



## Pesticides, nonylphenols and polybrominated diphenyl ethers in marine bivalves from France: A pilot study

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### ABSTRACT

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

### 1. Introduction

Coastal waters have been subjected to various contaminants leaching from urban, industrial and agricultural activities worldwide for many years. Numerous persistent chemicals reaching the estuarine environment via rivers, wastewater treatment plants and catchment leaching will accumulate in seawater, sediments and/or aquatic organisms. Some coastal ecosystems exposed to anthropogenic contaminants are the most productive ecosystems in the world (Luna-Acosta et al., 2015a). The Pertuis-Charentais littoral area, in south-west France, is one of them. This is a zone of transition between the Atlantic Ocean and the estuaries of rivers Sèvre, Charente and Seudre. This region produces 22% of the French shellfish production and France is the second biggest bivalve producer in Europe. Yet, over the past decades, high mortality rates of bivalves have been observed. In 2008, 40 to 100% of oyster spat mortality was recorded, and between 2014 and 2016, 50 to 100% of mussel mortality was observed (Coehennec-Laureau and Baud, 2011; Mille, 2011; Travers et al., 2016). Multiple causes are suspected to be involved

in those mortalities, among them are the occurrence of pathogens associated with specific abiotic conditions represent an important threat (Fleury et al., 2020). Moreover, questions have been raised about the role of organic chemical pollution such as pesticides in the quality of surrounding waters but this has yet to be elucidated.

If numerous studies were led on heavy metals contamination in littoral ecosystem, much fewer were led on persistent organic pollutants (POPs) in the Pertuis Charentais region (Miramand et al., 2003; Munaron et al., 2006; Roméo et al., 2003). POPs are a family of chemicals resistant to environmental degradation resulting in their long-term circulation in the environment. They can travel long distances, bioaccumulate in animal tissue and biomagnify through the food chain. Organochlorine pesticides, polybromodimethylethers (PBDEs) and nonylphenols belong to the POPs family. Special attention has been raised on their potential impact on human health and the environment (Luna-Acosta et al., 2015b). They have been massively used in industry and agriculture across the world. Since the Stockholm Convention in 2001, they have been prohibited in most countries in the northern

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hemisphere, however, they are still used in southern areas such as in southeast Asia. Pesticides are an essential component of current intensive farming, as they are used to boost and maintain crops yields against a large biodiversity of bacteria, insects and other organisms considered as pests. In 2018, 70,000 tons of active substance were sold in France including 45% of herbicides, 37% of fungicide and 9% of insecticide (UIPP, 2019). PBDEs form a group of flame retardants used in plastic products, textiles and building materials (Besis and Samara, 2012). These organic compounds are widespread worldwide in the environment. Nonylphenols are mainly used as surfactant in the industry to produce paints, papers, cosmetics and cleaning products. They are also used for oil extraction and metal processing as well as in household products and are, therefore, very common. They have been added to the list of compounds of very high concern of the European Chemical Agency and the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) in 2017.

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

The present pilot study aimed to provide an overview of organic contaminant concentrations in the littoral ecosystems of the Pertuis seas in February 2019. The study determined the concentrations of twenty-nine pesticides, six nonylphenols and seven PBDEs in sediments, seawater, Pacific oyster (*Magallana gigas*) and blue mussel (*Mytilus edulis*). Those sentinel species were used to assess the POPs contamination pressure on the littoral ecosystem of the Pertuis seas. Contamination levels were discussed and compared to the available environmental guidelines.

## 2. Material and methods

### 2.1. Site description and physicochemical parameters

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

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

### 2.2. Sample collection

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

Diploid (F/2N,  $n = 5$ ) and triploid (F/3N,  $n = 6$ ) adult oysters of similar age (2.5 years) and life history were collected at “Le Martray” site. Other diploid oysters were collected at “Ronce” site (F/2N,  $n = 5$ ) and at “Ile d’Aix” site (W/2N,  $n = 5$ ) (Fig. 1). After their collection, mussels and oysters were transported on ice and then frozen at  $-20^{\circ}\text{C}$  until analyses. For each oyster and mussel collected at the different sites, the total length (cm), width (cm), thickness (cm) and total wet weight (g, ww) were measured and the resulting Index of Form (IF) was calculated as described in Gouletquer et al. (1998):

$$\text{IF} = (\text{Length} + \text{Thickness}) / \text{Width}$$

One surface sediment sample (5 cm depth) was collected at “Le Martray” site and the two exposed sites of “Pointe de la Fumée” and “Opposite Mus du Loup” (Fig. 1). One surface sea water sample was collected at “Le Martray” site and the exposed site of “Pointe de la Fumée” (Fig. 1). Sediment and water samples were frozen at  $-20^{\circ}\text{C}$  until analyses.

