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1 **Pesticides, nonylphenols and polybrominated diphenyl ethers in marine bivalves from**
2 **France: a pilot study**

3

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25

26 **Abstract**

27 The present pilot study aimed to provide an overview of organic contaminant concentration
28 levels in the littoral ecosystems of the Pertuis seas. The study determined the concentrations
29 of twenty-nine pesticides, six nonylphenols and seven polybrominated diphenyl ethers
30 (PBDEs) in sediments, seawater, Pacific oysters and blue mussels. Oysters accumulated a
31 higher number of pesticides than blue mussels. Indeed, alpha BHC (0.60 - 0.72 ng/g, ww),
32 chlorfenvinphos (1.65 - 2.12 ng/g, ww), chlorpyrifos (0.79 - 0.93 ng/g, ww), chlortoluron
33 (2.50 - 4.31 ng/g, ww), metholachlor (up to 0.38 ng/g, ww) and parathion (0.56 - 0.69 ng/g,
34 ww) were quantified in oysters whereas only alpha BHC (0.24 - 0.31 ng/g, ww), was
35 quantified in mussels. The present results also revealed that the POPs detected in water or
36 sediments were not ultimately found accumulated in bivalves. Other molecules such as
37 methylparathion and BDE47 were quantified in sediments. These molecules, BDE99 and one
38 nonylphenol (OP2OE) were quantified in seawater. Finally, the comparison with the
39 available environmental guidelines showed that the values measured were at concentrations
40 not considered to cause adverse effects at the populations level except for chlortoluron in
41 seawater (15 – 50 ng/L).

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52 **Introduction**

53 Coastal waters have been subjected to various contaminants leaching from urban, industrial
54 and agricultural activities worldwide for many years. Numerous persistent chemicals
55 reaching the estuarine environment *via* rivers, wastewater treatment plants and catchment
56 leaching will accumulate in seawater, sediments and/or aquatic organisms. Some coastal
57 ecosystems exposed to anthropogenic contaminants are the most productive ecosystems in
58 the world (Luna-Acosta *et al.*, 2015a). The Pertuis-Charentais littoral area, in south-west
59 France, is one of them. This is a zone of transition between the Atlantic Ocean and the
60 estuaries of rivers Sèvre, Charente and Seudre. This region produces 22% of the french
61 shellfish production and France is the second biggest bivalve producer in Europe. Yet, over
62 the past decades, high mortality rates of bivalves have been observed. In 2008, 40 to 100% of
63 oyster spat mortality was recorded, and between 2014 and 2016, 50 to 100% of mussel
64 mortality was observed (Cochennec-Laureau and Baud, 2011; Mille, 2011; Travers *et al.*,
65 2016). Multiple causes are suspected to be involved in those mortalities, among them are the
66 occurrence of pathogens associated with specific abiotic conditions represent an important
67 threat (Fleury *et al.*, 2020). Moreover, questions have been raised about the role of organic
68 chemical pollution such as pesticides in the quality of surrounding waters but this has yet to
69 be elucidated.

70 If numerous studies were led on heavy metals contamination in littoral ecosystem,
71 much fewer were led on persistent organic pollutants (POPs) in the Pertuis Charentais region
72 (Miramand *et al.*, 2003; Munaron *et al.*, 2006; Roméo *et al.*, 2003). POPs are a family of
73 chemicals resistant to environmental degradation resulting in their long-term circulation in
74 the environment. They can travel long distances, bioaccumulate in animal tissue and
75 biomagnify through the food chain. Organochlorine pesticides, polybromodimethylethers

76 (PBDEs) and nonylphenols belong to the POPs family. Special attention has been raised on
77 their potential impact on human health and the environment (Luna-Acosta *et al.*, 2015b).
78 They have been massively used in industry and agriculture across the world. Since the
79 Stockholm Convention in 2001, they have been prohibited in most countries in the northern
80 hemisphere, however, they are still used in southern areas such as in southeast Asia.
81 Pesticides are an essential component of current intensive farming, as they are used to boost
82 and maintain crops yields against a large biodiversity of bacteria, insects and other organisms
83 considered as pests. In 2018, 70 000 tons of active substance were sold in France including
84 45% of herbicides, 37% of fungicide and 9% of insecticide (UIPP, 2019). PBDEs form a
85 group of flame retardants used in plastic products, textiles and building materials (Besis and
86 Samara, 2012). These organic compounds are widespread worldwide in the environment.
87 Nonylphenols are mainly used as surfactant in the industry to produce paints, papers,
88 cosmetics and cleaning products. They are also used for oil extraction and metal processing
89 as well as in household products and are, therefore, very common. They have been added to
90 the list of compounds of very high concern of the European Chemical Agency and the
91 Convention for the Protection of the Marine Environment of the North-East Atlantic
92 (OSPAR) in 2017.

93 Since 2008, a survey of heavy metals and POPs concentration levels in oysters from several
94 sites is performed annually (ROCCH, Ifremer). This program includes measurements of
95 lindane, dichlorodiphenyltrichloroethane (DDT) and tributyltin in the Pertuis seas (Ifremer,
96 2016). A couple of other studies measured organochlorine pesticides in oysters collected in
97 the same littoral area (Luna-Acosta *et al.*, 2015a; Bretwieser *et al.*, 2016).

98 The present pilot study aimed to provide an overview of organic contaminant
99 concentrations in the littoral ecosystems of the Pertuis seas in February 2019. The study
100 determined the concentrations of twenty-nine pesticides, six nonylphenols and seven PBDEs

101 in sediments, seawater, Pacific oyster (*Magallana gigas*) and blue mussel (*Mytilus edulis*).
102 Those sentinel species were used to assess the POPs contamination pressure on the littoral
103 ecosystem of the Pertuis seas. Contamination levels were discussed and compared to the
104 available environmental guidelines.

105 **Material and Methods**

106 **Site description and physicochemical parameters**

107 Mussels, oysters, seawater and sediment samples were collected in February 2019 at seven
108 sites located in the Pertuis Charentais littoral area (Figure 1). One site was located in the
109 south west of “Ile de Ré” and named “Le Martray”. This site was the most distant from the
110 shore and the most influenced by oceanic waters from the Atlantic Ocean. More exposed sites
111 to anthropogenic release of contaminants were located in the estuaries of the Sèvre Niortaise
112 (“Marsilly” site), Charente (“Pointe de la Fumée”, “Ile d’Aix”, “Ile Madame” sites) and
113 Seudre (Opposite “Mus du Loup” and “Ronce” sites) Rivers (Figure 1).

114 Turbidity (NTU), chlorophyll *a* ($\mu\text{g/L}$), salinity (PSU), sea surface temperature (SST, $^{\circ}\text{C}$),
115 dissolved oxygen (mg/L) and pH were measured continuously (every 10 minutes) in the
116 Charente and Seudre estuaries by multi-parameters probes (SAMBAT sea, nke
117 instrumentation). Data recorded from the 1st to the 28th of February 2019 were used.

118 **Sample collection**

119 Adult farmed (F) mussels, were collected at “Ile Madame” site ($n = 4$) and “Marsilly” site (n
120 $= 6$), respectively. Adult wild (W) mussels were collected at “Le Martray” site ($n = 6$).

