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

3
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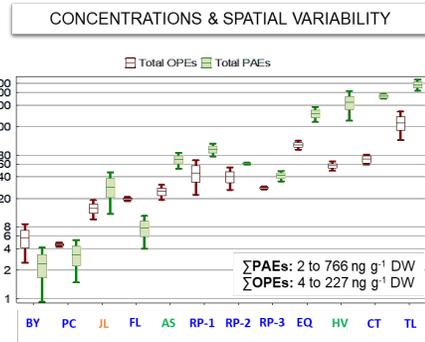
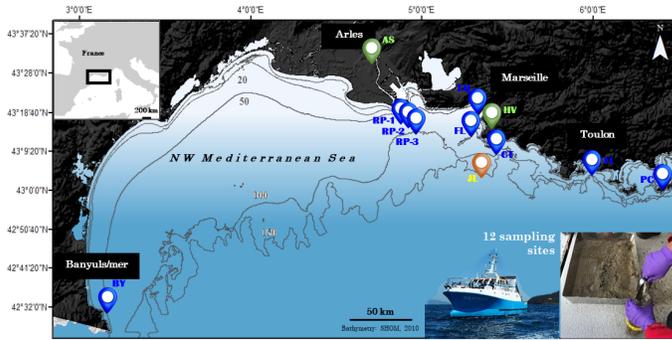
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1

2 **ABSTRACT**

3 Seven phthalate (PAEs) and nine organophosphate esters (OPEs) were measured
 4 in surface sediments across the Gulf of Lion (NW Mediterranean Sea) at twelve
 5 stations characterized by different anthropogenic signatures. Σ PAEs and Σ OPEs
 6 concentrations ranged from 2 to 766 ng/g DW (av. 196 ng/g DW) and from 4 to
 7 227 ng/g DW (av. 54 ng/g DW), respectively. Our analysis of the potential sources
 8 of these organic plastic additives in sediments of the Gulf of Lion suggests that the
 9 dominant factors affecting their occurrence and environmental distribution are port-
 10 based industrial activities and urban pressures. Indeed, the highest Σ PAE and Σ
 11 OPE concentrations were found close to the ports of Toulon and Marseille
 12 (Estaque) and at the sites impacted by the Marseille metropolitan area (i.e. at the
 13 outlets of the waste water treatment plant at Cortiou and at the mouth of the
 14 Huveaune River). The lowest levels were generally found in protected areas (e.g.
 15 Port-Cros) and at sites relatively far from the coast. DEHP was seen to be the
 16 most abundant PAE while TDCP, TEHP and TiBP were the most abundant OPEs
 17 in the area. Our results also expose the contribution of additives entering the Gulf
 18 of Lion via sedimentary material from the Rhône River, with positive correlations

1 between the total organic carbon (TOC) content in the sediment and the Σ PAEs
2 and Σ OPEs concentrations. However, additive concentrations decreased from
3 shore to offshore in the Rhône River discharge area, indicating an efficient dilution
4 of the contaminants accumulated at the river mouth area.

5

6 **Keywords:** Plastic additives; phthalates; organophosphate esters; sediment; Gulf
7 of Lion

8

1 **1. Introduction**

2 The increasing worldwide demand in recent years for plastics and
3 commonly used plastic additives has resulted in global awareness regarding the
4 presence of organic pollutants such as phthalate and organophosphate esters
5 (PAEs and OPEs, respectively) in all environments and their associated living
6 organisms (Net al al., 2015; Wei et al., 2015). In 2016 global plastic production
7 reached 355 million tons (PlasticsEurope, 2015), and plastic fragments can now
8 be found in the marine environment in unprecedented amounts (Barnes et al.,
9 2009). Since the beginning of the 20th century, PAEs have been used as
10 plasticizers to facilitate processing and to increase the flexibility and toughness of
11 manufactured plastic products: they are today in the class of synthetic chemicals
12 with high production volumes and toxicological properties (Schechter et al., 2013;
13 Wang et al., 2006). These chemicals are also added to paints, adhesives,
14 cosmetics and personal care products (Guo & Kannan, 2012; Cao, 2010). In 2009,
15 global PAE production stood at 6.2 million tons, of which 1.3 million tons were
16 produced in China, mainly di- (2-ethylhexyl) phthalate (DEHP) and di-n-butyl
17 phthalate (DnBP) (He et al., 2019). OPEs are listed among the most highly
18 produced chemicals due to their high worldwide consumption (Yang et al., 2019)
19 and their widespread used in numerous applications such as flame retardants,
20 plasticizers and lubricants (Wei et al., 2015).

