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Phthalates and organophosphate esters in surface water, sediments and zooplankton of the NW Mediterranean Sea: exploring links with microplastic abundance and accumulation in the marine food web

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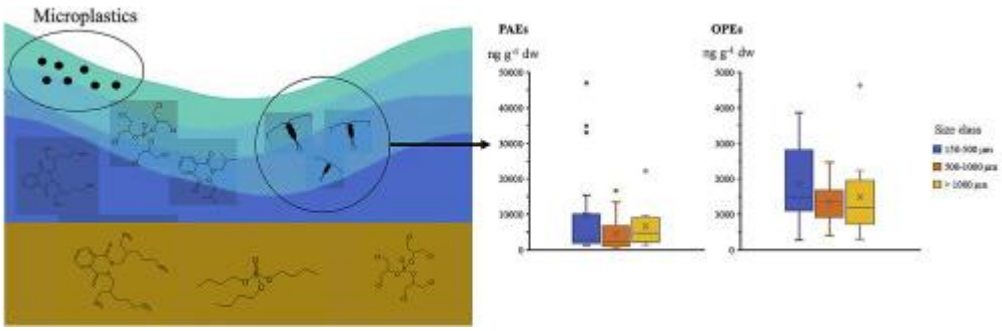
Abstract :

In this study, surface seawater, sediment and zooplankton samples were collected from three different sampling stations in Marseille Bay (NW Mediterranean Sea) and were analyzed for both microplastics and organic plastic additives including seven phthalates (PAEs) and nine organophosphate esters (OPEs). PAE concentrations ranged from 100 to 527 ng L-1 (mean 191±123 ng L-1) in seawater, 12 to 610 ng g-1 dw (mean 194±193 ng g-1 dw) in sediment and 0.9 to 47 µg g-1 dw (mean 7.2±10 µg g-1 dw) in zooplankton, whereas OPE concentrations varied between 9-1013 ng L-1 (mean 243±327 ng L-1) in seawater, 13-49 ng g-1 dw (mean 25±11 ng g-1 dw) in sediment and 0.4-4.6 µg g-1 dw (mean 1.6±1.0 µg g-1 dw) in zooplankton. Microplastic counts in seawater ranged from 0 to 0.3 items m-3 (mean 0.05±0.05 items m-3). We observed high fluctuations in contaminant concentrations in zooplankton between different sampling events. However, the smallest zooplankton size class generally exhibited the highest PAE and OPE concentrations. Field-derived bioconcentration factors (BCFs) showed that certain compounds are prone to bioaccumulate in zooplankton, including some of the most widely used chlorinated OPEs, but with different intensity depending on the zooplankton size-class. The concentration of plastic additives in surface waters and the abundance of microplastic particles were not correlated, implying that they are not necessarily good indicators for each other in this compartment. This is the first comprehensive study on the occurrence and temporal variability of PAEs and OPEs in the coastal Mediterranean based on the parallel collection of water, sediment and differently sized zooplankton samples.

Graphical abstract



Highlights

► High $\sum_7$PAE concentrations detected in zooplankton (up to 47 µg g^{-1} dw). ► Zooplankton sized 150–500 µm most concerned by chemical contamination. ► Several PAEs & OPEs (e.g. EHDPP) have field-derived bioconcentration factors >5000. ► No correlation between OPE & PAE concentrations and MP abundance in seawater.

Keywords : Microplastics, plasticizers flame, retardant, s bioaccumulation, Mediterranean Sea

Introduction

The chemical pollution of watercourses and the oceans is one of the main man-made threats to aquatic biodiversity (Young et al., 2016). The number of pollutants present in the aquatic environment is constantly increasing, with compounds of emerging concern adding up to legacy toxic organic chemicals such as polychlorinated biphenyls (PCBs) or polycyclic aromatic hydrocarbons (PAHs). Two chemical families of plastic additives and/or flame retardants considered to be of emerging concern are phthalate esters (PAEs) and organophosphate esters (OPEs). PAEs are widely used in the manufacturing of PVC and other plastics, but also as solvents in cosmetics and paints, among others (Net et al., 2015), while OPEs are commonly incorporated in polyurethane foams and electronic devices (Marklund, 2005; van der Veen and de Boer, 2012; Yang et al., 2019). These additives are not covalently bound to the polymeric matrix and are thus prone to leach from the materials, especially if exposed to UV radiation, heat (Paluselli et al., 2019) or prokaryotes, although direct additive inputs from manufacturing processes or wastewater treatment plants (WWTP) might be the predominant means of entry into the environment (Sánchez-Avila et al., 2012). In the last decades, the presence of PAEs and OPEs in the environment has been reported in numerous studies (Castro-Jiménez et al., 2016, 2014; Ma et al., 2017; Pantelaki and Voutsa, 2019; Peijnenburg and Struijs, 2006; Reemtsma et al., 2008; Sánchez-Avila et al., 2012; Sousa et al., 2018; Wang et al., 2015; Wolschke et al., 2015). In surface waters of the Bay of Marseille in the NW Mediterranean Sea, PAEs have previously been reported at concentrations of 130-1330 ng L^{-1} ($\sum_6$ PAEs) (Paluselli et al., 2018b). Few studies report on OPEs and PAEs in zooplankton, in spite of their pivotal role in the aquatic food web and increasing evidence that exposure to these chemicals can severely harm zooplanktonic organisms, especially larvae. Negative effects of diethylhexyl phthalate (DEHP), one of the most common PAEs, on copepods, reach hereby from lower egg production rates in females to increased nauplii mortality (Heindler et al., 2017). Developmental toxicity on zebrafish embryo exposed to several PAEs, with effects including cardia edema and death, as well as estrogenic activity of butyl benzyl phthalate (BBzP), i.e. endocrine disrupting activity was reported (Chen et al., 2014). An OPE exposure study using the model organism *Daphnia magna* showed that OPE toxicity was correlated with log K_{OW} values, and furthermore, that the joint toxicity of multiple OPEs was additive (Cristale et al., 2013). Neurotoxic effects of OPEs on aquatic organisms include the increased occurrence of malformations as well as reduced heart rates (Sun et al., 2016).

Wang et al. (2019) measured OPEs in zooplankton from Taihu Lake, China, and concluded that relative abundances of individual OPEs between water and zooplankton samples were significantly different. Various studies have reported on the occurrence of OPEs and PAEs in sediments, such as Ma et al. (2017) who found that in the North Pacific and the Arctic Ocean, halogenated OPEs were more abundant than non-halogenated OPEs. A recent study in Marseille Bay reported that PAE concentrations in sediments were 3-33 times higher than OPE concentrations with up to 328 ng g^{-1} dw ($\sum_7$ PAEs) (Castro-Jiménez and Ratola, 2020).

Another threat to the environment is microplastics (MPs) (i.e., plastics ≤ 5 mm), particularly in the marine environment, which receives substantial microplastic loads from rivers (Horton et al., 2017; Lebreton et al., 2017; van Wijnen et al., 2019), coastal cities (Liubartseva et al., 2018; Schmidt et al., 2018), and through maritime traffic and fishing activities (Liubartseva et al., 2018). MPs have recently received considerable attention from the media and scientific community due to their omnipresence and their potential deleterious effects, such as ingestion by a wide variety of aquatic species (Cole et al., 2013; Duncan et al., 2019; Silva-Cavalcanti et al., 2017; Zhu et al., 2019). Hotspots and accumulation zones have been identified, including the East Asian Seas with concentrations of up to 491 items m^{-3} (Isobe et al., 2015), and the Mediterranean Sea (Suaria et al., 2016). In Marseille Bay, highly variable microplastic concentrations have already been reported (0.01 items m^{-2}, Collignon et al., 2012; $6 \cdot 10^3$ to $1 \cdot 10^6$ items km^{-2}, Schmidt et al., 2018).

The objectives of this study are i) to investigate PAE and OPE occurrence as well as spatial and temporal variability in water, sediment and zooplankton samples in the Bay of Marseille during one year, ii) to examine their potential to bioconcentrate at the base of the Mediterranean food web and iii) to provide data on microplastic abundance and size in order to iv) examine the relationship between organic plastic additive concentrations and microplastic abundances in surface waters.

Material & Methods

Study area

The Bay of Marseille is located at the eastern edge of the Gulf of Lion (NW Mediterranean Sea) and is influenced by strong wind regimes (mainly the northwestern

Mistral wind), high solar radiation (Sempéré et al., 2015) and episodic intrusions from the Rhône River (Fraysse et al., 2014), which provide important inputs of particle and dissolved organic matter (Para et al., 2010) as well as organic contaminants (Schmidt et al., 2019). The sampling stations chosen for this study are influenced by harbor activity (L'Estaque station), tourism and fish-farming (Frioul station) and the outlet of Marseille's municipal wastewater treatment plant (WWTP; Cortiou station) (Fig. 1). Due to its geographical position, L'Estaque station is particularly prone to be influenced by freshwater intrusions from the Rhône River (Schmidt et al., 2019). On the other hand, episodic intrusions of the Mediterranean Northern Current can enter the Bay of Marseille and, when coupled with a south-eastern wind regime, these intrusions can lead to a transport of particles from the WWTP to the inner bays (including Frioul island and L'Estaque station) (Millet et al., 2018). Marseille is one of the largest cities in the NW Mediterranean with a WWTP treating the effluents of 1.7 million inhabitant equivalents (Oursel et al., 2013). Marine resources play an important role in both the local economy and in traditional values (Ourgaud, 2015).