121 Diploid (F/ 2N, $n = 5$) and triploid (F/ 3N, $n = 6$) adult oysters of similar age (2.5 years) and
122 life history were collected at “Le Martray” site. Other diploid oysters were collected at
123 “Ronce” site (F/ 2N, $n = 5$) and at “Ile d’Aix” site (W/ 2N, $n = 5$) (Figure 1). After their
124 collection, mussels and oysters were transported on ice and then frozen at -20°C until
125 analyses. For each oyster and mussel collected at the different sites, the total length (cm),

126 width (cm), thickness (cm) and total wet weight (g, ww) were measured and the resulting
127 Index of Form (IF) was calculated as described in Gouletquer *et al.*, (1998):

$$128 \quad IF = (Length + Thickness) / Width$$

129 One surface sediment sample (5 cm depth) was collected at “Le Martray” site and the two
130 exposed sites of “Pointe de la Fumée” and “Opposite Mus du Loup” (Figure 1). One surface
131 sea water sample was collected at “Le Martray” site and the exposed site of “Pointe de la
132 Fumée” (Figure 1). Sediment and water samples were frozen at -20°C until analyses.

133 **Organic contaminants extraction and analyses**

134 Four to six bivalves from each site were thawed and the flesh of each bivalve was dissected
135 and cut into pieces. About 3 g were spiked with perdeuterated internal standards. Pesticides,
136 nonylphenols and PBDEs were extracted from biological matrix following the QuECHERS
137 method (Quick, Easy, Cheap, Efficient, Rugged and Safe) as briefly described: each sample
138 was mixed with a solution of acetonitrile for 1 min at 160 rpm, then 6 g of MgSO₄ and 1.5 g
139 of sodium acetate were added and the mixture incubated 10 minutes at 250 rpm and finally
140 centrifuged at 4700 rpm for 5 minutes at 5°C. A second extraction using the Stir Bar
141 Sorptive Extraction (SBSE) method was performed as follows: 10 mL of supernatant was
142 collected and mixed with 40 mL of NaCO₃ (0.1 M). A stir bar was inserted and the solution
143 incubated at 750 rpm during 16h in darkness and at room temperature. After the extraction,
144 the stir bars were carefully rinsed, dried and analysed by TD-GC-MS/MS.

145 One water sample for each site was used. About 10 mL of methanol containing the internal
146 standards was added to each sample of water (100 mL). A stir bar was then added to the
147 solution and the extraction performed using the SBSE method as described above for the
148 biological samples.

149 Prior to extraction, 10 g of each sediment samples were weighed and spiked with internal
150 standards as previously described. 20 mL of a methylene chloride / acetone (50/50 v/v) were

151 added to 10 g of each sediment sample and the extraction was performed using an ultrasonic
152 bath (3 times during 15 minutes each). After filtration with NaSO₄, the extract was
153 evaporated until it reached a volume of 250 µL. The extract was then diluted in 10 mL of
154 methanol and 100 mL of ultrapure water. Organic compounds were then extracted following
155 the SBSE protocol as described above.

156 Bars were subsequently analysed for all samples using a gas chromatography system Agilent
157 7890A coupled to an Agilent 7000 triple quadrupole mass spectrometer (Agilent
158 Technologies) and equipped with a Thermal Desorption Unit (TDU) combined with a Cooled
159 Injection System (Gerstel). Thermodesorption and GC-MS/MS analyses were performed as
160 previously described in Lacroix *et al.*, (2014). The interface temperature was 300°C and the
161 GC temperature gradient was 50°C (1 min) to 320°C (20 min) at 3°C/min. The carrier gas
162 was Helium at a constant flow of 1 ml/min. The capillary column used was a RXi 5-ms
163 (Restek, Bellefonte, USA): 30 m x 0.25 mm ID x 0.25 µm film thickness. The quadrupole was
164 used in the Electronic Impact mode (Electronic Impact: 70 eV. voltage: 2000V). The
165 extraction yield of each organic molecule was corrected using the standard reference
166 materials (SRM 1974 c). Blank samples were considered and analytes were quantified
167 relatively to deuterated compounds using a calibration curve. Limits of quantification (LOQ)
168 were calculated using the calibration curve method (Shrivastava et al, 2011) and limit of
169 detection (LOD) were estimated by dividing the LOQ by 3.

170 **Statistical analysis**

171 Statistical analyses were performed using R (version 3.1.2). The potential differences of
172 POPs concentrations measured across the sites were assessed using 1-way ANOVA test.
173 When significant, comparison for each site was assessed in pairs by the lsmean test. When
174 residuals were not normally distributed, comparison for each site was assessed by the

175 nonparametric Wilcoxon rank test. Post-hoc comparisons were performed using adjusted p
176 value according to the Bonferroni method.

177 **Results**

178 Biometric parameters measurements revealed that triploid oysters were heavier (total weight:
179 16.1 ± 7.6 g ww) than diploid oysters (total weight: 12.9 ± 3.4 g ww) at Le Martray site
180 (Table 1A). These diploid and triploid oysters from Le Martray were also significantly
181 heavier and taller (mean length: 9.4 ± 0.7 cm and 12.2 ± 1.1 cm for M2N and M3N
182 respectively) than oysters from the Charente estuary (total weight: 7.1 ± 1.1 g ww, mean
183 length: 8.4 ± 1.0 cm) and the Seudre estuary (total weight: 3.7 ± 0.4 g ww, mean length: $7.7 \pm$
184 0.2 cm) (Table 1A).

185 Mussels collected at the different sites displayed similar weights ($p > 0.05$) (Table 1B) and
186 were taller at the Charente estuary (mean length: 4.4 ± 0.3 cm) than at Le Martray (mean
187 length: 3.9 ± 0.2 cm) (Table 1B). Further details on width, thickness and IF are provided in
188 supplementary material (Text S1).

189 **Physico-chemical parameters**

190 The mean turbidity, chlorophyll a and temperature, averaged over the month of February
191 2019, were different between the Charente and the Seudre sites ($p < 0.05$) (Table 2). The
192 Charente estuary was characterised by a lower mean temperature (10.5 °C) and a higher mean
193 concentration in chlorophyll a (1.61 µg/L) than the Seudre estuary (mean temperature of 11.2
194 °C and mean concentration in chlorophyll a of 1.28 µg/L) (Table 2). The mean salinity and
195 dissolved oxygen were similar for both sites ($p > 0.05$) (Table 2).

196 **Levels of POPs in sediments, seawater, oysters and mussel**

197 The analyses of contaminant concentrations in the seawater, sediments, oysters and mussels
198 were performed for forty-two POPs compounds: twenty-nine pesticides, six nonylphenols
199 and seven PBDEs. Most of the concentrations were below the limit of detection (LOD) or

200 between the LOD and the limit of quantification (LOQ) (Table 3). More POPs were
201 quantified in oysters (six pesticides) (Table 3C) than in mussels (one pesticide) (Table 3D).