21 PAEs and OPEs are among the most abundant organic plastic additives to
22 be released into the environment during polymer degradation/aging (Meng et al.,
23 2014; Net et al., 2015; Paluselli et al., 2019). The assimilation and subsequent

1 bioaccumulation of certain PAE and OPEs by living organisms may cause serious
2 risks due to their carcinogenic and estrogenic effects on human and animal health,
3 with potential impacts similar to those provoked by persistent organic pollutants
4 (POPs) (Wei et al., 2015). More specifically, PAEs may induce endocrine
5 disruption in both wild fish and mammals, as well as in humans, and may thus
6 affect reproduction, fertility and development (Net et al., 2015). Neurotoxic,
7 carcinogenic, mutagenic and hormone disturbance effects linked to some OPEs
8 have been observed in extensive studies on humans and animals (Andresen &
9 Bester, 2004; Lai et al., 2015; Zeng et al., 2014). Several phthalates are listed as
10 priority pollutants by diverse national and international regulatory organizations
11 including the United States Environmental Protection Agency (EPA) (Pan & Xing,
12 2008; Bernaldo de Quirós et al., 2019).

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

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

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

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

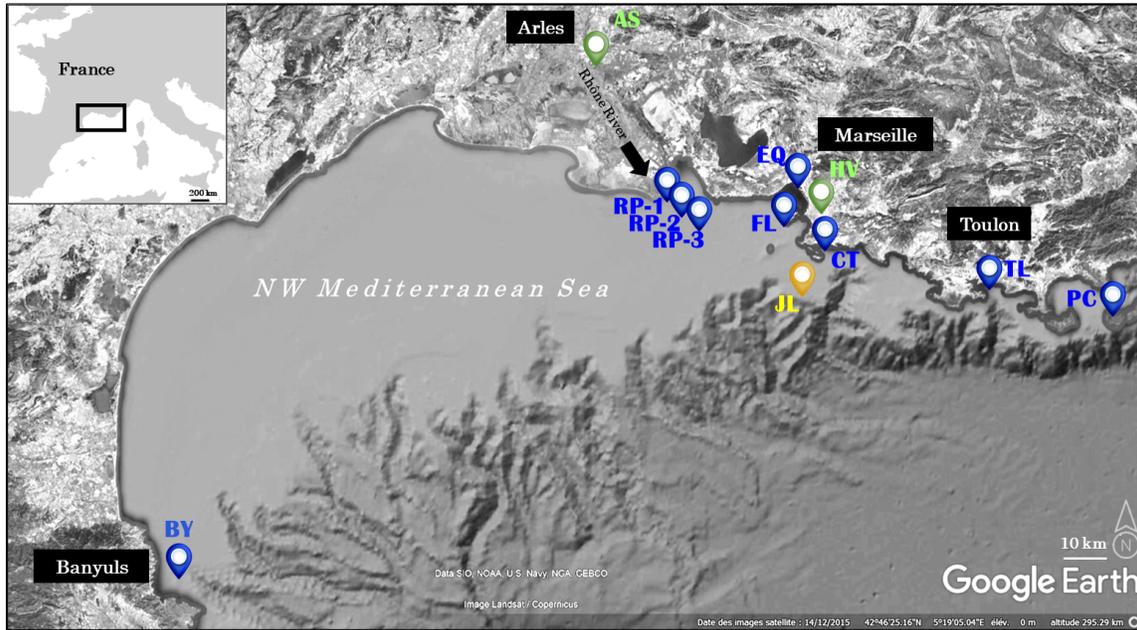
22 **2. Materials and methods**

23

1 *2.1. Study Area and Sampling*

2

3 Surface sediment samples (n=12) were collected on board the R/V Antedon
4 using a stainless-steel grab sampler at various stations across the Gulf of Lion
5 (43°32'N, 06°36'E) in the NW Mediterranean Sea from January-July 2018 (Fig. 1,
6 Table 1). Our strategy was to select sites subject to different anthropogenic
7 pressures: “Banyuls” (BY) and “Port-Cros” (PC) are located in marine protected
8 areas in the NW Mediterranean. The “Toulon” site (TL) is influenced by the
9 enclosed military and domestic port areas of the city of Toulon, whereas “Estaque”
10 (EQ) is subject to the influence of the commercial port/harbor of the city of
11 Marseille. “Cortiou” (CT) is near the outlet of Marseille’s sewage treatment plant,
12 and “Frioul” (FL), while located on the short passenger ferry crossing between
13 Marseille and the Frioul archipelago, is less exposed to Rhône River or urban
14 discharges. Additional sites are located offshore on the continental margin (“Julio”
15 (JL)), and in the Rhône River dilution plume (RP1-3) with increasing salinities from
16 RP1 to RP3. Two riverine sites were also investigated, the first in the Rhône River
17 at “Arles” station (AS) and the second in the smaller “Huveaune” (HV) River, which
18 discharges close to the Marseille beach area. Manual sampling was performed 3-
19 4 m from the shore at these fluvial sites using a stainless-steel bucket. The content
20 was poured onto a pre-cleaned stainless-steel tray, the first 2-5 cm of the sediment
21 surface was collected in a pre-cleaned glass bottle (0.5-1 kg of material) and was
22 then stored at -20 °C. All use of plastic materials was avoided during sampling and
23 storage.



