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## Organophosphate esters (OPEs) in the marine environment: Spatial distribution and profiles in French coastal bivalves

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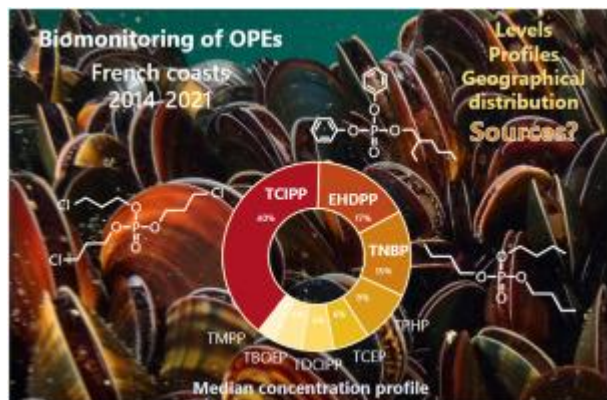
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### Abstract :

Organophosphate esters (OPEs), chemicals widely used in industrial production, electronics and domestic products, have become ubiquitous environmental contaminants. In this study, the levels and spatial distribution of 11 OPEs (aryl, alkyl and halogenated) were investigated in over 100 samples of filter-feeding bivalves collected yearly between 2014 and 2021 at sites of contrasted pressure along the French coasts. OPEs were found in virtually all samples, indicating their widespread spatial and temporal occurrence in coastal bivalves and the relevance of their biomonitoring. The median concentrations were between 0.4 (TMPP) and 4.9 ng g<sup>-1</sup> dry weight (TCIPP), with TCIPP, TNBP and EHDPP found at the highest median values. TCEP and TBOEP were not frequently detected overall, but each year, the same sites showed repeatedly high concentrations. Structurally-related OPEs generally correlated, but the geographical distributions were not predictable from known anthropogenic pressures (population in the catchment area, industry), with little comparability with other hydrophobic contaminants. If the relation between sources of OPEs and bioaccumulated levels remains uncertain, local hotspots, rather than riverine/atmospheric transportation, could account for their geographical distribution. A systematic review of the levels of OPEs found in filter-feeding bivalves worldwide revealed comparable levels in our study with those reported elsewhere; however, the levels across and within (when available) studies generally spanned several orders of magnitude, indicating high spatial and temporal heterogeneity. In view of the growing concerns regarding OPEs, this study provides essential reference data for future studies of their occurrence on European coasts and supports the need for a more systematic (bio)monitoring of this class of contaminant.

## Graphical abstract



## Highlights

► Investigation of OPEs in bivalves from French coasts collected between 2014 and 2021. ► TDCIPP, TPHP and TNBP found in over half of the samples. ► Highest median concentrations were found for TCIPP, EHDPP, and TNBP. ► OPE profiles are site-specific. ► OPE spatial distribution differs from that of other bioaccumulative contaminants.

**Keywords** : Coastal marine environment, Bioaccumulation, Shellfish, Flame retardants, Plasticizers

## 48 **1. Introduction**

49 Organophosphate esters (OPEs), chemicals used as flame retardants, plasticizers, antifoaming  
50 agents, lubricants, and hydraulic fluids, have been extensively added to a variety of  
51 commercial products like plastics, textiles, electronics, and building materials (van der Veen  
52 and de Boer, 2012; Wei et al., 2015). In 2006, the total consumption of flame retardants in  
53 Europe was estimated to be 465,000 tons, 20% of which were OPEs (93,000 tons) (van der  
54 Veen and de Boer, 2012). The global market volume of OPEs was estimated to be 620,000  
55 tons in 2013 (Sühling et al., 2016); in 2022, OPEs are still assumed to account for  
56 approximately 15% of the total flame-retardant market (Xie et al., 2022). With over 1,000  
57 tons imported and/or produced in the European Union per year, several OPEs are considered  
58 high production volume (HPV) chemicals, including: triethyl phosphate (TEP), tri-n-butyl  
59 phosphate (TNBP), tris(2-butoxyethyl) phosphate (TBOEP), tris(2-ethylhexyl) phosphate  
60 (TEHP), tris(1,3-dichloro-2-propyl) phosphate (TDCIPP), tri-phenyl phosphate (TPHP), tri-  
61 methylphenyl phosphate (TMPP), and 2-ethylhexyl diphenyl phosphate (EHDPP). Beside  
62 their high usage, OPEs are suspected to exert toxic effects on humans and ecosystems (Wei et

63 al., 2015). OPEs have been proposed as an alternative to brominated flame retardants (BFRs),  
64 since the production and use of several BFRs, including penta-, octa-, and decabromodiphenyl  
65 ethers (PBDEs) have been banned for their persistence, toxicity, and bioaccumulation  
66 (Stockholm Convention, 2009; van der Veen and de Boer, 2012). Unlike BFRs, OPEs differ  
67 widely in their structures and chemical and physical properties, resulting in potentially  
68 contrasted environmental behaviour within this class. OPEs span log  $K_{ow}$  from 0.8 for TEP to  
69 9.49 for TEHP (Reemtsma et al., 2008). Light-weight OPEs, such as TEP and tris(2-  
70 chloroethyl) phosphate (TCEP), have high volatility, with a vapor pressure higher than that of  
71 naphthalene (a known volatile contaminant) and 6 orders of magnitude higher than the least  
72 volatile of the HPV OPEs, TMPP and TEHP (van der Veen and de Boer, 2012). The soil  
73 adsorption coefficient and bioconcentration factors computed in their study also showed a  
74 wide range of values.

75 OPEs are released from consumer and industrial products to the environment by  
76 volatilization, leaching, and abrasion (Xie et al., 2022). Emissions from direct industrial  
77 inputs, wastewater treatment facilities, and e-waste recycling activities are of importance, and  
78 their relative contributions depend on the anthropogenic pressures on a given watershed (Liu  
79 et al., 2022; Wei et al., 2015). To better apportion OPE sources in the Guangdong-Hong  
80 Kong-Macao Greater Bay (China), the correlations between water concentrations from 16  
81 sites were tested against several socio-economic indicators (Gao et al., 2021). The authors  
82 showed that population density, wastewater discharge, manufacturing industry, construction  
83 industry, vehicles, and shipping transport were determinants of OPE levels. In addition to  
84 these multiple sources, leaching from plastic debris is also a speculated source (Xie et al.,  
85 2022), but a substantiated evaluation of its magnitude with regards to other sources is lacking.  
86 Riverine and atmospheric transportation, as well as direct coastal discharges, lead to their  
87 presence in the global ocean and in remote marine regions (McDonough et al., 2018).

88 First detected in river waters in the USA (Sheldon and Hites, 1978), OPEs have been  
89 reported ubiquitously in the marine environment. In surface waters of the German Bight, the  
90 total concentration of 16 OPEs ranged from 5 to 50 ng L<sup>-1</sup>, with a riverine export of 50 t y<sup>-1</sup>  
91 into the North Sea from the German tributaries alone (Bollmann et al., 2012). Concentrations  
92 of individual OPEs in harbour waters in the United Kingdom were as high as 100–260 ng L<sup>-1</sup>  
93 (EHDPP, TCIPP), with an enrichment in the surface microlayer (Aminot et al., 2017). In  
94 sediments of the Korean coast, 10 out of the 18 studied OPEs were detected with >50%  
95 detection rate, with TCIPP having the highest median concentrations of 30 ng g<sup>-1</sup> dry weight  
96 (dw) (Choi et al., 2020). With significantly higher concentrations in harbour zones, the  
97 authors identified shipping activity as a putative source of OPEs in coastal environments. In  
98 San Francisco Bay (USA), OPEs were also widely detected in sediment, particularly the most  
99 hydrophobic OPEs like TEHP (median: 8.2 ng g<sup>-1</sup> dw), TMPP (3.4 ng g<sup>-1</sup> dw) and TPHP  
100 (1.9 ng g<sup>-1</sup> dw) (Sutton et al., 2019). Water and sediment concentrations were over one order  
101 of magnitude higher for OPEs than for PBDEs.