202 **POPs in sediments and seawater.** Two POPs were quantified in sediments: methylparathion
203 and BDE47 (Table 3A), and four POPs were quantified in seawater: methylparathion,
204 BDE47, BDE99 and OP2OE (Table 3B). Methylparathion was quantified in sediments and
205 seawater at the Charente, Le Martray and Seudre (in sediments only) sites. The mean
206 concentration in methylparathion ranged between 0.16 and 0.41 ng/g in sediments (Table 3A)
207 and between 1.51 and 1.97 ng/L in seawater (Table 3B).

208 BDE 47 was quantified in sediments and seawater collected at the Charente, Le
209 Martray and Seudre (in sediments only) sites and the mean concentrations ranged between
210 0.2 and 0.6 ng/g in sediments (Table 3A) and between 1.13 and 1.88 ng/L in seawater (Table
211 3B). BDE 99 was quantified in the Charente seawater at a mean concentration of 9.8 ng/L but
212 was not detected at Le Martray (Table 3B). In sediments, the BDE99 mean concentration was
213 not detected at Le Martray and Charente sites (< 0.20 ng/g) and was below the LOQ (0.67
214 ng/g) at the Seudre site (Table 3A).

215 OP2OE was quantified in seawater only, at Le Martray and Charente sites, with mean
216 concentrations ranging between 7.37 and 8.62 ng/L (Table 3B). In sediments, the OP2OE
217 mean concentration ranged between the LOD (0.20 ng/g) and the LOQ (0.67 ng/g) at Le
218 Martray and Seudre sites and was below the LOD at the Charente site (Table 3A).

219 Other compounds were measured at the different sites and their concentrations ranged
220 between the LOD and the LOQ in sediments for alpha BHC, gamma BHC and acetochlor
221 (between 0.04 and 0.13 ng/g) (Table 3A), and in seawater for alpha BHC (between 0.30 and 1
222 ng/L), gamma BHC (between 0.30 and 1 ng/L), chlortoluron (between 15 and 50 ng/L) and
223 metolachlor (between 1.5 and 5 ng/L) (Table 3B). Contrarily to seawater samples, no
224 chlortoluron neither metolachlor were detected in sediment samples (Table 3A).

225 **POPs in the Pacific oysters.** Chlortoluron, alpha BHC, chlorpyrifos, parathion,
226 chlorfenvinphos and metolachlor were quantified in oysters from the different sites (Figure
227 2). The M3N oysters from Le Martray were characterized by their concentration in
228 metolachlor (0.38 ng/g ww) contrary to the concentrations found below the LOQ in oysters
229 from other sites (Figure 2, Table 3C). The oysters from Le Martray (M2N) and the Charente
230 site were characterized by their concentration in parathion whereas the oysters from the
231 Seudre estuary (Ronce) were characterized by their concentration in chlortoluron,
232 chlorpyrifos, alpha BHC and chlorfenvinphos (Figure 2).

233 The mean concentration in chlortoluron measured in oysters from the Seudre site (Ronce)
234 was almost two times higher (4.31 ng/g ww) ($p < 0.05$) than in oysters from Le Martray and
235 the Charente estuary (Table 3C). Among other compounds that were quantified in oysters
236 from all sites, the concentration in alpha BHC ranged between 0.60 and 0.72 ng/g ww, in
237 chlorpyrifos between 0.79 and 0.93 ng/g ww, in parathion between 0.56 and 0.69 ng/g ww
238 and in chlorfenvinphos between 1.65 and 2.12 ng/g ww (Table 3C).

239 Some other compounds were found between the LOD and the LOQ in oysters from all sites:
240 beta BHC (0.10 – 0.33 ng/g ww), gamma BHC (0.10 – 0.33 ng/g ww), diazinon (0.50 – 1.67
241 ng/g ww), delta BHC (0.10 – 0.33 ng/g ww), acetochlor (0.50 – 1.67 ng/g ww), aldrine (0.50
242 – 1.67 ng/g ww) and metolachlor (0.50 – 1.67 ng/g ww) (Table 3C).

243 **POPs in the blue mussels.** The alpha BHC was the only pollutant that could be quantified in
244 mussels (Table 3D). The concentrations were similar across sites (between 0.24 and 0.31 ng/g
245 ww) and were significantly lower than the concentrations measured in oysters ($p < 0.05$)
246 (Table 3D). Delta BHC (0.10 – 0.33 ng/g ww), metolachlor (0.50 – 1.67 ng/g ww) and
247 chlorpyrifos (0.50 – 1.67 ng/g ww) were found between the LOD and the LOQ in mussels
248 from the different sites (Table 3D).

249 The concentration results obtained in sediment, seawater or biota were compared to
250 the Environmental Guidance Values (EGV) or Predicted No Effect Concentration (PNEC)
251 when available (Table 4).

252

253 **Discussion**

254 The present study showed that triploid oysters were heavier than diploid ones, when
255 rigorously comparing the 2.5 years old M3N and M2N oysters from Le Martray that were
256 characterised by the same exposure history at the farming site and origin as they were
257 obtained from the same hatchery at the spat stage. This was expected as they are growing
258 faster than diploid oysters making them attractive for oyster farmers. They represent today
259 50% of the oyster production in the Pertuis Charentais region. The present variation in
260 biometry when comparing oysters and mussels from all sites is likely due to the difference of
261 origin, age, genetics and farmers' manipulations rather than the subtle difference measured in
262 chlorophyll *a* or temperature between the Charente and Sèvre estuaries.

263 Pollutants that were quantified in sediments and seawater were not necessarily
264 detected or quantified in living organisms. Two POPs were quantified in sediments:
265 methylparathion and BDE47, and four POPs were quantified in seawater: methylparathion,
266 BDE47, BDE99 and OP2OE. Methylparathion is an organophosphorus compound used as a
267 broad-spectrum insecticide in crops. The present results showed low concentrations in
268 sediments (0.16 to 0.41 ng/g) and in seawater (1.51 to 1.97 ng/L). Only a few studies sought
269 this pesticide in those compartments. The values found in sediments were lower than the
270 concentration of 16.8 ng/g measured in sediment of the Dniester River, Moldavia
271 (Sapozhnikova *et al.*, 2005). Because of its relatively short half-life (1-9 weeks), the
272 quantification of low concentrations could indicate a chronic release in rivers and estuaries.
273 The concentrations measured in water were 10 times below the PNEC value of 16 ng/L and

274 are thus too low to represent a risk for populations. Parathion concentrations measured in
275 oysters ranged between 0.56 and 0.69 ng/g and were below the LOD of 0.1 ng/g in mussels.
276 Those concentrations measured in oysters were consistent with the concentrations of
277 methylparathion measured in the 90s, in mussel, clam and oysters from the bays of the Ebro
278 delta, Spain, that ranged from 0.7 to 0.9 ng/g on average (Solé *et al.*, 2000). Other studies
279 neither detected parathion in mussels (*P. perna*) neither in oysters (*C. gigas*) (< 0.1 ng/g)
280 collected in the bays of Santa Catarina, Brazil (de Souza *et al.*, 2016).