1

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

7

8 **Table 1**

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

10

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

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

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

6

7 2.2. Chemicals and Reagents

8

9 Dichloromethane (DCM), hexane, ethyl acetate (EtOAc), acetone,
10 methanol, and toluene were purchased from Promochem (Picograde, LGC
11 standard). Ultrapure water (MQ) was obtained from a Millipore (resistivity > 18.2
12 MΩ) Milli-Q system. Resprep activated copper granules (99.5%) were supplied by
13 Restek (Bellefonte, PA, USA) and aluminum oxide 90 active neutral (alumina, 70-
14 230 mesh ASTM) and sodium sulfate was purchased from Merck (Darmstadt,
15 Germany). Labelled and native PAEs were obtained from Supelco (Bellefonte, PA,
16 USA). Labelled OPEs were purchased from C/D/N Isotopes Inc. (Pointe-Claire,
17 Canada) (TBP-d₂₇, TPhP-d₁₅, TPrP- d₂₁) and from Cambridge Isotope

1 Laboratories, Inc. (Tewksbury, MA, USA) (TCPP-d₁₈, TDCP-d₁₅ and TCEP-d₁₂).
2 Native OPEs were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany).
3 All details are presented in Table S2.

4

5 *2.3. C, N, P determinations*

6

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

13

14 *2.4. Pretreatment and extraction*

15

16 Sediment samples were freeze-dried using a Christ Beta 2-4 LO Plus LT
17 then sieved through a pre-cleaned stainless-steel sieve (500 µm diameter) before
18 extraction. Sediment samples (3.000 ± 0.005 g DW) were placed into pre-cleaned
19 glass centrifuge tubes, mixed with about 0.5-1 g of active copper, then spiked (100
20 ng/sample) with labeled surrogate standards (TBP-d₂₇, TCPP-d₁₈, TDCP-d₁₅,
21 DnBP-d₄) to monitor the overall extraction efficiency of the target compounds and
22 left to equilibrate for about 15 min. Four replicates (i.e. separated extractions) were
23 carried out for each sampling site. For each extraction, after the addition of 5 mL

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

21 *2.5. Instrumental analysis*

22

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

6

7 *2.6. Quality assurance/quality control (QA/QC)*

8

9 Strict measures were taken to prevent potential cross-contamination during
10 OPE and PAE analysis. First, the use of plastic material was avoided at all times
11 and all glassware was cleaned overnight with detergent, rinsed with tap water +
12 MQ water and then baked at 450 °C for 6 h before use. Alumina and sodium sulfate
13 were also baked overnight at 450 °C before use. Sample pre-treatment (except
14 freeze-drying) and extraction/clean-up steps were performed entirely in an
15 International Standards Organization (ISO) 6 cleanroom (22 °C, SAS +15 Pa
16 cleanroom pressure, 50 vol h⁻¹ brewing rate) (Paluselli et al., 2018). Four
17 replicates of sediment samples were extracted for each site except for CT (due to
18 limited available material), and method blanks relating to all steps were made for
19 each batch of extractions. The retention time and the response factors of GC-MS
20 were evaluated for each analytical sequence by regularly injecting different
21 calibration levels. One hexane injection was performed every 4-5 samples to check
22 and monitor potential cross contamination along the sequence.

1 After correction by blanks and determination of the naturally occurring
2 amounts of target compounds in the selected sediment (spiking experiment
3 performed on sediment FL), recoveries ranged from $66 \pm 3.2\%$ - $109 \pm 4.3\%$ and
4 $52 \pm 15\%$ - $131 \pm 17\%$ for native PAEs and OPEs, respectively (Table S3). In
5 addition, all samples analyzed (n=46) were spiked with labelled surrogates,
6 showing average recoveries varying from $77 \pm 22\%$ for TBP-d₂₇, $47 \pm 18\%$ for
7 TCPP-d₁₈, $70 \pm 13\%$ for TDCP-d₁₅ and $97 \pm 10\%$ for DnBP-d₄ (Table S3). Mean
8 blank values (n=7) varied from 0.001 to 8.62 ng depending on the compound
9 (Table S4). For the three compounds undetected in the blanks (i.e. DMP, TiBP and
10 TEHP), the corresponding instrumental limits of quantification (LOQ) were used.
11 For most compounds the values in the blanks represented <17% of the values in
12 the real samples on average. Slightly higher average contributions were observed
13 for two OPEs (i.e TPP and TnBP) representing between the 21-24% of values on
14 the samples. This contribution approached the 50% for only 4 compounds
15 (i.e=DEP, DiBP, DnBP and EHDPP) which exhibited general lower concentrations
16 in the sediments, explaining this higher % with respect to the blanks. All results
17 presented are blank corrected by subtracting the corresponding mean blank value.
18 The LOQ were determined based on a signal-to-noise (S/N) ratio of ≥ 10 at the
19 lowest calibration level, and varied from 0.0001 to 0.01ng depending on the
20 compound (Table S4).

