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

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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^{-1} 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

29 showed repeatedly high concentrations. Structurally-related OPEs generally correlated, but

30 the geographical distributions were not predictable from known anthropogenic pressures

31 (population in the catchment area, industry), with little comparability with other hydrophobic

32 contaminants. If the relation between sources of OPEs and bioaccumulated levels remains

33 uncertain, local hotspots, rather than riverine/atmospheric transportation, could account for

34 their geographical distribution. A systematic review of the levels of OPEs found in filter-

35 feeding bivalves worldwide revealed comparable levels in our study with those reported

36 elsewhere; however, the levels across and within (when available) studies generally spanned

37 several orders of magnitude, indicating high spatial and temporal heterogeneity. In view of the

38 growing concerns regarding OPEs, this study provides essential reference data for future

39 studies of their occurrence on European coasts and supports the need for a more systematic

40 (bio)monitoring of this class of contaminant.

41

42 **Keywords**

43 Coastal marine environment; Bioaccumulation; Shellfish; Flame retardants; Plasticizers

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45 **Highlights**

46 Investigation of OPEs in bivalves from French coasts collected between 2014–2021

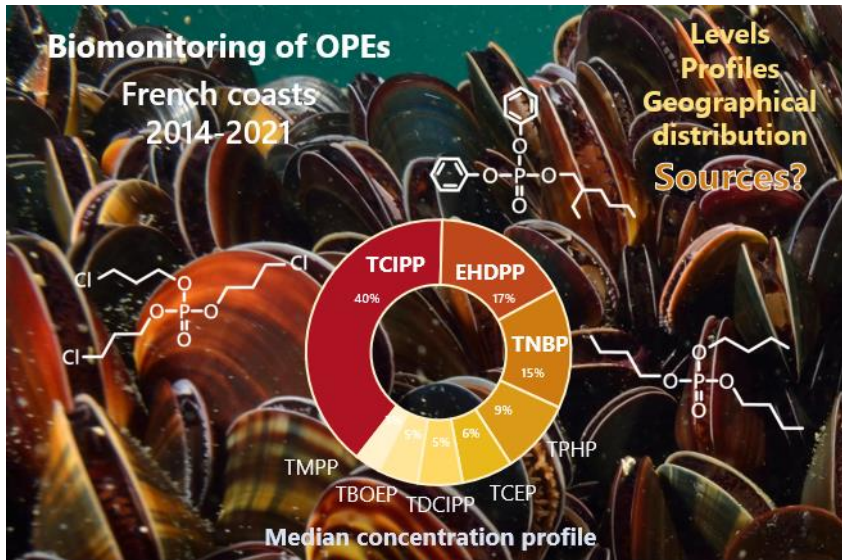47 TDCIPP, TPHP and TNBP found in over half of the samples

48 Highest median concentrations were found for TCIPP, EHDPP, and TNBP

49 OPE profiles are site-specific

50   OPE spatial distribution differs from that of other bioaccumulative contaminants

51

52   **Graphical abstract**

54   **1. Introduction**

55   Organophosphate esters (OPEs), chemicals used as flame retardants, plasticizers, antifoaming

56   agents, lubricants, and hydraulic fluids, have been extensively added to a variety of

57   commercial products like plastics, textiles, electronics, and building materials (van der Veen

58   and de Boer, 2012; Wei et al., 2015). In 2006, the total consumption of flame retardants in

59   Europe was estimated to be 465,000 tons, 20% of which were OPEs (93,000 tons) (van der

60   Veen and de Boer, 2012). The global market volume of OPEs was estimated to be 620,000

61   tons in 2013 (Sühring et al., 2016); in 2022, OPEs are still assumed to account for

62   approximately 15% of the total flame-retardant market (Xie et al., 2022). With over 1,000

63   tons imported and/or produced in the European Union per year, several OPEs are considered

64   high production volume (HPV) chemicals, including: triethyl phosphate (TEP), tri-n-butyl

65   phosphate (TNBP), tris(2-butoxyethyl) phosphate (TBOEP), tris(2-ethylhexyl) phosphate

66   (TEHP), tris(1,3-dichloro-2-propyl) phosphate (TDCIPP), tri-phenyl phosphate (TPHP), tri-

3

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

OPEs are released from consumer and industrial products to the environment by
volatilization, leaching, and abrasion (Xie et al., 2022). Emissions from direct industrial
inputs, wastewater treatment facilities, and e-waste recycling activities are of importance, and
their relative contributions depend on the anthropogenic pressures on a given watershed (Liu
et al., 2022; Wei et al., 2015). To better apportion OPE sources in the Guangdong-Hong
Kong-Macao Greater Bay (China), the correlations between water concentrations from 16
sites were tested against several socio-economic indicators (Gao et al., 2021). The authors
showed that population density, wastewater discharge, manufacturing industry, construction
industry, vehicles, and shipping transport were determinants of OPE levels. In addition to
these multiple sources, leaching from plastic debris is also a speculated source (Xie et al.,
2022), but a substantiated evaluation of its magnitude with regards to other sources is lacking.

4

92   Riverine and atmospheric transportation, as well as direct coastal discharges, lead to their

93   presence in the global ocean and in remote marine regions (McDonough et al., 2018).

94   First detected in river waters in the USA (Sheldon and Hites, 1978), OPEs have been

95   reported ubiquitously in the marine environment. In surface waters of the German Bight, the

96   total concentration of 16 OPEs ranged from 5 to 50 ng L^{-1}, with a riverine export of 50 t y^{-1}

97   into the North Sea from the German tributaries alone (Bollmann et al., 2012). Concentrations

98   of individual OPEs in harbour waters in the United Kingdom were as high as 100–260 ng L^{-1}

99   (EHDPP, TCIPP), with an enrichment in the surface microlayer (Aminot et al., 2017). In

100   sediments of the Korean coast, 10 out of the 18 studied OPEs were detected with >50%

101   detection rate, with TCIPP having the highest median concentrations of 30 ng g^{-1} dry weight

102   (dw) (Choi et al., 2020). With significantly higher concentrations in harbour zones, the

103   authors identified shipping activity as a putative source of OPEs in coastal environments. In

104   San Francisco Bay (USA), OPEs were also widely detected in sediment, particularly the most

105   hydrophobic OPEs like TEHP (median: 8.2 ng g^{-1} dw), TMPP (3.4 ng g^{-1} dw) and TPHP

106   (1.9 ng g^{-1} dw) (Sutton et al., 2019). Water and sediment concentrations were over one order

107   of magnitude higher for OPEs than for PBDEs.