281 BDE47 and BDE99 are the predominant flame-retardant molecules found in
282 commercial composition of BDEs mixtures (Abbasi *et al.*, 2019). These molecules are
283 ubiquitously distributed in the littoral environment and their concentrations have been
284 scarcely described in sediments and seawater of coastal areas of France. Some studies led on
285 the Atlantic coast of France found that PBDEs accumulated in fish, the European sturgeon
286 (*Acipenser sturio*) from the Gironde estuary (South Pertuis seas) (Acolas *et al.*, 2019) and the
287 European eel (*Anguilla anguilla*) from the Loire estuary, North Pertuis seas (Couderc *et al.*,
288 2015). The authors found very low concentration of PBDEs (mostly BDE47) from 10 to 100
289 pg/g of plasma in sturgeons (Acolas *et al.*, 2019). In the muscle of eels, the sum of PBDE
290 concentrations ranged from 25.9 to 46.2 ng/g (Couderc *et al.*, 2015). Low concentrations of
291 BDE 47 and BDE 99 were measured in oysters *C. gigas* from the Pertuis Charentais and
292 ranged from 0.4 to 1.5 ng/g for BDE 47 and up to 0.9 ng/g for BDE 99 (Luna-Acosta *et al.*,
293 2014). The present results showed that the concentrations of BDE 47 and 99 were below the
294 LD of 0.2 ng/g in oysters highlighting a decline between 2008 and 2019. In our study, BDE
295 47 was quantified at concentrations of 0.2-0.6 ng/g in sediments and 1.13-1.88 ng/L in
296 seawater, and BDE 99 was only quantified in seawater, at a concentration of 9.8 ng/L in the
297 Charente estuary. These concentrations were comparable to the values of BDE47 (0.96 ng/L)
298 and BDE99 (1.4 ng/L) measured in water and lower than the BDE-47 concentration measured

299 in sediment (2.3 ng/g) in an impacted, e-waste dismantling region in eastern China (Ling *et*
300 *al.*, 2021). In coastal rivers of North China the concentrations measured in water samples
301 were much lower: 1.12 pg/L for BDE99 and 0.82 pg/L for BDE47 (Liu *et al.*, 2021). In
302 sediment samples from the Thau Lagoon, France, all PBDEs concentrations measured were
303 also very low, below the LOD set at 10–100 pg/ g (Hong *et al.*, 2009). Our results showed
304 that the predominant BDEs were quantified at low concentrations in sediments and seawater.
305 Because the BDE99 concentrations measured in water samples of the Charente river were the
306 highest and comparable to the values measured at some impacted areas it would be relevant
307 to monitor this pollutant in the future. However, this compound was nor detected in oyster
308 neither in mussel in their early adult stage, revealing a low accumulation in marine bivalves,
309 in the present study.

310 Although nonylphenols can act as endocrine disruptors at low concentrations and are
311 ubiquitous in the environment, available data on their water concentrations in freshwater,
312 estuarine and marine ecosystems are scarce. Concentrations of OP2OE in seawater measured
313 in the present study ranged between 7.37 and 8.62 ng/L. Those concentrations were in the
314 range of the alkylphenol concentrations (that did not include OP2OE) measured in
315 Mediterranean coastal water that varied from 2 to 19 ng/L (Munaron *et al.*, 2012), and a
316 thousand times lower than the concentration of alkylphenol ethoxylates (including OP2OE)
317 measured in Israeli rivers that ranged from 11.83 to 55.32 µg/L (Houshan and Zoller, 2021).
318 Water concentrations of alkylphenol ethoxylates that are relatively recent aquatic pollutants
319 need to be sought in monitoring programs to better understand their distribution and fate in
320 aquatic systems.

321 Chlortoluron is a commonly used herbicide in wheat and barley crops, however, there
322 is only a few available studies reporting seawater concentrations in French estuaries. The
323 seawater concentration of chlortoluron measured in the present study was relatively low and

324 ranged between 15 and 50 ng/L, the LOD and LOQ respectively. These concentrations were
325 lower than the chlortoluron concentrations measured in the water of the Gironde estuary
326 (South Pertuis) of 71 ng/L in February 2015 (Levesque *et al.*, 2018) and about seven times
327 lower than the concentrations found in the Vilaine estuary (North Pertuis) where the values
328 ranged from 125 to 330 ng/L (Caquet *et al.*, 2013). The chlortoluron concentrations measured
329 in the present study were above the detection limit of 15 ng/L which is above the VGE in
330 seawater of 10 ng/L. Therefore, this molecule deserves a particular attention and should be
331 monitored as it may represent a risk for aquatic populations. The present results showed that
332 the concentrations of chlortoluron reached 4.31 ng/g in oysters from the Seudre estuary. To
333 our knowledge, no data on chlortoluron concentrations in marine bivalves contaminated in
334 their natural environment is available in the published literature.

335 Metolachlor was a broad-spectrum herbicide used in corn crops. It was replaced by
336 the active enantiomer S-metolachlor, after being prohibited in France in 2003. Our results
337 showed concentrations within the range of 1.5 - 5 ng/L (the LOD and LOQ respectively).
338 These concentrations were much lower than the values previously measured in North and
339 South areas off the Pertuis seas: 16 ng/L in the Gironde estuary in February 2015 (Levesque
340 *et al.*, 2018) to 70 ng/L (Farcy *et al.*, 2013) and 330 ng/L (Caquet *et al.*, 2013) in the Vilaine
341 estuary. Metolachlor accumulated in triploid oysters at a concentration of 0.38 ng/g and in
342 other diploid oysters at a concentration below the LOQ of 0.33 ng/g. Mussels also
343 concentrated this molecule at a concentration found between 0.5 ng/g (LOD) and 1.67 ng/g
344 (LOQ). Data published on metolachlor contamination of marine bivalves exposed in French
345 littoral areas are scarce.

346 Chlorfenvinphos and chlorpyrifos were widely used organophosphorus insecticides
347 and were banned in Europe, in 2007 and 2020, respectively. In oysters, the present
348 concentrations ranged between 0.79 and 0.93 ng/g for chlorpyrifos and between 1.65 and

349 2.12 ng/g for chlorfenvinphos. Chlorpyrifos has been quantified in various surface waters of
350 the world (Huang *et al.*, 2020), however, data on bivalve contamination in their natural
351 environment are scarce. In the early 90s, the concentrations in chlorpyrifos measured in
352 mussel, oyster and clam from the Ebro Delta, North West of the Mediterranean Sea, Spain,
353 ranged from 0.7 to 1.9 ng/g (Solé *et al.*, 2000). The capacity of those contaminants to
354 bioaccumulate in marine bivalves was observed a few years later by Serrano *et al.*, (1997)
355 who showed that chlorpyrifos and chlorfenvinphos bioaccumulated in the Mediterranean
356 mussel (*Mytilus galloprovincialis*). Studies led under laboratory conditions confirmed that
357 marine bivalves accumulated chlorpyrifos (reviewed in Huang *et al.*, 2020) but studies
358 monitoring the actual concentrations of chlorfenvinphos and chlorpyrifos in sentinel species
359 from the marine environment are rare. These studies are essential to evaluate the actual risk
360 due to these contaminations on marine environmental health.