21

22 *2.7. Statistical analysis*

23

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

7

8

9 **3. Results and discussion**

10

11 *3.1. Total carbon, nitrogen and phosphorus in the sediments*

12

13 TC ranged from 1.8-12.7 %, while TOC varied between 0.3-5.4 %.
14 Relatively high TOC values were detected at stations under the influence of the
15 Rhône River (Table 2 and Fig. S1)., Our results show, however, that TOC values
16 were higher in stations with high terrestrial inputs, namely TL, HV and EQ (Fig.
17 S1). The highest N (%) values were measured at TL station, followed by those at
18 EQ and RP stations. Our results also indicate that the N (%) level decreased from
19 shore to offshore at the stations in the discharge area of the Rhône River. The
20 highest organic phosphorus values were detected at TL and JL stations, and the
21 highest inorganic phosphorus values were found at AS and EQ stations. Levels of
22 inorganic phosphorus were found to be 2-6 times higher than levels of organic
23 phosphorus at AS, RP (1-3) and EQ stations.

24

1 **Table 2**

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

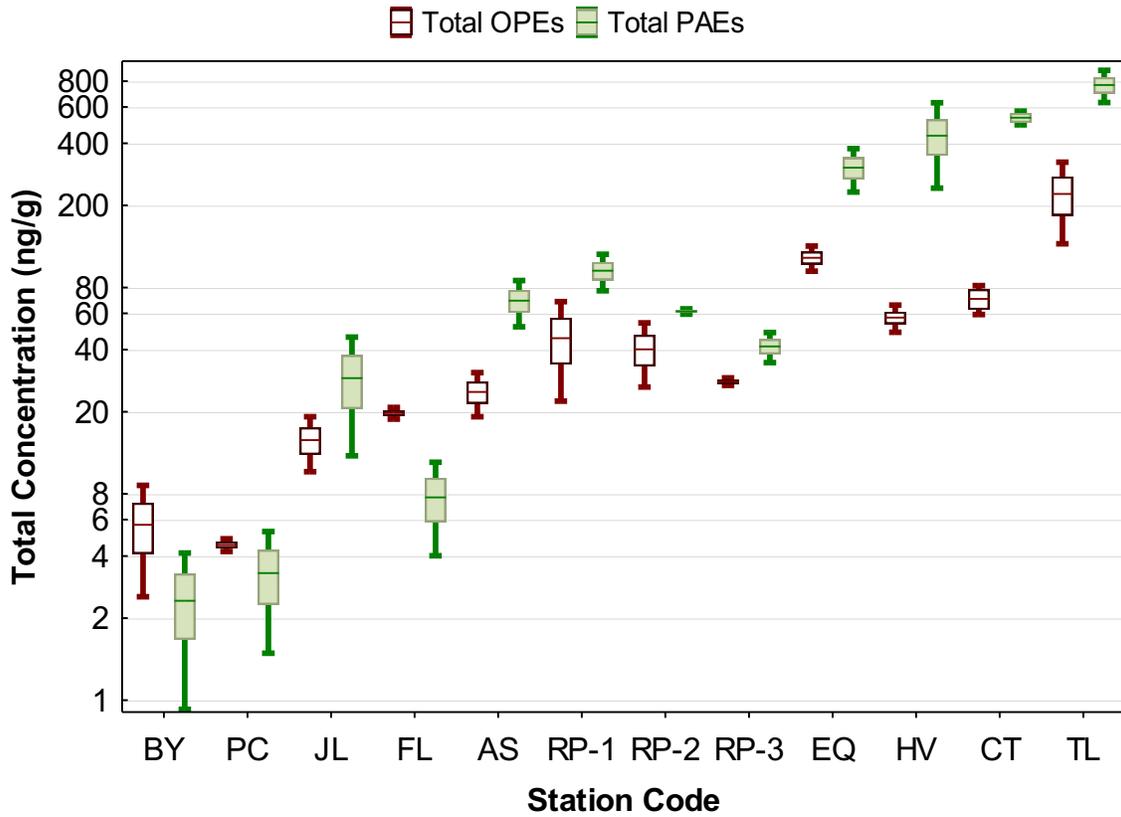
4 *3.2. Environmental levels and relative abundances*

5

6

7 Σ PAEs and Σ OPEs sediment concentrations in the Gulf of Lion ranged from
8 2 to 766 ng/g DW (av. 196 ng/g DW) and from 4 to 227 ng/g DW (av. 54 ng/g DW),
9 respectively (Table 1, Fig. 2, Figs. S2a-S2b; Tables S5-S6). Σ PAE and Σ OPE
10 showed higher concentrations in areas subject to substantial anthropogenic
11 activities such as the military port of Toulon (TL), Marseille's Huveaune River
12 mouth (HV) and the Cortiou Wastewater Treatment Plant (WWTP) discharge area
13 (CT), as well as the harbor at Estaque (EQ), just next to Marseille (Figs. S3-S4).
14 Lower concentrations were found in more remote areas including the Port-Cros
15 (PC) Marine Protected Area, Banyuls Bay (BY), Frioul Island (FL) off Marseille and
16 at the offshore Julio (JL) station (Figs. S3-S4). It should be noted that sediment
17 concentrations of Σ PAE and Σ OPEs decreased from shore to offshore at all
18 stations near the Rhône River mouth (RP stations), highlighting the inputs of

1 additives associated with the sedimentary material transported by this river.
 2 Furthermore, this dilution gradient suggests the efficient dispersal of additives in
 3 the sediments across the Rhône's discharge area.



