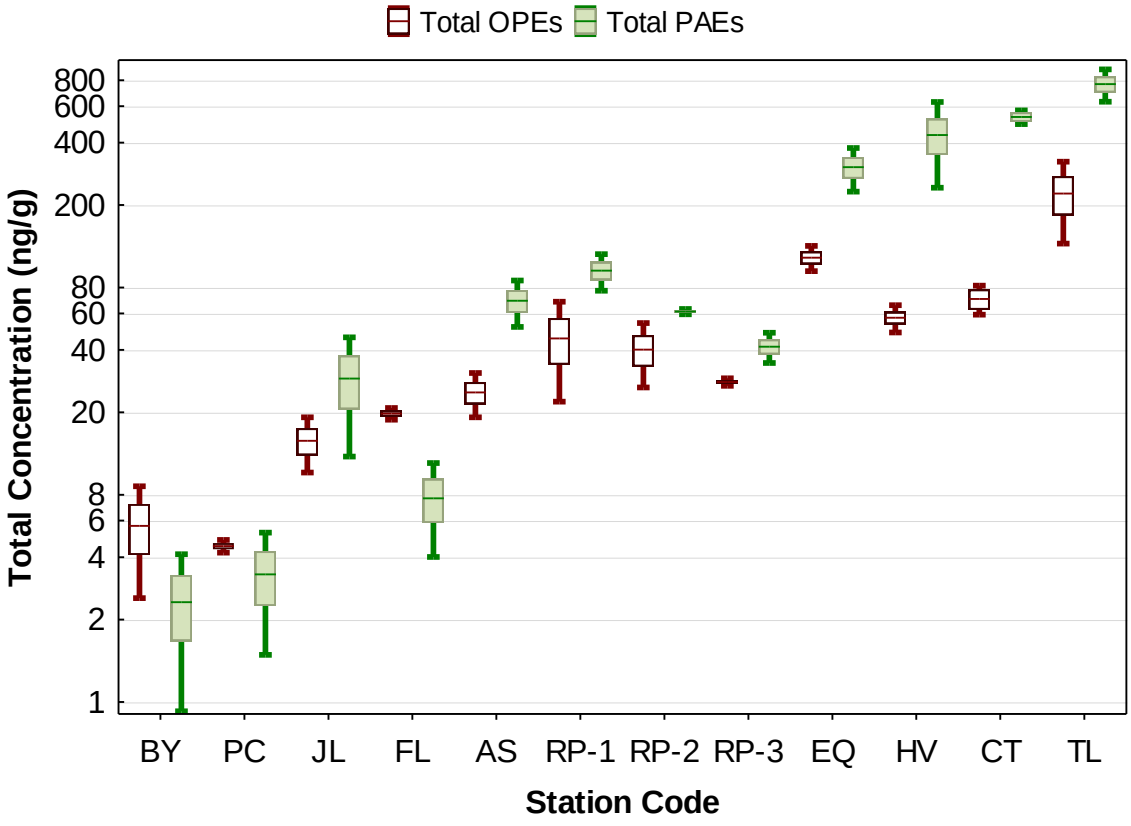

Fig. 2. ∑PAEs and ∑OPEs in sediment samples across the Gulf of Lion in the NW Mediterranean Sea (the Y axis is a logarithmic scale). **BY**: Banyuls, **AS**: Arles (Rhône River), **RP-1**: Rhône plume-1, **RP-2**: Rhône plume-2, **RP-3**: Rhône plume-3, **HV**: Huveaune River, **JL**: Julio, **TL**: Toulon, **PC**: Port-Cros, **CT**: Cortiou, **FL**: Frioul, **EQ**: Estaque (AS and HV= rivers, JL= offshore site, others= coastal marine sites).

Total PAE ($\sum_6$PAEs) concentrations (DEP, DiBP, DnBP, BBP, DCHP, and DEHP) were reported at similar levels (1.37 to 24.6 ng/g DW) in the sediments from the Bohai and Yellow Seas (Mi et al., 2019), and at slightly higher levels (17-530 ng/g DW) for the Jiulong River (Li et al. 2016). The highest concentrations (2.27 µg/g to 74.94 µg/g DW) were reported for the $\sum_{16}$PAEs concentrations of sediments from Guangzhou lakes (Zeng et al., 2008). In another study, concentrations of total PAEs of sediments from the Guanting Reservoir and the Yongding River, Beijing, China were determined at between 478 and ~2120 ng/g DW, with an average of 1137 ng/g DW (Wang et al., 2006). ∑PAE were found in the range of 654-2603 ng/g DW in Hungzhou Bay, Taizhou Bay and Wenzhou Bay sediment in East China Sea (Hu et al., 2020). ∑PAE concentrations were determined range from 462.1-15133 ng/g DW Jiaozhou Bay in China (Zhang et al., 2020). In our study, the maximum ∑PAE concentrations detected at the stations in the Gulf of Lion ranged from 2 to 766 ng/g DW. However, data comparability can be very tricky, so these comparisons must be interpreted very carefully. Factors like the differential content and type of OC in the sediment could explain part of the variability among different geographical areas. In addition, not all the studies measured the same type and number of PAEs.