108   Alongside hydrophobicity, metabolizability is a key driver of bioaccumulation (Walters et

109   al., 2016). With reports of OPE biotransformation (Muir and Grift, 1981; Wang et al., 2019),

110   there is conflicting evidence on the potential for bioaccumulation and biomagnification of

111   OPEs, although they are found in measurable quantities in marine organisms (Xie et al.,

112   2022). Here, we focus on bivalves, organisms of lower trophic levels which show a low

113   ability to metabolize organic contaminants in comparison to fish and crustaceans (Farrington

114   et al., 2016). In mussels (*Mytilus edulis*) and oysters (*Crassostrea gigas*) from Korea, 5 OPEs

115   (TEHP, TCIPP, EHDPP, TEP and TCEP) were found in over half of the samples, with

116   median concentrations between 0.56 and 1.4 ng g^{-1} dw, except for TCIPP, which was found at

117 11.7 ng g^{-1} dw (Choi et al., 2020). In San Francisco Bay, TDCIPP was found in all 6 samples of

118 transplanted mussels (*Mytilus californianus*) at the highest levels (median: 4.5 ng g^{-1} dw,

119 comparable to BDE-47, 3.1 ng g^{-1} dw), with TPHP, EHDPP, TNBP, TBOEP, and TCIPP

120 being detected in over half of the samples (Sutton et al., 2019). In several European

121 aquaculture sites, OPE levels were several orders of magnitude higher than other chlorinated

122 and brominated FRs, with a predominance of TNBP in the studied mussels (Aznar-Alemany

123 et al., 2018). Filter-feeding bivalves, particularly mussels and oysters, are widely-used

124 organisms for the biomonitoring of bioaccumulative contaminants (Beyer et al., 2017).

125 Beyond the commonly-monitored legacy contaminants (PCDD/Fs, PCBs, OCPs, and PAHs),

126 contaminants of emerging concern have been included in such biomonitoring programs

127 worldwide, ultimately contributing evidence for their widespread occurrence in biota and

128 leading to regulations (e.g. PBDEs, HBCDDs).

129   In light of the paucity of data on OPEs in marine bivalves, we have expanded the French

130 national biomonitoring program to this class of compounds on a yearly basis since 2017. The

131 objective of this study was to investigate their occurrence and spatial distribution in marine

132 shellfish collected from sites under contrasted anthropogenic pressure along French coasts.

133

134 **2. Materials and methods**

135   2.1 Chemicals and reagents

136 All chemicals were of trace analysis grade. Picograde® solvents (methanol, ethyl acetate,

137 acetone, cyclohexane, n-hexane) and Florisil® (100–200 mesh) were purchased from

138 Promochem (Germany) or LGC Standards (France). Aminopropyl cartridges (Discovery®

139 DSC-NH$_2$, 500 mg, 6 mL) and graphite cartridges (Supelclean™ ENVI-Carb™, 500 mg, 6 mL)

140 were obtained from Merck (Darmstadt, Germany). Trimethylphenyl phosphate (TMPP),

141 methylphenyldiphenyl phosphate (MPDPP), 2-ethylhexyldiphenyl phosphate (EHDPP),

142 isodecyldiphenyl phosphate (IDDPP), triphenyl phosphate (TPHP), triethyl phosphate (TEP),

143 tripropyl phosphate (TPRP), tripentyl phosphate (TPEP), tri-n-butyl phosphate (TNBP), tris(2-

144 ethylhexyl) phosphate (TEHP), tris(2-butoxyethyl) phosphate (TBOEP), tris(2-chloroethyl)

145 phosphate (TCEP), tris(chloro-2-propyl) phosphate (TCIPP), tris(1,3-dichloro-2-propyl)

146 phosphate (TDCIPP), tris(2,3-dibromopropyl) phosphate (TDBPP), and

147 tris(tribromoneopentyl) phosphate (TTBNPP) were acquired from Accustandards (New Haven,

148 USA). Triphenyl phosphate-$^{13}C_8$ (TPHP-$^{13}C_8$), triphenyl phosphate-D_{15} (TPHP-D_{15}), triethyl

149 phosphate-D_{15} (TEP-D_{15}), tripropyl phosphate-D_{21} (TPRP-D_{21}), tri-n-butyl phosphate-D_{27}

150 (TNBP-D_{27}), tris(2-butoxyethyl) phosphate-$^{13}C_2$ (TBOEP-$^{13}C_2$), tris(2-chloroethyl) phosphate-

151 D_{12} (TCEP-D_{12}), and tris(1,3-dichloro-2-propyl) phosphate-D_{15} (TDCIPP-D_{15}) were acquired

152 from Wellington Laboratories (Guelph, Canada). Trimethylphenyl phosphate-D_{21} (TMPP-D_{21}),

153 tris(2-ethylhexyl) phosphate-D_{51} (TEHP-D_{51}), tris(2-butyloxyethyl) phosphate-D_{27} (TBOEP-

154 D_{27}), tris(1-chloro-2-propyl) phosphate-D_{18} (TCIPP-D_{18}), and tris(2,3-dibromopropyl)

155 phosphate-D_{15} (TDBPP-D_{15}) were acquired from TRC Canada (Toronto, Canada).