4
 5 **Fig. 2.** Σ PAEs and Σ OPEs in sediment samples across the Gulf of Lion in the NW
 6 Mediterranean Sea (the Y axis is a logarithmic scale). **BY:** Banyuls, **AS:** Arles
 7 (Rhône River), **RP-1:** Rhône plume-1, **RP-2:** Rhône plume-2, **RP-3:** Rhône
 8 plume-3, **HV:** Huveaune River, **JL:** Julio, **TL:** Toulon, **PC:** Port-Cros, **CT:** Cortiou,
 9 **FL:** Frioul, **EQ:** Estaque (AS and HV= rivers, JL= offshore site, others= coastal
 10 marine sites).

11

1 Total PAE (\sum_6 PAEs) concentrations (DEP, DiBP, DnBP, BBP, DCHP, and
2 DEHP) were reported at similar levels (1.37 to 24.6 ng/g DW) in the sediments
3 from the Bohai and Yellow Seas (Mi et al., 2019), and at slightly higher levels (17-
4 530 ng/g DW) for the Jiulong River (Li et al. 2016). The highest concentrations
5 (2.27 μ g/g to 74.94 μ g/g DW) were reported for the \sum_{16} PAEs concentrations of
6 sediments from Guangzhou lakes (Zeng et al., 2008). In another study,
7 concentrations of total PAEs of sediments from the Guanting Reservoir and the
8 Yongding River, Beijing, China were determined at between 478 and ~2120 ng/g
9 DW, with an average of 1137 ng/g DW (Wang et al., 2006). \sum PAE were found in
10 the range of 654-2603 ng/g DW in Hungzhou Bay, Taizhou Bay and Wenzhou Bay
11 sediment in East China Sea (Hu et al., 2020). \sum PAE concentrations were
12 determined range from 462.1-15133 ng/g DW Jiaozhou Bay in China (Zhang et
13 al., 2020). In our study, the maximum \sum PAE concentrations detected at the
14 stations in the Gulf of Lion ranged from 2 to 766 ng/g DW. However, data
15 comparability can be very tricky, so these comparisons must be interpreted very
16 carefully. Factors like the differential content and type of OC in the sediment could
17 explain part of the variability among different geographical areas. In addition, not
18 all the studies measured the same type and number of PAEs.

19 We found that DEHP was generally the most abundant PAE in the study
20 area, representing 6-98 % (av. 67) of the \sum PAEs (Fig. 3a) and being slightly less
21 abundant at the three other sites (i.e. BY, EQ, TL) (Figs. 3a-3b and Tables S5 and
22 S6). Indeed, the relative abundance of DnBP was greater than 50 % at TL and EQ
23 stations, whereas at BY, DiBP represented 46 % of the sum of PAEs. The relative

1 abundance of DMP at FL and PC stations and of DEP at BY and PC stations was
2 significantly higher ($p < 0.05$) than values at other stations (Table S5, Fig. 3a).
3 Relative abundances of BBzP, DnOP, DiBP and DEP in the more pristine stations
4 (BY, PC, JL, FL) were higher than values detected at other stations that are more
5 exposed to anthropogenic pressures. The relative abundance of DEHP was found
6 to be as high as 90% and 98% in HV and CT stations, respectively: these two
7 stations are both close to urban centers and are affected by associated pressures
8 (Table S7). DEHP was also largely predominant (50-70%) at the stations in the
9 Rhône River and at those in its area of influence. The relative abundance of DnBP,
10 another dominant PAE compound, was found to be 54 % and 65 % at EQ and TL
11 stations, respectively (Table S5, Fig. 3a). DEHP was also shown to be the most
12 abundant PAE in the sediments of the Bohai and Yellow Seas (with maximum
13 DEHP concentrations of 15.9 ng/g DW and 15.6 ng/g DW, respectively, Mi et al.,
14 2019), as well as in the sediments of Taihu Lake, China (Wang et al., 2003), of the
15 Qiantang River, China (Sun et al., 2013), and of the Pearly River, China (Liu et al.,
16 2014) where concentrations were 10 times higher.