361 Our study was also interested in the fate of aldrin, an organochlorine insecticide
362 widely used in the 50s-60s and banned in France, in 1992. The present results revealed a
363 decrease in marine bivalves from the Charente estuary of the Pertuis seas. Indeed, values
364 decreased from 4.15 ng/g ww in the scallops (*Mimachlamys varia*) in March 2014
365 (Bretwieser *et al.*, 2016) to reach values < LOQ of 1.67 ng/g in oysters (*C. gigas*) or < LOD
366 of 0.5 ng/g in mussels (*M. edulis*) in February 2019, in the present study.

367 DDT was widely used as a potent insecticide from the 40s and was banned for
368 agricultural uses in Europe in March 1983 (Directive 83/131/EEC). However, the subsequent
369 use of “Dicophol” that contained DDT, was only banned in France in March 2010. Because
370 they have been prohibited for many years, the concentrations of DDT and its byproducts were
371 expected to be very low in the marine environment and to gradually decrease in the years to
372 come. In our study, 2,4- and 4,4-DDT were below the LOD in mussels (< 0.5 ng/g) and
373 oysters (< 0.2 and 0.5 ng/g, respectively). These findings were consistent with the results

374 found by Luna-Acosta *et al.* (2015a) in oysters (*C. gigas*) from the Charente and Seudre
375 estuaries where these molecules were found at levels below the LOD or at very low
376 concentration (0.8 ng/g) respectively (Luna-Acosta *et al.*, 2015a). Lindane is another
377 insecticide that has been widely used during the same period (40s-70s), especially in France,
378 one of the main countries using it in Europe, before being banned in 1998. Alpha-BHC, a
379 byproduct of lindane present in commercial grade insecticide solution to treat a wide variety
380 of crops (corn, beet, cereals, flax and colza) was quantified in oysters (0.60 and 0.72 ng/g)
381 and mussels (0.24 and 0.31 ng/g) in the present study. The concentrations measured in
382 oysters encompass the guidance concentration in the flesh of bivalves of 0.53 ng/g. The past
383 high emission and persistence of lindane in the environment, and the likely erosion and
384 removal of contaminated river sediments into estuaries may explain the post-ban presence of
385 the byproducts in marine bivalves as found in the present study.

386 Most of the POPs are found in very low concentrations in sediments, seawater and
387 biota. Of the 42 compounds analysed in this study, most of them were not detected or
388 detected below the LOD or LOQ. The LOD and LOQ in mussels and oysters were not the
389 same for all chemicals. Those differences are due to a better extraction yield for oysters than
390 for mussels, and have to be considered when interpreting POPs concentration levels between
391 species. Moreover, the higher number of pesticides quantified in the Pacific oysters (*C. gigas*)
392 than in the blue mussels (*M. edulis*) confirm the relevance of studying this species in POPs
393 biomonitoring programme. The seek for POPs in the different compartments of the
394 environment (water, sediment and biota) is also necessary for a better understanding of the
395 fate of pollutants in the aquatic ecosystems. Finally, future studies could analyse POPs in
396 older bivalve species (up to 3 or 4 years for adult oysters) to obtain further information on
397 organic contaminant accumulation over time.

398

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551

552 **Figure and Table Legend.**

553 **Figures.**

554 **Figure 1.** Map showing the location of all the samples collected in the Pertuis-Charentais
555 region, France.

556 **Figure 2.** Principal component analysis showing the distribution of POPs according to their
557 concentration levels in oysters from the Seudre, Martray (diploid, M2N and triploid, M3N)
558 and Charente Sites.

559 **Tables.**

560 **Table 1.** Measurement of total length (cm), width (cm), thickness (cm), total weight (g, ww)
561 and resulting Index of Form (IF) of the oysters (A) and mussels (B) (mean \pm SD, $n = 4$ to 6)
562 collected at the different sites. *: significantly different ($p < 0.05$).

563 **Table 2.** Turbidity, chlorophyll a, salinity, SST, dissolved oxygen and pH measured in
564 Charente and Seudre by multi parameters probes in February 2019 (mean, $n = 3303$).

565 **Table 3.** A, B, C and D. Pesticides, nonylphenols and PBDEs concentrations measured by
566 GCMS/MS in sediments (A), seawater (B), oysters (C) and mussels (D) samples collected at
567 the different sites: Martray, Charente and Seudre. nd : non detected, <LOD : below limit of
568 detection, <LOQ : below limit of quantification. Units are expressed in ng/g of sediments (n

569 = 1 per site), ng/L of seawater ($n = 1$ per site) or ng/g of tissue wet weight (mean, $n = 5$ to 6
570 oysters or 4 to 6 mussels per site).

571 **Table 4.** Guidance and measured values in different matrix (sediment in ng/g, seawater in
572 ng/L, biota in ng/g wet weight), for different POPs (in orange: the LOD was higher than the
573 guidance value, in red: the LOD was lower than the guidance value).

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577 Figure 1.