### 2.3. Organic contaminants extraction and analyses

Four to six bivalves from each site were thawed and the flesh of each bivalve was dissected and cut into pieces. About 3 g were spiked with perdeuterated internal standards. Pesticides, nonylphenols and PBDEs were extracted from biological matrix following the QuEChERS method (Quick, Easy, Cheap, Efficient, Rugged and Safe) as briefly described: each sample was mixed with a solution of acetonitrile for 1 min at 160 rpm, then 6 g of  $\text{MgSO}_4$  and 1.5 g of sodium acetate were added and the mixture incubated 10 min at 250 rpm and finally centrifuged at 4700 rpm for 5 min at  $5^{\circ}\text{C}$ . A second extraction using the Stir Bar Sorptive Extraction (SBSE) method was performed as follows: 10 mL of supernatant was collected and mixed with 40 mL of  $\text{NaCO}_3$  (0.1 M). A stir bar was inserted and the solution incubated at 750 rpm during 16 h in darkness and at room temperature. After the extraction, the stir bars were carefully rinsed, dried and analysed by TD-GC-MS/MS.

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

Prior to extraction, 10 g of each sediment samples were weighed and spiked with internal standards as previously described. 20 mL of a methylene chloride/acetone (50/50 v/v) were added to 10 g of each sediment sample and the extraction was performed using an ultrasonic bath (3 times during 15 min each). After filtration with  $\text{NaSO}_4$ , the extract was evaporated until it reached a volume of 250  $\mu\text{L}$ . The extract was then diluted in 10 mL of methanol and 100 mL of ultrapure water. Organic compounds were then extracted following the SBSE protocol as described above.