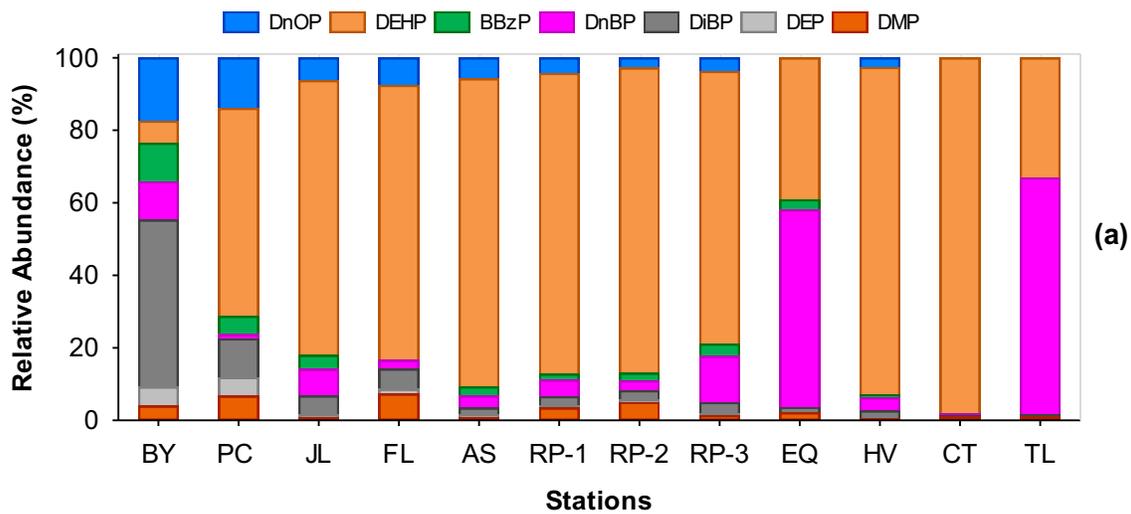
17 Concerning OPEs, total concentrations (Σ OPE) found in the Gulf of Lion
18 stations were in line with or slightly higher than those reported in previous studies
19 including Ontario, Lakes and Superior (Canada) and Michigan (USA), Lake Taihu,
20 China (lake surface sediments (2.16-16.6 ng/g DW; Cao et al., 2012, 2017), the
21 Evrotas River Basin, Greece (10.4 ng/g DW; Giulivo et al., 2017), the North Pacific
22 Ocean and Arctic Ocean (0.878 ng/g DW; Ma et al., 2017), the Yellow Sea (0.411
23 ng/g DW; Zhong et al., 2018), the coasts and rivers of Taiwan (7.38 ng/g DW;

1 Chung & Ding, 2009), and the northern part of the East Chinese Sea (12.7 ng/g
2 DW; Liao et al., 2019). Similar or higher average OPEs concentrations were
3 reported in sediments from Lake Shihwa (inshore; 31.1 ± 15.6 ng/g DW and
4 offshore region; 16.6 ± 15.7 ng/g DW), from surrounding creeks (1200 ± 1337 ng/g
5 DW) and from sediments sampled next to a submarine WWTP outfall (26.2 ± 22.4
6 ng/g DW) in South Korea (Lee et al., 2018).

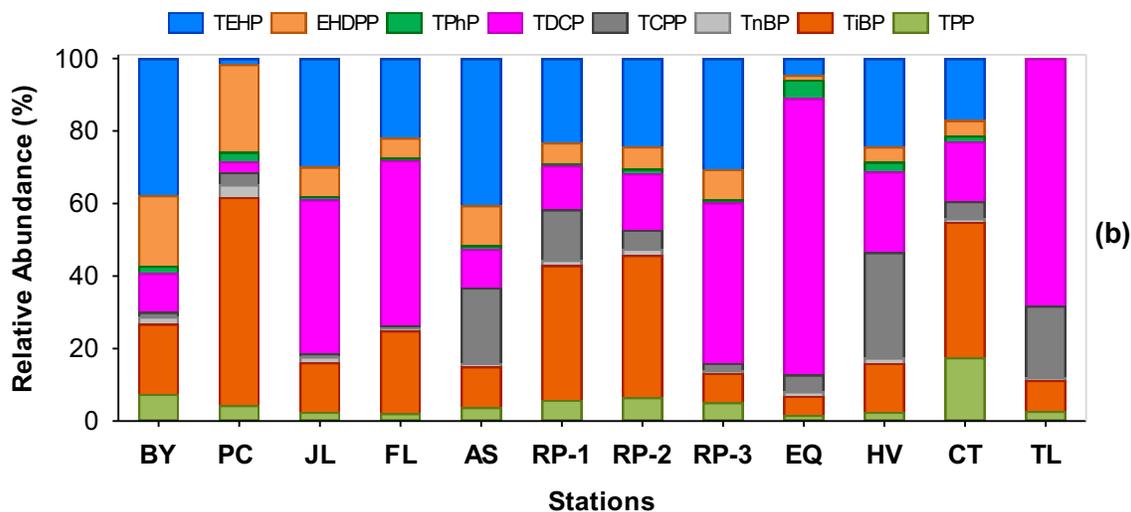
7 Our results indicate that in the studied areas, TDCP, TEHP and TiBP were
8 the most abundant OPEs (Fig. 3b). TDCP peaked at EQ (76 %), TL (68 %) and
9 FL (45 %) stations. The relative abundance of TCPP was 29 % at HV, 20 % at AS
10 and 19 % at TL stations. Relative abundance of TCCP decreased from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