FIGURE 1: (A) Map of the Mediterranean Sea indicating the position of the sampling area, (B) zoom showing the Gulf of Lions with schematic representations of the Mediterranean Northern Current and the Rhône River plume, both of which can influence the Bay of Marseille via episodic intrusions. (C) Map of the Bay of Marseille showing the three sampling stations L'Estaque, Frioul Island and Cortiou.

Sampling and sample processing

One-liter seawater samples were gathered in duplicate using a stainless-steel collector on six occasions between May 2017 and March 2018 from the R/V Antedon II, were poured into pre-combusted (450 °C, 6 h) 1 L glass bottles and were filtered (GF/F, 0.7 µm retention size) within three hours of collection. The samples were either stored in the dark at 4 °C and extracted within 24 h, or were otherwise stored in the dark at -20 °C until extraction. Sediments were collected using a Van Veen grab sampler. The upper 5 cm of the samples were immediately removed and transferred into pre-combusted glass bottles. Once in the MIO laboratory, the sediments were stored in the freezer (in the dark; -20 °C) and afterwards lyophilized. Finally, they were sieved to a size class ≤ 500 µm using a pre-cleaned stainless steel sieve.

Zooplankton and microplastic samples were collected using a manta net (opening area 40 x 70 cm, mesh size 150 µm), which was towed horizontally at a speed of 2-3 knots for 20 minutes. A floater on each side of the net resulted in only half of the net height being submerged in the water, leaving an opening area of 20 x 70 cm that was used for the calculation of microplastic concentrations. The samples were poured into glass bottles and kept in cool and dark conditions until reaching the laboratory. They were left for 24 h to enable the zooplankton to defecate so as to avoid a falsification of, or interference with, the chemical analysis. Next, using metal sieves, three zooplankton and MP size classes were separated to obtain the following size ranges: 150-500 µm, 500-1000 µm and >1000 µm. The advantage of analyzing different zooplankton size classes as opposed to pooled samples is that size-specific differences in contaminant uptake (due to different surface area/volume ratios, feeding behaviors or developmental stages) can be investigated (Hargrave et al., 2000). The samples were thoroughly rinsed using ultrapure water. Next, MPs were sorted out within each size class using a dissecting microscope and tweezers. Fibers were excluded due to the high risk of contamination. No polymer characterizations were performed to verify the nature of the items, meaning that despite all efforts to maximize result reliability, it cannot be excluded that some non-plastic items were considered as microplastics. MPs were counted and their size was measured using a ZooScan (HYDROPTIC SARL). To do so, each item was placed on the screen of the ZooScan without water. Surface area measurements in pixels were obtained with the ImageJ software and then converted into mm^2. Other debris items (e.g., plant debris) were also removed from the samples. The plankton samples were then frozen (-20 °C), lyophilized and ground using an agate mortar and pestle. Details on sampling dates, GPS positions, temperature (surface and bottom), salinity (surface and bottom) and sediment collection depth are given in Table S1 (Supplementary Material).

Contaminant extraction

Seawater samples

Dissolved contaminants were solid phase extracted (SPE) according to Fauvelle et al. (2018). The filtered samples were thus spiked with labeled surrogate standards (100 ng $sample^{-1}$ of D_{27}-TBP, D_{18}-TCPP, D_{15}-TDCP and D_4-DnBP), thoroughly shaken, passed through pre-cleaned and conditioned glass cartridges containing 250 mg Oasis HLB sorbent using inert polytetrafluoroethylene (PTFE) liners, washed with ultrapure water, vacuum-dried

and the compounds eluted using 5 mL hexane and 5 mL hexane/dichloromethane (50/50, v/v), before being collected in pre-combusted glass tubes and reduced to approximately 50 µL using pure N_2.

Sediment and zooplankton samples

Freeze-dried sediments (3 g) and zooplankton (100 mg) were put into glass tubes, spiked with surrogate standards as indicated above, vortexed and left to equilibrate for about 30 min. Activated copper was added to sediment samples before extraction and to zooplankton samples directly into the final extract. Next, 5 mL of hexane was added and an ultrasound (Elmasonic X-tra TT 120 H, extraction power 800 W) extraction was performed during 15 min without heating. The extract was then cleaned in glass cartridges containing 250 mg of Oasis MAX sorbent. The cartridges had previously been washed three times using a sequence of solvents (~5 mL each of acetone, ethyl acetate and dichloromethane). The processed extracts were collected in glass tubes. The extraction and subsequent procedure were repeated once more with 5 mL of hexane and twice more with 5 mL hexane/dichloromethane (50/50, v/v), for a total of four extraction steps. The extracts were concentrated using N_2 to obtain a final volume of approximately 100 µL. All glassware used was pre-combusted (450°C, 6 h).

GC/MS analysis

Water, sediment and zooplankton samples were spiked with internal standards (100 ng sample^{-1} of D_4-DEP, D_4-DEHP, D_{21}-TPrP, D_{12}-TCEP and D_{15}-TPhP) and injected into GC/MS in Selected Ion Monitoring (SIM) mode. GC/MS conditions were the same for all matrixes and can be found in the Supplementary Material (Text S1). Seven PAEs (dimethyl phthalate -DMP-, diethyl phthalate -DEP-, di-n-butyl phthalate -DnBP-, diisobutyl phthalate -DiBP-, benzylbutyl phthalate -BzBP-, diethylhexyl phthalate -DEHP- and di-n-octyl phthalate -DnOP-) and nine OPEs (tripropyl phosphate -TPP-, tri-iso-buthyl phosphate -TiBP-, tri-n-butyl phosphate -TnBP-, tris-(2-chloroethyl) phosphate -TCEP-, tris-(2-chloro, 1-methylethyl) phosphate -TCPP-, tris-(2-chloro-, 1-chloromethylethyl) phosphate -TDCP-, triphenyl phosphate -TPhP-, 2- ethylhexyl-diphenyl phosphate -EHDPP- and tris(2-ethylhexyl) phosphate -TEHP-) were quantified.

Quality Assurance / Quality Control

Ultrasound extraction recovery experiments were performed by spiking 3 g of freeze-dried sediment and 100 mg zooplankton with a PAE and OPE analytical standard mixture (50 ng sample^{-1}). Seawater was spiked with 150 ng L^{-1} of the analytical standard mixture (Fauvelle et al., 2018). Recoveries were then calculated by subtracting the measured concentrations in the spiked samples from those in the non-spiked samples (see Table S2 for recovery rates). Furthermore, surrogates were added to each sample prior to extraction and their recovery rates were monitored for each individual extraction. Mean surrogate recoveries in water, sediment and zooplankton samples, respectively, were as follows: 94% (±11% SD), 90% (±4.6% SD) and 90% (±18% SD) (D_4-DnBP), 87% (±9.8% SD), 86% (±7.6% SD) and 96% (±7.8% SD) (D_{27}-TBP), 80% (±12% SD), 40% (±7% SD) and 53% (±9.4% SD) (D_{18}-TCPP) and 88% (±8.5% SD), 73% (±16% SD) and 68% (±4.2% SD) (D_{15}-TDCP). Results presented in this work were not recovery corrected. Extraction blanks were made for all sample batches to monitor possible contamination (see Table S3 for all blank values). The results presented here are blank-corrected by subtracting the blank value corresponding to the extraction batch. Certain zooplankton samples (especially in the size class >1000 µm) did not contain sufficient biomass to perform an extraction, and in other samples (particularly those from Frioul station), matrix interferences inhibited the quantification of TCPP and TDCP. Instrumental limits of quantification (LOQ) ranged from 1 pg to 10 pg (Fauvelle et al., 2018).

Results & Discussion

Surface waters

Total PAE and OPE concentrations varied in water samples between 100-527 ng L^{-1} and 9-1013 ng L^{-1}, respectively (Fig. 2 A-C). TPP was never detected whereas TEHP was detected in 28% of samples, followed by DnOP (39%), TDCP (56%), BzBP (67%), DEP (72%), TnBP and TCEP (89%) and TPhP (94%). DMP, DnBP, DiBP, DEHP, TiBP, TCPP and EHDPP were found in 100% of water samples. Of all PAEs, DEHP was predominant with 62-454 ng L^{-1} (50-90% relative abundance), while TCPP was the dominant OPE with 6-876 ng L^{-1} (28-91% relative abundance). At L'Estaque station, highest OPE concentrations were observed in September 2017 (S3), when a high TPhP peak (24 ng L^{-1}) was detected. By

contrast, we found the highest PAE concentration in the November 2017 (S4) sample at L'Estaque station. Another interesting observation is the high amount of TCEP detected in March 2018 (S6) at L'Estaque (19 ng L^{-1}) and Frioul (26 ng L^{-1}) stations (Fig. 2 A-B). Total PAE and OPE concentrations in water samples from all stations were not correlated (R^2 = 0.14; p-value > 0.01; Figure S1), pointing to different sources and/or environmental occurrence in the study area. Positive linear correlations between dissolved organic carbon (DOC) and TiBP (p-value < 0.001), TDCP (p-value < 0.001), TCPP (p-value < 0.01) and TnBP (p-value < 0.01) concentrations were observed (Figure S2).