We found that DEHP was generally the most abundant PAE in the study area, representing 6-98 % (av. 67) of the ∑PAEs (Fig. 3a) and being slightly less abundant at the three other sites (i.e. BY, EQ, TL) (Figs. 3a-3b and Tables S5

and S6). Indeed, the relative abundance of DnBP was greater than 50 % at TL and EQ stations, whereas at BY, DiBP represented 46 % of the sum of PAEs. The relative abundance of DMP at FL and PC stations and of DEP at BY and PC stations was significantly higher ($p<0.05$) than values at other stations (Table S5, Fig. 3a). Relative abundances of BBzP, DnOP, DiBP and DEP in the more pristine stations (BY, PC, JL, FL) were higher than values detected at other stations that are more exposed to anthropogenic pressures. The relative abundance of DEHP was found to be as high as 90% and 98% in HV and CT stations, respectively: these two stations are both close to urban centers and are affected by associated pressures (Table S7). DEHP was also largely predominant (50-70%) at the stations in the Rhône River and at those in its area of influence. The relative abundance of DnBP, another dominant PAE compound, was found to be 54 % and 65 % at EQ and TL stations, respectively (Table S5, Fig. 3a). DEHP was also shown to be the most abundant PAE in the sediments of the Bohai and Yellow Seas (with maximum DEHP concentrations of 15.9 ng/g DW and 15.6 ng/g DW, respectively, Mi et al., 2019), as well as in the sediments of Taihu Lake, China (Wang et al., 2003), of the Qiantang River, China (Sun et al., 2013), and of the Pearly River, China (Liu et al., 2014) where concentrations were 10 times higher.

Concerning OPEs, total concentrations (∑OPE) found in the Gulf of Lion stations were in line with or slightly higher than those reported in previous studies including Ontario, Lakes and Superior (Canada) and Michigan (USA), Lake Taihu, China (lake surface sediments (2.16-16.6 ng/g DW; Cao et al., 2012,

2017), the Evrotas River Basin, Greece (10.4 ng/g DW; Giulivo et al., 2017), the North Pacific Ocean and Arctic Ocean (0.878 ng/g DW; Ma et al., 2017), the Yellow Sea (0.411 ng/g DW; Zhong et al., 2018), the coasts and rivers of Taiwan (7.38 ng/g DW; Chung & Ding, 2009), and the northern part of the East Chinese Sea (12.7 ng/g DW; Liao et al., 2019). Similar or higher average OPEs concentrations were reported in sediments from Lake Shihwa (inshore; 31.1 ± 15.6 ng/g DW and offshore region; 16.6 ± 15.7 ng/g DW), from surrounding creeks (1200 ± 1337 ng/g DW) and from sediments sampled next to a submarine WWTP outfall (26.2 ± 22.4 ng/g DW) in South Korea (Lee et al., 2018).

Our results indicate that in the studied areas, TDCP, TEHP and TiBP were the most abundant OPEs (Fig. 3b). TDCP peaked at EQ (76 %), TL (68 %) and FL (45 %) stations. The relative abundance of TCPP was 29 % at HV, 20 % at AS and 19 % at TL stations. Relative abundance of TCCP decreased from shore to offshore while TDCP increased at the stations located in the Rhône River area. We found that the relative abundance of TPP was higher at CT station than at other stations, while TiBP constituted 35-40 % of total OPEs at PC, RP1-2 and CT stations. TEHP relative abundance varied from 1.6 to 40.6 % and was present at most sites, though not at TL and PC (Table S6, Fig. 3b).

When all the stations are taken into consideration, TDCP stands out as the dominant OPE. However, dominant species diversity exceeded the PAE profile. The relative abundance of TCPP decreases from shore to offshore in the Rhône River and the stations the river impacts (Fig. 3b). TCEP and TiBP were

found to be the most abundant OPEs in the North Pacific and the Arctic Ocean sediments (Ma et al., 2017), whereas TiBP was shown to be the most common OPE compound in sediment core samples on the northern Chinese coast (Liao et al., 2019).