16 When all the stations are taken into consideration, TDCP stands out as the
17 dominant OPE. However, dominant species diversity exceeded the PAE profile.
18 The relative abundance of TCPP decreases from shore to offshore in the Rhône
19 River and the stations the river impacts (Fig. 3b). TCEP and TiBP were found to
20 be the most abundant OPEs in the North Pacific and the Arctic Ocean sediments
21 (Ma et al., 2017), whereas TiBP was shown to be the most common OPE
22 compound in sediment core samples on the northern Chinese coast (Liao et al.,
23 2019).

1



2



3

4 **Fig. 3.** Relative abundance of PAEs (a) and OPEs (b) in sediments from the
5 different stations in the Gulf of Lion in the NW Mediterranean. **BY:** Banyuls,
6 **AS:** Arles (Rhône River), **RP-1:** Rhône plume-1, **RP-2:** Rhône plume-2, **RP-**
7 **3:** Rhône plume-3, **HV:** Huveaune River, **JL:** Julio, **TL:** Toulon, **PC:** Port-Cros, **CT:**
8 Cortiou, **FL:** Frioul, **EQ:** Estaque (AS and HV= rivers, JL= offshore site, others=
9 coastal marine sites).

10

1

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

16 In this study we determine a wide range of pollutant ratios for the marine
17 environment in accordance with many factors such as sediment origin (river/sea),
18 distance from the shore, and anthropogenic pressure. The TCPP/TDCP ratio was
19 higher in river sediments than in marine sediments. The value of DnOP/DiBP in
20 the Rhône River decreased threefold from shore to offshore. Our results show that
21 the TiBP/TnBP ratio was about 10 and that the TEHP/EHDPP ratio was about 3-4
22 in sediment samples from most of the stations. The DEHP/DnBP ratio was greater
23 than 20 at the stations close to the river mouth and exceeded 100 at CT station.

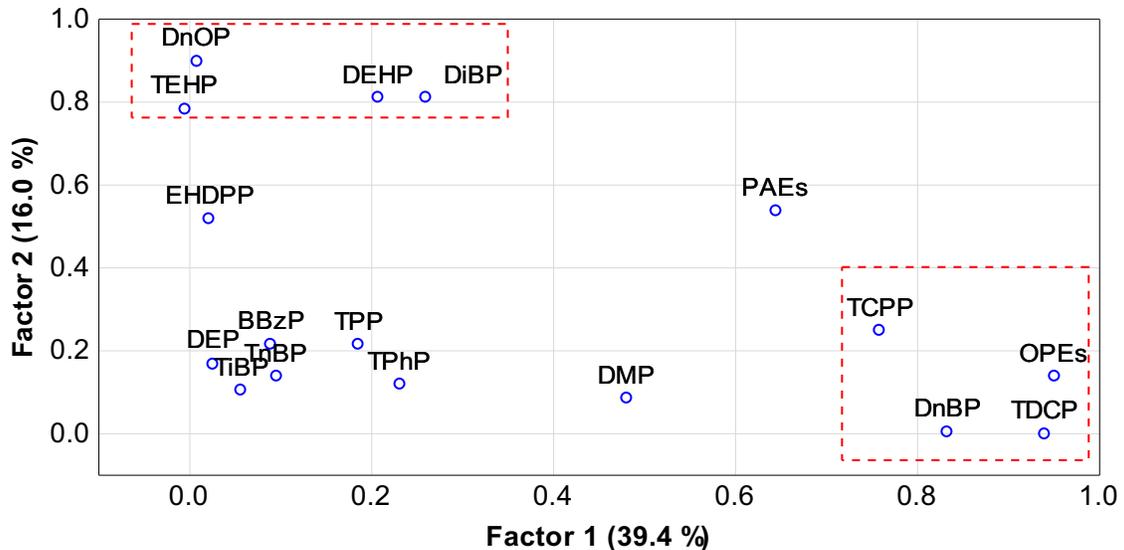
1 The DEHP/DiBP ratio was greater than 20 at most of the stations and exceeded
2 400 at CT station. The DnBP/DEHP ratio was approximately twice as high at EQ
3 and TL stations where industrial activities are widespread.