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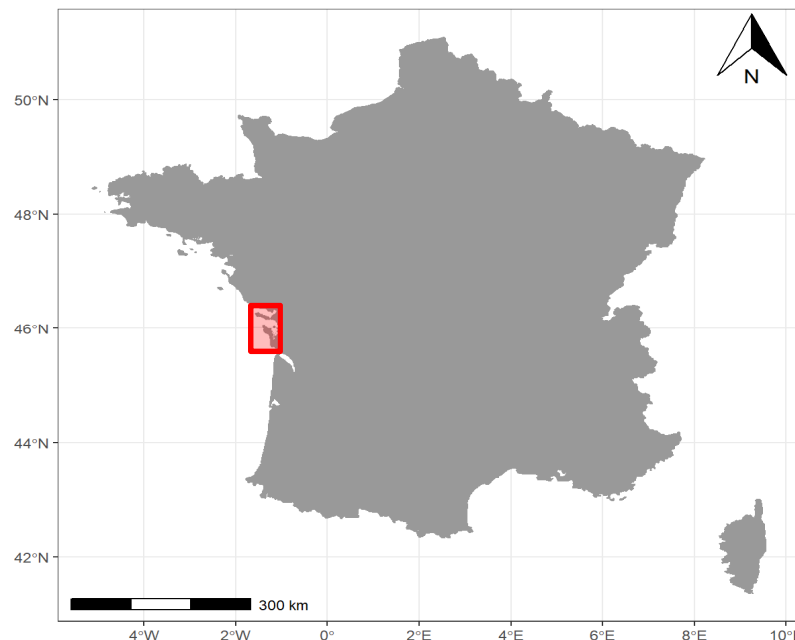
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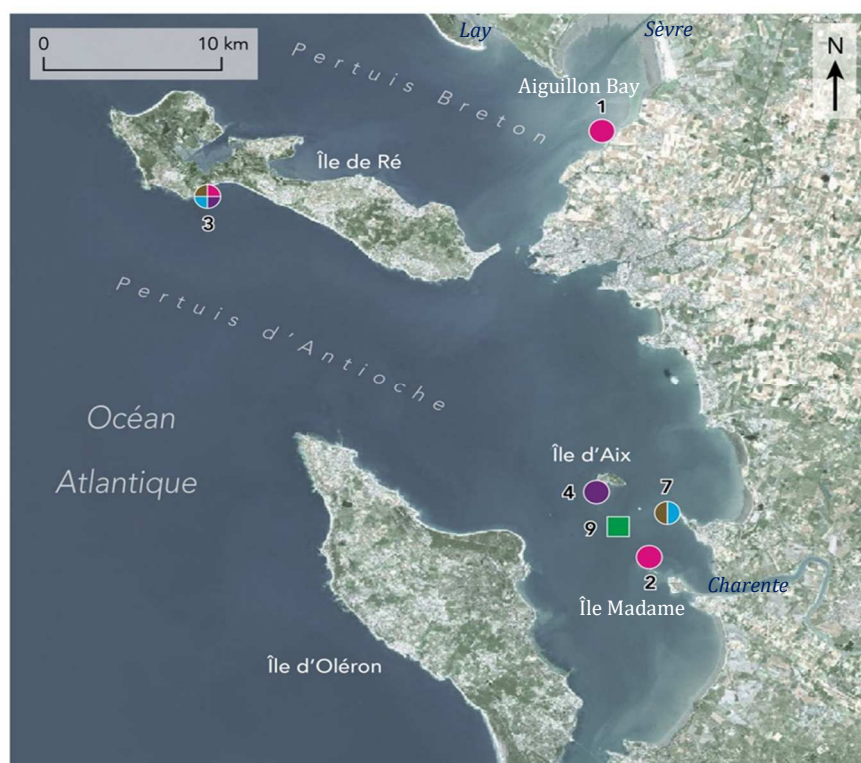
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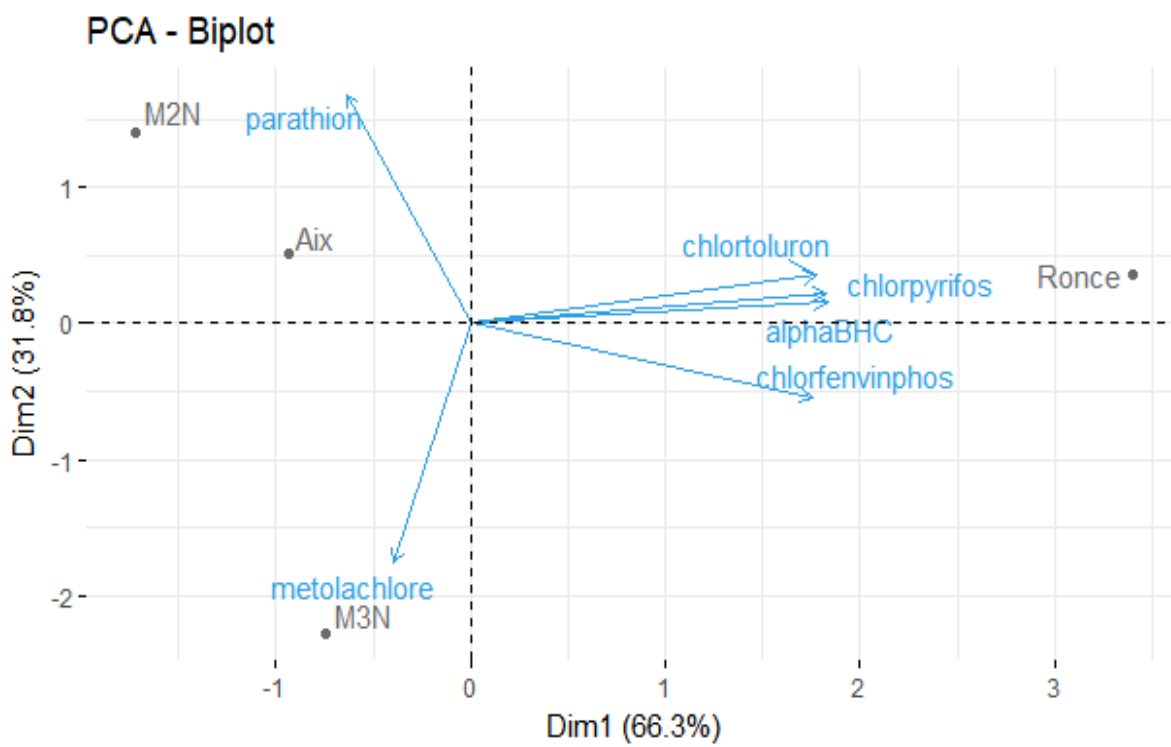
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596 Figure 2.



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607 Table 1.

A

	Total length (cm)	Width (cm)	Thickness (cm)	Total weight (g ww)	IF
Charente (Ile d'Aix)	8.4 ± 1.0	4.4 ± 0.3	2.4 ± 0.5	7.1 ± 1.1	2.5 ± 0.2
Seudre (Ronc les Bains)	7.7 ± 0.2	4.1 ± 0.2	1.9 ± 0.4	3.7 ± 0.4	2.4 ± 0.2
Martray 2N (M2N)	9.4 ± 0.7	5.3 ± 0.6	3.0 ± 0.3	12.9 ± 3.4 *	2.3 ± 0.2
Martray 3N (M3N)	12.2 ± 1.1	5.4 ± 0.3	3.7 ± 0.6	16.1 ± 7.6 *	2.9 ± 0.3*

B

	Total Length (cm)	Width (cm)	Thickness (cm)	Total weight (g ww)	IF
Marsilly (Sèvre)	4.2 ± 0.3	2 ± 0.1	1.8 ± 0.2*	2.3 ± 0.5	3 ± 0.2*
Charente (Ile Madame)	4.4 ± 0.3	2.2 ± 0.1*	1.6 ± 0.1	1.8 ± 0.2	2.7 ± 0.0
Martray	3.9 ± 0.2	2.1 ± 0.1	1.5 ± 0.1	1.9 ± 0.5	2.6 ± 0.2

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Table 2.

	Turbidity (NTU)	Chlorophyll a ($\mu\text{g/L}$)	Salinity (PSU)	Temperature ($^{\circ}\text{C}$)	Dissolved oxygen (mg/L)
Probe 1 Charente	4.3 ± 0.9	1.61 ± 0.06	29.4 ± 0.4	10.5 ± 0.04	10.9 ± 0.02
Probe 2 Seudre	16.7 ± 0.1	1.28 ± 0.04	29.2 ± 0.2	11.2 ± 0.03	10.9 ± 0.03

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Table 3A.