A previous study related to OPE occurrence in Mediterranean dissolved seawater samples (~60 km north-east of Barcelona, Spain) indicated a total concentration of 10.5±1.0 ng L^{-1} (Σ_5 OPEs), with TiBP being predominant (3.7±1.3 ng L^{-1}) with an averaged concentration comparable to that measured in our study area (8.3±10 ng L^{-1}) (Vila-Costa et al., 2019). The higher standard deviation in our case can be explained by the well differentiated characteristics of the sampling stations, with Cortiou exhibiting ≥ 4-times the concentrations detected at Frioul and L'Estaque stations. For comparison, <DL-4.4 ng L^{-1} of Σ_{11} OPEs were recently detected in Canadian Arctic surface waters (McDonough et al., 2018) and 7.3-100 ng L^{-1} of Σ_7 OPEs in the Bohai, Yellow and East China Seas (Zhong et al., 2020). Concerning PAEs, we found that the Σ_7 PAE concentration at Cortiou station (264 ng L^{-1}) was close to the one reported by Paluselli et al. (2018a) in 2014 for the same sampling station (213 ng L^{-1}).

FIGURE 2: PAE and OPE concentrations measured in filtered water samples during six sampling events (S1-S6) at L'Estaque (A), Frioul (B) and Cortiou (C) stations in the Bay of Marseille.

Sediments

In sediment samples, PAE (12-610 ng g^{-1} dw) concentrations were generally higher than OPEs (13-49 ng g^{-1} dw) (Fig. 3 A-C). DMP, DEP, DnBP, DiBP, DEHP, TnBP and TCEP had a detection frequency of 100%. TPP and TDCP were not detected in any samples, DnOP was found in 11% of samples, followed by BzBP (28%), TiBP (67%), TPhP (72%), EHDPP (78%), TEHP (89%) and TCPP (94%). TnBP was usually the most abundant OPE,

with concentrations ranging from 2.2 to 32 ng g^{-1} dw, followed by TCPP (1.0-20 ng g^{-1} dw) and TEHP (0.3-9.5 ng g^{-1} dw). These concentrations are slightly higher than those reported for sediment samples from the Bohai and Yellow Seas (China), where TCPP was detected at 0.029-1.5 ng g^{-1} dw and TEHP at 8-3,445 pg g^{-1} dw (Zhong et al., 2018). Therein, the authors noted that halogenated OPEs were more abundant than non-halogenated OPEs, which was not the case in our study. Another study in the Bohai Sea found TnBP to be predominant in surface (0-20 cm) sediments, with a relative abundance of 34-60% (Wang et al., 2017). Those authors pointed out that TnBP is commonly used in hydraulic fluids and lubricating oils (see also van der Veen & de Boer, 2012), which may also explain the important abundance of TnBP in our sediment samples, given that the Bay of Marseille is influenced by marine traffic of all kinds. Sediments from the North Pacific and Arctic Oceans yielded lower OPE loads (<1-460 pg g^{-1} dw TCPP and 19-209 pg g^{-1} dw TnBP; Ma et al., 2017) and TCEP and TiBP were the dominant compounds in these samples.

When comparing sampling stations, highest mean PAE and OPE concentrations (404 and 33 ng g^{-1} dw, respectively) were found at Cortiou station, followed by L'Estaque (140 and 24 ng g^{-1} dw) and finally, Frioul station (37 and 20 ng g^{-1} dw). While a weak positive correlation of total PAE and OPE concentrations in sediment samples was observed (R^2 = 0.32; Figure S1), this correlation was not statistically significant (p-value > 0.01), suggesting a similar situation as in surface waters for both families of plastic additives when considered a group.

FIGURE 3: PAE and OPE concentrations measured in sediment samples during six sampling events (S1-S6) at L'Estaque (A), Frioul (B) and Cortiou (C) stations in the Bay of Marseille.

Zooplankton samples

Concentrations at stations and per size class

As was seen in sediment samples, PAE concentrations (mean 7,230 ± 10,100 ng g^{-1} dw) in zooplankton samples were generally higher than OPE concentrations (mean 1,590 ± 990 ng g^{-1} dw) (Table S4 & S5). DEHP was found to be the most abundant PAE in all zooplankton samples, with a maximum concentration of ~43,000 ng g^{-1} dw at Cortiou station

near the WWTP outlet. TDCP was the predominant OPE, with concentrations of up to 2,610 ng g^{-1} dw. This means that while DEHP (log K_{ow} of 7.6) was the dominant PAE in all matrixes, for OPEs the relative composition of individual compounds changed depending on the environmental compartment, with a dominance of TCPP (log K_{ow} of 2.6) in seawater, TnBP (log K_{ow} of 4.0) in sediments and TDCP (log K_{ow} of 3.7) in zooplankton. Wang et al. (2019) made a similar observation (TCPP was dominant in their seawater samples but not detected in zooplankton samples) and concluded that OPEs with low log K_{ow} values, and therefore low hydrophobicity, do not easily accumulate in zooplankton.

Cortiou station exhibited the highest PAE and OPE concentrations (all size classes combined; Fig. 4 A & B). Interestingly, averaged Σ_7 PAE and Σ_9 OPE concentrations varied with the zooplankton size classes, the highest concentrations being observed for the smallest size class, followed by the largest size class, whereas the lowest concentrations were observed for the middle-sized organisms (Fig. 4 C & D). In total, 46% of PAEs and 40% of OPEs were detected in the smallest size class (150-500 μm) (Fig. 4 E & F). The high concentrations observed in small-sized plankton are probably due to the higher surface area/volume ratio, which can lead to a rapid uptake of contaminants from the surrounding medium (DeLorenzo et al., 2002; Hargrave et al., 2000). However, this does not explain why the middle-sized class (500-1000 μm) is generally the least contaminated. A lower lipid content might be an explanation; however, lipid contents were not determined in this study due to sample size limitations. In addition, a previous report showed that zooplankton of the 500-1000 μm size class in the study area exhibited the highest lipid contents (Chen et al., 2019).

The high standard deviation values underline an important variability between sampling events, possibly linked to the planktonic life cycle and/or to changes in the water column conditions across the sampling year. Indeed, a seasonality of bioaccumulation in zooplankton has already been observed for certain organochlorine chemicals such as PCBs, and those authors suggested that a varying lipid content in zooplankton due to reproduction and growth might be an explanation (Hargrave et al., 2000).

FIGURE 4: Box plots indicating PAE (A) and OPE (B) concentrations per sampling station as well as PAE (C) and OPE (D) concentrations per zooplankton size class. The pie charts indicate the percentage of PAEs (E) and OPEs (F) found in the different

zooplankton size classes (e.g. 46% of all PAEs detected were found in size class 150-500 µm).

A previous study analyzing PAEs in zooplankton samples from the NW Mediterranean Sea (including coastal and open sea stations) detected Σ_7 PAEs at concentrations of 17-4580 ng g^{-1} dw, with DEHP concentrations of up to 2700 ng g^{-1} dw (mean 679±739) (Baini et al., 2017). This mean DEHP concentration is lower than our mean DEHP concentration in zooplankton samples, even if we exclude the highly contaminated WWTP outlet at Cortiou station (i.e., 2010±1400 ng g^{-1} dw without Cortiou station), indicating that the Bay of Marseille could be a PAE contamination hotspot. Apart from a previous study reporting OPEs concentrations in freshwater zooplankton (Taihu Lake, China) (10.8±0.5 ng g^{-1} ww of Σ_{11} OPEs; Wang et al., 2019), a recent study investigated OPE occurrence in a tropical marine food web. The authors hereby reported a mean Σ_{11} OPEs concentration of 660±246 ng g^{-1} dw in zooplankton samples (Ding et al., 2020) and furthermore noted that OPEs underwent trophic dilution rather than biomagnification. It has elsewhere been reported that zooplankton are also impacted by other organic contaminants, such as PCBs (14.2-88.1 ng g^{-1} dw Σ_7 PCBs in Marseille Bay; Tiano et al., 2014) and perfluorooctane sulfonate (PFOS) (4.18 ng g^{-1} ww in Gaobeidian Lake, China; Li et al., 2008). Since zooplankton are at the base of the marine food web, negative implications for organisms of higher trophic levels cannot be excluded and the consequences for local marine resources should be investigated. More data from other parts of the Mediterranean Sea, and elsewhere, are urgently needed for comparison.

Bioconcentration

To obtain an idea of the bioconcentration potential of the studied compounds, the bioconcentration factors (BCF) of PAEs and OPEs were calculated for the three zooplankton size classes using the following equation:

$$\mathrm{BCF} = \frac{[zooplankton](mg\ kg^{-1})}{[water](mg\ L^{-1})}$$

Since the wet weight is used for the BCF calculation, zooplankton concentrations were converted from ng g^{-1} dw to ng g^{-1} ww using a conversion factor of 0.2 (Håkanson and

Boulion, 2003; Pagano and Saint-Jean, 1994). For the scope of this work, diet is not considered in the BCF calculation in any of the zooplankton size classes. Therefore, the BCFs calculated here represent the ratio of the concentration of the chemical in a given zooplankton size class to the corresponding dissolved chemical concentration in the surrounding water column. We acknowledge the limitations of these calculations, but provide the first field-derived BCFs for PAEs and OPEs in coastal Mediterranean waters. Table 1 presents the estimated BCFs for each individual compound and size class using the average and the median contaminant concentration measured in zooplankton. Between size classes, the calculated BCFs were at times variable, but with no clear trends. Furthermore, no relationship between BCF values and log K_{ow} of contaminants was observed. The highest calculated median BCF was ~117,000 for TEHP (size class 150-500 μm). In contrast, lowest BCFs were calculated for DEP (359-519, depending on size class) and DiBP (264-687). Our median DEHP BCF (2,500-4,600) is consistent with the reported DEHP BCF of 2,700 for *Gammarus*, an amphipod genus (JRC Risk Assesment Report, 2008). For comparison with other organic contaminants, the average BCF of endosulfan, an agricultural pesticide, was reported as 3,300 in freshwater zooplankton (DeLorenzo et al., 2002).