156   2.2 Sampling strategy

157 Mussels (*Mytilus spp*) and oysters (*Crassostrea gigas*) were collected annually in autumn (out

158 of spawning season) from 2017 to 2021 at the same selected locations in the English Channel,

159 the Atlantic Ocean and along Mediterranean coasts, as shown in Figure 1, for a total of 103

160 samples (an additional 5 samples from 2014–2016 were analysed to confirm site specificities).

161 These locations cover main estuaries and deltas (Seine, Loire, Gironde, Rhône), together with

162 smaller tributaries and sites away from direct sources. The shellfish were collected and handled

163 in accordance with international guidelines for the monitoring of contaminants in biota

164 (OSPAR, 2018). Briefly, a composite sample consisted of at least 50 mussels of similar size

165 (30–60 mm shell length) or 10 oysters (90–140 mm shell length), and each individual had spent

7

at least 6 months *in situ* beforehand. All samples were depurated in settled water from the site

for 24 h, shelled, homogenized (whole soft body), and stored at -20 °C prior to freeze-drying.

The average dry weight (dw) was 19.9 ± 5.2 % (n = 108), and the average total lipid content

was 9.7 ± 1.8% dw (determined gravimetrically from a dried hexane/acetone [80:20 v:v]

extract). The dried samples were stored in amber glass containers in a cool, dry, dark place until

further analysis.
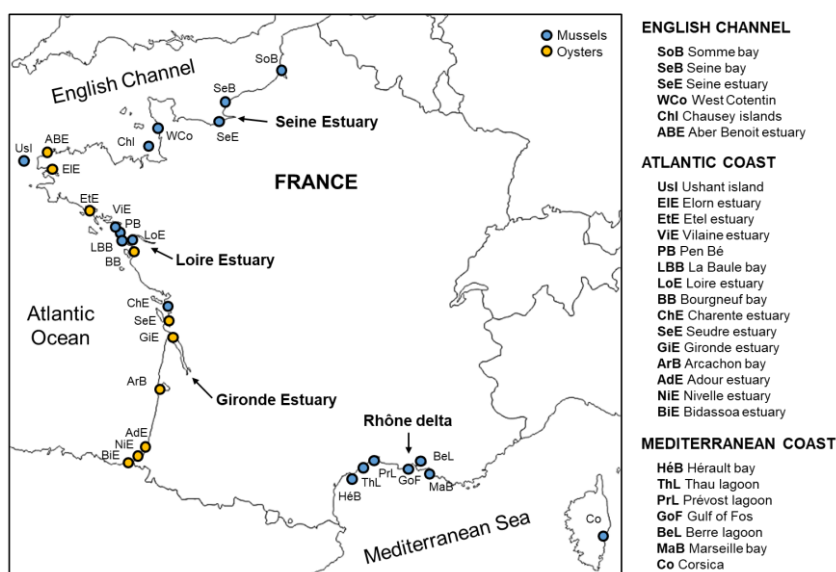
Figure 1. Sampling sites for bivalves collected from 2017 to 2021 from the English Channel,

Atlantic Ocean and Mediterranean coasts.

2.3 Extraction method

Samples were extracted using pressurized liquid extraction (ASE350, Dionex, USA), in a pre-

cleaned 66 mL stainless steel cell, filled with: cellulose filter, Florisil (15 g, 100–200 mesh),

and dry sample (1 g). Before extraction, 5 ng (50 µL, 0.1 ng µL^{-1} in toluene) of each labelled

standard (Table S2) were added to the sample for internal standard quantification by isotopic

dilution. The extraction cell was filled with ethyl acetate/cyclohexane (4:1 v:v) and brought to

100 °C and 100 bar for a 5 min static extraction (constant P and T). Fresh solvent was introduced

8

183   into the cell (flushing volume 100%), and the extraction cycle was repeated once more. The

184   extraction cells were precleaned by running a first complete cycle with Florisil and no sample,

185   a step found to be essential to limit blank contamination.The extract was concentrated to 1 mL

186   with a rotary evaporator before clean-up.

187   2.4 Solid phase extraction clean-up method

188   Clean-up was performed on NH_2 and graphite sorbents. The NH_2 sorbent was conditioned with

189   5 mL of ethyl acetate/cyclohexane (1:1 v:v) followed by 5 mL of cyclohexane. After sample

190   loading, OPEs were eluted in two separate fractions of: (1) ethyl acetate/cyclohexane (4 mL,

191   1:4 v:v) and (2) ethyl acetate/cyclohexane (5 mL, 1:1 v:v). Each fraction was concentrated to

192   100 µL under nitrogen, and 1 mL of hexane/acetone (1:1 v:v) was added before loading on an

193   ENVI-Carb sorbent (conditioned with 10 mL of acetone and 10 mL of hexane/acetone, 1:1,

194   v/v). OPEs were eluted with 20 mL of hexane/acetone (1:1, v/v) and this fraction was

195   concentrated to 100 µL under nitrogen and transferred to a glass injection vial. The recoveries

196   obtained for standards on NH_2 and graphite sorbents are provided in Figure S1. Injection

197   standards (Table S2) were added (5 ng), and the final extract was evaporated to dryness and

198   further reconstituted in 100 µL of methanol and 100 µL of water.

199   2.5 Instrumental method

200   Analysis of the OPEs was performed on an ultra-performance liquid chromatography (UPLC)

201   I-Class coupled to a triple quadrupole Xevo TQS-µ (Waters, USA) using positive electrospray

202   ionization mode (ESI+). Separation was achieved on a 50 mm x 2.1 mm BEH C_{18} column

203   (particle size 1.7 µm, Waters, France), maintained at 50 °C, using a gradient of methanol and

204   ammonium acetate (20 mM) at a flow rate of 0.5 mL/min. The gradient from solvent A

205   (ammonium acetate 20 mM) to solvent B (100% methanol) was as follows: 0 min (25% B), 0.5

min (25% B), 5 min (85% B), 5.1 min (100% B), 6 min (100% B), 6.1 min (25% B), 9 min

(25% B).