102 Alongside hydrophobicity, metabolizability is a key driver of bioaccumulation (Walters et  
103 al., 2016). With reports of OPE biotransformation (Muir and Grift, 1981; Wang et al., 2019),  
104 there is conflicting evidence on the potential for bioaccumulation and biomagnification of  
105 OPEs, although they are found in measurable quantities in marine organisms (Xie et al.,  
106 2022). Here, we focus on bivalves, organisms of lower trophic levels which show a low  
107 ability to metabolize organic contaminants in comparison to fish and crustaceans (Farrington  
108 et al., 2016). In mussels (*Mytilus edulis*) and oysters (*Crassostrea gigas*) from Korea, 5 OPEs  
109 (TEHP, TCIPP, EHDPP, TEP and TCEP) were found in over half of the samples, with  
110 median concentrations between 0.56 and 1.4 ng g<sup>-1</sup> dw, except for TCIPP, which was found at  
111 11.7 ng g<sup>-1</sup> dw (Choi et al., 2020). In San Francisco Bay, TDCIPP was found in all 6 samples of  
112 transplanted mussels (*Mytilus californianus*) at the highest levels (median: 4.5 ng g<sup>-1</sup> dw,

113 comparable to BDE-47, 3.1 ng g<sup>-1</sup> dw), with TPHP, EHDPP, TNBP, TBOEP, and TCIPP  
114 being detected in over half of the samples (Sutton et al., 2019). In several European  
115 aquaculture sites, OPE levels were several orders of magnitude higher than other chlorinated  
116 and brominated FRs, with a predominance of TNBP in the studied mussels (Aznar-Alemany  
117 et al., 2018). Filter-feeding bivalves, particularly mussels and oysters, are widely-used  
118 organisms for the biomonitoring of bioaccumulative contaminants (Beyer et al., 2017).  
119 Beyond the commonly-monitored legacy contaminants (PCDD/Fs, PCBs, OCPs, and PAHs),  
120 contaminants of emerging concern have been included in such biomonitoring programs  
121 worldwide, ultimately contributing evidence for their widespread occurrence in biota and  
122 leading to regulations (e.g. PBDEs, HBCDDs).

123 In light of the paucity of data on OPEs in marine bivalves, we have expanded the French  
124 national biomonitoring program to this class of compounds on a yearly basis since 2017. The  
125 objective of this study was to investigate their occurrence and spatial distribution in marine  
126 shellfish collected from sites under contrasted anthropogenic pressure along French coasts.

127

## 128 **2. Materials and methods**

### 129 2.1 Chemicals and reagents

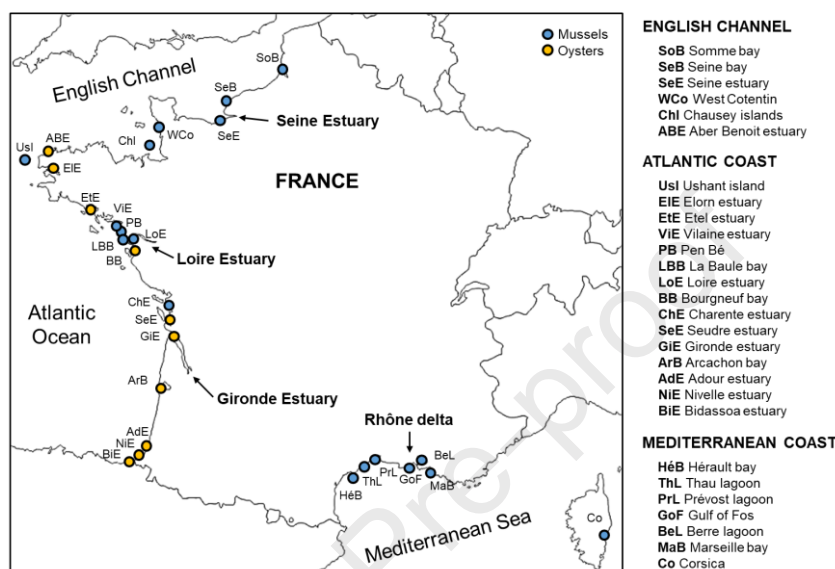
130 All chemicals were of trace analysis grade. Picograde® solvents (methanol, ethyl acetate,  
131 acetone, cyclohexane, n-hexane) and Florisil® (100–200 mesh) were purchased from  
132 Promochem (Germany) or LGC Standards (France). Aminopropyl cartridges (Discovery®  
133 DSC-NH<sub>2</sub>, 500 mg, 6 mL) and graphite cartridges (Supelclean™ ENVI-Carb™, 500 mg, 6 mL)  
134 were obtained from Merck (Darmstadt, Germany). Trimethylphenyl phosphate (TMPP),  
135 methylphenyldiphenyl phosphate (MPDPP), 2-ethylhexyldiphenyl phosphate (EHDPP),  
136 isodecyldiphenyl phosphate (IDDPP), triphenyl phosphate (TPHP), triethyl phosphate (TEP),

137 tripropyl phosphate (TPRP), tripentyl phosphate (TPEP), tri-n-butyl phosphate (TNBP), tris(2-  
138 ethylhexyl) phosphate (TEHP), tris(2-butoxyethyl) phosphate (TBOEP), tris(2-chloroethyl)  
139 phosphate (TCEP), tris(chloro-2-propyl) phosphate (TCIPP), tris(1,3-dichloro-2-propyl)  
140 phosphate (TDCIPP), tris(2,3-dibromopropyl) phosphate (TDBPP), and  
141 tris(tribromoneopentyl) phosphate (TTBNPP) were acquired from Accustandards (New Haven,  
142 USA). Triphenyl phosphate-<sup>13</sup>C<sub>8</sub> (TPHP-<sup>13</sup>C<sub>8</sub>), triphenyl phosphate-D<sub>15</sub> (TPHP-D<sub>15</sub>), triethyl  
143 phosphate-D<sub>15</sub> (TEP-D<sub>15</sub>), tripropyl phosphate-D<sub>21</sub> (TPRP-D<sub>21</sub>), tri-n-butyl phosphate-D<sub>27</sub>  
144 (TNBP-D<sub>27</sub>), tris(2-butoxyethyl) phosphate-<sup>13</sup>C<sub>2</sub> (TBOEP-<sup>13</sup>C<sub>2</sub>), tris(2-chloroethyl) phosphate-  
145 D<sub>12</sub> (TCEP-D<sub>12</sub>), and tris(1,3-dichloro-2-propyl) phosphate-D<sub>15</sub> (TDCIPP-D<sub>15</sub>) were acquired  
146 from Wellington Laboratories (Guelph, Canada). Trimethylphenyl phosphate-D<sub>21</sub> (TMPP-D<sub>21</sub>),  
147 tris(2-ethylhexyl) phosphate-D<sub>51</sub> (TEHP-D<sub>51</sub>), tris(2-butyloxyethyl) phosphate-D<sub>27</sub> (TBOEP-  
148 D<sub>27</sub>), tris(1-chloro-2-propyl) phosphate-D<sub>18</sub> (TCIPP-D<sub>18</sub>), and tris(2,3-dibromopropyl)  
149 phosphate-D<sub>15</sub> (TDBPP-D<sub>15</sub>) were acquired from TRC Canada (Toronto, Canada).