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

### 2.4. Statistical analysis

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

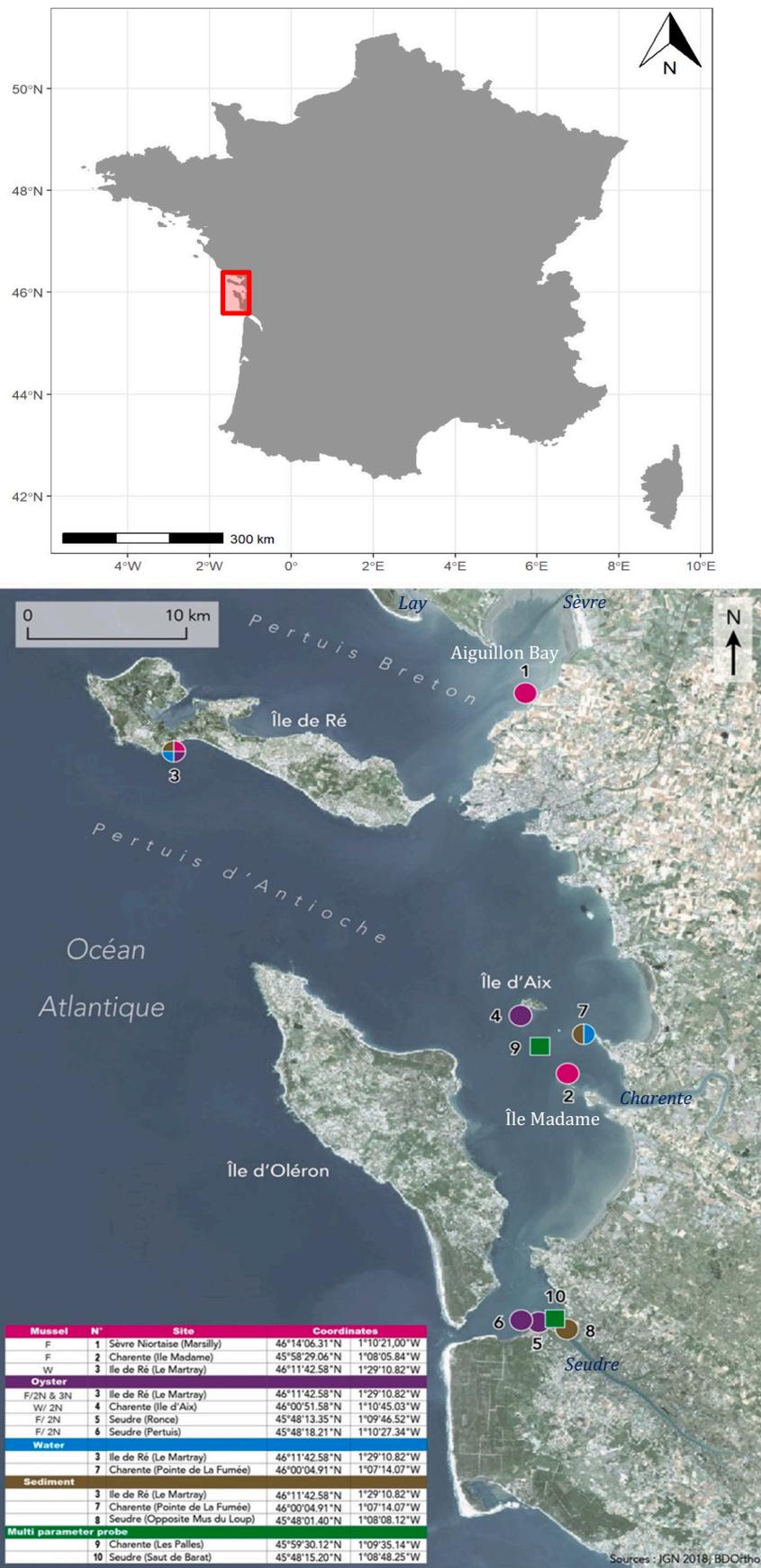


Fig. 1. Map showing the location of all the samples collected in the Pertuis-Charentais region, France.

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

### 3. Results

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

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

#### 3.1. Physico-chemical parameters

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

#### 3.2. Levels of POPs in sediments, seawater, oysters and mussel

The analyses of contaminant concentrations in the seawater, sediments, oysters and mussels were performed for forty-two POPs compounds: twenty-nine pesticides, six nonylphenols and seven PBDEs. Most of the concentrations were below the limit of detection (LOD) or between the LOD and the limit of quantification (LOQ) (Table 3). More POPs were quantified in oysters (six pesticides) (Table 3C) than in mussels (one pesticide) (Table 3D).

##### 3.2.1. POPs in sediments and seawater

Two POPs were quantified in sediments: methylparathion and

**Table 1**

Measurement of total length (cm), width (cm), thickness (cm), total weight (g, ww) and resulting Index of Form (IF) of the oysters (A) and mussels (B) (mean  $\pm$  SD,  $n = 4$  to 6) collected at the different sites.

	Total length (cm)	Width (cm)	Thickness (cm)	Total weight (g ww)	IF
<b>A</b>					
Charente (Ile d'Aix)	$8.4 \pm 1.0$	$4.4 \pm 0.3$	$2.4 \pm 0.5$	$7.1 \pm 1.1$	$2.5 \pm 0.2$
Seudre (Ronces les Bains)	$7.7 \pm 0.2$	$4.1 \pm 0.2$	$1.9 \pm 0.4$	$3.7 \pm 0.4$	$2.4 \pm 0.2$
Martray 2N (M2N)	$9.4 \pm 0.7$	$5.3 \pm 0.6$	$3.0 \pm 0.3$	$12.9 \pm 3.4^*$	$2.3 \pm 0.2$
Martray 3N (M3N)	$12.2 \pm 1.1$	$5.4 \pm 0.3$	$3.7 \pm 0.6$	$16.1 \pm 7.6^*$	$2.9 \pm 0.3^*$
<b>B</b>					
Marsilly (Sèvre)	$4.2 \pm 0.3$	$2 \pm 0.1$	$1.8 \pm 0.2^*$	$2.3 \pm 0.5$	$3 \pm 0.2^*$
Charente (Ile Madame)	$4.4 \pm 0.3$	$2.2 \pm 0.1^*$	$1.6 \pm 0.1$	$1.8 \pm 0.2$	$2.7 \pm 0.0$
Martray	$3.9 \pm 0.2$	$2.1 \pm 0.1$	$1.5 \pm 0.1$	$1.9 \pm 0.5$	$2.6 \pm 0.2$

\* Significantly different ( $p < 0.05$ ).