The mass spectrometric detection was completed in multiple reaction monitoring (MRM) mode

(Table S2), with the following source parameters: capillary voltage 3 kV, cone voltage 10 V,

and desolvation flow 900 L/hr.

2.6 Method validation, quality assurance and quality control

The method was validated according to the accuracy profile procedure (NFT90-210, 2009).

Briefly, it consisted of assessing the accuracy of the calibration function, the intermediate

precision, and bias and comparing it to tolerance intervals (more details in supplementary

information Text S1 and S2, Table S3). Validation criteria were met for 11 of the 16 targeted

OPEs. With high absolute bias for TPEP, IDDPP and MPDPP, their analysis was considered

semi-quantitative only. In addition, TEHP and TTBNPP were not detected because of an

important matrix effect.

The method limit of quantification (LOQ), as per the EU commission regulation 2017/644, is

defined for each analyte in each sample as the concentration for which the instrumental response

of the less sensitive MRM transition yields a S/N (signal/noise) ratio of 3:1 (Table 1). TBOEP,

TCIPP, TPHP, and TDCIPP have been commonly detected at high levels (>1 ng m^{-3}) in both

indoor particulate and gas phases (Brandsma et al., 2013; Brommer et al., 2014). OPE glassware

contamination can be expected from deposition from ambient air and potential carryover. All

glassware was treated at 450 °C overnight and pre-cleaned with ethyl acetate before use. The

entire sample preparation and subsequent analyses were performed in clean laboratories, under

a low-dust atmosphere and positive pressure (ISO 8 class according to NF EN ISO 14644). As

contamination can also come from the detection system itself (Brandsma et al., 2013), a delay

column was installed between the pump and the injector to separate instrument-related peaks

from the actual sample peaks. This approach, commonly used in the analysis of analyses

perfluoroalkyl substances (PFAS), was successfully implemented for OPEs here (see Figure

S2). Procedural blanks (excluding sampling, freeze-drying and homogenization) were

extracted, purified, and analyzed within each sample batch. Concentrations in samples were

corrected for blank contamination: the mass of analyte (ng) found in the blanks was subtracted

from the mass (ng) found in the samples, provided that the analyte mass in the sample was

above 3 times that of the blank. According to the EU commission regulation 2017/644, the

reporting level shall be demonstrated to be different from the procedure's blank samples at least

by a factor of three. The LOQ was therefore fixed at three times the value of blank.

In addition to the initial method validation described in SI Text S2, one in-house spiked

reference material was extracted for each batch of 10–12 analyses, with overall deviation

between 7% (TNBP) and 48% (TDBPP). In all samples together (n = 108), the labelled internal

standards were recovered with a mean between 24% (TMPP-D$_{21}$) and 137% (TNBP-D$_{27}$),

indicative of a matrix effect. Laboratory blank levels (8 blanks processed in total) were between

73 pg g^{-1} dw (TMPP) and 1379 pg g^{-1} dw (TCIPP), with acceptable repeatability over the 5

years of analysis (23%–88%). The highest values (>500 pg) were observed for the chlorinated

OPEs TCIPP and TCEP, TEP and TNBP (alkyl), and EHDPP (aryl). These values led to LOQs

higher than those strictly instrument-derived and ranged on average from 54 pg g^{-1} dw (TPRP)

to 3089 pg g^{-1} dw (TCIPP). Blank contamination (see Figure S3) was partly attributed to the

contribution of the solvents used and concentrated in the final extract as between 5% (TBOEP)

and 64% (TCEP) of the blank contamination could be traced to the solvents. The levels of OPEs

found after evaporation of an ASE cell blank, without Florisil, were not significantly different

from the levels found after evaporation of the same volumes, without running through the ASE

system, suggesting its minimal contribution. Analysis of diatomaceous earth (Hydromatrix,

255 Agilent Technologies) exposed prior to sample extraction revealed that neither sampling,

256 handling or freeze-drying caused a significant contamination of the samples (Figure S4).

257

258 Table 1. QA/QC parameters: labeled compound recoveries, limits of quantification (LOQs) resulting

259 from blank contamination, LOQs extrapolated from the method sensitivity, and detection frequencies

260 per contaminant.

| Individual compound	n samples / n batches	^{2}H / ^{13}C standard recoveries	LOQ blank	LOQ method	Detection frequency
		(%)	pg g^{-1} dw	pg g^{-1} 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

261

3. Results

3.1 Levels and profiles of OPEs

264 Among the 103 samples analysed over the 5-year study, TDCIPP, TPHP, and TNBP were quantified

265 in over half of the samples (detection frequency, DF: 85%, 69%, and 61%, respectively), TMPP,

266 TCIPP, TCEP and EHDPP in 37%–43%, and TBOEP in 13% of the samples (DFs). OPEs were not

267 quantified in only 3 samples, indicating their widespread occurrence. The highest median

268 concentrations (Figure 2) were found for TCIPP at 4.93 ng g^{-1} dw (range: 1.9–18.6 ng g^{-1} dw), EHDPP

269 at 2.07 ng g^{-1} dw (range: 0.6–12.3 ng g^{-1} dw), and TNBP at 1.82 ng g^{-1} dw (range: 0.4–13.9 ng g^{-1} dw).