## 150 2.2 Sampling strategy

151 Mussels (*Mytilus spp*) and oysters (*Crassostrea gigas*) were collected annually in autumn (out  
152 of spawning season) from 2017 to 2021 at the same selected locations in the English Channel,  
153 the Atlantic Ocean and along Mediterranean coasts, as shown in Figure 1, for a total of 103  
154 samples (an additional 5 samples from 2014–2016 were analysed to confirm site specificities).  
155 These locations cover main estuaries and deltas (Seine, Loire, Gironde, Rhône), together with  
156 smaller tributaries and sites away from direct sources. The shellfish were collected and handled  
157 in accordance with international guidelines for the monitoring of contaminants in biota  
158 (OSPAR, 2018). Briefly, a composite sample consisted of at least 50 mussels of similar size  
159 (30–60 mm shell length) or 10 oysters (90–140 mm shell length), and each individual had spent  
160 at least 6 months *in situ* beforehand. All samples were depurated in settled water from the site  
161 for 24 h, shelled, homogenized (whole soft body), and stored at -20 °C prior to freeze-drying.

162 The average dry weight (dw) was  $19.9 \pm 5.2$  % ( $n = 108$ ), and the average total lipid content  
 163 was  $9.7 \pm 1.8$ % dw (determined gravimetrically from a dried hexane/acetone [80:20 v:v]  
 164 extract). The dried samples were stored in amber glass containers in a cool, dry, dark place until  
 165 further analysis.



166  
 167 **Figure 1.** Sampling sites for bivalves collected from 2017 to 2021 from the English Channel,  
 168 Atlantic Ocean and Mediterranean coasts.

### 170 2.3 Extraction method

171 Samples were extracted using pressurized liquid extraction (ASE350, Dionex, USA), in a pre-  
 172 cleaned 66 mL stainless steel cell, filled with: cellulose filter, Florisil (15 g, 100–200 mesh),  
 173 and dry sample (1 g). Before extraction, 5 ng ( $50 \mu\text{L}$ ,  $0.1 \text{ ng } \mu\text{L}^{-1}$  in toluene) of each labelled  
 174 standard (Table S2) were added to the sample for internal standard quantification by isotopic  
 175 dilution. The extraction cell was filled with ethyl acetate/cyclohexane (4:1 v:v) and brought to  
 176  $100 \text{ }^\circ\text{C}$  and 100 bar for a 5 min static extraction (constant P and T). Fresh solvent was introduced  
 177 into the cell (flushing volume 100%), and the extraction cycle was repeated once more. The  
 178 extraction cells were precleaned by running a first complete cycle with Florisil and no sample,



179 a step found to be essential to limit blank contamination. The extract was concentrated to 1 mL  
180 with a rotary evaporator before clean-up.

#### 181 2.4 Solid phase extraction clean-up method

182 Clean-up was performed on NH<sub>2</sub> and graphite sorbents. The NH<sub>2</sub> sorbent was conditioned with  
183 5 mL of ethyl acetate/cyclohexane (1:1 v:v) followed by 5 mL of cyclohexane. After sample  
184 loading, OPEs were eluted in two separate fractions of: (1) ethyl acetate/cyclohexane (4 mL,  
185 1:4 v:v) and (2) ethyl acetate/cyclohexane (5 mL, 1:1 v:v). Each fraction was concentrated to  
186 100 µL under nitrogen, and 1 mL of hexane/acetone (1:1 v:v) was added before loading on an  
187 ENVI-Carb sorbent (conditioned with 10 mL of acetone and 10 mL of hexane/acetone, 1:1,  
188 v/v). OPEs were eluted with 20 mL of hexane/acetone (1:1, v/v) and this fraction was  
189 concentrated to 100 µL under nitrogen and transferred to a glass injection vial. The recoveries  
190 obtained for standards on NH<sub>2</sub> and graphite sorbents are provided in Figure S1. Injection  
191 standards (Table S2) were added (5 ng), and the final extract was evaporated to dryness and  
192 further reconstituted in 100 µL of methanol and 100 µL of water.

#### 193 2.5 Instrumental method

194 Analysis of the OPEs was performed on an ultra-performance liquid chromatography (UPLC)  
195 I-Class coupled to a triple quadrupole Xevo TQS-µ (Waters, USA) using positive electrospray  
196 ionization mode (ESI+). Separation was achieved on a 50 mm x 2.1 mm BEH C<sub>18</sub> column  
197 (particle size 1.7 µm, Waters, France), maintained at 50 °C, using a gradient of methanol and  
198 ammonium acetate (20 mM) at a flow rate of 0.5 mL/min. The gradient from solvent A  
199 (ammonium acetate 20 mM) to solvent B (100% methanol) was as follows: 0 min (25% B), 0.5  
200 min (25% B), 5 min (85% B), 5.1 min (100% B), 6 min (100% B), 6.1 min (25% B), 9 min  
201 (25% B).

202 The mass spectrometric detection was completed in multiple reaction monitoring (MRM) mode  
203 (Table S2), with the following source parameters: capillary voltage 3 kV, cone voltage 10 V,  
204 and desolvation flow 900 L/hr.

205

## 206 2.6 Method validation, quality assurance and quality control

207 The method was validated according to the accuracy profile procedure (NFT90-210, 2009).  
208 Briefly, it consisted of assessing the accuracy of the calibration function, the intermediate  
209 precision, and bias and comparing it to tolerance intervals (more details in supplementary  
210 information Text S1 and S2, Table S3). Validation criteria were met for 11 of the 16 targeted  
211 OPEs. With high absolute bias for TPEP, IDDPP and MPDPP, their analysis was considered  
212 semi-quantitative only. In addition, TEHP and TTBNPP were not detected because of an  
213 important matrix effect.

214 The method limit of quantification (LOQ), as per the EU commission regulation 2017/644, is  
215 defined for each analyte in each sample as the concentration for which the instrumental response  
216 of the less sensitive MRM transition yields a S/N (signal/noise) ratio of 3:1 (Table 1). TBOEP,  
217 TCIPP, TPHP, and TDCIPP have been commonly detected at high levels ( $>1 \text{ ng m}^{-3}$ ) in both  
218 indoor particulate and gas phases (Brandsma et al., 2013; Brommer et al., 2014). OPE glassware  
219 contamination can be expected from deposition from ambient air and potential carryover. All  
220 glassware was treated at 450 °C overnight and pre-cleaned with ethyl acetate before use. The  
221 entire sample preparation and subsequent analyses were performed in clean laboratories, under  
222 a low-dust atmosphere and positive pressure (ISO 8 class according to NF EN ISO 14644). As  
223 contamination can also come from the detection system itself (Brandsma et al., 2013), a delay  
224 column was installed between the pump and the injector to separate instrument-related peaks  
225 from the actual sample peaks. This approach, commonly used in the analysis of analyses

226 perfluoroalkyl substances (PFAS), was successfully implemented for OPEs here (see Figure  
227 S2). Procedural blanks (excluding sampling, freeze-drying and homogenization) were  
228 extracted, purified, and analyzed within each sample batch. Concentrations in samples were  
229 corrected for blank contamination: the mass of analyte (ng) found in the blanks was subtracted  
230 from the mass (ng) found in the samples, provided that the analyte mass in the sample was  
231 above 3 times that of the blank. According to the EU commission regulation 2017/644, the  
232 reporting level shall be demonstrated to be different from the procedure's blank samples at least  
233 by a factor of three. The LOQ was therefore fixed at three times the value of blank.