Molécules	Concentrations in sediments* (ng/g)			LOD (ng/g)	LOQ (ng/g)
	Ile de Ré	Charente	Seudre		
acetochlore	<LOD	<LOQ	<LOQ	0.04	0.13
alachlore	<LOD	<LOD	<LOD	0.20	0.67
aldrine	<LOD	<LOD	<LOD	0.20	0.67
alpha-BHC	<LOQ	<LOQ	<LOQ	0.04	0.13
beta-BHC	<LOD	<LOD	<LOQ	0.04	0.13
delta-BHC	<LOD	<LOD	<LOD	0.04	0.13
gamma-BHC	<LOQ	<LOQ	<LOQ	0.04	0.13
chlorfenvinphos	<LOD	<LOD	<LOD	0.20	0.67
chlorpyrifos	<LOD	<LOD	<LOD	0.04	0.13
chlortoluron	<LOD	<LOD	<LOD	2.00	6.67
2,4-ddd	<LOD	<LOD	<LOD	0.20	0.67
4,4-ddd	<LOD	<LOD	<LOD	0.20	0.67
2,4-dde	<LOD	<LOD	<LOD	0.20	0.67
4,4-dde	<LOD	<LOD	<LOD	0.20	0.67
2,4-ddt	<LOD	<LOD	<LOD	0.20	0.67
4,4-ddt	<LOD	<LOD	<LOD	0.20	0.67
diazinon	<LOD	<LOD	<LOD	2.00	6.67
dieldrine	<LOQ	<LOD	<LOQ	0.04	0.13
diuron	nd	nd	nd	nd	nd
endosulfan alpha	<LOD	<LOD	<LOD	0.04	0.13
endosulfan beta	<LOD	<LOD	<LOD	0.20	0.67
endosulfan sulfate	<LOD	<LOD	<LOD	0.20	0.67
endrine	<LOD	<LOD	<LOD	0.20	0.67

isodrine	<LOD	<LOD	<LOD	0.20	0.67
metazachlore	<LOD	<LOD	<LOD	0.20	0.67
methylparathion	0.20	0.41	0.16	0.04	0.13
metolachlore	<LOD	<LOD	<LOD	0.20	0.67
oxadiazon	<LOD	<LOD	<LOD	0.20	0.67
parathion	<LOD	<LOD	<LOD	0.20	0.67
NP1OE	nd	nd	nd	nd	nd
NP2OE	nd	nd	nd	nd	nd
OP1OE	nd	nd	nd	nd	nd
OP2OE	<LOQ	<LOD	<LOQ	0.20	0.67
4-octylphenol	<LOD	<LOD	<LOD	0.04	0.13
4-nonylphenol	nd	nd	nd	nd	nd
BDE 28	<LOD	<LOD	<LOQ	0.04	0.13
BDE 47	0.39	0.20	0.60	0.04	0.13
BDE 99	<LOD	<LOD	<LOQ	0.20	0.67
BDE 100	<LOD	<LOD	<LOD	0.20	0.67
BDE 153	<LOD	<LOD	<LOD	0.20	0.67
BDE 154	<LOD	<LOD	<LOD	0.20	0.67
BDE 183	<LOD	<LOD	<LOD	0.20	0.67

*concentration range colour code:

<LOD	<LOQ	0.2 < x < 0.5	0.5 < x < 1.5	1.5 < x < 2.5
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646 Table 3B.

Molecules	Concentrations in seawater* (ng/L)		LOD (ng/L)	LOQ (ng/L)
	Martray	Charente		
acetochlore	<LOD	<LOQ	0.30	1.00
alachlore	<LOD	<LOD	1.50	5.00
aldrine	<LOD	<LOD	1.50	5.00
alpha-BHC	<LOQ	<LOQ	0.30	1.00
beta-BHC	<LOD	<LOD	0.30	1.00
delta-BHC	<LOD	<LOD	0.30	1.00
gamma-BHC	<LOQ	<LOQ	0.30	1.00
chlorfenvinphos	<LOD	<LOD	1.50	5.00
chlorpyrifos	<LOD	<LOD	0.30	1.00
chlortoluron	<LOQ	<LOQ	15.00	50.00
2,4-ddd	<LOD	<LOD	1.50	5.00
4,4-ddd	<LOD	<LOD	1.50	5.00
2,4-dde	<LOD	<LOD	1.50	5.00
4,4-dde	<LOD	<LOD	1.50	5.00
2,4-ddt	<LOD	<LOD	1.50	5.00
4,4-ddt	<LOD	<LOD	1.50	5.00
diazinon	<LOD	<LOD	3.00	10.00
dieldrine	<LOD	<LOD	0.30	1.00
diuron	nd	nd	nd	nd
endosulfan alpha	<LOD	<LOD	0.30	1.00
endosulfan beta	<LOD	<LOD	1.50	5.00
endosulfan sulfate	<LOD	<LOD	1.50	5.00
endrine	<LOD	<LOD	1.50	5.00

isodrine	<LOD	<LOD	1.50	5.00
metazachlore	<LOD	<LOD	1.50	5.00
methylparathion	1.51	1.97	0.30	1.00
metolachlore	<LOQ	<LOQ	1.50	5.00
oxadiazon	<LOD	<LOD	1.50	5.00
parathion	<LOD	<LOD	1.50	5.00
NP1OE	nd	nd	nd	nd
NP2OE	nd	nd	nd	nd
OP1OE	nd	nd	nd	nd
OP2OE	8.62	7.37	1.50	5.00
4-nonylphenol	nd	nd	nd	nd
4-octylphenol	<LOD	<LOD	0.30	1.00
BDE 28	<LOD	<LOD	0.30	1.00
BDE 47	1.13	1.88	0.30	1.00
BDE 99	<LOD	9.80	1.50	5.00
BDE 100	<LOD	<LOD	1.50	5.00
BDE 153	<LOD	<LOQ	1.50	5.00
BDE 154	<LOD	<LOD	1.50	5.00
BDE 183	<LOD	<LOD	1.50	5.00

*concentration range colour code:

<LD	<LQ	0.5 < x < 1.5	1.5 < x < 2.5	6.5 < x < 7.5	8.5 < x < 9.5	9.5 < x < 10.5
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647 Table 3C.

Molecules	Concentrations in oysters* (ng/g ww)				LOD (ng/g ww)	LOQ (ng/g ww)
	Martray (2N)	Martray (3N)	Charente	Seudre		
acetochlore	<LOQ	<LOQ	<LOQ	<LOQ	0.50	1.67
alachlore	<LOQ	<LOQ	<LOQ	<LOQ	0.50	1.67
aldrine	<LOQ	<LOQ	<LOQ	<LOQ	0.50	1.67
alpha-BHC	0.60	0.62	0.62	0.72	0.10	0.33
beta-BHC	<LOQ	<LOQ	<LOQ	<LOQ	0.10	0.33
gamma-BHC	<LOQ	<LOQ	<LOQ	<LOQ	0.10	0.33
delta-BHC	<LOQ	<LOQ	<LOQ	<LOQ	0.10	0.33
chlorfenvinphos	1.65	1.89	1.72	2.12	0.50	1.67
chlorpyrifos	0.79	0.80	0.81	0.93	0.10	0.33
chlortoluron	2.64	2.50	2.46	4.31	0.50	1.67
2,4-ddd	<LOD	<LOD	<LOD	<LOD	0.20	0.67
4,4-ddd	<LOD	<LOD	<LOD	<LOD	0.50	1.67
2,4-dde	<LOD	<LOD	<LOD	<LOD	0.50	1.67
4,4-dde	<LOD	<LOD	<LOD	<LOD	0.20	0.67
2,4-ddt	<LOD	<LOD	<LOD	<LOD	0.50	1.67
4,4-ddt	<LOD	<LOD	<LOD	<LOD	0.20	0.67
diazinon	<LOQ	<LOQ	<LOQ	<LOQ	0.50	1.67
dieldrine	0.27	<LOD	<LOD	<LOD	0.20	0.67
diuron	nd	nd	nd	nd	nd	nd
endosulfan alpha	<LOD	<LOD	<LOD	<LOD	0.20	0.67
endosulfan beta	<LOD	<LOD	<LOD	<LOD	1.00	3.33
endosulfan sulfate	<LOD	<LOD	<LOD	<LOD	0.20	0.67
endrine	<LOD	<LOD	<LOD	<LOD	0.20	0.67
isodrine	<LOD	<LOD	<LOD	<LOD	0.10	0.33
metazachlore	<LOD	<LOD	<LOD	<LOD	0.50	1.67