4

5 3.3. Potential sources in the study area

6

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



13

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

15

1 The first factor, which can be defined as port-based industrial pollution,
2 accounts for 39 % of the total variance and focuses heavily on Σ OPEs, TDCP,
3 DnBP and TCPP mainly at TL station (a closed harbor/military port) and EQ station
4 (Estaque), near Marseille's commercial port/harbor. Generally speaking, ports and
5 harbors exert an important environmental impact due to naval construction,
6 maintenance and repair. In addition to these activities, numerous important
7 environmental pollution problems occur during routine operations. These include
8 the leaching of chemicals from antifouling paints, accidental spills of hydraulic fluid
9 or lubricant oil from operational devices, and the discharge of hazardous waste
10 (Čulin & Bielić, 2015; Tornero & Hanke, 2016). Toulon Bay, which makes a
11 maximum contribution to Factor 1, is a semi-enclosed bay accommodating several
12 sources of anthropogenic pollution, notably a) harbor, urban, industrial,
13 agricultural, and tourism activities (Pougnnet et al., 2014; Tessier et al., 2011; Duc
14 et al., 2015) and b) the two urbanized river (Eygoutier R, Las R) outlets (Dang et
15 al., 2018). The second major contribution to Factor 1 is Estaque (EQ) station,
16 located next to the port of Marseille which is France's busiest oil port and most
17 important commercial center. Indicator parameters of Factor 1 are TDCP and
18 TCPP (OPEs with low K_{ow}), and DnBP: all are used as flame retardants and
19 plasticizers in industry (Andresen & Bester, 2004). Plasticizers are also used in
20 antifouling paints at a rate of 2% due to their flexibility and durability in a wide
21 variety of industrial and consumer products, including paints (Faÿ et al., 2019). In
22 addition, they are also used as anti-foaming stabilizers and as additives to floor
23 polishes, lubricants, lacquers and hydraulic fluids (Marklund et al., 2005).

1 The second factor represents 16 % of the total variance and concerns
2 DnOP, DEHP, DiBP, and TEHP, contaminants with a high log Kow value (≥ 7.6)
3 and HMW (except DiBP: log Kow=4.1), primarily at HV and CT stations. The
4 Huveaune River is one of the most polluted rivers in the Mediterranean Basin
5 (Kanzari et al., 2014) with several sources of pollution including a very high degree
6 of urbanization as well as the presence of both heavy industry and intense
7 agricultural activity. Marseille's Cortiou WWTP is the largest in the region (Kanzari
8 et al., 2014). Some pollutants in Mediterranean sediments are thought to have
9 discharged via the Huveaune River after passing untreated through the Cortiou
10 sewage outlet discharge during episodes of high rainfall (Kanzari et al., 2014). In
11 our study, the highest organic carbon values in sediments were found at Huveaune
12 (HV) station. The high log K_{ow} of DnOP, DEHP, and TEHP compounds underlines
13 their tendency to be adsorbed on particulate matter. F2 can be explained by the
14 interaction of PAE and OPE compounds of similar environmental sources and
15 behavior: both are urban-based anthropogenic in origin (such as car wash
16 detergents/ cleaning materials/ sewage) and are linked to the high particulate
17 matter transported by the rivers.

18 Factor 3 represents 12 % of the total variance and relates to BBzP, which
19 exhibits the highest concentrations at Estaque (EQ) and Huveaune (HV) stations.
20 Over 90% of BBzP is used for the plasticizing of PVC or other polymers with
21 consumer and industrial applications, such as floorings, sealants, adhesives,
22 caulking, coatings and paints (Koch et al., 2007). Factor 3 can be therefore linked
23 to industrial applications of this additive, which finds its way into urban effluent.

1 The other factors accounted for ≤ 10 % of the total variance and were not
2 considered as driving factors of the occurrence of PAE and OPEs in the area.

3

4 **4. Conclusions**

5

6 This work represents the first study of the environmental occurrence and
7 spatial patterns of PAEs and OPEs in sediments across the Gulf of Lion in the NW
8 Mediterranean Sea. High levels of some PAE and OPE compounds have been
9 detected, with DEHP and DnBP being identified as predominant PAEs and TDCP
10 and TiBP as predominant OPEs within the study area. Our analysis of potential
11 sources of these families of organic plastic additives points to port-based industrial
12 activities and urban pressures as the dominant factors affecting their occurrence
13 and environmental distribution in sediments of the Gulf of Lion. The TCPP/TDCP
14 ratio appears as a good indicator for riverine inputs of OPEs associated to
15 sedimentary material, exhibiting higher values in riverine rather than in marine
16 sediments. In addition, DEHP/DnBP and DEHP/DiBP ratios may provide useful
17 information on WWTP inputs of PAEs. Our study shows that the Rhône River
18 inputs of these two families of organic plastic additives are not only associated to
19 their transport via surface waters as recently reported, but also to riverine
20 sediments, providing important data for a more accurate estimation of their global
21 inputs by the Rhône River, which is the main freshwater source in the NW
22 Mediterranean Sea. However, concentrations of these additives decrease from

1 shore to offshore at the Rhône River stations indicating an efficient dilution of the
2 contaminants accumulated at the river mouth area

3 .

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16

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