234 In addition to the initial method validation described in SI Text S2, one in-house spiked  
235 reference material was extracted for each batch of 10–12 analyses, with overall deviation  
236 between 7% (TNBP) and 48% (TDBPP). In all samples together ( $n = 108$ ), the labelled internal  
237 standards were recovered with a mean between 24% (TMPP-D<sub>21</sub>) and 137% (TNBP-D<sub>27</sub>),  
238 indicative of a matrix effect. Laboratory blank levels (8 blanks processed in total) were between  
239 73 pg g<sup>-1</sup> dw (TMPP) and 1379 pg g<sup>-1</sup> dw (TCIPP), with acceptable repeatability over the 5  
240 years of analysis (23%–88%). The highest values (>500 pg) were observed for the chlorinated  
241 OPEs TCIPP and TCEP, TEP and TNBP (alkyl), and EHDPP (aryl). These values led to LOQs  
242 higher than those strictly instrument-derived and ranged on average from 54 pg g<sup>-1</sup> dw (TPRP)  
243 to 3089 pg g<sup>-1</sup> dw (TCIPP). Blank contamination (see Figure S3) was partly attributed to the  
244 contribution of the solvents used and concentrated in the final extract as between 5% (TBOEP)  
245 and 64% (TCEP) of the blank contamination could be traced to the solvents. The levels of OPEs  
246 found after evaporation of an ASE cell blank, without Florisil, were not significantly different  
247 from the levels found after evaporation of the same volumes, without running through the ASE  
248 system, suggesting its minimal contribution. Analysis of diatomaceous earth (Hydromatrix,  
249 Agilent Technologies) exposed prior to sample extraction revealed that neither sampling,  
250 handling or freeze-drying caused a significant contamination of the samples (Figure S4).

251

252 Table 1. QA/QC parameters: labeled compound recoveries, limits of quantification (LOQs) resulting  
 253 from blank contamination, LOQs extrapolated from the method sensitivity, and detection frequencies  
 254 per contaminant.

| Individual compound | n samples / n batches | <sup>2</sup> H / <sup>13</sup> C standard recoveries | LOQ blank             | LOQ method            | Detection frequency |
|---------------------|-----------------------|--|-----------------------|-----------------------|---------------------|
|                     |                       | (%)  | pg g <sup>-1</sup> dw | pg g <sup>-1</sup> dw | (%)                 |
| TEP                 | 108 / 12              | 80 ± 15  | 678 ± 677             | 223 ± 30              | 0                   |
| TPRP                |                       | no labelled std                                      | not found in blanks   | 54 ± 38               | 0                   |
| TNBP                |                       | 137 ± 53   | 669 ± 223             | 27 ± 2                | 61                  |
| TBOEP               |                       | 98 ± 16  | 254 ± 130             | 53 ± 3                | 13                  |
| TCEP                |                       | 65 ± 17  | 994 ± 910             | 53 ± 3                | 37                  |
| TCIPP               |                       | 73 ± 17  | 3089 ± 1158           | 214 ± 14              | 42                  |
| TDCIPP              |                       | 64 ± 24  | 252 ± 107             | 53 ± 3                | 85                  |
| TDBPP               |                       | 44 ± 23  | not found in blanks   | 95 ± 33               | 0                   |
| TPHP                |                       | 80 ± 9   | 281 ± 96              | 53 ± 3                | 69                  |
| TMPP                |                       | 24 ± 9   | 159 ± 81              | 88 ± 51               | 43                  |
| EHDPP               |                       | no labelled std                                      | 806 ± 208             | 107 ± 7               | 37                  |

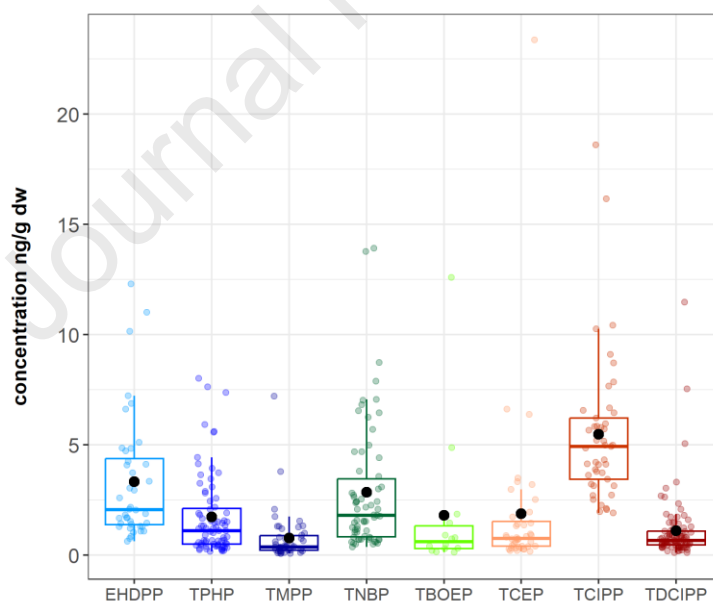
255

### 256 3. Results

#### 257 3.1 Levels and profiles of OPEs

258 Among the 103 samples analysed over the 5-year study, TDCIPP, TPHP, and TNBP were quantified  
 259 in over half of the samples (detection frequency, DF: 85%, 69%, and 61%, respectively), TMPP,  
 260 TCIPP, TCEP and EHDPP in 37%–43%, and TBOEP in 13% of the samples (DFs). OPEs were not  
 261 quantified in only 3 samples, indicating their widespread occurrence. The highest median  
 262 concentrations (Figure 2) were found for TCIPP at 4.93 ng g<sup>-1</sup> dw (range: 1.9–18.6 ng g<sup>-1</sup> dw), EHDPP  
 263 at 2.07 ng g<sup>-1</sup> dw (range: 0.6–12.3 ng g<sup>-1</sup> dw), and TNBP at 1.82 ng g<sup>-1</sup> dw (range: 0.4–13.9 ng g<sup>-1</sup> dw).  
 264 As reported by the European Chemicals Agency (ECHA; <https://echa.europa.eu/>), these higher  
 265 concentrations are consistent with their usage in Europe (TCIPP reported at 10 000–100 000 t y<sup>-1</sup> in  
 266 2018 [no production/import reported in 2022]; TNBP and EHDPP tonnage band 1,000–10,000 t y<sup>-1</sup> in  
 267 2022). Conversely, the absence of the bromine-containing TDBPP is consistent with its heavy

268 restrictions in the EU; this compound is indeed rarely found in the environment or at very low  
269 concentrations (Allan et al., 2018). Also undetected despite high production/import tonnage (>10,000 t  
270  $y^{-1}$  for TEP), the alkyl OPEs TEP and TPRP, have low  $\log K_{ow}$  (0.8 and 1.87, respectively), suggesting  
271 lower bioaccumulative tendencies (Mackay and Fraser, 2000). However, the chlorinated OPEs (TCEP,  
272 TCIPP, and TDCIPP) are also of relatively low  $\log K_{ow}$  (1.47, 2.59, and 3.27, respectively) but were  
273 found in our study at relatively higher concentrations and/or detection frequencies. This observation  
274 suggests that hydrophobicity only is insufficient to describe their bioaccumulation or that levels in  
275 surrounding waters are high. The field-derived bioconcentration factor (BCF) of TCEP in zooplankton  
276 has also been reported to be one of the highest among the monitored OPEs (Schmidt et al., 2021),  
277 whilst no relationship was found between BCFs and  $\log K_{ow}$ . In Korean coastal waters, the biota-  
278 sediment accumulation factor calculated for TCEP in mussels and oysters was higher than those  
279 determined for TEP, TCIPP, and TEHP (Choi et al., 2020), suggesting the peculiarity of this  
280 compound.