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

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

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

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

##### 3.2.2. POPs in the Pacific oysters

Chlortoluron, alpha BHC, chlorpyrifos, parathion, chlorfenvinphos and metolachlor were quantified in oysters from the different sites (Fig. 2). The M3N oysters from Le Martray were characterized by their concentration in metolachlor (0.38 ng/g ww) contrary to the concentrations found below the LOQ in oysters from other sites (Fig. 2, Table 3C). The oysters from Le Martray (M2N) and the Charente site were characterized by their concentration in parathion whereas the oysters from the Seudre estuary (Ronces) were characterized by their concentration in chlortoluron, chlorpyrifos, alpha BHC and chlorfenvinphos (Fig. 2).

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

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

##### 3.2.3. POPs in the blue mussels

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

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

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

	Turbidity (NTU)	Chlorophyll <i>a</i> (µg/L)	Salinity (PSU)	Temperature (°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

#### 4. Discussion

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

Pollutants that were quantified in sediments and seawater were not necessarily detected or quantified in living organisms. Two POPs were quantified in sediments: methylparathion and BDE47, and four POPs were quantified in seawater: methylparathion, BDE47, BDE99 and OP2OE. Methylparathion is an organophosphorus compound used as a broad-spectrum insecticide in crops. The present results showed low concentrations in sediments (0.16 to 0.41 ng/g) and in seawater (1.51 to 1.97 ng/L). Only a few studies sought this pesticide in those compartments. The values found in sediments were lower than the concentration of 16.8 ng/g measured in sediment of the Dniester River, Moldavia (Sapozhnikova et al., 2005). Because of its relatively short half-life (1–9 weeks), the quantification of low concentrations could indicate a chronic release in rivers and estuaries. The concentrations measured in water were 10 times below the PNEC value of 16 ng/L and are thus too low to represent a risk for populations. Parathion concentrations measured in oysters ranged between 0.56 and 0.69 ng/g and were below the LOD of 0.1 ng/g in mussels. Those concentrations measured in oysters were consistent with the concentrations of methylparathion measured in the 90s, in mussel, clam and oysters from the bays of the Ebro delta, Spain, that ranged from 0.7 to 0.9 ng/g on average (Solé et al., 2000). Other studies neither detected parathion in mussels (*P. perna*) neither in oysters (*C. gigas*) (<0.1 ng/g) collected in the bays of Santa Catarina, Brazil (de Souza et al., 2016).

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

BDE99 (1.4 ng/L) measured in water and lower than the BDE-47 concentration measured in sediment (2.3 ng/g) in an impacted, e-waste dismantling region in eastern China (Ling et al., 2021). In coastal rivers of North China the concentrations measured in water samples were much lower: 1.12 pg/L for BDE99 and 0.82 pg/L for BDE47 (Liu et al., 2021). In sediment samples from the Thau Lagoon, France, all PBDEs concentrations measured were also very low, below the LOD set at 10–100 pg/g (Hong et al., 2009). Our results showed that the predominant BDEs were quantified at low concentrations in sediments and seawater. Because the BDE99 concentrations measured in water samples of the Charente river were the highest and comparable to the values measured at some impacted areas it would be relevant to monitor this pollutant in the future. However, this compound was not detected in oyster neither in mussel in their early adult stage, revealing a low accumulation in marine bivalves, in the present study.

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

Chlortoluron is a commonly used herbicide in wheat and barley crops, however, there is only a few available studies reporting seawater concentrations in French estuaries. The seawater concentration of chlortoluron measured in the present study was relatively low and ranged between 15 and 50 ng/L, the LOD and LOQ respectively. These concentrations were lower than the chlortoluron concentrations measured in the water of the Gironde estuary (South Pertuis) of 71 ng/L in February 2015 (Levesque et al., 2018) and about seven times lower than the concentrations found in the Vilaine estuary (North Pertuis) where the values ranged from 125 to 330 ng/L (Caquet et al., 2013). The chlortoluron concentrations measured in the present study were above the detection limit of 15 ng/L which is above the VGE in seawater of 10 ng/L. Therefore, this molecule deserves a particular attention and should be monitored as it may represent a risk for aquatic populations. The present results showed that the concentrations of chlortoluron reached 4.31 ng/g in oysters from the Seudre estuary. To our knowledge, no data on chlortoluron concentrations in marine bivalves contaminated in their natural environment is available in the published literature.