Indeed, zooplankton are thought to accumulate a significant fraction of organic contaminants from the dissolved water phase (Borgå et al., 2005), justifying the use of the BCF as a basic risk assessment tool. In Annex D of the Stockholm Convention on Persistent Organic Pollutants, a BCF $\geq$ 5000 L kg^{-1} is listed as a criterion that identifies a chemical as bioaccumulative. If we apply this criterion to the median BCFs, DMP (for size class > 1000 μm), BzBP (all size classes), DnOP (all size classes), TiBP (all size classes), TCEP (size classes 150-500 μm & 500-1000 μm), TDCP (size class 150-500 μm), EHDPP (all size classes) and TEHP (size classes 150-500 μm & 500-1000 μm) can be considered as bioaccumulative. The quality threshold is hereby exceeded by up to 23-fold. If the BCF calculated using average concentrations is considered, even more compounds, including DnBP, DEHP, TnBP and TPhP exceed the BCF criterion as defined by the Stockholm Convention. Bioconcentration of PAEs and OPEs at the base of the marine food web could cause negative effects at higher trophic levels. Field data, as provided here, are therefore essential and can help to improve existing risk assessment models.

TABLE 1: Average and median bioconcentration factors (BCF) for seven phthalates and nine organophosphate esters, calculated for the three zooplankton size classes.

405

406 *Microplastic abundance and relationships with additives*

407 Microplastic density in surface waters varied between 0 and 0.308 items per cubic
408 meter (mean 0.051 items m^{-3}). Surprisingly, the highest mean MP abundance was found at
409 Frioul Island (0.081 items m^{-3}), the station where generally lower contaminant concentrations
410 were detected in comparison with the two other stations and, more specifically, with Cortiou
411 station. By contrast, we observed the lowest mean MP density (0.025 items m^{-3}) at Cortiou
412 station (Fig. 5) suggesting that (1) the water near the outfall is well mixed, leading to a more
413 homogeneous microplastic distribution in the whole water column and therefore lower MP
414 concentrations at the surface, or (2) that the contaminants may originate from various sources,
415 such as household greywater, leaching from PVC pipes (e.g. from the sewage system) or
416 industrial inputs, and not solely from plastic litter. A regression analysis confirmed that
417 waterborne PAE and OPE concentrations at the three sampling stations were not correlated
418 with the corresponding microplastic abundances (p-value = 0.7). This indicates that in coastal
419 systems microplastic abundances cannot be taken as a proxy of contamination by organic
420 plastic additives and *vice versa*. When compared with the literature, our observed MP density
421 is at the lower limit of previous studies. For example, a mean abundance of 0.15 items m^{-3}
422 was measured in the Central-Western Mediterranean Sea (de Lucia et al., 2014). Therein, the
423 authors observed lower MP concentrations close to the shore (0.01±0.00 - 0.18±0.03 items m^{-3})
424 than in off-shore waters (up to 0.35±0.11 items m^{-3}). In the Atlantic Ocean (Portuguese
425 coast), mean MP concentrations ranging from 0.002±0.001 to 0.036±0.027 items m^{-3} have
426 been reported (Frias et al., 2014).

427 At L'Estaque station, small MPs (surface area < 1 mm^2) were predominant with 90.1%
428 relative abundance, followed by MPs with surface areas between 1 and 5 mm^2 (8.5%) and
429 between 5 and 10 mm^2 (1.4%). At Cortiou station, the percentage of particles sized 1-5 mm^2
430 (35.5%) and 5-10 mm^2 (3.2%) was higher, but the small-sized items < 1 mm^2 remained
431 dominant (61.3%). Finally, at Frioul station, items sized < 1 mm^2 and 1-5 mm^2 had similar
432 relative abundances (40.5% and 44.0%, respectively), as did MPs with surface areas of 5-10
433 mm^2 and > 10 mm^2 (6.7% and 8.6%, respectively) (Fig. 5). This indicates that the size
434 distribution in samples can differ even at a small spatial scale. In a previous study analyzing
435 MPs at three sampling stations in the Bay of Marseille (all close to Frioul Island), a size
436 distribution similar to ours (at Frioul station) was observed, but with an even higher

437 percentage of items sized 1-5 mm^2 (55%; compared to 27% of items < 1 mm^2) (Schmidt et al.,
438 2018).

439 Microplastics at Cortiou station may represent inputs from the WWTP outlet, while
440 MPs those from Frioul and L'Estaque stations may originate from the city of Marseille or
441 have been transported to the sampling stations via currents. A previous study involving *in situ*
442 data and numerical simulations showed that contaminants (perfluoroalkyl substances) from
443 the Rhône River can reach the Bay of Marseille, and particularly L'Estaque station through
444 freshwater intrusions (Schmidt et al., 2019). This might be the case for microplastics as well.

445

446 **FIGURE 5: Microplastic density (items/m^3) observed on each of the six sampling dates**
447 **at the three stations (upper right corner) and distribution of microplastic surface area**
448 **(mm^2) along stations (left).**

449

450 **Conclusion**

451 This is the first comprehensive study on the occurrence and temporal variability of
452 PAEs and OPEs in coastal Mediterranean based on the parallel collection of water, sediment
453 and differently sized zooplankton samples. PAEs and OPEs were detected at high
454 (zooplankton), moderate (water) and low (sediment) concentrations in Marseille Bay. PAEs
455 were generally more abundant than OPEs, with DEHP being the predominant PAE in all
456 matrixes. Zooplankton samples in particular collected near the municipal WWTP outlet
457 exhibited alarmingly high DEHP concentrations (up to 43 $\mu g\ g^{-1}$ dw), raising questions about
458 potential toxicity and impacts on the local marine food web. Variability in contaminant
459 concentrations within the same zooplankton size class and sampling station were found,
460 possibly due to the life cycle of zooplanktonic organisms or to a different species composition
461 of the samples. The smallest zooplankton size class generally exhibited the highest PAE and
462 OPE concentrations. These differences in contaminant concentrations between size classes
463 require further investigation, warranting further research and laboratory experimentation.
464 Furthermore, analyzing the lipid content and taxonomical composition of each future sample
465 could shed light on the remaining questions. Certain compounds exhibited median BCFs >
466 5000, suggesting a potential for bioaccumulation, including some of the most widely used
467 chlorinated OPEs, like TDCP. This was not, however, the case for DEHP and TCPP,

generally the most abundant PAE/OPE found in environmental samples, indicating that dietary intake might be more important than waterborne bioconcentration mechanisms for these two compounds. Our results and the first field-derived BCFs in coastal Mediterranean waters fill an important data gap and could help to fine tune existing risk assessments methodologies regarding PAEs and OPEs. The amounts of dissolved organic plastic additives in surface waters and the abundance of microplastic particles were not correlated, implying that they are not necessarily good indicators for each other in this compartment.

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References

Baini, M., Martellini, T., Cincinelli, A., Campani, T., Minutoli, R., Panti, C., Finoia, M.G., Fossi, M.C., 2017. First detection of seven phthalate esters (PAEs) as plastic tracers in superficial neustonic/planktonic samples and cetacean blubber. Anal. Methods 9, 1512–1520. https://doi.org/10.1039/c6ay02674e

Borgå, K., Fisk, A.T., Hargrave, B., Hoekstra, P.F., Swackhamer, D., Muir, D.C.G., 2005. Bioaccumulation factors for PCBs revisited. Environ. Sci. Technol. 39, 4523–4532. https://doi.org/10.1021/es050376i

Castro-Jiménez, J., Berrojalbiz, N., Pizarro, M., Dachs, J., 2014. Organophosphate ester (OPE) flame retardants and plasticizers in the open mediterranean and black seas atmosphere. Environ. Sci. Technol. 48, 3203–3209. https://doi.org/10.1021/es405337g

Castro-Jiménez, J., Casal, P., González-Gaya, B., Pizarro, M., Dachs, J., 2016. Organophosphate ester flame retardants and plasticizers in the global oceanic atmosphere. Environ. Sci. Technol 50, 12831–12839.

Castro-Jiménez, J., Ratola, N., 2020. An innovative approach for the simultaneous

quantitative screening of organic plastic additives in complex matrices in marine coastal areas. Environ. Sci. Pollut. Res. 27, 11450–11457. https://doi.org/10.1007/s11356-020-08069-9

Chen, C.T., Bănaru, D., Carlotti, F., Faucheux, M., Harmelin-Vivien, M., 2019. Seasonal variation in biochemical and energy content of size-fractionated zooplankton in the Bay of Marseille (North-Western Mediterranean Sea). J. Mar. Syst. 199. https://doi.org/10.1016/j.jmarsys.2019.103223

Chen, X., Xu, S., Tan, T., Lee, S.T., Cheng, S.H., Lee, F.W.F., Xu, S.J.L., Ho, K.C., 2014. Toxicity and estrogenic endocrine disrupting activity of phthalates and their mixtures. Int. J. Environ. Res. Public Health 11, 3156–3168. https://doi.org/10.3390/ijerph110303156

Cole, M., Lindeque, P., Fileman, E., Halsband, C., Goodhead, R., Moger, J., Galloway, T.S., 2013. Microplastic Ingestion by Zooplankton. Environ. Sci. Technol 47, 6646–6655. https://doi.org/10.1021/es400663f

Collignon, A., Hecq, J.H., Glagani, F., Voisin, P., Collard, F., Goffart, A., 2012. Neustonic microplastic and zooplankton in the North Western Mediterranean Sea. Mar. Pollut. Bull. 64, 861–864. https://doi.org/10.1016/j.marpolbul.2012.01.011