281  
282 Figure 2. Concentration ( $ng\ g^{-1}\ dw$ ) distributions of the OPEs found in coastal bivalves of the French  
283 coasts above LOQs ( $n = 14$  [TBOEP] to 92 [TDCIPP]). The black circles represent the mean value for  
284 individual OPEs.

285

286 Statistically significant correlations (Spearman's rank correlations) were generally observed for  
287 structurally-related OPE concentrations. In particular, all three aryl OPEs were correlated, suggesting  
288 similar sources and/or environmental behaviour (Table S4), with TMPP and TPHP having the  
289 strongest correlations ( $\rho = 0.69$ ,  $p < 0.0001$ ; compounds co-occurring in 39% of the samples). Other  
290 significantly correlated OPEs were TCIPP and TDCIPP ( $\rho = 0.43$ ,  $p = 0.004$ ; co-occurrence 40%),  
291 TPHP and TNBP ( $\rho = 0.41$ ,  $p = 0.002$ ; co-occurrence 50%), and TCEP and EHDPP ( $\rho = -0.671$ ,  $p =$   
292  $0.02$ , but co-occurrence only 11%). In a previous study, it was found that similar OPEs to those  
293 studied here did not correlate in bivalve tissues, even if they had strong positive correlations in the  
294 surrounding sediments, a result attributed to their likely rapid biotransformation (Choi et al., 2020).  
295 Similarly, the significant correlation observed between the chlorinated OPEs TCEP, TCIPP, and  
296 TDCIPP, in the dissolved phase were not found in mussel tissues nor in harbour seal blubber from San  
297 Francisco Bay (Sutton et al., 2019). If the existence of OPE-specific differences in biotransformation  
298 kinetics is a plausible hypothesis, it may also relate to the range of log  $K_{ow}$  (and subsequent  
299 bioaccumulation factor, BAF) spanned by the whole family, as compounds with higher BAF take  
300 longer to reach steady state. This would cause compound-specific exchange kinetics between bivalves  
301 and the dynamic tidal waters and confound relative concentrations in water vs. in bivalves. In our  
302 study, the correlation found between TCIPP and TDCIPP still suggests some similarities in their  
303 partition behaviour. Regarding aryl OPEs, concentrations of MPDPP and IDDPP were not calculated  
304 because of their low accuracy in our method (see Section 2.6); however, it is noteworthy that the  
305 highest signals for these aryl compounds were measured in samples with high  $\sum$ aryl OPE levels  
306 (TPHP, EHDPP, TMPP). A Mann-Whitney non-parametric test indicates significantly higher TPHP  
307 levels ( $p = 0.0002$ ) in those 59% of samples for which MPDPP was also qualitatively detected in  
308 comparison with those where it was not. The same difference was observed when considering the 18%  
309 of samples in which IDDPP was also detected ( $p = 0.003$ ).

310 OPEs were the most abundant of all hydrophobic contaminants analysed in the same samples (for  
311 further details, refer to Aminot et al., 2021; Munschy et al., 2019, 2015, 2013), with concentrations  
312 decreasing as follows: OPEs > polycyclic musks ( $\text{ng g}^{-1} \text{dw}$ ); followed by: perfluorocarboxylates ( $\sum$   
313  $\text{C}_9\text{-C}_{14}$  PFCAs) > perfluorooctane sulfonate (PFOS)  $\sim$  polybrominated diphenyl ethers ( $\sum$  8 OSPAR

314 PBDE congeners) > hexabromocyclododecane (hundreds of  $\text{pg g}^{-1}$  dw); followed by: nitromusks and  
315 alternative brominated flame retardants (BTBPE, DBDPE) tens of  $\text{pg g}^{-1}$ . OPEs are rarely reported  
316 alongside other hydrophobic contaminants in the literature on mollusc contamination. When they have  
317 been, their concentrations were comparable or exceeded those of other contaminants, which is in  
318 agreement with our findings (Aznar-Aleman et al., 2018; Brandsma et al., 2015; Fu et al., 2020;  
319 Sutton et al., 2019).

320

### 321 3.2 Geographical distribution

322 The relative interquartile range (RIQR; IQR divided by the median, in percentage) was calculated to  
323 evaluate the spread of OPE concentrations over the 5-year study. The RIQR was high for the sum of  
324 all quantified OPEs (147%) and for the individual compounds EHDPP (145%), TPHP (146%), TMPP  
325 (173%), TNBP (147%), TBOEP (167%), and TCEP (146 %), indicating notable spatiotemporal  
326 variability; however, the RIQR for TCIPP and TDCIPP was 56% and 91%, respectively, indicating a  
327 more uniform distribution.

328 Interestingly, the highest concentrations of  $\sum$ OPEs were consistently found in the same sites. For each  
329 year, concentrations found in the Nivelle (NiE), Elorn (EIE), and Etel (EtE) estuaries, as well as the  
330 Arcachon Bay (ArB), were above the 3<sup>rd</sup> quartile of all measurements. Specific OPE contributions  
331 indicate different patterns in these samples (Figure 3). TNBP is abundant in these four sites with  
332 median values in the range of 1.6–7.5  $\text{ng g}^{-1}$  dw and to a lesser extent in other sites of the Atlantic  
333 coast (Vilaine: ViE; Seudre: SeE; Adour: AdE; Bidassoa: BiE; estuaries that have values above the 3<sup>rd</sup>  
334 quartile). High TNBP concentrations were also found in additional samples taken prior to 2017 in the  
335 Etel estuary (2014–2016, 3–7.9  $\text{ng g}^{-1}$  dw), in the Elorn estuary (2016, 1.8  $\text{ng g}^{-1}$  dw), and the  
336 Arcachon Bay (2016, 3.6  $\text{ng g}^{-1}$  dw), which suggests regular inputs of this contaminant in these sites.  
337 If the Nivelle and Elorn estuaries have been previously identified as sites under anthropogenic  
338 pressure (Aminot et al., 2021; Munsch et al., 2015), the case of the Etel estuary is peculiar,  
339 considering this is a site under the influence of a small rural catchment area, with no major city or  
340 particular industry, and for which the other contaminants followed in our surveys have always been  
341 low. The high TNBP concentrations detected in the above-mentioned low impacted sites warrant