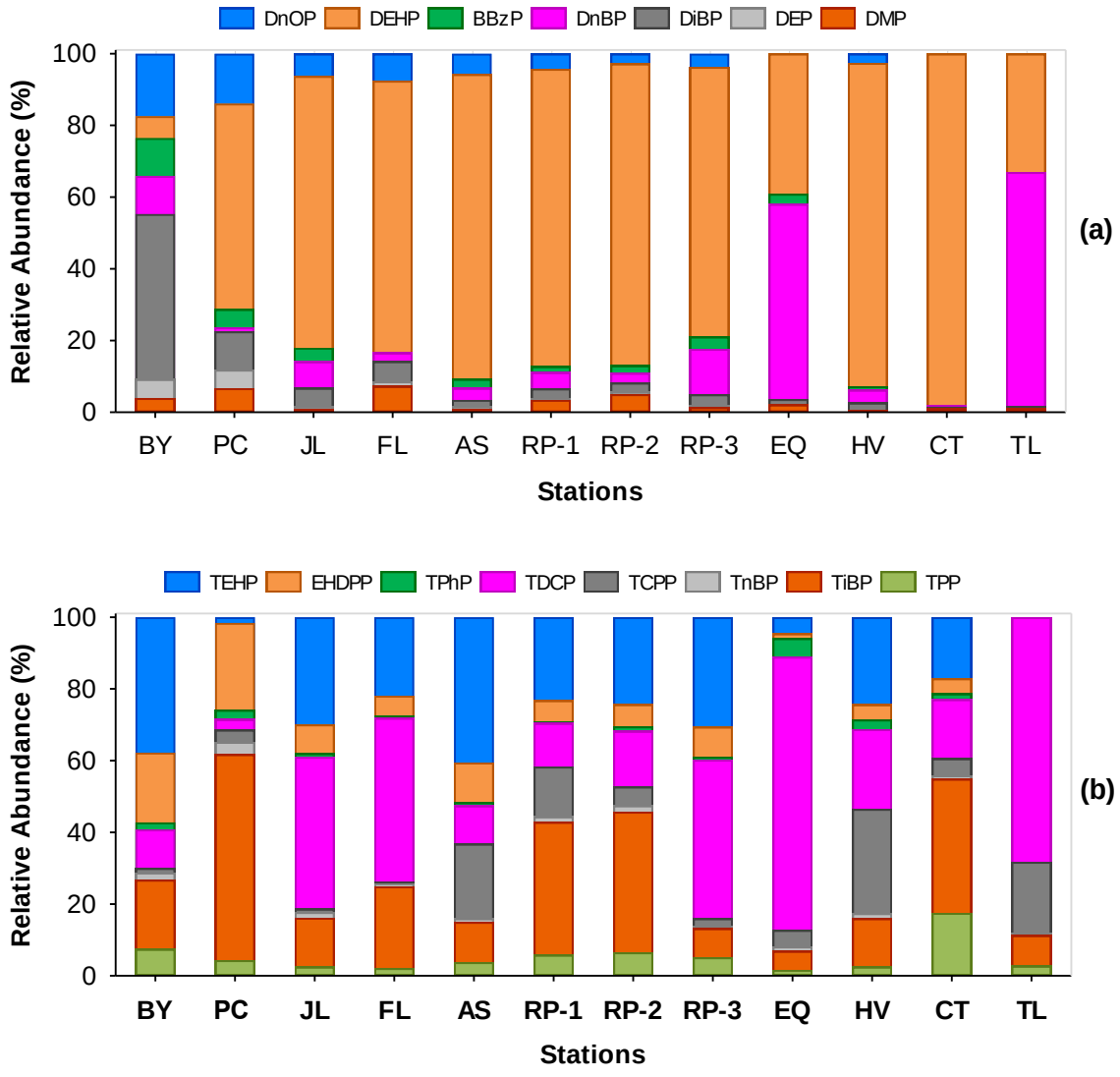

Fig. 3. Relative abundance of PAEs (a) and OPEs (b) in sediments from the different stations in the Gulf of Lion in the NW Mediterranean. **BY**: Banyuls, **AS**: Arles (Rhône River), **RP-1**: Rhône plume-1, **RP-2**: Rhône plume-2, **RP-**

3: Rhône plume-3, **HV**: Huveaune River, **JL**: Julio, **TL**: Toulon, **PC**: Port-Cros, **CT**: Cortiou, **FL**: Frioul, **EQ**: Estaque (AS and HV= rivers, JL= offshore site, others= coastal marine sites).