270 As reported by the European Chemicals Agency (ECHA; https://echa.europa.eu/), these higher

271 concentrations are consistent with their usage in Europe (TCIPP reported at 10 000-100 000 t y^{-1} in

272   2018 [no production/import reported in 2022]; TNBP and EHDPP tonnage band 1,000–10,000 t y^{-1} in

273   2022). Conversely, the absence of the bromine-containing TDBPP is consistent with its heavy

274   restrictions in the EU; this compound is indeed rarely found in the environment or at very low

275   concentrations (Allan et al., 2018). Also undetected despite high production/import tonnage (>10,000 t

276   y^{-1} for TEP), the alkyl OPEs TEP and TPRP, have low log K_{ow} (0.8 and 1.87, respectively), suggesting

277   lower bioaccumulative tendencies (Mackay and Fraser, 2000). However, the chlorinated OPEs (TCEP,

278   TCIPP, and TDCIPP) are also of relatively low log Kow (1.47, 2.59, and 3.27, respectively) but were

279   found in our study at relatively higher concentrations and/or detection frequencies. This observation

280   suggests that hydrophobicity only is insufficient to describe their bioaccumulation or that levels in

281   surrounding waters are high. The field-derived bioconcentration factor (BCF) of TCEP in zooplankton

282   has also been reported to be one of the highest among the monitored OPEs (Schmidt et al., 2021),

283   whilst no relationship was found between BCFs and log K_{ow}. In Korean coastal waters, the biota-

284   sediment accumulation factor calculated for TCEP in mussels and oysters was higher than those

285   determined for TEP, TCIPP, and TEHP (Choi et al., 2020), suggesting the peculiarity of this

286   compound.
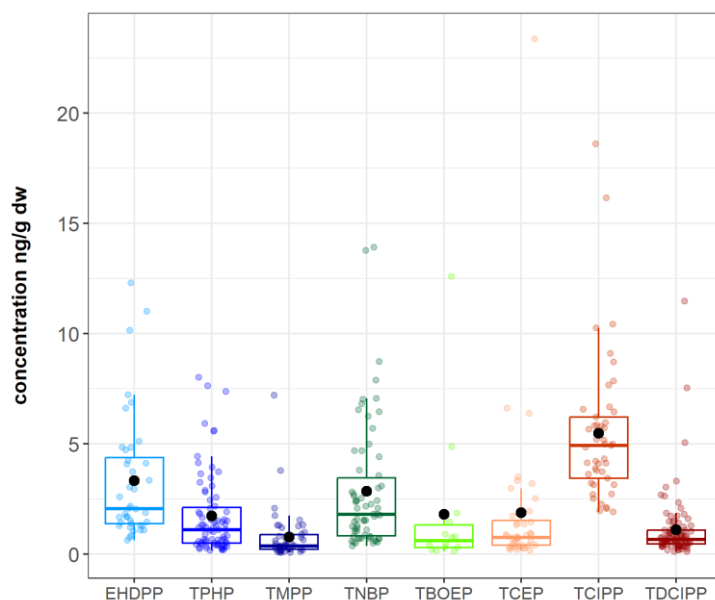
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288   Figure 2. Concentration (ng g^{-1} dw) distributions of the OPEs found in coastal bivalves of the French

289   coasts above LOQs (n = 14 [TBOEP] to 92 [TDCIPP]). The black circles represent the mean value for

290   individual OPEs.

291

292   Statistically significant correlations (Spearman's rank correlations) were generally observed for

293   structurally-related OPE concentrations. In particular, all three aryl OPEs were correlated, suggesting

294   similar sources and/or environmental behaviour (Table S4), with TMPP and TPHP having the

295   strongest correlations ($\rho = 0.69$, $p < 0.0001$; compounds co-occurring in 39% of the samples). Other

296   significantly correlated OPEs were TCIPP and TDCIPP ($\rho = 0.43$, $p = 0.004$; co-occurrence 40%),

297   TPHP and TNBP ($\rho = 0.41$, $p = 0.002$; co-occurrence 50%), and TCEP and EHDPP ($\rho = -0.671$, $p=$

298   0.02, but co-occurrence only 11%). In a previous study, it was found that similar OPEs to those

299   studied here did not correlate in bivalve tissues, even if they had strong positive correlations in the

300   surrounding sediments, a result attributed to their likely rapid biotransformation (Choi et al., 2020).

301   Similarly, the significant correlation observed between the chlorinated OPEs TCEP, TCIPP, and

302   TDCIPP, in the dissolved phase were not found in mussel tissues nor in harbour seal blubber from San

303   Francisco Bay (Sutton et al., 2019). If the existence of OPE-specific differences in biotransformation

304   kinetics is a plausible hypothesis, it may also relate to the range of log Kow (and subsequent

305   bioaccumulation factor, BAF) spanned by the whole family, as compounds with higher BAF take

306   longer to reach steady state. This would cause compound-specific exchange kinetics between bivalves

307   and the dynamic tidal waters and confound relative concentrations in water vs. in bivalves. In our

308   study, the correlation found between TCIPP and TDCIPP still suggests some similarities in their

309   partition behaviour. Regarding aryl OPEs, concentrations of MPDPP and IDDPP were not calculated

310   because of their low accuracy in our method (see Section 2.6); however, it is noteworthy that the

311   highest signals for these aryl compounds were measured in samples with high $\sum$aryl OPE levels

312   (TPHP, EHDPP, TMPP). A Mann-Whitney non-parametric test indicates significantly higher TPHP

313   levels ($p = 0.0002$) in those 59% of samples for which MPDPP was also qualitatively detected in

314   comparison with those where it was not. The same difference was observed when considering the 18%

315   of samples in which IDDPP was also detected ($p = 0.003$).

316   OPEs were the most abundant of all hydrophobic contaminants analysed in the same samples (for

317   further details, refer to Aminot et al., 2021; Munschy et al., 2019, 2015, 2013), with concentrations

318   decreasing as follows: OPEs > polycyclic musks (ng g^{-1} dw); followed by: perfluorocarboxylates ($\sum$

319   C_9–C_{14} PFCAs) > perfluorooctane sulfonate (PFOS) ~ polybrominated diphenyl ethers ($\sum$ 8 OSPAR

320   PBDE congeners) > hexabromocyclododecane (hundreds of pg g^{-1} dw); followed by: nitromusks and

321   alternative brominated flame retardants (BTBPE, DBDPE) tens of pg g^{-1}. OPEs are rarely reported

322   alongside other hydrophobic contaminants in the literature on mollusc contamination. When they have

323   been, their concentrations were comparable or exceeded those of other contaminants, which is in

324   agreement with our findings (Aznar-Alemany et al., 2018; Brandsma et al., 2015; Fu et al., 2020;

325   Sutton et al., 2019).

326

327   **3.2 Geographical distribution**

328   The relative interquartile range (RIQR; IQR divided by the median, in percentage) was calculated to

329   evaluate the spread of OPE concentrations over the 5-year study. The RIQR was high for the sum of

330   all quantified OPEs (147%) and for the individual compounds EHDPP (145%), TPHP (146%), TMPP

331   (173%), TNBP (147%), TBOEP (167%), and TCEP (146 %), indicating notable spatiotemporal

332   variability; however, the RIQR for TCIPP and TDCIPP was 56% and 91%, respectively, indicating a

333   more uniform distribution.