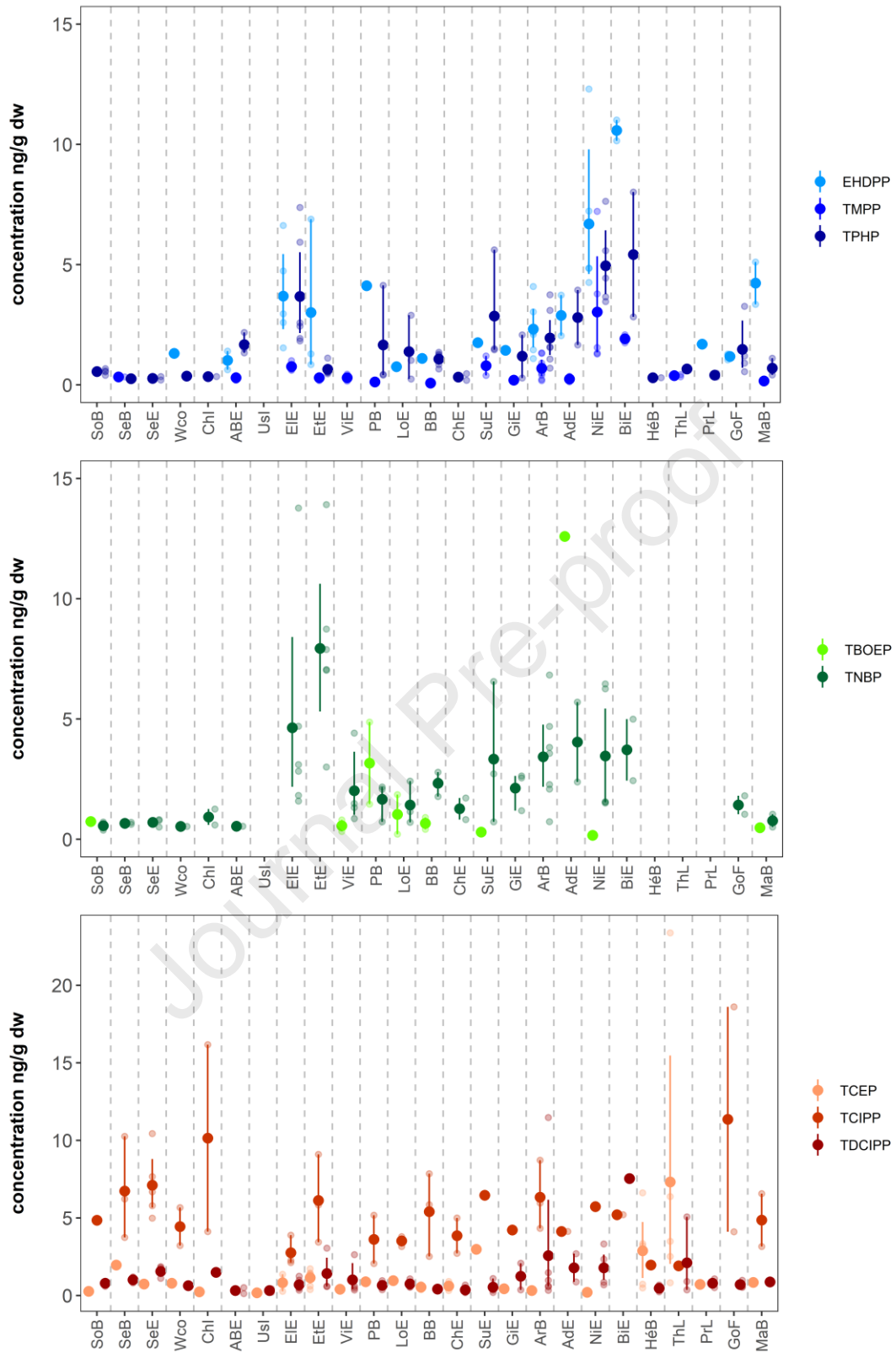
342 further research into the sources of this compound into coastal waters, as most of the industrial sources  
343 identified by Gao et al. (2021) are unlikely here. Used in particular for its thermal stability, resistance  
344 to oxidation, and viscosity, some TNBP applications include coating products, polymers, adhesives,  
345 and sealants. ECHA identified potential releases of TNBP in relation with transports (ships), and  
346 previous reviews indicate its inclusion as a plasticizer in marine paint in particular (Brigham and  
347 Landrigan, 1985). Yachting and/or shipbuilding, generally found in the previously mentioned sites, are  
348 speculative sources of these compounds to the marine environment. It is corroborated by results from  
349 Korea, where sediments from near-harbour sites showed the highest  $\Sigma$ OPE concentrations, although  
350 contributions from single compounds were not specified (Choi et al., 2020). TNBP was also  
351 predominant in coastal waters of the Beibu Gulf (China), a result attributed to lubricants used in  
352 fishing vessels (Liu et al., 2022), whilst shipping activity near Hong Kong remained a source of TNBP  
353 in the bay (Gao et al., 2021).

354 Most of the positive detections of the other alkyl OPE, TBOEP, occurred in four neighbouring sites on  
355 the Atlantic coast (8 out of the 14 > LOQ), with consistently high concentrations in the site Pen-Bé  
356 (PB) and generally low levels of other monitored contaminants. The specific sources of TBOEP in this  
357 area need investigation, as none of its described uses clearly relate to local activities (used in washing  
358 and cleaning products, polishes and waxes, as a plasticizer in vinyl plastics and rubber stoppers, in  
359 plant protection products and water treatment chemicals, ECHA). Consistently high concentrations of  
360 TCEP occurred in the Hérault Bay (HéB, range: 3.2–23.4 ng g<sup>-1</sup> dw) and the Thau Lagoon (ThL,  
361 range: 0.49–6.4 ng g<sup>-1</sup> dw), two neighbouring Mediterranean sites of otherwise low OPE  
362 contamination. This high level of concentrations in mussel tissues is noteworthy considering its near-  
363 absence in most sites. Identified as a substance of very high concern by ECHA, TCEP is not currently  
364 being manufactured in and / or imported to the European Economic Area, and such contamination  
365 might result from historical inputs or release from articles containing it and used in this area.

366 Regarding aryl OPEs, concentrations of all three compounds were high in the Nivelle estuary (NiE;  
367 means between 3.0 and 6.7 ng g<sup>-1</sup> dw), a site also showing higher contamination of PBDE and  
368 HBCDD flame retardants (Munsch et al., 2013). The neighbouring sites of the Adour estuary (AdE)  
369 and particularly the Bidassoa estuary (BiE), all three within a 30-km distance and added to the survey



370 in 2020–2021, also have high concentrations, indicating a regional contamination rather than a local  
371 hotspot. Concentrations of TPHP were generally higher on the Atlantic coast and in the Gulf of Fos  
372 (GoF, Mediterranean coast). High EHDPP concentrations were observed on the Atlantic coast in the  
373 Elorn and Etel estuaries and in Arcachon Bay, as well as in Marseille Bay (MaB) on the  
374 Mediterranean coast. These compounds have previously been attributed to the industry of electronic  
375 equipment (in thermoplastics of electric enclosures for televisions, computers, monitors, and printers)  
376 or in relation with electronic waste recycling facilities (Gao et al., 2021). The aforementioned sites do  
377 not share a similar pressure pattern (e.g. Arcachon Bay and the Nivelle and Etel estuaries are exempt  
378 of major industrial discharge) and unequivocal source tracking of aryl OPEs remains challenging.  
379



380

381 Figure 3. Geographical distribution of the OPE concentrations ( $\text{ng g}^{-1} \text{ dw}$ ) found in coastal bivalves of382 the French coasts above LOQs. Data shown as mean  $\pm$  standard deviations (individual values in

383

transparency).