Cristale, J., García Vázquez, A., Barata, C., Lacorte, S., 2013. Priority and emerging flame retardants in rivers: Occurrence in water and sediment, Daphnia magna toxicity and risk assessment. Environ. Int. 59, 232–243. https://doi.org/10.1016/j.envint.2013.06.011

de Lucia, G.A., Caliani, I., Marra, S., Camedda, A., Coppa, S., Alcaro, L., Campani, T., Giannetti, M., Coppola, D., Cicero, A.M., Panti, C., Baini, M., Guerranti, C., Marsili, L., Massaro, G., Fossi, M.C., Matiddi, M., 2014. Amount and distribution of neustonic micro-plastic off the western Sardinian coast (Central-Western Mediterranean Sea). Mar. Environ. Res. 100, 10–16. https://doi.org/10.1016/j.marenvres.2014.03.017

DeLorenzo, M.E., Taylor, L.A., Lund, S.A., Pennington, P.L., Strozier, E.D., Fulton, M.H., 2002. Toxicity and bioconcentration potential of the agricultural pesticide endosulfan in phytoplankton and zooplankton. Arch. Environ. Contam. Toxicol. 42, 173–181. https://doi.org/10.1007/s00244-001-0008-3

Ding, Y., Han, M., Wu, Z., Zhang, R., Li, A., Yu, K., Wang, Y., Huang, W., Zheng, X., Mai, B., 2020. Bioaccumulation and trophic transfer of organophosphate esters in tropical

529 marine food web, South China Sea. Environ. Int. 143.
530 https://doi.org/10.1016/j.envint.2020.105919

531 Duncan, E.M., Broderick, A.C., Fuller, W.J., Galloway, T.S., Godfrey, M.H., Hamann, M.,
532 Limpus, C.J., Lindeque, P.K., Mayes, A.G., Omeyer, L.C.M., Santillo, D., Snape,
533 R.T.E., Godley, B.J., 2019. Microplastic ingestion ubiquitous in marine turtles. Glob.
534 Chang. Biol. 25, 744–752. https://doi.org/10.1111/gcb.14519

535 Fauvelle, V., Castro-Jiménez, J., Schmidt, N., Carlez, B., Panagiotopoulos, C., Sempéré, R.,
536 2018. One-Single Extraction Procedure for the Simultaneous Determination of a Wide
537 Range of Polar and Nonpolar Organic Contaminants in Seawater. Front. Mar. Sci. 5, 1–
538 10. https://doi.org/10.3389/fmars.2018.00295

539 Fraysse, M., Pairaud, I., Ross, O.N., Faure, V.M., Pinazo, C., 2014. Intrusion of Rhone River
540 diluted water into the Bay of Marseille: Generation processes and impacts on ecosystem
541 functioning. J. Geophys. Res. Ocean. 119, 6535–6556.
542 https://doi.org/10.1002/2014JC010022.Received

543 Frias, J.P.G.L., Otero, V., Sobral, P., 2014. Evidence of microplastics in samples of
544 zooplankton from Portuguese coastal waters. Mar. Environ. Res. 95, 89–95.
545 https://doi.org/10.1016/j.marenvres.2014.01.001

546 Håkanson, L., Boulion, V. V., 2003. A general dynamic model to predict biomass and
547 production of phytoplankton in lakes. Ecol. Modell. 165, 285–301.
548 https://doi.org/10.1016/S0304-3800(03)00096-6

549 Hargrave, B.T., Phillips, G.A., Vass, W.P., Bruecker, P., Welch, H.E., Siferd, T.D., 2000.
550 Seasonality in bioaccumulation of organochlorines in lower trophic level arctic marine
551 biota. Environ. Sci. Technol. 34, 980–987. https://doi.org/10.1021/es990871c

552 Heindler, F.M., Alajmi, F., Huerlimann, R., Zeng, C., Newman, S.J., Vamvounis, G., van
553 Herwerden, L., 2017. Toxic effects of polyethylene terephthalate microparticles and
554 Di(2-ethylhexyl)phthalate on the calanoid copepod, Parvocalanus crassirostris.
555 Ecotoxicol. Environ. Saf. 141, 298–305. https://doi.org/10.1016/j.ecoenv.2017.03.029

556 Horton, A.A., Walton, A., Spurgeon, D.J., Lahive, E., Svendsen, C., 2017. Microplastics in
557 freshwater and terrestrial environments: Evaluating the current understanding to identify
558 the knowledge gaps and future research priorities. Sci. Total Environ. 586, 127–141.
559 https://doi.org/10.1016/j.scitotenv.2017.01.190

Isobe, A., Uchida, K., Tokai, T., Iwasaki, S., 2015. East Asian seas: A hot spot of pelagic microplastics. Mar. Pollut. Bull. 101, 618–623. https://doi.org/10.1016/j.marpolbul.2015.10.042

Lebreton, L.C.M., Van Der Zwet, J., Damsteeg, J.W., Slat, B., Andrady, A., Reisser, J., 2017. River plastic emissions to the world's oceans. Nat. Commun. 8, 1–10. https://doi.org/10.1038/ncomms15611

Li, X., Yin Yeung, L.W., Xu, M., Taniyasu, S., Lam, P.K.S., Yamashita, N., Dai, J., 2008. Perfluorooctane sulfonate (PFOS) and other fluorochemicals in fish blood collected near the outfall of wastewater treatment plant (WWTP) in Beijing. Environ. Pollut. 156, 1298–1303. https://doi.org/10.1016/j.envpol.2008.03.008

Liubartseva, S., Coppini, G., Lecci, R., Clementi, E., 2018. Tracking plastics in the Mediterranean: 2D Lagrangian model. Mar. Pollut. Bull. 129, 151–162. https://doi.org/10.1016/j.marpolbul.2018.02.019

Ma, Y., Xie, Z., Lohmann, R., Mi, W., Gao, G., 2017. Organophosphate Ester Flame Retardants and Plasticizers in Ocean Sediments from the North Pacific to the Arctic Ocean. Environ. Sci. Technol. 51, 3809–3815. https://doi.org/10.1021/acs.est.7b00755

Marklund, A., 2005. Levels and Sources of Organophosphorus Flame Retardants and Plasticizers in.

McDonough, C.A., De Silva, A.O., Sun, C., Cabrerizo, A., Adelman, D., Soltwedel, T., Bauerfeind, E., Muir, D.C.G., Lohmann, R., 2018. Dissolved Organophosphate Esters and Polybrominated Diphenyl Ethers in Remote Marine Environments: Arctic Surface Water Distributions and Net Transport through Fram Strait. Environ. Sci. Technol. 52, 6208–6216. https://doi.org/10.1021/acs.est.8b01127

Millet, B., Pinazo, C., Banaru, D., Pagès, R., Guiart, P., Pairaud, I., 2018. Unexpected spatial impact of treatment plant discharges induced by episodic hydrodynamic events: Modelling Lagrangian transport of fine particles by Northern current intrusions in the bays of marseille (France). PLoS One 13, 0–25. https://doi.org/10.1371/journal.pone.0195257

Net, S., Sempéré, R., Delmont, A., Paluselli, A., Ouddane, B., 2015. Occurrence, fate, behavior and ecotoxicological state of phthalates in different environmental matrices. Environ. Sci. Technol. 49, 4019–4035. https://doi.org/10.1021/es505233b

Ourgaud, M., 2015. Influence des apports anthropiques sur les flux de carbone et de contaminants dans les réseaux trophiques de “poissons” de l’écosystème à Posidonia oceanica. Aix-Marseille Université.

Oursel, B., Garnier, C., Durrieu, G., Mounier, S., Omanović, D., Lucas, Y., 2013. Dynamics and fates of trace metals chronically input in a Mediterranean coastal zone impacted by a large urban area. Mar. Pollut. Bull. 69, 137–149. https://doi.org/10.1016/j.marpolbul.2013.01.023

Pagano, M., Saint-Jean, L., 1994. In situ metabolic budget for the calanoid copepod Acartia clausi in a tropical brackish water lagoon (Ebrié Lagoon, Ivory Coast). Hydrobiologia 272, 147–161. https://doi.org/10.1007/BF00006518

Paluselli, A., Aminot, Y., Galgani, F., Net, S., Sempéré, R., 2018a. Occurrence of phthalate acid esters (PAEs) in the northwestern Mediterranean Sea and the Rhone River. Prog. Oceanogr. 163, 221–231. https://doi.org/10.1016/j.pocean.2017.06.002

Paluselli, A., Fauvelle, V., Galgani, F., Sempéré, R., 2019. Phthalate release from plastic fragments and degradation in seawater. Environ. Sci. Technol. 53, 166–175. https://doi.org/10.1021/acs.est.8b05083

Paluselli, A., Fauvelle, V., Schmidt, N., Galgani, F., Net, S., Sempéré, R., 2018b. Distribution of phthalates in Marseille Bay (NW Mediterranean Sea). Sci. Total Environ. 621, 578–587. https://doi.org/10.1016/j.scitotenv.2017.11.306

Pantelaki, I., Voutsa, D., 2019. Organophosphate flame retardants (OPFRs): A review on analytical methods and occurrence in wastewater and aquatic environment. Sci. Total Environ. 649, 247–263. https://doi.org/10.1016/j.scitotenv.2018.08.286

Peijnenburg, W.J.G.M., Struijs, J., 2006. Occurrence of phthalate esters in the environment of the Netherlands. Ecotoxicol. Environ. Saf. 63, 204–215. https://doi.org/10.1016/j.ecoenv.2005.07.023

Reemtsma, T., Quintana, J.B., Rodil, R., García-López, M., Rodríguez, I., 2008. Organophosphorus flame retardants and plasticizers in water and air I. Occurrence and fate. Trends Anal. Chem. 27, 727–737. https://doi.org/10.1016/j.trac.2008.07.002

Report, J.R.A., 2008. Summary Risk Assessment Report - Bis(2-Ethylhexyl) phthalate (DEHP). Eur. Communities 80, 204–211.