334   Interestingly, the highest concentrations of $\sum$OPEs were consistently found in the same sites. For each

335   year, concentrations found in the Nivelle (NiE), Elorn (ElE), and Etel (EtE) estuaries, as well as the

336   Arcachon Bay (ArB), were above the 3rd quartile of all measurements. Specific OPE contributions

337   indicate different patterns in these samples (Figure 3). TNBP is abundant in these four sites with

338   median values in the range of 1.6–7.5 ng g^{-1} dw and to a lesser extent in other sites of the Atlantic

339   coast (Vilaine: ViE; Seudre: SeE; Adour: AdE; Bidassoa: BiE; estuaries that have values above the 3rd

340   quartile). High TNBP concentrations were also found in additional samples taken prior to 2017 in the

341   Etel estuary (2014–2016, 3–7.9 ng g^{-1} dw), in the Elorn estuary (2016, 1.8 ng g^{-1} dw), and the

342   Arcachon Bay (2016, 3.6 ng g^{-1} dw), which suggests regular inputs of this contaminant in these sites.

343   If the Nivelle and Elorn estuaries have been previously identified as sites under anthropogenic

344   pressure (Aminot et al., 2021; Munschy et al., 2015), the case of the Etel estuary is peculiar,

345   considering this is a site under the influence of a small rural catchment area, with no major city or

346   particular industry, and for which the other contaminants followed in our surveys have always been

347 low. The high TNBP concentrations detected in the above-mentioned low impacted sites warrant

348 further research into the sources of this compound into coastal waters, as most of the industrial sources

349 identified by Gao et al. (2021) are unlikely here. Used in particular for its thermal stability, resistance

350 to oxidation, and viscosity, some TNBP applications include coating products, polymers, adhesives,

351 and sealants. ECHA identified potential releases of TNBP in relation with transports (ships), and

352 previous reviews indicate its inclusion as a plasticizer in marine paint in particular (Brigham and

353 Landrigan, 1985). Yachting and/or shipbuilding, generally found in the previously mentioned sites, are

354 speculative sources of these compounds to the marine environment. It is corroborated by results from

355 Korea, where sediments from near-harbour sites showed the highest $\sum$OPE concentrations, although

356 contributions from single compounds were not specified (Choi et al., 2020). TNBP was also

357 predominant in coastal waters of the Beibu Gulf (China), a result attributed to lubricants used in

358 fishing vessels (Liu et al., 2022), whilst shipping activity near Hong Kong remained a source of TNBP

359 in the bay (Gao et al., 2021).

360 Most of the positive detections of the other alkyl OPE, TBOEP, occurred in four neighbouring sites on

361 the Atlantic coast (8 out of the 14 > LOQ), with consistently high concentrations in the site Pen-Bé

362 (PB) and generally low levels of other monitored contaminants. The specific sources of TBOEP in this

363 area need investigation, as none of its described uses clearly relate to local activities (used in washing

364 and cleaning products, polishes and waxes, as a plasticizer in vinyl plastics and rubber stoppers, in

365 plant protection products and water treatment chemicals, ECHA). Consistently high concentrations of

366 TCEP occurred in the Hérault Bay (HéB, range: 3.2–23.4 ng g^{-1} dw) and the Thau Lagoon (ThL,

367 range: 0.49–6.4 ng g^{-1} dw), two neighbouring Mediterranean sites of otherwise low OPE

368 contamination. This high level of concentrations in mussel tissues is noteworthy considering its near-

369 absence in most sites. Identified as a substance of very high concern by ECHA, TCEP is not currently

370 being manufactured in and / or imported to the European Economic Area, and such contamination

371 might result from historical inputs or release from articles containing it and used in this area.

372 Regarding aryl OPEs, concentrations of all three compounds were high in the Nivelle estuary (NiE;

373 means between 3.0 and 6.7 ng g^{-1} dw), a site also showing higher contamination of PBDE and

374 HBCDD flame retardants (Munschy et al., 2013). The neighbouring sites of the Adour estuary (AdE)

375 and particularly the Bidassoa estuary (BiE), all three within a 30-km distance and added to the survey

376 in 2020–2021, also have high concentrations, indicating a regional contamination rather than a local

377 hotspot. Concentrations of TPHP were generally higher on the Atlantic coast and in the Gulf of Fos

378 (GoF, Mediterranean coast). High EHDPP concentrations were observed on the Atlantic coast in the

379 Elorn and Etel estuaries and in Arcachon Bay, as well as in Marseille Bay (MaB) on the

380 Mediterranean coast. These compounds have previously been attributed to the industry of electronic

381 equipment (in thermoplastics of electric enclosures for televisions, computers, monitors, and printers)

382 or in relation with electronic waste recycling facilities (Gao et al., 2021). The aforementioned sites do

383 not share a similar pressure pattern (e.g. Arcachon Bay and the Nivelle and Etel estuaries are exempt

384 of major industrial discharge) and unequivocal source tracking of aryl OPEs remains challenging.