OPE compounds with high log K_{ow} values, such as EHDPP and TEHP, were found to be relatively high at stations with high TOC. A similar trend can be seen for high K_{ow} PAE compounds such as DEHP and DnOP. A statistically highly positive correlation ($p<0.05$) was found between TOC and the ΣPAEs ($r=0.97$), while a moderate positive correlation was seen between TOC and the Σ OPEs ($r=0.64$) concentrations. The TOC/TC ratio was roughly 45 % at HV and TL stations where we found high PAE and OPE concentrations, for example for DEHP and TDCP, which are among the most used industrial plastic additives. This ratio was between 20-30 % at BY, PC, AS, RP and EQ stations, but only 2-4 % at JL, FL and CT stations. It decreased from 27% to 17% at the RP stations from shore to offshore. Low-molecular weight PAEs (DiBP and DnBP) and OPEs (TCPP, TDCP) were positively correlated ($p<0.05$) with TOC and TON. Other high molecular weight phthalates (BBzP, DnOP and DEP) and an OPE compound, TnBP, were found to be highly correlated with inorganic phosphorus.

In this study we determine a wide range of pollutant ratios for the marine environment in accordance with many factors such as sediment origin (river/sea), distance from the shore, and anthropogenic pressure. The TCPP/TDCP ratio was higher in river sediments than in marine sediments. The value of DnOP/DiBP in

the Rhône River decreased threefold from shore to offshore. Our results show that the TiBP/TnBP ratio was about 10 and that the TEHP/EHDPP ratio was about 3-4 in sediment samples from most of the stations. The DEHP/DnBP ratio was greater than 20 at the stations close to the river mouth and exceeded 100 at CT station. The DEHP/DiBP ratio was greater than 20 at most of the stations and exceeded 400 at CT station. The DnBP/DEHP ratio was approximately twice as high at EQ and TL stations where industrial activities are widespread.

3.3. Potential sources in the study area

Factor analysis was carried out using PAE and OPE concentrations in all sediment samples. Results of factor loadings with varimax rotation, eigenvalues, and communalities are presented in Tables S8 and S9. Five factors were found with eigenvalues above 1, which correspond to 85 % of the total variance. Since the contribution of factor 1 and 2 only was about 55 %, our discussion hereafter mostly focuses on these two factors (Fig. 4).

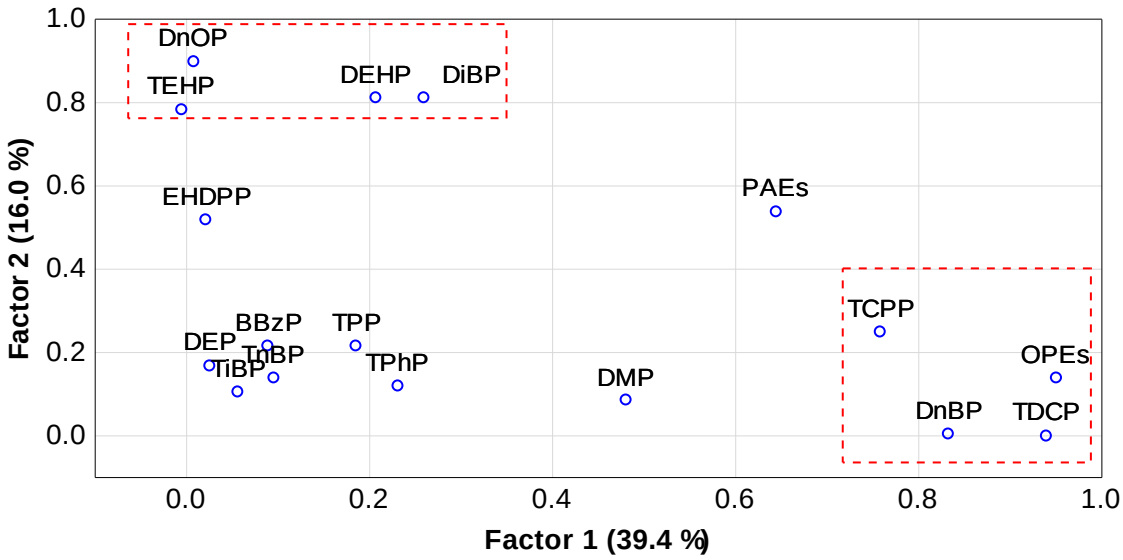

Fig. 4. Factor analysis score plots for OPEs and PAEs in Gulf of Lion sediments

The first factor, which can be defined as port-based industrial pollution, accounts for 39 % of the total variance and focuses heavily on ∑OPEs, TDCP, DnBP and TCPP mainly at TL station (a closed harbor/military port) and EQ station (Estaque), near Marseille's commercial port/harbor. Generally speaking, ports and harbors exert an important environmental impact due to naval construction, maintenance and repair. In addition to these activities, numerous important environmental pollution problems occur during routine operations. These include the leaching of chemicals from antifouling paints, accidental spills of hydraulic fluid or lubricant oil from operational devices, and the discharge of hazardous waste (Čulin & Bielić, 2015; Tornero & Hanke, 2016). Toulon Bay, which makes a maximum contribution to Factor 1, is a semi-enclosed bay accommodating several sources of anthropogenic pollution, notably a) harbor, urban, industrial, agricultural, and tourism activities (Pougnet et al., 2014; Tessier

et al., 2011; Duc et al., 2015) and b) the two urbanized river (Eygoutier R, Las R) outlets (Dang et al., 2018). The second major contribution to Factor 1 is Estaque (EQ) station, located next to the port of Marseille which is France's busiest oil port and most important commercial center. Indicator parameters of Factor 1 are TDCP and TCPP (OPEs with low K_{ow}), and DnBP: all are used as flame retardants and plasticizers in industry (Andresen & Bester, 2004). Plasticizers are also used in antifouling paints at a rate of 2% due to their flexibility and durability in a wide variety of industrial and consumer products, including paints (Faÿ et al., 2019). In addition, they are also used as anti-foaming stabilizers and as additives to floor polishes, lubricants, lacquers and hydraulic fluids (Marklund et al., 2005).

The second factor represents 16 % of the total variance and concerns DnOP, DEHP, DiBP, and TEHP, contaminants with a high log K_{ow} value (≥7.6) and HMW (except DiBP: log K_{ow}=4.1), primarily at HV and CT stations. The Huveaune River is one of the most polluted rivers in the Mediterranean Basin (Kanzari et al., 2014) with several sources of pollution including a very high degree of urbanization as well as the presence of both heavy industry and intense agricultural activity. Marseille's Cortiou WWTP is the largest in the region (Kanzari et al., 2014). Some pollutants in Mediterranean sediments are thought to have discharged via the Huveaune River after passing untreated through the Cortiou sewage outlet discharge during episodes of high rainfall (Kanzari et al., 2014). In our study, the highest organic carbon values in sediments were found at Huveaune (HV) station. The high log K_{ow} of DnOP, DEHP, and TEHP compounds underlines their tendency to be adsorbed on particulate matter. F2

can be explained by the interaction of PAE and OPE compounds of similar environmental sources and behavior: both are urban-based anthropogenic in origin (such as car wash detergents/ cleaning materials/ sewage) and are linked to the high particulate matter transported by the rivers.

Factor 3 represents 12 % of the total variance and relates to BBzP, which exhibits the highest concentrations at Estaque (EQ) and Huveaune (HV) stations. Over 90% of BBzP is used for the plasticizing of PVC or other polymers with consumer and industrial applications, such as floorings, sealants, adhesives, caulking, coatings and paints (Koch et al., 2007). Factor 3 can be therefore linked to industrial applications of this additive, which finds its way into urban effluent. The other factors accounted for ≤10 % of the total variance and were not considered as driving factors of the occurrence of PAE and OPEs in the area.

4. Conclusions

This work represents the first study of the environmental occurrence and spatial patterns of PAEs and OPEs in sediments across the Gulf of Lion in the NW Mediterranean Sea. High levels of some PAE and OPE compounds have been detected, with DEHP and DnBP being identified as predominant PAEs and TDCP and TiBP as predominant OPEs within the study area. Our analysis of potential sources of these families of organic plastic additives points to port-based industrial activities and urban pressures as the dominant factors affecting their occurrence and environmental distribution in sediments of the Golf of Lion.

The TCPP/TDCP ratio appears as a good indicator for riverine inputs of OPEs associated to sedimentary material, exhibiting higher values in riverine rather than in marine sediments. In addition, DEHP/DnBP and DEHP/DiBP ratios may provide useful information on WWTP inputs of PAEs. Our study shows that the Rhône River inputs of these two families of organic plastic additives are not only associated to their transport via surface waters as recently reported, but also to riverine sediments, providing important data for a more accurate estimation of their global inputs by the Rhône River, which is the main freshwater source in the NW Mediterranean Sea. However, concentrations of these additives decrease from shore to offshore at the Rhône River stations indicating an efficient dilution of the contaminants accumulated at the river mouth area

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