621 Sánchez-Avila, J., Tauler, R., Lacorte, S., 2012. Organic micropollutants in coastal waters
622 from NW Mediterranean Sea: Sources distribution and potential risk. Environ. Int. 46,
623 50–62. https://doi.org/10.1016/j.envint.2012.04.013

624 Schmidt, N., Fauvelle, V., Castro-Jiménez, J., Lajaunie-Salla, K., Pinazo, C., Yohia, C.,
625 Sempéré, R., 2019. Occurrence of perfluoroalkyl substances in the Bay of Marseille
626 (NW Mediterranean Sea) and the Rhône River. Mar. Pollut. Bull. 149, 110491.
627 https://doi.org/10.1016/j.marpolbul.2019.110491

628 Schmidt, N., Thibault, D., Galgani, F., Paluselli, A., Sempéré, R., 2018. Occurrence of
629 microplastics in surface waters of the Gulf of Lion (NW Mediterranean Sea). Prog.
630 Oceanogr. 163, 214–220. https://doi.org/10.1016/j.pocean.2017.11.010

631 Sempéré, R., Para, J., Tedetti, M., Charrière, B., Mallet, M., 2015. Variability of Solar
632 Radiation and CDOM in Surface Coastal Waters of the Northwestern Mediterranean Sea.
633 Photochem. Photobiol. 91, 851–861. https://doi.org/10.1111/php.12434

634 Silva-Cavalcanti, J.S., Silva, J.D.B., França, E.J. de, Araújo, M.C.B. de, Gusmão, F., 2017.
635 Microplastics ingestion by a common tropical freshwater fishing resource. Environ.
636 Pollut. 221, 218–226. https://doi.org/10.1016/j.envpol.2016.11.068

637 Sousa, J.C.G., Ribeiro, A.R., Barbosa, M.O., Pereira, M.F.R., Silva, A.M.T., 2018. A review
638 on environmental monitoring of water organic pollutants identified by EU guidelines. J.
639 Hazard. Mater. 344, 146–162. https://doi.org/10.1016/j.jhazmat.2017.09.058

640 Suaria, G., Avio, C.G., Mineo, A., Lattin, G.L., Magaldi, M.G., Belmonte, G., Moore, C.J.,
641 Regoli, F., Aliani, S., 2016. The Mediterranean Plastic Soup: Synthetic polymers in
642 Mediterranean surface waters. Sci. Rep. 6, 1–10. https://doi.org/10.1038/srep37551

643 Sun, L., Tan, H., Peng, T., Wang, S., Xu, W., Qian, H., Jin, Y., Fu, Z., 2016. Developmental
644 neurotoxicity of organophosphate flame retardants in early life stages of Japanese
645 medaka (Oryzias latipes). Environ. Toxicol. Chem. 35, 2931–2940.
646 https://doi.org/10.1002/etc.3477

647 Tiano, M., Tronczyński, J., Harmelin-Vivien, M., Tixier, C., Carlotti, F., 2014. PCB
648 concentrations in plankton size classes, a temporal study in Marseille Bay, Western
649 Mediterranean Sea. Mar. Pollut. Bull. 89, 331–339.
650 https://doi.org/10.1016/j.marpolbul.2014.09.040

van der Veen, I., de Boer, J., 2012. Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis. Chemosphere 88, 1119–1153. https://doi.org/10.1016/j.chemosphere.2012.03.067

van Wijnen, J., Ragas, A.M.J., Kroeze, C., 2019. Modelling global river export of microplastics to the marine environment: Sources and future trends. Sci. Total Environ. 673, 392–401. https://doi.org/10.1016/j.scitotenv.2019.04.078

Vila-Costa, M., Sebastián, M., Pizarro, M., Cerro-Gálvez, E., Lundin, D., Gasol, J.M., Dachs, J., 2019. Microbial consumption of organophosphate esters in seawater under phosphorus limited conditions. Sci. Rep. 9, 1–11. https://doi.org/10.1038/s41598-018-36635-2

Wang, R., Tang, J., Xie, Z., Mi, W., Chen, Y., Wolschke, H., Tian, C., Pan, X., Luo, Y., Ebinghaus, R., 2015. Occurrence and spatial distribution of organophosphate ester flame retardants and plasticizers in 40 rivers draining into the Bohai Sea, north China. Environ. Pollut. 198, 172–178. https://doi.org/10.1016/j.envpol.2014.12.037

Wang, X., Zhong, W., Xiao, B., Liu, Q., Yang, L., Covaci, A., Zhu, L., 2019. Bioavailability and biomagnification of organophosphate esters in the food web of Taihu Lake, China: Impacts of chemical properties and metabolism. Environ. Int. 125, 25–32. https://doi.org/10.1016/j.envint.2019.01.018

Wang, Y., Wu, X., Zhang, Q., Hou, M., Zhao, H., Xie, Q., Du, J., Chen, J., 2017. Organophosphate esters in sediment cores from coastal Laizhou Bay of the Bohai Sea, China. Sci. Total Environ. 607–608, 103–108. https://doi.org/10.1016/j.scitotenv.2017.06.259

Wolschke, H., Sühring, R., Xie, Z., Ebinghaus, R., 2015. Organophosphorus flame retardants and plasticizers in the aquatic environment: A case study of the Elbe River, Germany. Environ. Pollut. 206, 488–493. https://doi.org/10.1016/j.envpol.2015.08.002

Yang, C., Harris, S.A., Jantunen, L.M., Siddique, S., Kubwabo, C., Tsirlin, D., Latifovic, L., Fraser, B., St-Jean, M., De La Campa, R., You, H., Kulka, R., Diamond, M.L., 2019. Are cell phones an indicator of personal exposure to organophosphate flame retardants and plasticizers? Environ. Int. 122, 104–116. https://doi.org/10.1016/j.envint.2018.10.021

Young, H.S., McCauley, D.J., Galetti, M., Dirzo, R., 2016. Patterns, Causes, and Consequences of Anthropocene Defaunation. Annu. Rev. Ecol. Evol. Syst. 47, 333–358.

https://doi.org/10.1146/annurev-ecolsys-112414-054142

Zhong, M., Tang, J., Guo, X., Guo, C., Li, F., Wu, H., 2020. Occurrence and spatial distribution of organophosphorus flame retardants and plasticizers in the Bohai , Yellow and East China seas. Sci. Total Environ. 741, 140434. https://doi.org/10.1016/j.scitotenv.2020.140434

Zhong, M., Wu, H., Mi, W., Li, F., Ji, C., Ebinghaus, R., Tang, J., Xie, Z., 2018. Occurrences and distribution characteristics of organophosphate ester flame retardants and plasticizers in the sediments of the Bohai and Yellow Seas, China. Sci. Total Environ. 615, 1305–1311. https://doi.org/10.1016/j.scitotenv.2017.09.272

Zhu, J., Yu, X., Zhang, Q., Li, Y., Tan, S., Li, D., Yang, Z., Wang, J., 2019. Cetaceans and microplastics: First report of microplastic ingestion by a coastal delphinid, Sousa chinensis. Sci. Total Environ. 659, 649–654. https://doi.org/10.1016/j.scitotenv.2018.12.389