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

**Table 3**

A, B, C and D. Pesticides, nonylphenols and PBDEs concentrations measured by GCMS/MS in sediments (A), seawater (B), oysters (C) and mussels (D) samples collected at the different sites: Martray, Charente and Seudre. nd: non detected, <LOD: below limit of detection, <LOQ: below limit of quantification. Units are expressed in ng/g of sediments ( $n = 1$  per site), ng/L of seawater ( $n = 1$  per site) or ng/g of tissue wet weight (mean,  $n = 5$  to 6 oysters or 4 to 6 mussels per site).

Molécules	Concentrations in sediments* (ng/g)			LOD (ng/g)	LOQ (ng/g)
	Ile de Ré	Charente	Seudre		
acetochlor	<LOD	<LOQ	<LOQ	0.04	0.13
alachlor	<LOD	<LOD	<LOD	0.20	0.67
aldrin	<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
dieldrin	<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
endrin	<LOD	<LOD	<LOD	0.20	0.67
isodrin	<LOD	<LOD	<LOD	0.20	0.67
metazachlor	<LOD	<LOD	<LOD	0.20	0.67
methylparathion	0.20	0.41	0.16	0.04	0.13
metolachlor	<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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Molecules	Concentrations in seawater* (ng/L)		LOD (ng/L)	LOQ (ng/L)
	Martray	Charente		
	acetochlor	<LOD		
alachlor	<LOD	<LOD	1.50	5.00
aldrin	<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
dieldrin	<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
endrin	<LOD	<LOD	1.50	5.00
isodrin	<LOD	<LOD	1.50	5.00
metazachlor	<LOD	<LOD	1.50	5.00
methylparathion	1.51	1.97	0.30	1.00
metolachlor	<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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Molecules	Concentrations in oysters* (ng/g ww)				LOD (ng/g ww)	LOQ (ng/g ww)
	Martray (2N)	Martray (3N)	Charente	Seudre		
acetochlor	<LOQ	<LOQ	<LOQ	<LOQ	0.50	1.67
alachlor	<LOQ	<LOQ	<LOQ	<LOQ	0.50	1.67
aldrin	<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
dieldrin	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
endrin	<LOD	<LOD	<LOD	<LOD	0.20	0.67
isodrin	<LOD	<LOD	<LOD	<LOD	0.10	0.33
metazachlor	<LOD	<LOD	<LOD	<LOD	0.50	1.67
methylparathion	<LOQ	<LOQ	<LOQ	<LOQ	0.50	1.67
metolachlor	<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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Molecules	Concentrations in mussels* (ng/g ww)			LOD (ng/g ww)	LOQ (ng/g ww)
	Martray	Charente	Sevre		
acetochlor	<LOD	<LOD	<LOD	0.50	1.67
alachlor	<LOD	<LOD	<LOD	0.50	1.67
aldrin	<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
dieldrin	<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
endrin	<LOD	<LOD	<LOD	0.50	1.67
isodrin	<LOD	<LOD	<LOD	0.50	1.67
metazachlor	<LOD	<LOD	<LOD	0.50	1.67
methylparathion	<LOD	<LOD	<LOD	0.50	1.67
metolachlor	<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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metolachlor contamination of marine bivalves exposed in French littoral areas are scarce.

Chlorfenvinphos and chlorpyrifos were widely used organophosphorus insecticides and were banned in Europe, in 2007 and 2020, respectively. In oysters, the present concentrations ranged between 0.79 and 0.93 ng/g for chlorpyrifos and between 1.65 and 2.12 ng/g for chlorfenvinphos. Chlorpyrifos has been quantified in various surface waters of the world (Huang et al., 2020), however, data on bivalve contamination in their natural environment are scarce. In the early 90s, the concentrations in chlorpyrifos measured in mussel, oyster and clam from the Ebro Delta, North West of the Mediterranean Sea, Spain, ranged from 0.7 to 1.9 ng/g (Solé et al., 2000). The capacity of those contaminants to bioaccumulate in marine bivalves was observed a few years later by Serrano et al. (1997) who showed that chlorpyrifos and chlorfenvinphos bioaccumulated in the Mediterranean mussel (*Mytilus galloprovincialis*). Studies led under laboratory conditions confirmed that

marine bivalves accumulated chlorpyrifos (reviewed in Huang et al., 2020) but studies monitoring the actual concentrations of chlorfenvinphos and chlorpyrifos in sentinel species from the marine environment are rare. These studies are essential to evaluate the actual risk due to these contaminations on marine environmental health.