385

386
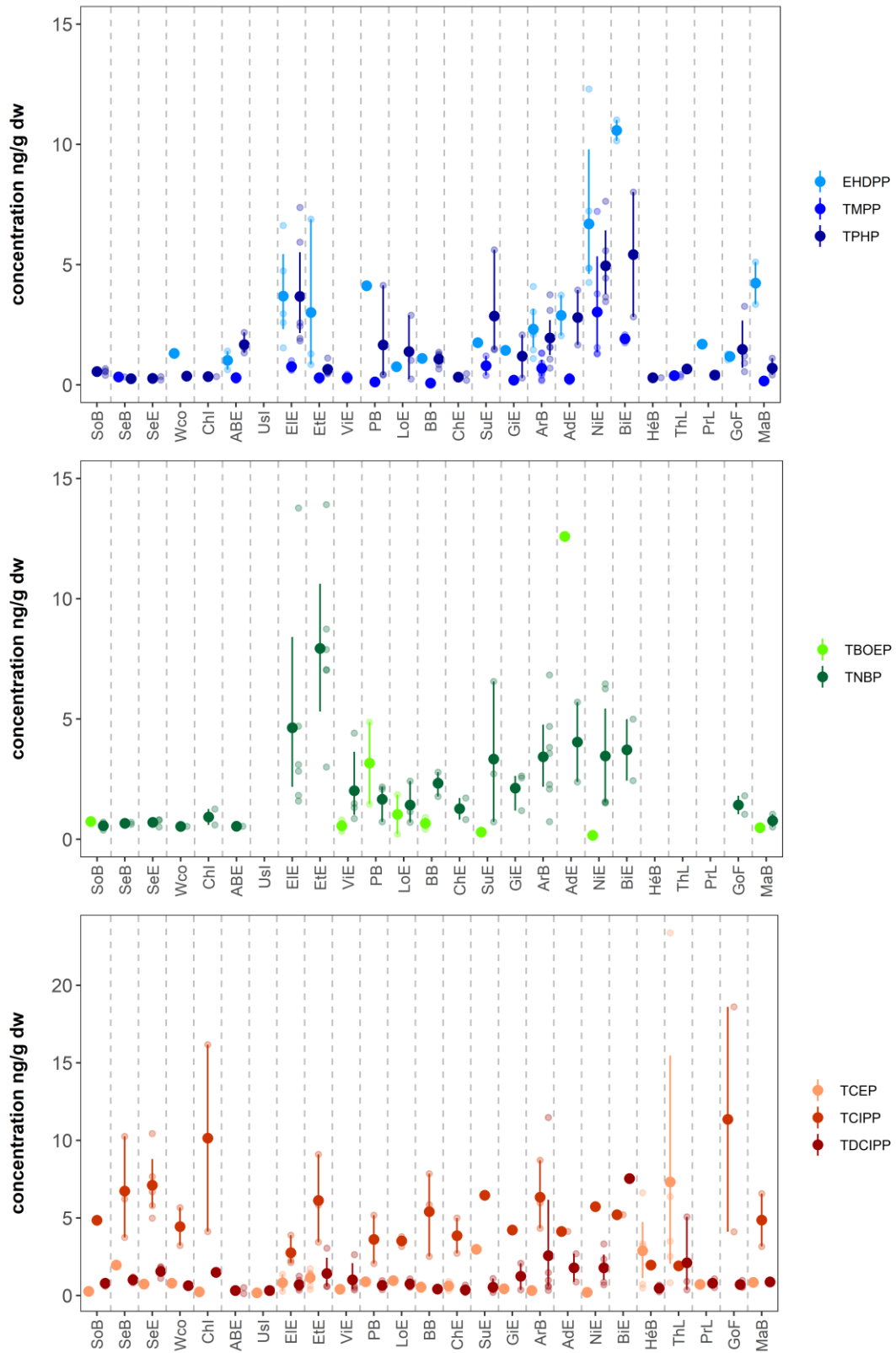
Figure 3. Geographical distribution of the OPE concentrations (ng g^{-1} dw) found in coastal bivalves of

the French coasts above LOQs. Data shown as mean ± standard deviations (individual values in

transparency).

390

391 Previous studies often related OPE levels in the marine coastal environment to wastewater discharges

392 (Kim et al., 2011; Sutton et al., 2019; Wei et al., 2015), as effluents have been reported as an important

393 source of OPEs (Xie et al., 2022). Here, concentrations in mussels from the Seine estuary (SeE) and

394 bay (SeB) were low for all OPEs (within the exception of the ubiquitous TCIPP), despite being under

395 the influence of its highly anthropized catchment area (*ca.* 17 million inhabitants and industries). A

396 Spearman correlation test between AHTN, a synthetic musk of known urban origin (Aminot et al.,

397 2021 and references herein), and any of the OPEs in our dataset revealed no significance. We also

398 observed a different geographical distribution to the one found for hydrophobic organic contaminants

399 (Munschy et al., 2015), which have shown higher concentrations in sites such as estuaries and deltas

400 with large catchment areas, industrial areas, and urban areas (e.g. Seine estuary and Rhône delta).

401 Previous studies on OPE distribution and source apportionment have generally focused on study sites

402 of regional scale. A thorough spatial pattern analysis of Hong Kong Bay waters revealed multiple

403 sources of OPEs, including human settlement, wastewater, manufacturing industry, construction

404 industry, vehicles, and shipping transport (Gao et al., 2021). In addition to shipping, other sources

405 include aquaculture (Aznar-Alemany et al., 2018; Zhang et al., 2020) or influences of local point

406 sources such as airports (Sundkvist et al., 2010). Besides, evidence for OPEs' degradability in marine

407 environments (Castro-Jiménez et al., 2022) suggests a rather limited potential for widespread

408 distribution, unlike other hydrophobic organic contaminants. Based on our data and literature

409 evidence, we hypothesize here that the OPE levels in coastal bivalves mostly relate to local hotspots

410 and that our understanding of contamination patterns in the marine environment is impeded by both

411 the huge diversity of their applications and their lower persistence. Selecting study sites based on

412 expected pressure and on the knowledge gained from other contaminants may consequently fail to

413 encompass the breadth of coastal OPE contamination. This limitation affects biomonitoring studies,

414 including ours, until better source identification is achieved.