methylparathion	<LOQ	<LOQ	<LOQ	<LOQ	0.50	1.67
metolachlore	<LOQ	0.38	<LOQ	<LOQ	0.10	0.33
oxadiazon	<LOD	<LOD	<LOD	<LOD	0.50	1.67
parathion	0.69	0.56	0.63	0.61	0.10	0.33
NP1OE	nd	nd	nd	nd	nd	nd
NP2OE	nd	nd	nd	nd	nd	nd
OP1OE	<LOD	<LOD	<LOD	<LOD	0.50	1.67
OP2OE	<LOD	<LOD	<LOD	<LOD	0.50	1.67
4-nonylphenol	nd	nd	nd	nd	nd	nd
4-octylphenol	<LOD	<LOD	<LOD	<LOD	0.10	0.33
BDE 28	<LOD	<LOD	<LOD	<LOD	0.50	1.67
BDE 47	<LOD	<LOD	<LOD	<LOD	0.20	0.67
BDE 99	<LOD	<LOD	<LOD	<LOD	0.20	0.67
BDE 100	<LOD	<LOD	<LOD	<LOD	0.20	0.67
BDE 153	<LOD	<LOD	<LOD	<LOD	0.20	0.67
BDE 154	<LOD	<LOD	<LOD	<LOD	0.20	0.67
BDE 183	<LOD	<LOD	<LOD	<LOD	0.50	1.67

*concentration range colour code:

<LOD	<LOQ	0.2 < x < 0.5	0.5 < x < 1.5	1.5 < x < 2.5	2.5 < x < 3.5	3.5 < x < 4.5
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650 Table 3D.

Molecules	Concentrations in mussels* (ng/g ww)			LOD (ng/g ww)	LOQ (ng/g ww)
	Martray	Charente	Sevre		
acetochlore	<LOD	<LOD	<LOD	0.50	1.67
alachlore	<LOD	<LOD	<LOD	0.50	1.67
aldrine	<LOD	<LOD	<LOD	0.50	1.67
alpha-BHC	0.31	0.26	0.24	0.10	0.33
beta-BHC	<LOD	<LOD	<LOD	0.50	1.67
delta-BHC	<LOQ	<LOQ	<LOQ	0.10	0.33
gama bhc	<LOD	<LOD	<LOD	0.10	0.33
chlorfenvinphos	nd	nd	nd	nd	nd
chlorpyrifos	<LOQ	<LOQ	<LOQ	0.50	1.67
chlortoluron	<LOD	<LOD	<LOD	0.50	1.67
2,4-ddd	<LOD	<LOD	<LOD	0.50	1.67
4,4-ddd	<LOD	<LOD	<LOD	0.50	1.67
2,4-dde	<LOD	<LOD	<LOD	0.10	0.33
4,4-dde	<LOD	<LOD	<LOD	0.50	1.67
2,4-ddt	<LOD	<LOD	<LOD	0.50	1.67
4,4-ddt	<LOD	<LOD	<LOD	0.50	1.67
diazinon	<LOD	<LOD	<LOD	0.50	1.67
dieldrine	<LOD	<LOD	<LOD	0.50	1.67
diruon	nd	nd	nd	nd	nd
endosulfan alpha	<LOD	<LOD	<LOD	0.10	0.33
endosulfan beta	<LOD	<LOD	<LOD	1.00	3.33
endosulfan sulfate	<LOD	<LOD	<LOD	0.10	0.33
endrine	<LOD	<LOD	<LOD	0.50	1.67
isodrine	<LOD	<LOD	<LOD	0.50	1.67
metazachlore	<LOD	<LOD	<LOD	0.50	1.67
methylparathion	<LOD	<LOD	<LOD	0.50	1.67
metolachlore	<LOQ	<LOQ	<LOQ	0.50	1.67

oxadiazon	<LOD	<LOD	<LOD	0.10	0.33
parathion	<LOD	<LOD	<LOD	0.10	0.33
NP1OE	nd	nd	nd	nd	nd
NP2OE	nd	nd	nd	nd	nd
OP1OE	nd	nd	nd	nd	nd
OP2OE	nd	nd	nd	nd	nd
4-nonylphenol	nd	nd	nd	nd	nd
4-octylphenol	<LOD	<LOD	<LOD	0.10	0.33
BDE 28	<LOD	<LOD	<LOD	1.00	3.33
BDE 47	<LOD	<LOD	<LOD	1.00	3.33
BDE 99	<LOD	<LOD	<LOD	1.00	3.33
BDE 100	<LOD	<LOD	<LOD	1.00	3.33
BDE 153	<LOD	<LOD	<LOD	0.50	1.67
BDE 154	<LOD	<LOD	<LOD	0.50	1.67
BDE 183	<LOD	<LOD	<LOD	0.50	1.67

*concentration range colour code:

<LOD	<LOQ	0.2 < x < 0.5
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Table 4.

	Sediment (ng/g)		Seawater (ng/L)		Biota (ng/g ww)	
	Guidance	Measured	Guidance	Measured	Guidance	Measured
acetochlore			2.6 ^b	< 1		
alpha BHC			2 ^c	0.3 < x < 1	0.53	0.60 – 0.72
gamma BHC	2.4 ^a	0.04 < x < 0.13	2	0.3 < x < 1		
chlorfenvinphos			100 ^b	< 1.5	30.9 ^d	1.65 – 2.12
chlorpyrifos			30 ^b	< 0.3	10.32	0.78 – 0.93
chlortoluron			10^b	15 < x < 50		
endosulfan alpha			0.5 ^a	< 0.3		
metazachlore	8.0 ^a	< 0.2	2 ^b	< 1.5		
methylparathion			16 ^a	1.97		
octylphenol			10 ^c	8	2.29 ^d	< 0.5
oxadiazon	0.04^a	< 0.2	9 ^b	< 1.5		

656 ^a: PNEC, ^b: VGE, ^c: NQE and ^d: VGE mollusk.

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675 **Supplementary material**

676 Biometric parameters measurements revealed that oysters collected at the different sites were
677 of similar width and thickness ($p > 0.05$). Triploid oysters possessed a higher IF (2.9 ± 0.3)
678 than diploid oysters (mean IF: 2.3 ± 0.2) at Le Martray site (Table 1A).

679 Mussels from the Sèvre estuary displayed the highest IF (mean: 3 ± 0.2) (Table 1B). Mussels
680 from the Charente were wider (width: 2.2 ± 0.1 cm) than mussels from the Sèvre (width: $2 \pm$
681 0.1 cm). Mussels from the Sèvre were thicker (thickness: 1.8 ± 0.2 cm) than at Le Martray
682 (thickness: 1.5 ± 0.1 cm) (Table 1B).