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

DDT was widely used as a potent insecticide from the 40s and was banned for agricultural uses in Europe in March 1983 (Directive 83/131/EEC). However, the subsequent use of “Dicophol” that contained

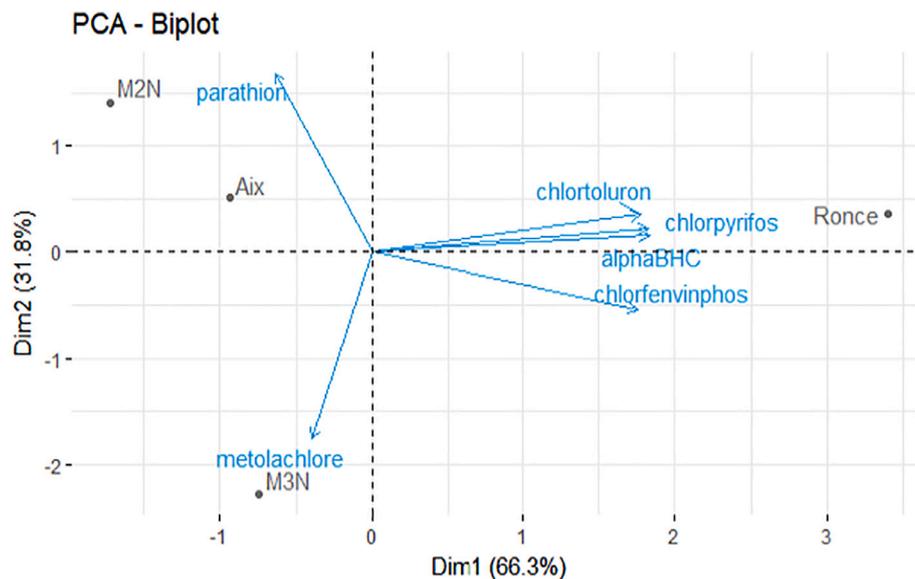


Fig. 2. Principal component analysis showing the distribution of POPs according to their concentration levels in oysters from the Seudre, Martray (diploid, M2N and triploid, M3N) and Charente Sites.

Table 4

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

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

<sup>a</sup>: PNEC, <sup>b</sup>: VGE, <sup>c</sup>: NQE and <sup>d</sup>: VGE mollusk.

DDT, was only banned in France in March 2010. Because they have been prohibited for many years, the concentrations of DDT and its byproducts were expected to be very low in the marine environment and to gradually decrease in the years to come. In our study, 2,4- and 4,4-DDT were below the LOD in mussels (<0.5 ng/g) and oysters (<0.2 and 0.5 ng/g, respectively). These findings were consistent with the results found by Luna-Acosta et al. (2015a) in oysters (*C. gigas*) from the Charente and Seudre estuaries where these molecules were found at levels below the LOD or at very low concentration (0.8 ng/g) respectively (Luna-Acosta et al., 2015a). Lindane is another insecticide that has been widely used during the same period (40s–70s), especially in France, one of the main countries using it in Europe, before being banned in 1998. Alpha-BHC, a byproduct of lindane present in commercial grade insecticide solution to treat a wide variety of crops (corn, beet, cereals, flax and colza) was quantified in oysters (0.60 and 0.72 ng/g) and mussels (0.24 and 0.31 ng/g) in the present study. The concentrations measured in oysters encompass the guidance concentration in the flesh of bivalves of 0.53 ng/g. The past high emission and persistence of lindane in the environment, and the likely erosion and removal of contaminated river sediments into estuaries may explain the post-ban presence of the

byproducts in marine bivalves as found in the present study.

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

#### CRediT authorship contribution statement

None to declare.

## 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.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2021.112956>.

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