415

416 **3.3 Comparison with worldwide levels**

417   A systematic review was conducted to screen for OPE concentrations reported in marine bivalves in

418   the published literature (see SI Text S3 for search terms). Since 2007, 12 articles were found and 1

419   report was also included (NIVA - Norwegian Environment Agency), with a total of 15 distinct zones

420   available (some studies described separate sampling areas) in Europe, Asia, and North America

421   (Figure 4 and Table 2). TCEP, TCIPP, TDCIPP, TBOEP, TPHP and TNBP were the most studied

422   compounds, reported in 11 zones. TMPP, EHDPP, and TEHP were also frequently reported (9 zones),

423   whilst TEP, MPDPP, TPEP, TPRP, and TDBPP were only studied in 1–3 zones. Globally, the

424   concentrations reported in our study compare with the concentrations reported worldwide, but with

425   ranges spanning several orders of magnitude, a fine comparison is challenging. TCIPP, the prevailing

426   OPE in our study (median: 4.93 ng g^{-1} dw) and the most homogeneously distributed, is also the most

427   abundant OPE worldwide (inter-study median: 17.3 ng g^{-1} dw). High concentrations of TBOEP (inter-

428   study median: 8.1 ng g^{-1} dw) have also been reported elsewhere, which tend to be higher than our

429   findings (median: 0.61 ng g^{-1} dw). We showed that this compound exhibited one of the highest IQR,

430   indicating strong spatial and temporal variabilities. We also found that TCEP concentrations were

431   strongly site-dependent, and if our median concentration (0.77 ng g^{-1} dw) is lower than the inter-study

432   median of concentrations retrieved from other published studies (4.1 ng g^{-1} dw), concentrations in HeB

433   and ThL, the two sites of the Mediterranean coastline with repeatably high levels, are comparable

434   (median of both sites: 3.28 ng g^{-1} dw. maximum 23.4 ng g^{-1} dw). Conversely, TNBP in our study

435   (median: 1.81 ng g^{-1} dw) was above the median of concentrations reported worldwide (inter-study

436   median: 1.40 ng g^{-1} dw). Undetected in our study, TEP was also generally unquantified or found at

437   low levels elsewhere. Regarding aryl OPEs in our samples, comparable levels were reported

438   worldwide for TPHP and EHDPP. In 8 studies (9 zones), TMPP was investigated with contrasted

439   results, either unquantified or found at notably high values. With the highest interquartile range

440   reported in our study, this compound also appears to be heterogeneously distributed. Quantified across

441   the 2 studies where MPDPP was targeted, it was qualitatively found in a large number of our samples

442   and deserves further interest. TEHP was not included in our work because of methodological

443   limitations, but we recommend further monitoring as it has been reported in several other studies.

444
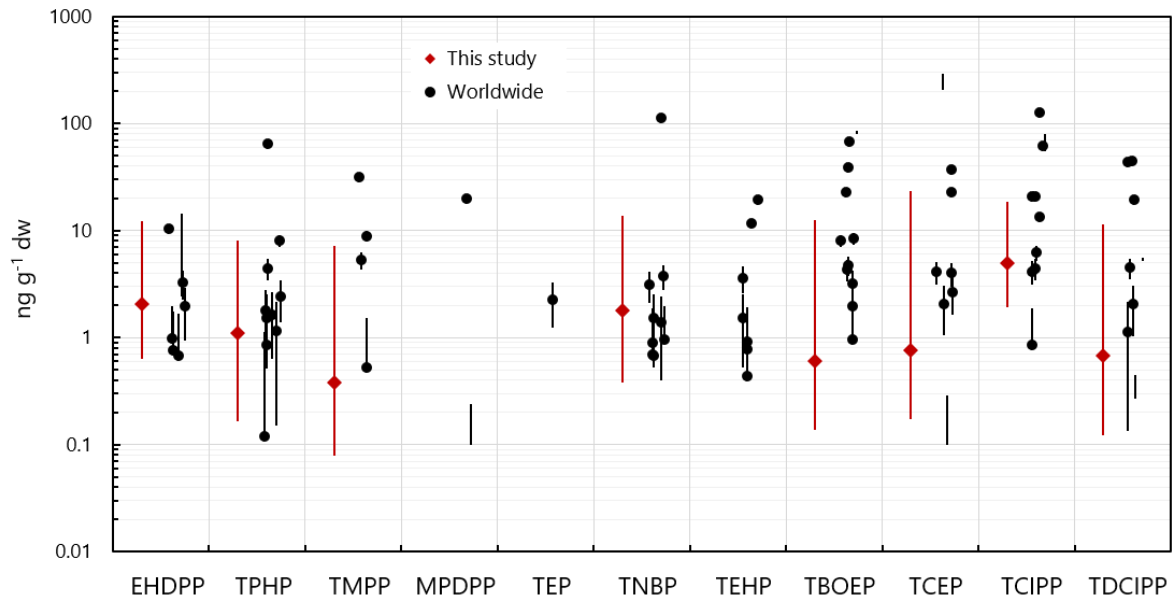
Figure 4. OPE concentrations (ng g^{-1} dw) in this study (median and minimum – maximum) and in other studies on marine filter-feeding bivalves worldwide (median or mean, and minimum – maximum when available). MPDPP and TEHP, not quantified in this study; TEP, not detected in this study.

Table 2. OPE concentrations (range and mean or median, in ng g^{-1} 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													
		EHDPP	TPHP	TMPP	MPDPP	TEP	TPRP	TNBP	TEHP	TBOEP	TCEP	TCIPP	TDCIPP	TDBPP	Reference
Europe															
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
Asia															
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
North America															
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 (Munschy 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. Munschy: Conceptualization, Investigation, Writing – review & editing, Funding acquisition. L. Tao: Methodology, Investigation, Writing – original draft. M. O'Loghlin: Investigation, Data curation. K. Héas-Moisan: Data acquisition, QA/QC. C. Pollono: Methodology, Data acquisition, QA/QC.

Declaration of competing interest

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