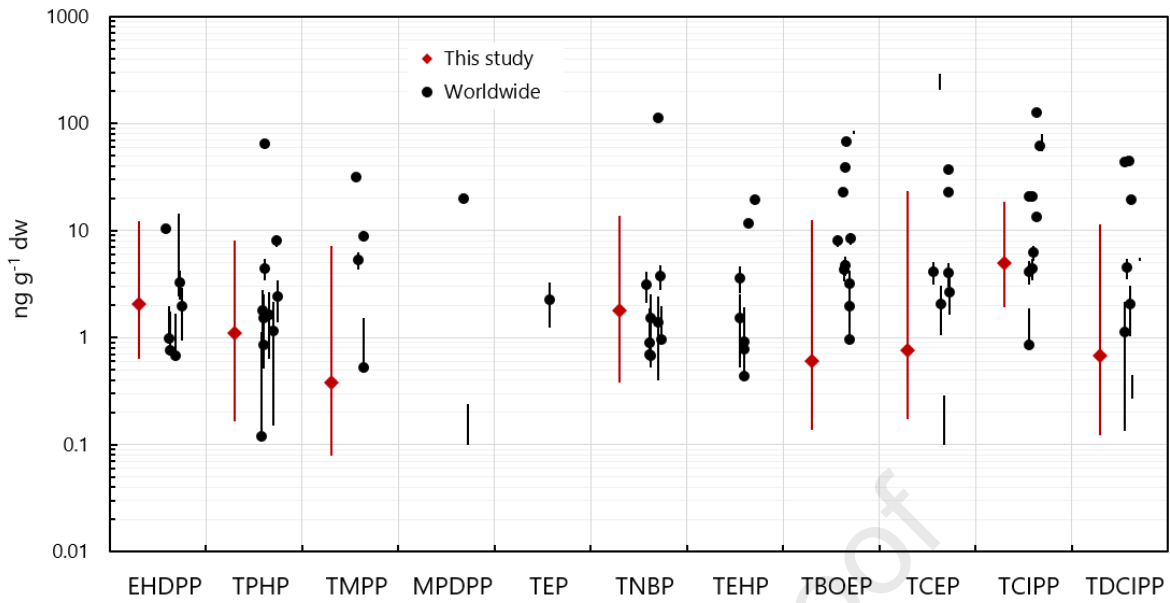
384

385 Previous studies often related OPE levels in the marine coastal environment to wastewater discharges  
386 (Kim et al., 2011; Sutton et al., 2019; Wei et al., 2015), as effluents have been reported as an important  
387 source of OPEs (Xie et al., 2022). Here, concentrations in mussels from the Seine estuary (SeE) and  
388 bay (SeB) were low for all OPEs (within the exception of the ubiquitous TCIPP), despite being under  
389 the influence of its highly anthropized catchment area (*ca.* 17 million inhabitants and industries). A  
390 Spearman correlation test between AHTN, a synthetic musk of known urban origin (Aminot et al.,  
391 2021 and references herein), and any of the OPEs in our dataset revealed no significance. We also  
392 observed a different geographical distribution to the one found for hydrophobic organic contaminants  
393 (Munsch et al., 2015), which have shown higher concentrations in sites such as estuaries and deltas  
394 with large catchment areas, industrial areas, and urban areas (e.g. Seine estuary and Rhône delta).  
395 Previous studies on OPE distribution and source apportionment have generally focused on study sites  
396 of regional scale. A thorough spatial pattern analysis of Hong Kong Bay waters revealed multiple  
397 sources of OPEs, including human settlement, wastewater, manufacturing industry, construction  
398 industry, vehicles, and shipping transport (Gao et al., 2021). In addition to shipping, other sources  
399 include aquaculture (Aznar-Alemany et al., 2018; Zhang et al., 2020) or influences of local point  
400 sources such as airports (Sundkvist et al., 2010). Besides, evidence for OPEs' degradability in marine  
401 environments (Castro-Jiménez et al., 2022) suggests a rather limited potential for widespread  
402 distribution, unlike other hydrophobic organic contaminants. Based on our data and literature  
403 evidence, we hypothesize here that the OPE levels in coastal bivalves mostly relate to local hotspots  
404 and that our understanding of contamination patterns in the marine environment is impeded by both  
405 the huge diversity of their applications and their lower persistence. Selecting study sites based on  
406 expected pressure and on the knowledge gained from other contaminants may consequently fail to  
407 encompass the breadth of coastal OPE contamination. This limitation affects biomonitoring studies,  
408 including ours, until better source identification is achieved.

409

410 **3.3 Comparison with worldwide levels**

411 A systematic review was conducted to screen for OPE concentrations reported in marine bivalves in  
412 the published literature (see SI Text S3 for search terms). Since 2007, 12 articles were found and 1  
413 report was also included (NIVA - Norwegian Environment Agency), with a total of 15 distinct zones  
414 available (some studies described separate sampling areas) in Europe, Asia, and North America  
415 (Figure 4 and Table 2). TCEP, TCIPP, TDCIPP, TBOEP, TPHP and TNBP were the most studied  
416 compounds, reported in 11 zones. TMPP, EHDPP, and TEHP were also frequently reported (9 zones),  
417 whilst TEP, MPDPP, TPEP, TPRP, and TDBPP were only studied in 1–3 zones. Globally, the  
418 concentrations reported in our study compare with the concentrations reported worldwide, but with  
419 ranges spanning several orders of magnitude, a fine comparison is challenging. TCIPP, the prevailing  
420 OPE in our study (median: 4.93 ng g<sup>-1</sup> dw) and the most homogeneously distributed, is also the most  
421 abundant OPE worldwide (inter-study median: 17.3 ng g<sup>-1</sup> dw). High concentrations of TBOEP (inter-  
422 study median: 8.1 ng g<sup>-1</sup> dw) have also been reported elsewhere, which tend to be higher than our  
423 findings (median: 0.61 ng g<sup>-1</sup> dw). We showed that this compound exhibited one of the highest IQR,  
424 indicating strong spatial and temporal variabilities. We also found that TCEP concentrations were  
425 strongly site-dependent, and if our median concentration (0.77 ng g<sup>-1</sup> dw) is lower than the inter-study  
426 median of concentrations retrieved from other published studies (4.1 ng g<sup>-1</sup> dw), concentrations in HeB  
427 and ThL, the two sites of the Mediterranean coastline with repeatably high levels, are comparable  
428 (median of both sites: 3.28 ng g<sup>-1</sup> dw. maximum 23.4 ng g<sup>-1</sup> dw). Conversely, TNBP in our study  
429 (median: 1.81 ng g<sup>-1</sup> dw) was above the median of concentrations reported worldwide (inter-study  
430 median: 1.40 ng g<sup>-1</sup> dw). Undetected in our study, TEP was also generally unquantified or found at  
431 low levels elsewhere. Regarding aryl OPEs in our samples, comparable levels were reported  
432 worldwide for TPHP and EHDPP. In 8 studies (9 zones), TMPP was investigated with contrasted  
433 results, either unquantified or found at notably high values. With the highest interquartile range  
434 reported in our study, this compound also appears to be heterogeneously distributed. Quantified across  
435 the 2 studies where MPDPP was targeted, it was qualitatively found in a large number of our samples  
436 and deserves further interest. TEHP was not included in our work because of methodological  
437 limitations, but we recommend further monitoring as it has been reported in several other studies.  
438



439

440 Figure 4. OPE concentrations ( $\text{ng g}^{-1} \text{dw}$ ) in this study (median and minimum – maximum) and in  
 441 other studies on marine filter-feeding bivalves worldwide (median or mean, and minimum – maximum  
 442 when available). MPDPP and TEHP, not quantified in this study; TEP, not detected in this study.