Figures and tables

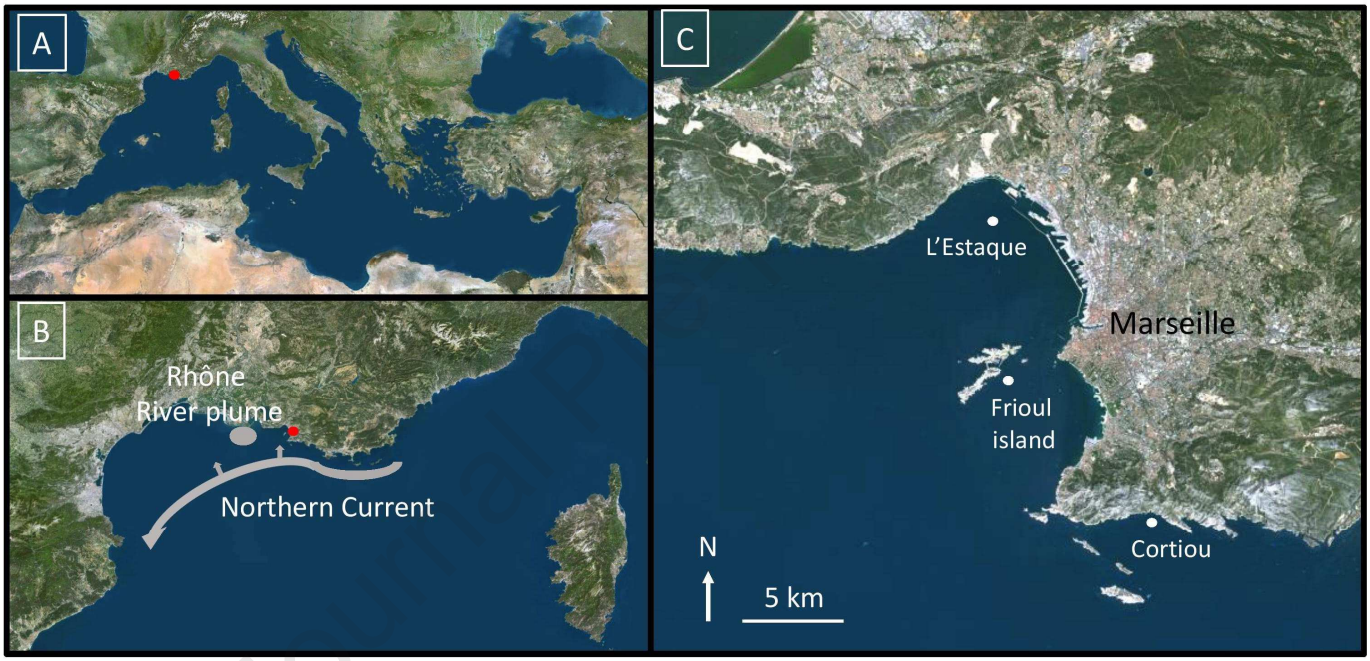
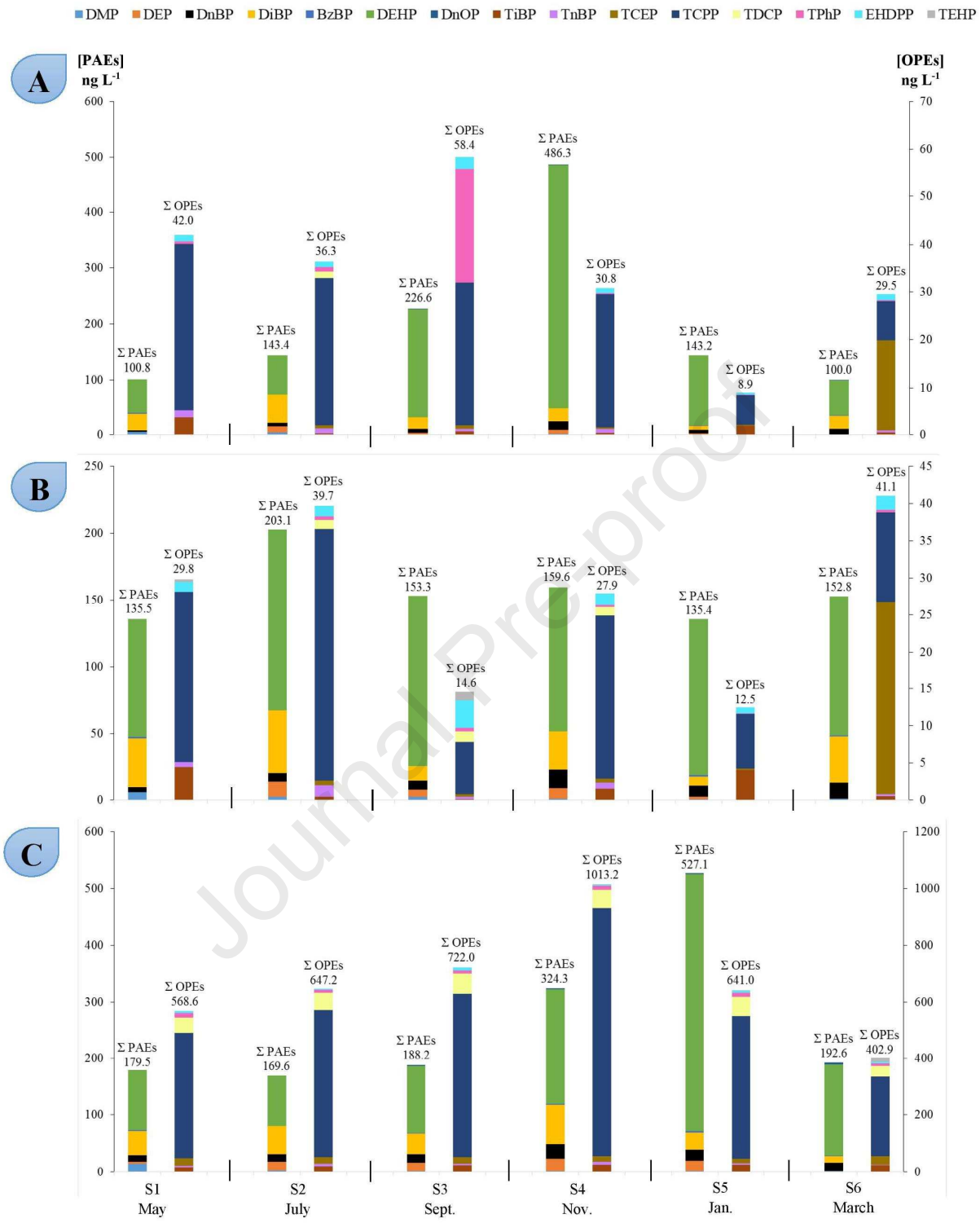


Figure 1: (A) Map of the Mediterranean Sea indicating the position of the sampling area, (B) zoom showing the Gulf of Lions with schematic representations of the Mediterranean Northern Current and the Rhône River plume, both of which can influence the Bay of Marseille *via* episodic intrusions. (C) Map of the Bay of Marseille showing the three sampling stations L'Estaque, Frioul Island and Cortiou.



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722 Fig. 2: PAE and OPE concentrations measured in filtered water samples during six sampling
723 events (S1-S6) at L'Estaque (A), Frioul (B) and Cortiou (C) stations in the Bay of Marseille.
724 Note the different scales for PAE (left) and OPE (right) concentrations.

725

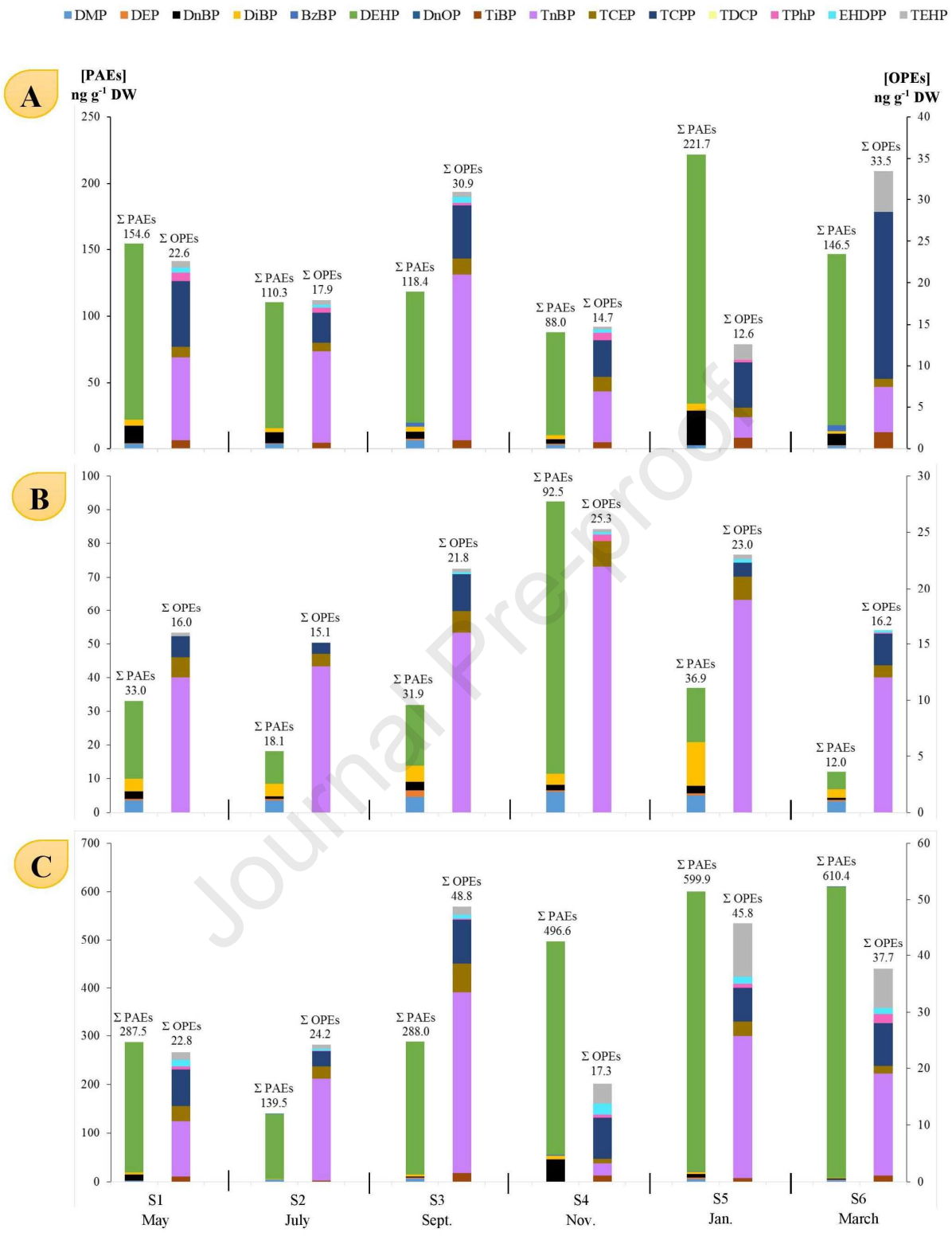
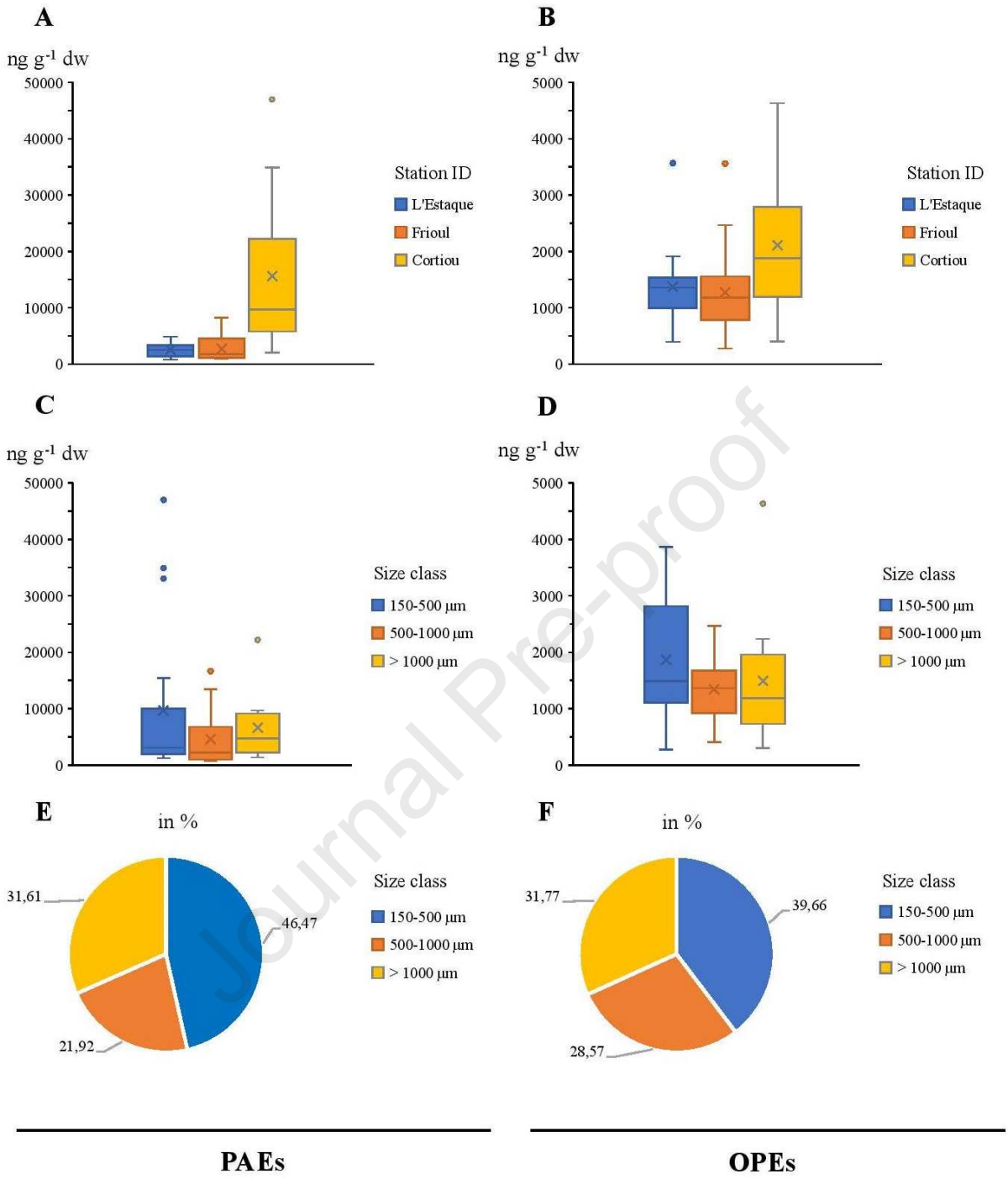