443

444

Table 2. OPE concentrations (range and mean or median, in ng g<sup>-1</sup> dw) in marine filter-feeding bivalves from all coastal locations found in a systematic review. na: not analysed.

|                              | year of sampling | OPE concentration in ng/g dw. min-max/mean or median |                |                |           |              |       |                |               |                |                |                |                |          | Reference                       |
|------------------------------|------------------|--|----------------|----------------|-----------|--------------|-------|----------------|---------------|----------------|----------------|----------------|----------------|----------|---------------------------------|
|                              |                  | EHDPP  | TPHP           | TMPP           | MPDPP     | TEP          | TPRP  | TNBP           | TEHP          | TBOEP          | TCEP           | TCIPP          | TDCIPP         | TDBPP    |                                 |
| <b>Europe</b>                |                  |  |                |                |           |              |       |                |               |                |                |                |                |          |                                 |
| France, whole coast          | 2014-2021        | 0.63-12.3/2.07                                       | 0.17-8.01/1.12 | 0.08-7.21/0.38 | detected  | <1.0         | <0.05 | 0.38-13.9/1.82 | detected      | 0.14-12.6/0.61 | 0.17-23.4/0.77 | 1.91-18.6/4.93 | 0.12-11.5/0.68 | <0.10    | This study                      |
| France, Bay of Marseille     | 2018             | 10.4   | 2.4            | na             | na        | na           | <10   | 1.4            | 11.8          | na             | 4.1            | 21             | 19.5           | na       | Castro-Jiménez and Ratola, 2020 |
| Netherlands, Scheldt estuary | 2008             | <0.44  | 1.64           | <0.24          | na        | na           | na    | na             | 0.44          | 8.4            | <0.24          | 4.4            | 2.04           | na       | Brandsma et al., 2015           |
| Sweden, North Sea            | 2007             | 0.67   | 0.86           | 0.53           | na        | na           | na    | 0.67           | na            | <0.34          | <0.53          | 6.2            | <0.16          | na       | Sundkvist et al., 2010          |
| Sweden, Baltic Sea           | 2007             | 0.768  | 4.46           | 5.28           | na        | na           | na    | 0.96           | na            | <0.82          | 2.64           | 62             | <0.39          | na       | Sundkvist et al., 2010          |
| Norway, Oslo fjord           | 2014             | <3.6-8.4   | <31.6          | <0.8           | na        | na           | na    | <59            | <2.4          | <80-85         | <206-293       | 77-81          | 5.2-5.6        | na       | Ruus et al., 2019               |
| Spain, Galician coast        | 2017             | <1-2   | <0.8-291/64.5  | na             | na        | na           | na    | <0.4-4.4/3.1   | <0.5-2.0/1.5  | 2-5.8/4.7      | na             | <1-14/4.2      | na             | na       | Castro et al., 2020             |
| Spain, Ebro Delta            | 2013             | na   | na             | na             | na        | na           | na    | na             | na            | 3.2            | <0.75          | <1.5           | na             | na       | Álvarez-Muñoz et al., 2015      |
| Italy, Po Delta              | 2013             | na   | na             | na             | na        | na           | na    | na             | na            | 39.4           | <0.75          | <1.5           | na             | na       | Álvarez-Muñoz et al., 2015      |
| Portugal, Tagus estuary      | 2013             | na   | na             | na             | na        | na           | na    | na             | na            | 22.8           | <0.75          | na             | na             | na       | Álvarez-Muñoz et al., 2015      |
| Portugal, Aveiro lagoon      | 2016-2017        | <0.7   | <0.7           | na             | <0.1-0.24 | na           | na    | <0.7           | <0.2          | <0.1           | <0.7           | <1.5           | 0.27-0.45      | na       | Gadelha et al., 2019            |
| <b>Asia</b>                  |                  |  |                |                |           |              |       |                |               |                |                |                |                |          |                                 |
| Japan, Maizuru Bay           | 2009             | na   | 8              | 32             | 20        | <4           | <4    | 92-136/112     | na            | <4-48/8        | <4-12/4        | na             | 24-60/44       | na       | Harino et al., 2014             |
| China, Beibu Gulf            | 2015             | na   | 0.12           | <1.36          | na        | na           | na    | 0.49-1.3/0.9   | 0.11-1.4/0.78 | <1.6-3.9/2.0   | 18-28/23       | 6.7-25/14      | <0.37-3/1.1    | na       | Zhang et al. 2020               |
| Korea, whole coast           | 2016             | <0.3-9.6/3.3   | <0.3-31/1.5    | <0.5-58/8.9    | na        | <0.1-2.2/2.2 | na    | <0.08-9.4/1.5  | <0.13-18/3.6  | <0.37-48/4.3   | <0.12-5.1/2.1  | <0.3-216/21    | <0.26          | na       | Choi et al. 2020                |
| China, Weizhou Island        | 2018             | na   | 1.81           | <0.45          | na        | na           | na    | 3.8            | 19.4          | 68             | 37             | 126            | 45             | na       | Ding et al., 2020               |
| <b>North America</b>         |                  |  |                |                |           |              |       |                |               |                |                |                |                |          |                                 |
| USA, San Francisco Bay       | 2014             | <0.4-4/0.98  | <0.4-1.6/1.2   | <0.25          | na        | <0.1         | <0.25 | <0.15-1.6/0.69 | <0.3-1.3/0.9  | <0.3-2.0/1.0   | <0.1-0.3       | <0.15-3.6/0.9  | 0.38-8.9/4.5   | <0.8-1.6 | Sutton et al. 2019              |

#### 4. Conclusions

Widespread occurrence of OPEs was revealed, confirming the relevance of their inclusion in biomonitoring programs. TCIPP, TNBP, and EHDPP were found at the highest median concentrations, indicating that out of the targeted compounds all three subclasses of OPEs (chlorinated, aryl, and alkyl) were of environmental relevance. Interestingly, we noted that TCEP, TCIPP, and TDCIPP, of relatively low log Kow (1.47, 2.59, and 3.27, respectively), could be found at high concentrations in the sampled bivalves, highlighting that the processes leading to bioaccumulation in marine organisms remain unclear (Xie et al., 2022). Geographical distributions were not predictable from known anthropogenic pressures such as population in the catchment area, or previously identified industrial sources and differed from those established for other flame retardants (Munsch et al., 2015) or urban-related synthetic musks (Aminot et al., 2021). In line with other studies, we suggest that ports and/or marinas in relation with shipping and yachting are potential sources of TNBP, hypothesis needing further investigations. Less persistent than other POPs, local hotspots, rather than riverine/atmospheric transportation, could drive the geographical distribution of OPEs in coastal environments. Still, ubiquitous detection at levels exceeding those of brominated flame retardants deserves a stronger focus from regulators and environment monitoring authorities. With some recent regulations (e.g. TCIPP and TDCIPP in the EU) and growing scientific concerns (Blum et al., 2019), it is essential to acquire baseline levels and continue (bio)monitoring with the objective of identifying long-term time trends in the environment.

#### Author statement

Y. Aminot: Methodology, Investigation, Formal analysis, Statistical analysis, QA/QC, Writing – original draft, Writing – review & editing. C. Munsch: Conceptualization, Investigation, Writing – review & editing, Funding acquisition. L. Tao: Methodology, Investigation, Writing – original draft. M. O’Loughlin: Investigation, Data curation. K. Héas-Moisan: Data acquisition, QA/QC. C. Pollono: Methodology, Data acquisition, QA/QC.

### Declaration of competing interest

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.

### Acknowledgments

The authors would like to thank the OFB (Office Français de la Biodiversité) for its financial support. IFREMER staff from coastal laboratories are gratefully acknowledged for performing the sampling campaigns. LT is grateful to Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China, for supporting a doctoral mobility grant in Ifremer.

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**Author statement**

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**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:

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