Fig. 3: PAE and OPE concentrations measured in sediment samples during six sampling events (S1-S6) at L'Estaque (A), Frioul (B) and Cortiou (C) stations in the Bay of Marseille. Note the different scales for PAE (left) and OPE (right) concentrations.



730

731 Fig. 4: Box plots indicating PAE (A) and OPE (B) concentrations per sampling station as well
732 as PAE (C) and OPE (D) concentrations per zooplankton size class. The pie charts indicate
733 the percentage of PAEs (E) and OPEs (F) found in the different zooplankton size classes (e.g.,
734 46% of all PAEs detected were found in size class 150-500 µm).

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736

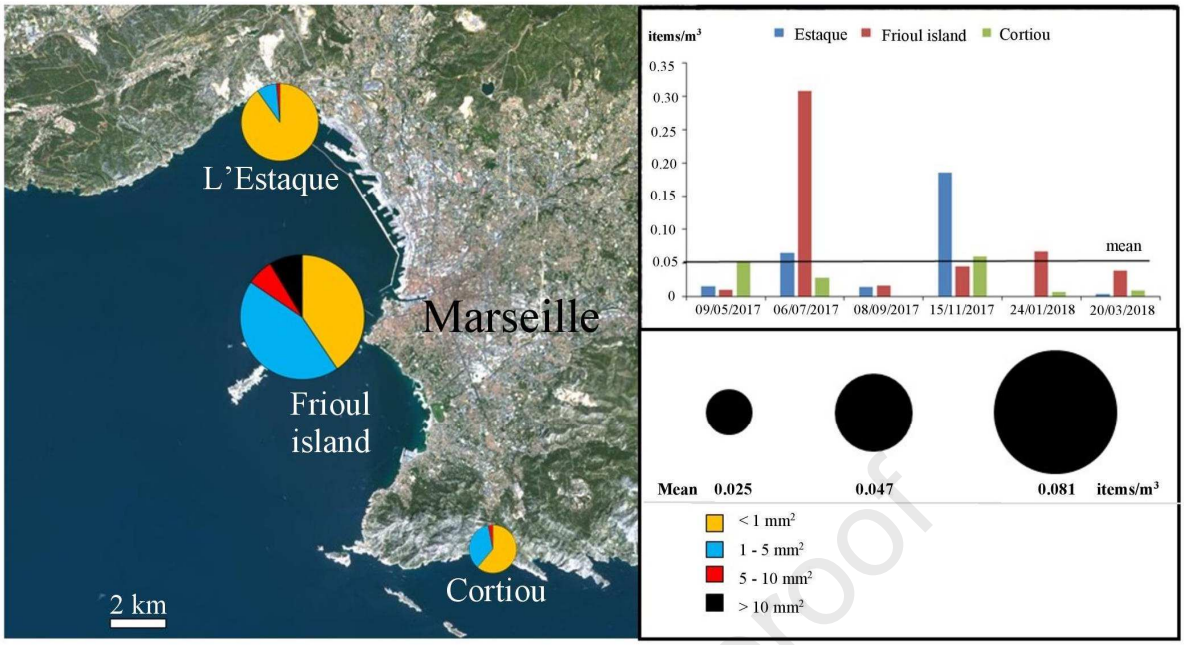

Fig. 5: Microplastic density (items/m^3) observed on each of the six sampling dates at the three stations (upper right corner) and distribution of microplastic surface area (mm^2) along stations (left).

753 Table 1: Average (± SD) and median bioconcentration factors (BCF) for seven phthalates and
754 nine organophosphate esters, calculated for the three zooplankton size classes.

	Average			Median		
	>1000 µm	**500-1000 µm**	**150-500 µm**	**>1000 µm**	**500-1000 µm**	**150-500 µm**
DMP	32 800 (± 58 100)	3 400 (± 4 500)	7 800 (± 15 500)	8 700	1 900	3 300
DEP	518 (± 464)	523 (± 406)	697 (± 639)	410	359	519
DnBP	5 400 (± 5 000)	3 800 (± 4 800)	5 700 (± 8 500)	3 500	2 700	1 900
DiBP	979 (± 777)	275 (± 151)	690 (± 670)	687	264	350
BzBP	30 500 (± 11 300)	29 400 (± 22 200)	25 700 (± 22 000)	31 900	25 500	23 300
DEHP	6 900 (± 7 500)	5 900 (± 6 300)	13 200 (± 18 900)	3 600	2 500	4 600
DnOP	55 700 (± 21 300)	47 100 (± 44 600)	100 000 (± 100 000)	65 500	33 700	50 000
TPP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
TiBP	183 000 (± 476 000)	27 300 (± 37 100)	138 000 (± 432 000)	28 100	8 500	7 200
TnBP	4 300 (± 6 600)	2 800 (± 4 000)	6 500 (± 13 500)	2 100	1 300	2 500
TCEP	25 000 (± 36 900)	79 600 (± 146 000)	50 700 (± 67 100)	1 800	14 400	22 700
TCPP	1 600 (± 1 400)	2 800 (± 4 800)	3 400 (± 6 400)	1 800	868	1 600
TDCP	6 200 (± 5 100)	28 000 (± 39 700)	84 800 (± 141 000)	4 700	3 300	5 800
TPhP	4 600 (± 5 900)	9 400 (± 12 800)	7 300 (± 9 200)	1 700	3 900	1 100
EHDPP	7 400 (± 6 100)	11 500 (± 11 200)	24 300 (± 27 400)	6 100	6 200	12 600
TEHP	n.a.	41 900 (± 61 700)	117 000 (± 158 000)	n.a.	11 200	116 900

755 n.a. = not available.

- High $\sum_7$PAE concentrations detected in zooplankton (up to 47 µg g^{-1} dw)
- Zooplankton sized 150-500 µm most concerned by chemical contamination
- Several PAEs & OPEs (e.g. EHDPP) have field-derived bioconcentration factors > 5000
- No correlation between OPE & PAE concentrations and MP abundance in seawater

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: