



## Organochlorines in the Vaccarès Lagoon trophic web (Biosphere Reserve of Camargue, France)

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### ABSTRACT

During a decade (1996–2006), ecotoxicological studies were carried out in biota of the Vaccarès Lagoon (Biosphere Reserve in Rhone Delta, France). A multicontamination was shown at all levels of the trophic web due to a direct bioconcentration of chemical from the medium combined with a food transfer. Here, the pollutants investigated were organochlorines, among which many compounds banned or in the course of prohibition (or restriction) (PCB, lindane, *pp'*-DDE, dieldrin, aldrin, heptachlor, endosulfan...) and some substances likely still used in the Rhone River basin (diuron, fipronil). The results confirmed the ubiquity of contamination. It proves to be chronic, variable and tends to regress; however contamination levels depend on the trophic compartment. A biomagnification process was showed. A comparison of investigation methods used in other Mediterranean wetlands provides basis of discussion, and demonstrates the urgent need of modelling to assess the ecotoxicological risk in order to improve the management of such protected areas.

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### 1. Introduction

The inter-connections of wetlands with agricultural areas or other adjacent habitats lead subsequently to a chronic contamination of aquatic ecosystems and their trophic webs. Due to their position as sinks of wastewater from irrigation agriculture fields and run off, the Camargue wetlands are particularly endangered. They receive residues of agrochemical sprayings, from continuous or intermittent inputs, likely transferred to the organisms during the bioaccumulation process (Albanis et al., 1996; van der Oost et al., 1996; Mackay and Fraser, 2000; Weber and Goerke, 2003; Gewurtz et al., 2006). The qualitative and quantitative distribution of organic pollutants in the aquatic biota is largely dependent on the solubility of the molecule in water or in lipids. Bioaccumulation proceeds overall in two ways: a direct transfer through the teguments (skin and gills) and/or by ingestion, or a transfer along the food chain, from preys to predators.

In a bioconcentration process, aquatic organisms retain and concentrate chemical compounds from their environment (Ramade, 2007). When inputs are chronic and regular, the longevity

and the sedentariness of the organisms are prevailing factors, then the oldest individuals, which are usually the biggest ones, would be the more contaminated. At the opposite, if pollutant discharges are accidental or occasional (field treatments, atmospheric drift, soil leaching, etc.), the ratio 'exposed body surface'/body volume' is determining for the contamination level, since this ratio is generally higher in the smallest organisms (Randall et al., 1998; Fant and Reindelder, 2003; Xiulin and Zauke, 2004). According to this concept, within a food web, bioconcentration is higher at the low trophic levels (TLs) than in predators. This empirical theory, also suffers from exceptions due to the morphology and the surface structure of organisms (gill surface area in fishes, chitin in invertebrates, etc.).

Conversely, a trophic transfer leading to an increasing concentration along a food chain is named the biomagnification process, according to which the bioaccumulation is higher in a consumer than in its food. Nevertheless, the two phenomena are often concomitant. Even if the high liposolubility of Persistent Organic Pollutants (POPs) renders such compounds more subject to biomagnification, their contamination ability in biota remains dependent on the physiological functions of species: i.e. assimilation, excretion and biodegradation. Biomagnification has been well described in long marine food chains (Wilson et al., 1995; Borga et al., 2001) or more generally in open ecosystems (Muir et al., 1996),

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but, in shortest trophic webs composed of multi-food chains, the demonstration is challenging (Kidd et al., 2001), as in Lake Erie (Kwon et al., 2006) or in a coastal lagoon (Menone et al., 2000).

Due to its geographical location, in the centre of the Rhone delta, the Biosphere Reserve of Camargue, and in spite of its multiple statutes of protection (MAB–UNESCO), is exposed to random natural or anthropogenic disturbances, linked to a complex hydrological system and human activities developed nearby. Among them, the rice fields requires large volumes of water, so the Vaccarès Lagoon, the main water body of the Reserve, receives the effluents loaded with agrochemical products, as well as pesticides coming from the Rhone River Valley.

Since 1996, several research programs including biomonitoring, devoted to the study of aquatic organisms exposed to POPs, were carried out in the Vaccarès Lagoon (Roche et al., 2000, 2002a,b). Initially the projects were devoted to an ecotoxicological assessment in the eels (Oliveira Ribeiro et al., 2005, 2008; Buet et al., 2006). This common fish of Mediterranean coastal brackish wetlands fill all the required properties as a bioindicator species. Nevertheless, its decline became alarming. Considering that the observed contamination was obviously due to a long history of pesticide use with chemicals often banned (Roche et al., 2002a), our researches have addressed the transfer of pollutants into the aquatic trophic web of the Vaccarès water body. The contamination by pesticides and PCB in species sampled in spring and autumn 2002 and 2005, were compared in this paper. The liposolubility of substances, characterized by their octanol–water partition coefficient ( $\log K_{ow}$ ) exceeding 5, would potentially generate a biomagnification process. However, as highlighted by McIntyre and

Beauchamp (2007) and at the opposite of a widespread idea, we virtually never observe any causal relationship between the lipid contents of organisms and the concentrations of POPs, as Kucklick and Baker (1998) in the Lake Superior. Stable nitrogen isotope was used as an indicator of trophic position (Minagawa and Wada, 1984; Vander Zanden and Rasmussen, 2001; McIntyre and Beauchamp, 2007) and biomagnification factors, adjusted for TL, were reported. So, the present article is devoted to the synthesis of numerous results obtained during the last decade. Here, such a collection provides the discussion basis about the trophic transfer of organochlorine contaminants in Mediterranean wetlands.

## 2. Material and methods

### 2.1. Studied site

The Reserve of Camargue-Rhone Delta nominated in 1977 by UNESCO as an 'International Reserve of Biosphere' (position revised in 2006), ranks as the largest protected coastal wetland in Mediterranean Europe (32 000 Ha.). As a deltaic complex of terrestrial, coastal and aquatic areas the Reserve displays a remarkable variety of natural habitat as well of plant and animal communities. Therefore, the Camargue Reserve stands as a major hot spot of Mediterranean coastal wetland biodiversity. Here, attention was focused on aquatic species living in the brackish waters of the Vaccarès Lagoon (43°30' N 4°30' E), the largest water body of the Reserve (6500 Ha) (Fig. 1).

### 2.2. Organism sampling

Eels were caught in spring and in autumn during a decade (1996–2005). The eels' samples were divided into 4 stages of growth (juvenile, immature type 1, immature type 2 and yellow eels). A total of 17 other aquatic species were sampled from La Capelière site in the Vaccarès Lagoon during 6 campaign experiments



Fig. 1. The Rhone Delta, Biosphere Reserve of Camargue (France).

conducted in spring 2001, in autumn 2003 and in spring and autumn 2002 and 2005. The studied organisms were zooplankton (copepods sp. + larvae), *Sphaeroma* sp, cockles (*Cerastoderma glaucum*), mysids, gammarids (*Gammarus salinus*), pink shrimps (*Crangon crangon*), brown shrimps (*Palaemonetes varians*), sand smelts (*Atherina boyeri*), gobies (*Pomatoschistus* sp.), sticklebacks (*Gastrosteus aculeatus*), pipefish (*Syngnatus acus*), not to mention occasionally, common soles (*Solea solea*), breams (*Abramis brama*), pikeperch (*Sander lucioperca*), and juvenile mullets (*Mugilidae* sp). One plant of brackish and marine waters (*Zostera noltii*) (Helobiales), water and sedimentary organic matter (SOM) were also collected in spring 2005. The selected zooplankton, invertebrate and fish species differed in their trophic habits and ecological niches as estimated by the annual NNRC biodiversity report compiled by the French National Nature Conservancy Society (SNPN) (internal publication).

Fishing nets and metallic-mesh strainers were used for fish and bivalve capture, respectively; crustaceans were trawled in the sampling site. The samples were transported frozen to the laboratory at the University Paris 11 (France).

Lipid extraction (dichloromethane/methanol treatment) was carried out prior to N isotopic analyses performed on the same sample; individual data were recorded for fishes and pooled data for invertebrates. The measurements were performed on the whole body mass of organism with the exception of eel, sole, bream, pikeperch and common sunfish, whose only dorsal muscle was analyzed.

### 2.3. Trophic level (TL) and biomagnification factor (BMF) determinations

The lipid-free tissues were filtered, freeze-dried and powdered. The 1 mg powder sub-samples were packed into 3.3 × 5 mm tin capsules for N isotope measurements performed with a continuous flow isotope ratio mass spectrometer (VG Optima; Model NA-1500, Carlo Erba). As previously described, the TL of each of the organisms was assessed on the basis of  $\delta^{15}\text{N}$  enrichment (Persic et al., 2004; Voltaire et al., 2007). The TL of consumers ranged from 2 in zooplankton to 4.39 in the yellow eels (Table 1).

The biomagnification factor between trophic guilds was calculated using the formula:

$$\text{BMF} = \left[ \frac{(\text{OC}_{\text{TGN}}/\text{OC}_{\text{TGN-1}}/\text{OC}_{\text{TGN-1}})}{(\text{TL}_{\text{TGN}}/\text{TL}_{\text{TGN-1}})} \right]$$

Where  $\text{OC}_{\text{TGN}}$  and  $\text{OC}_{\text{TGN-1}}$  were the lipid-normalized concentration of organochlorines in trophic guilds.

### 2.4. Chemical analyses

Muscles of fishes and invertebrate bodies were dissected for pesticides analysis. Total lipids were gravimetrically determined after extraction using a dichloromethane/methanol solution (1:2 v/v) following a method adapted of Folch et al. (1957). Pesticides were extracted from muscle or whole organism lipids or from pools of individuals, and purified by solid phase extraction (SPE) on florisil ( $\text{MgO}_3\text{Si}$ ), following the EPA method 3620 (Bond Elut Florisil, 1 g, 200  $\mu\text{m}$  particle size, Varian,

Les Ulis France), first with hexane, to eluate  $\Sigma\text{DDT}$ , HCB and PCB, then with hexane/diethylether (90/10) for OCPs clean-up.

The quantitative and qualitative analyses of organochlorine compounds were achieved by gas chromatography with an AutoSystem XL (Perkin-Elmer), using ECD (electron capture detection) with an  $^{63}\text{Ni}$  Source and Nitrogen as make-up gas according an adapted procedure of the EPA Method 8081a, previously described (Oliveira Ribeiro et al., 2005, 2008). Compound detections were achieved using a 30 m column, internal diameter 0.25 mm, 0.25 mm PE5 fused silica column (PerkinElmer, Courtabouef, France) and nitrogen as carrier gas. The injector and detector temperatures were 280 °C and 350 °C, respectively. For OCPs, except HCB and  $\Sigma\text{DDT}$ , the initial GC oven temperature was 200 °C (12 min hold) followed by an increase (10 °C/min) to 210 °C (30 min) then a rapid increase (40 °C/min) to 260 °C (3 min hold). For PCBs, HCB and DDT, the GC conditions were: initial temperature 140 °C (12 min), the oven was ramped at 40 °C/min to 170 °C (19 min), then at 40 °C/min to 200 °C (25 min) and finally at 45 °C/min to 270 °C (4 min). Twenty-nine PCB congeners were retained for analysis, amongst them were the 7 indicator PCBs (IUPAC n° 28, 52, 101, 118, 138, 153, 180). Amongst the 14 dioxin-like PCBs, 10 were identified (77, 81, 105, 114, 118, 123, 126, 156/157, 169, 170). All reference materials were produced by the ISO9001 certified laboratories of Dr. Ehrenstorfer as part of the Reference Standards Program provided by the Society CIL Cluzeau, (Sainte Foy la Grande, France). Under the specified conditions, the detection limit ranged from 0.05 to 0.20 ng g<sup>-1</sup>dw (dry weight) in fish tissues (dry matter normalized data).

### 2.5. Statistical procedures

Statistics were performed with Statview 5.0 software (SAS institute, Cary, NC, USA). The Kolmogorov-Smirnov normality test was applied to  $\delta^{15}\text{N}$  and contaminant data in each trophic guilds ( $n > 45$ ). No statistical transformation of data was necessary to reach normality. One-way ANOVA, followed by Scheffé and Bonferroni/Dunn post-hoc tests was performed to compare TL and pollutant concentrations in the different studied species or trophic guilds. Pearson correlations between contaminant concentrations and TL were checked. All tests were regarded as statistically significant when  $p$ -value < 0.05. Continuous variables were expressed as mean value  $\pm$  SD or [min-max] values, as appropriate.

## 3. Results and discussion

The Biosphere Reserve of Camargue is designated as one of the most important wetlands in Europe according to the Ramsar Convention (Designation date: 01-12-1986) ([http://www.ramsar.org/key\\_sitelist.htm](http://www.ramsar.org/key_sitelist.htm)). Nevertheless, this protected area is exposed to an inflow of pollutants coming from the Rhone River amounting to about  $400 \times 10^6 \text{ m}^3 \text{ y}^{-1}$  of water and by pesticides spraying in the bordering agrosystems, notably rice fields.

Recently, some reports from French governmental agencies revealed a significant PCBs contamination of the fish populations from the Rhone River (Babut and Miege, 2007) leading to the development of an action plan by the ministry in charge of the environmental protection (MEDAD et al., 2008).

For one decade, we clearly showed transfers of heterogeneous organic contaminants (agricultural inputs, pesticides, industrial products, hydrocarbons, etc.) in the Vaccarès Lagoon. Consequently, components of the food webs (pelagic and benthic organisms) were contaminated, notably top-consumers. Amongst them, eels developed necrosis and more or less reversible lesions, potentially in relation with this contamination (Roche et al., 2000, 2002a,b; Persic et al., 2004; Buet et al., 2006; Voltaire, 2007; Oliveira Ribeiro et al., 2005, 2008).

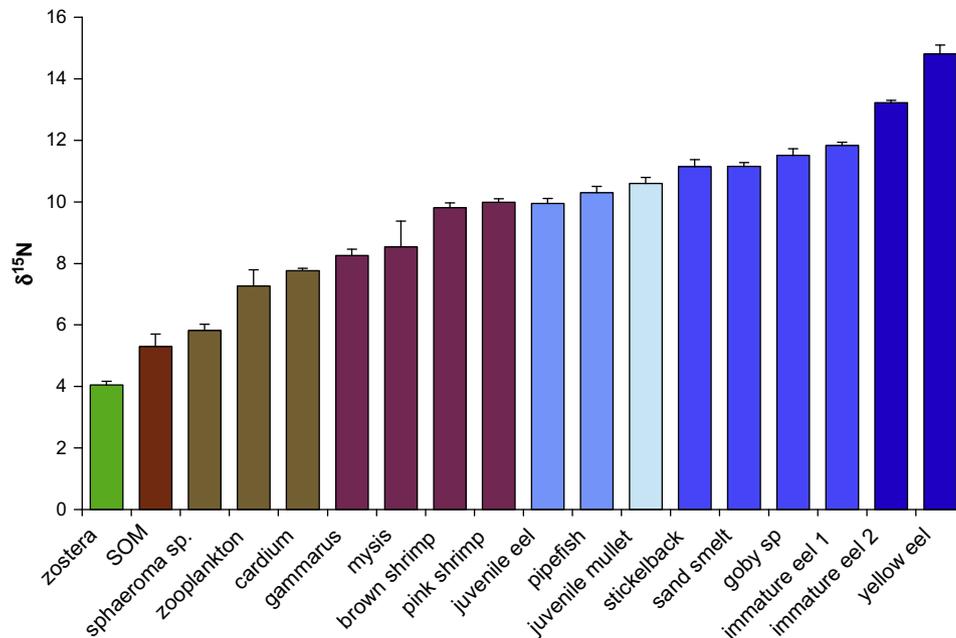
### 3.1. The trophic web of the Vaccarès Lagoon

The Fig. 2 shows a large interspecific variability in isotopic contents of the 335 samples. According to our previous study (Persic et al., 2004), the stable N isotopic values, ranging from  $5.81 \pm 0.20\text{‰}$  in isopods as *Sphaeroma* to  $14.8 \pm 0.31\text{‰}$  in yellow eel (*Anguilla anguilla*), with a mean trophic enrichment of  $3.2 \pm 0.14\text{‰}$  confirmed trophic emplacement of the selected organisms. Due to their specific life history traits, the eels showed a large intraspecific variability, they were present in 3 trophic sub-compartments: juvenile eels ( $18.3 \pm 5.9 \text{ g}$ ;  $21.2 \pm 2.2 \text{ cm}$ ); immature eels 1 ( $77 \pm 9 \text{ g}$ ;  $33.2 \pm 1.2 \text{ cm}$ ); immature eels 2 ( $105 \pm 14 \text{ g}$ ;  $37.7 \pm 1.4 \text{ cm}$ ) and

**Table 1**

Studied components of the Vaccarès trophic web, trophic levels (TLs) and guild classification designated on the  $^{15}\text{N}$  basis. SOM: sedimentary organic matter.

Guilds	Species	TL	Count	min-max
Producer	<i>Zostera</i> sp.	$0.99 \pm 0.04$	(6 pools)	[0.86–1.09]
	SOM	$1.38 \pm 0.13$	(5 × 100g)	[0.90–1.64]
Consumer I	<i>Sphaeroma</i> sp.	$1.55 \pm 0.07$	(6 pools)	[1.29–1.74]
	zooplankton	$2.00 \pm 0.16$	(8 pools)	[1.69–2.80]
	cockles	$2.15 \pm 0.02$	(36 pools)	[1.91–2.76]
	gammarids	$2.31 \pm 0.06$	(18 pools)	[1.68–2.74]
	mysids	$2.40 \pm 0.26$	(3 pools)	[2.08–2.91]
Consumer II-1	brown shrimp	$2.80 \pm 0.05$	(40)	[2.27–3.59]
	pink shrimp	$2.85 \pm 0.04$	(29)	[2.28–3.20]
	juvenile eel	$2.94 \pm 0.09$	(10)	[2.60–3.72]
Consumer II-2	pipefish	$2.95 \pm 0.06$	(18)	[2.48–3.40]
	mullet	$3.04 \pm 0.06$	(12)	[2.46–3.30]
	stickleback	$3.21 \pm 0.07$	(21)	[2.55–4.06]
	sand smelt	$3.21 \pm 0.04$	(68)	[2.56–3.94]
	goby sp.	$3.37 \pm 0.07$	(26)	[2.85–3.96]
	immature eel 1	$3.44 \pm 0.03$	(35)	[2.83–3.66]
	common sole	$3.49 \pm 0.08$	(4)	[3.31–3.65]
	bream	$3.62 \pm 0.07$	(7)	[3.48–4.02]
	pikeperch	$3.77 \pm 0.06$	(5)	[3.71–3.83]
	immature eel 2	$3.87 \pm 0.02$	(32)	[3.66–4.11]
Consumer II-3	yellow eel	$4.36 \pm 0.09$	(12)	[3.51–4.72]



**Fig. 2.**  $\delta^{15}\text{N}$  signature of components from the Vaccarès trophic web. SOM: sedimentary organic matter; immature eel 1: young eel stage 1; immature eel 2: young eels stage 2. ■ producers: plants ■ producers: organic matter (detritus, bacteria, etc.) ■ primary consumer invertebrates: detritivorous, decomposers, depositivorous, phytoplanktivorous; ■ secondary consumer invertebrates: zooplanktivorous; ■ invertebrate predators ■ herbivorous ■ piscivorous/omnivorous ■ top-consumers.

yellow eels ( $451 \pm 58$  g;  $59.5 \pm 2.7$  cm). We never analyzed sexually maturing eels (silver eels).

Here we chose to classify species in 3 trophic guilds on the basis of N isotopic measurements, namely: producers (SOM and zostera); primary consumers (consumer I) [phytoplanktivorous (zooplankton) and depositivorous (*sphaeroma*, cockles and gammarids)]; and secondary consumers (consumer II). These last ones may be divided in 3 sub-compartments: type 1 (consumer II-1) [zooplanktivorous (shrimps, mysids, immature eel)], secondary consumers type 2 (consumer II-2) [benthivorous fish (goby, pipefish, sand smelt), invertebrate predator or piscivorous fish (stickleback, bream, juvenile eel, sole and pike-perch)] and secondary consumers type 3 (consumer II-3) as yellow eel or top-consumer fish (Fig. 3).

Using a primary producer baseline, the calculated TL of species analyzed during our ecotoxicological projects, were ranked from 1.5 to 4.4. As showed in Table 2, the lipid contents were not dependent to the trophic guilds, whatever the capture season.

The stable isotope ratio analyses are useful tools for ecotoxicological studies, however a number of scientists warned about the lack of consideration toward the analytical constraints. Indeed, isotopic ratio is influenced by feeding level, metabolic rates (Gaye-Siessegger et al., 2004), seasonal variability (Perga and Gerdeaux, 2005), tissue constitution (Jardine et al., 2005; Voltaire et al., 2007) as others singularities of species phenology (Fisk et al., 2003). Nevertheless, in accordance with Gu et al. (1996), the  $\delta^{15}\text{N}$  has been used successfully to assess the TL of fish and invertebrates in the Vaccarès Lagoon. This littoral lagoon involves a rather short food chain from primary producers to top predators (excluding piscivorous birds and mammals), according to Vander Zanden and Fetzer (2007) who consider that food webs tend to have from 3 to 5 TL and underline the importance of the food chain length in productivity, structuring and functioning of ecosystem.

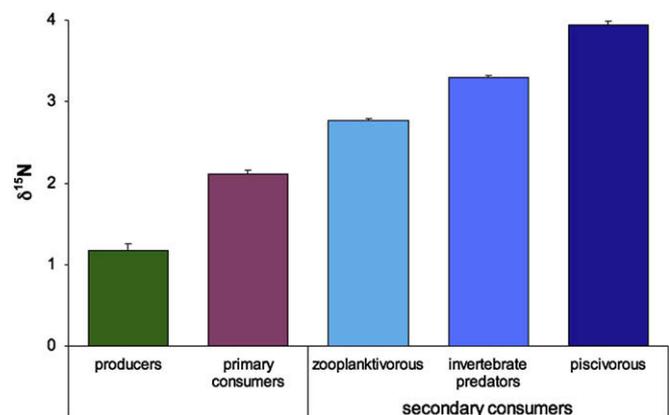
### 3.2. Contaminant bioaccumulation in the Vaccarès Lagoon trophic web

Since two decades, a number of papers have shown that aquatic organisms bioaccumulate lipophilic pollutants, notably

organochlorines, and some of them demonstrated a bio-magnification through a trophic transfer (Kidd et al., 1995; Rypel et al., 2007). Here, we report the global contamination analyses of trophic web elements, carried out in 2002 and 2005, at two seasons, spring and autumn.

#### 3.2.1. Organochlorine pesticides (OCP)

The contamination profiles of the trophic web in 2002 and 2005 are given in Tables 3 and 4. A total of 297 analyses were achieved in organisms (or pools of invertebrates) sampled before the summer (pre-summer period: March–April–May named ‘spring’) and after the summer (post-summer period: September–October named ‘autumn’). All investigated pesticides were found at every TL. Among the analyzed biocontaminants, as well agrochemical substances recently used in the vicinity of the lagoon (fipronil and diuron plus metabolite), as banned OCPs and their metabolites (or isomers), (lindane, heptachlor, endosulfan, dieldrin, aldrin, endrin, HCB and *pp'*-DDE) were detected. Residues of such pesticides



**Fig. 3.** The  $\delta^{15}\text{N}$  enrichment in the five trophic compartments of the Vaccarès Lagoon (Biosphere Reserve of Camargue).

**Table 2**  
Lipid tissue contents (mg g dw<sup>-1</sup>) in components of the Vaccarès trophic web.

Guilds	season	species	Mean ± sm	Count	[min–max]
producer	spring	<i>Zostera</i> sp.	185.8 ± 26.5	(6 pools)	[111–301]
Consumer I	spring	<i>Sphaeroma</i> sp.	221.7 ± 3.9	(6 pools)	[207–236]
	spring	copepods	382.7 ± 35.4	(8 pools)	[215–498]
	spring	mulletts	157.9 ± 23.8	(6)	[46.9–222]
	spring	cockles	72.9 ± 6.5	(11)	[33.5–116]
	spring	gammarids	182.7 ± 25.2	(7)	[87.0–246]
	autumn	cockles	71.9 ± 5.9	(15)	[33.4–116]
	autumn	gammarids	59.5 ± 16.7	(3)	[26.2–77.6]
Consumer II-1	spring	juvenile eels	123.1 ± 13.2	(8)	[72.5–174]
	spring	brown shrimps	138.0 ± 22.1	(21)	[30.3–316]
	spring	pink shrimps	155.4 ± 20.7	(20)	[38.6–299]
	spring	pipefish	108.7 ± 14.0	(10)	[49.2–166]
	autumn	juvenile eels	190.9 ± 71.7	(5)	[75.4–471]
	autumn	brown shrimps	192.1 ± 33.4	(8)	[77.0–323]
	autumn	pink shrimps	137.3 ± 63.8	(3)	[60.3–264]
	autumn	pipefish	149.9 ± 5.3	(5)	[132–162]
Consumer II-2	spring	immature eels 1	279.7 ± 35.8	(9)	[167–520]
	spring	sand smelts	143.5 ± 10.9	(25)	[23.6–231]
	spring	sticklebacks	109.5 ± 14.7	(11)	[56.6–196]
	spring	goby sp.	136.0 ± 7.2	(11)	[98.7–174]
	spring	immature eels 2	332.8 ± 41.2	(13)	[140–588]
	autumn	immature eels1	208.8 ± 44.5	(13)	[64.5–535]
	autumn	sand smelts	164.5 ± 18.5	(20)	[55.5–399]
	autumn	goby sp.	73.4 ± 7.4	(8)	[28.7–103]
	autumn	bream	44.2 ± 9.3	(7)	[20.0–95.8]
	autumn	immature eel 2	250.1 ± 39.7	(20)	[50.4–646]
Consumer II-3	autumn	yellow eel	516.2 ± 34.0	(9)	[350–666]
	autumn	pikeperch	76.1 ± 9.9	(5)	[66.3–86.0]
	autumn	common sole	101.7 ± 52.3	(4)	[38.5–257]

occurs commonly in a majority of the Mediterranean estuaries as Albanis et al. (1994) showed it in the wetland of the delta of the rivers Axios, Loudias and Aliakmon (Greece), or Villa et al. (2003) in the coastal lagoon Orbetello (Italy) as in Ebro delta (Spain) (Mañosa et al., 2001; Gómez-Gutiérrez et al., 2006), for example. Moreover, because of their high position in the Camargue trophic web, Berny et al. (2002) using predator birds as bioindicators, showed that little egrets' eggs accumulated contaminants such as lindane or DDT derivatives without reproductive effects in bird species.

Diuron was the most abundant contaminant in the Vaccarès trophic web, notably in 2005. This urea-substituted herbicide used in vine and fruit plantations in the Rhone River Valley, as its metabolite 3,4-dichloroaniline, appeared as well to be a major contaminant in Ebro basin (Spain) (Claver et al., 2006). The eels (immature and juvenile) were highly contaminated in spring until 1000 ng g<sup>-1</sup> dw, and up to 3000 ng g<sup>-1</sup> dw in autumn. The high level of diuron bioaccumulation in fish, was in contradiction with the results of Tucker et al. (2003) who showed a rather low transfer to fish, after experimental exposure consisting in nine consecutive weekly applications of diuron at 0.01 mg l<sup>-1</sup>.

At the opposite, a fipronil decrease was assumed from 2002 to 2005. In conventional rice fields, fipronil was used until 2003 for chironomid control (Mesleard et al., 2005). Comoretto et al. (2007) showed the difficulty to detect fipronil into the Vaccarès Lagoon water due to the low intensity of its overall use. The occurrence of a fipronil bioaccumulation in trophic webs of Mediterranean wetlands is not documented.

The mean detectable concentrations of lindane and its isomers ranked from 0.04 to 1043 ng g<sup>-1</sup> dw, with a maximum for the δ isomer. The highest levels of lindane were found in sand smelt and juvenile eel in autumn 2005. Generally, our results were much higher than those obtained in muscle tissue of whitefish (*Coregonus lavaretus*) (<2.4 ng g<sup>-1</sup> dw recalculated on the basis of 75% moisture) or European perch (*Perca fluviatilis*) (<0.05 ng g<sup>-1</sup> dw) from

lakes of central Italy (Orban et al., 2006, 2007) or in eels from Orbetello Lagoon (Italy) (range 4–160 ng g<sup>-1</sup> dw) (Corsi et al., 2005) (Tables 3 and 4).

The heptachlor concentrations varied from 0.22 to 556 ng g<sup>-1</sup> dw. The higher values (close to 300 ng g<sup>-1</sup> dw) were almost always found in juvenile eels and in brown shrimps collected in spring 2005, as well in sand smelt in autumn 2005. In spring 2002, only the juvenile mullets showed similar concentrations. Such values are higher to levels reported in studies conducted in others Mediterranean sites, where values are below the detection limit, as in Orbetello Lagoon (Italy) (Corsi et al., 2005) or <4 ng g<sup>-1</sup> dw in fishes from rivers in Cantabria (Spain) (Guitart et al., 2005), for example.

The endosulfan, notably its main metabolite, the endosulfan sulphate, showed a high level in eels and in gammarids sampled in March 2002. Moreover high values were found in some eels caught in autumn 2002. Currently, the endosulfan concentration showed a tendency to decrease in 2005, despite its strong persistence (Sethunathan et al., 2002).

Other banned pesticides were still present in 2002 and 2005, ranked according to ascending concentrations, they were HCB < pp'-DDE < dieldrin < aldrin < endrin (+endrin aldehyde). Their concentrations seldom exceeding 100 ng g<sup>-1</sup> dw were comparable with values found in biota from others European sites (Corsi et al., 2005; Mazet et al., 2005; Covaci et al., 2006; Schmid et al., 2007; Maes et al., 2008). In 1996, lindane and DDT metabolites were detected in all eggs of top-predator birds, and occasionally, heptachlor and endosulfan residues (Berny et al., 2002)

### 3.2.2. PCBs contamination

The concentrations of the four dominant PCBs (PCB 52; PCB 101; PCB 138; PCB 153) and their classes according to their chlorination level are given in Tables 5 and 6. PCB 52 accounting on average for 25% of the total PCB, tetra- penta- and hexa-chlorobiphenyls showed the higher concentrations.

**Table 3**  
Mean muscle tissue concentration and range [minimum–maximum] (ng g<sup>-1</sup> dw) of HCH, heptachlor and endosulfan (isomers and/or metabolite) in trophic web components of the Vaccarès Lagoon (Camargue, France), sampled in spring and autumn 2002 and 2005. (n) = counts of individuals, (n<sup>+</sup>) = count of pools. nm = not measured; nd = not detected.

species	Season of sampling	$\alpha$ -HCH	$\beta$ -HCH	$\gamma$ -HCH	$\delta$ -HCH	heptachlor	heptachlor-epoxide	$\alpha$ endosulfan	$\beta$ endosulfan	endosulfan sulphate
cardium	spring 2002 (13)	1.77 [nd–8.2]	nm	1.79 [nd–17.2]	7.56 [nd–46]	12.2 [0.17–36]	3.75 [0.23–24]	1.9 [nd–4.8]	0.4 [nd–3.32]	9.4 [nd–51.2]
	autumn 2002 (6)	0.12 [nd–0.69]	nm	0.45 [nd–2.70]	0.9 [nd–4.0]	0.8 [nd–3.31]	2.23 [nd–4.06]	1.4 [nd–7.3]	0.9 [nd–3.3]	14.8 [nd–86.3]
	spring 2005	nm	nm	nm	nm	nm	nm	nm	nm	nm
	autumn 2005	nm	nm	nm	nm	nm	nm	nm	nm	nm
gammarids	spring 2002 (4*)	24.6 [1.46–57.0]	nm	43.2 [20–69]	260 [90–476]	155 [21–324]	40.0 [16–94]	74.8 [63–101]	19.0 [nd–75]	336.5 [nd–1345]
	autumn 2002 (3*)	nd–	nm	2.95 [nd–4.96]	nd	39.8 [nd–83.8]	0.02 [nd–0.02]	6.2 [nd–10.7]	nd–	22.1 [nd–43]
	spring 2005 (6)	9.18 [3.09–18.6]	14.0 [nd–37]	20.8 [9.6–55]	6.8 [0.16–15]	1.54 [nd–5.91]	17.2 [nd–48.7]	25.6 [nd–37]	14.2 [nd–85]	64.2 [5.6–122]
	autumn 2005	nm	nm	nm	nm	nm	nm	nm	nm	nm
brown shrimp	spring 2002 (19)	2.21 [nd–6.5]	nm	1.78 [nd–10.5]	17.4 [nd–106]	18.3 [nd–97.7]	4.13 [nd–14.7]	6.2 [nd–21.1]	4.7 [nd–61.2]	38.1 [nd–182.1]
	autumn 2002 (7)	2.10 [nd–5.70]	nm	9.53 [nd–35.8]	32 [1.45–106]	26.9 [nd–71.2]	152.2 [nd–825]	12.6 [nd–47]	174 [nd–819]	54.6 [nd–255]
	spring 2005 (9)	6.77 [0.95–19.3]	1.8 [nd–9.5]	217 [0.9–51]	26 [0.21–75]	80 [31–169]	149 [26–476]	17.6 [nd–77]	11.4 [nd–23]	62.1 [nd–120]
	autumn 2005 (6)	6.32 [nd–13.8]	1.0 [nd–4.1]	46.8 [nd–120]	35.4 [8.9–61]	109 [nd–265]	224 [56–552]	14 [nd–77]	14.6 [5–31]	102 [16–289]
pink shrimp	spring 2002 (17)	7.04 [nd–21.2]	nm	5.66 [nd–20.9]	33 [nd–194]	71.1 [nd–480]	12.9 [nd–71.9]	20.5 [nd–117]	37 [nd–174]	49.6 [nd–400]
	autumn 2002 (3*)	4.71 [nd–14.1]	nm	5.08 [nd–8.6]	6.7 [nd–16]	16.3 [5.8–37]	8.3 [nd–13.2]	118 [3.4–335]	195 [4–562]	72.9 [3.98–203]
	spring 2005 (9)	12.1 [1.94–33.4]	37 [0.1–109]	65 [0.14–218]	49 [nd–157]	34 [nd–112]	52.6 [nd–144]	1.8 [nd–17]	22.8 [nd–69]	26.8 [nd–53.3]
	autumn 2005	nm	nm	nm	nm	nm	nm	nm	nm	nm
stickelback	spring 2002 (19)	5.92 [nd–19.1]	nm	12.5 [nd–64.9]	100 [nd–548]	38.5 [nd–130]	19.5 [nd–120.9]	29.3 [nd–166]	3.9 [nd–66.8]	1.7 [nd–10.4]
	autumn 2002 (2*)	6.45 [5.64–7.27]	nm	31 [6.24–55.7]	1044 [753–1334]	45.8 [25–67]	32.0 [21–44]	109 [20–197]	69 [19–120]	15.0 [nd–30.0]
	spring 2005	nm	nm	nm	nm	nm	nm	nm	nm	nm
	autumn 2005	nm	nm	nm	nm	nm	nm	nm	nm	nm
pipefish	spring 2002 (7)	2.38 [nd–8.4]	nm	22.1 [nd–93.0]	37 [nd–180]	248 [nd–1292]	12.4 [nd–66.2]	30.9 [nd–93]	nd	0.4 [nd–2.56]
	autumn 2002	nm	nm	nm	nm	nm	nm	nm	nm	nm
	spring 2005 (6*)	0.68 [nd–1.23]	3.6 [nd–6.9]	8.6 [2.6–14.2]	14.0 [nd–37]	1.56 [nd–4.07]	4.94 [nd–14.4]	nd	8.7 [2–17.0]	13.6 [nd–46.9]
	autumn 2005 (5*)	5.79 [1.05–18.0]	2.36 [nd–11]	29.6 [nd–58.9]	31.0 [10–55]	94.4 [44–198]	174.2 [35–295]	1.5 [nd–7.38]	15.8 [2–34]	15.6 [nd–48.2]
goby sp.	spring 2002 (17)	9.32 [nd–39.3]	nm	15.6 [nd–65]	18.0 [nd–94]	53.8 [3.5–156]	12.0 [nd–30.3]	38 [2.4–105]	14.2 [nd–74]	81.6 [nd–561]
	autumn 2002 (13)	5.94 [nd–30]	nm	3.88 [nd–21]	99 [nd–554]	37.9 [nd–225]	17.4 [nd–131.6]	17.5 [nd–132]	13.6 [nd–135]	27.8 [nd–152]
	spring 2005	nm	nm	nm	nm	nm	nm	nm	nm	nm
	autumn 2005	nm	nm	nm	nm	nm	nm	nm	nm	nm
juvenile mullet	spring 2002 (5)	18.9 [2.96–34.7]	nm	80.6 [58–107]	72.3 [13–122]	360 [8–1555]	26.6 [nd–72]	42.6 [5.5–98]	nd	0.05 [nd–0.09]
	autumn 2002	nm	nm	nm	nm	nm	nm	nm	nm	nm
	spring 2005 (6)	9.16 [2.74–36.2]	9.8 [5–16]	25.0 [9.4–61.]	68.4 [57–86]	2.55 [nd–6.39]	10.4 [4.03–32.7]	10.2 [nd–51]	46.7 [16–64]	nd
	autumn 2005	nm	nm	nm	nm	nm	nm	nm	nm	nm
sand smelt	spring 2002 (17)	12.8 [0.96–31.5]	nm	5.36 [nd–17.6]	33 [nd–200]	82.8 [nd–245]	13.7 [nd–84.4]	21.1 [nd–60]	16.7 [nd–113]	44.3 [nd–183]
	autumn 2002 (6)	14.0 [nd–28.4]	nm	9.21 [nd–49]	11.9 [nd–72]	16.2 [nd–46]	28.0 [nd–89]	53.8 [24–102]	44.0 [nd–88]	167 [79–334]
	spring 2005 (14)	8.61 [nd–64.2]	23.4 [nd–93]	654 [nd–1999]	122 [nd–407]	9.61 [nd–22.9]	3.3 [nd–16.0]	4.2 [nd–16.3]	17.5 [nd–58]	4.6 [nd–65]
	autumn 2005 (9)	8.52 [nd–28.1]	9.2 [nd–37]	10.2 [nd–54.1]	42 [nd–119]	77.4 [3.9–208]	212.6 [10–793]	19.3 [nd–53]	63 [2–496]	95 [nd–253]
juvenile eel	spring 2002 (3)	68.3 [33.1–88.8]	nm	2.78 [nd–8.3]	nd	30.0 [nd–90.0]	77.0 [55.0–100]	nd	44 [nd–131]	226 [128–356]
	autumn 2002	nm	nm	nm	nm	nm	nm	nm	nm	nm
	spring 2005 (3)	8.90 [4.82–11.9]	130 [76–205]	263 [165–424]	251 [150–404]	556 [379–805]	31.6 [nd–68.7]	nd	80 [39–102]	257 [88–511]
	autumn 2005 (3)	7.69 [nd–23.1]	1.5 [nd–4.4]	nd	42.2 [23–67]	124 [12–190]	63.2 [26.1–137]	14.0 [7.8–23]	6.0 [nd–18]	16 [nd–48]
immature eel 1	spring 2002 (6)	98 [6.5–378]	nm	27 [1.1–99]	0.23 [nd–0.7]	49.6 [nd–181]	45.0 [nd–150]	31.4 [nd–176]	163 [nd–953]	238 [nd–1429]
	autumn 2002 (6)	8.9 [nd–53.5]	nm	9.39 [nd–28]	nd	69.5 [nd–217]	10.3 [nd–28]	24.5 [nd–68]	9.5 [nd–24]	4.8 [nd–20]
	spring 2005 (4)	6.90 [1.7–18.6]	33 [nd–76]	272 [193–418]	125 [72–206]	133 [15–485]	44.5 [nd–165]	nd	23.9 [21–30]	9.8 [nd–22]
	autumn 2005 (7)	7.19 [nd–23.3]	1.56 [nd–8]	nd	58 [38–131]	230 [9.5–638]	35.4 [5.32–69.0]	22.7 [2–55]	12 [nd–37]	86.6 [nd–237]
immature eel 2	spring 2002 (3)	53.9 [10–121]	nm	12.5 [2.2–32]	27.5 [nd–77]	21.2 [nd–64]	43.6 [nd–106]	35.7 [3.4–95]	125 [nd–374]	924 [nd–2773]
	autumn 2002 (4)	15.3 [nd–61.2]	nm	5.77 [nd–11.8]	39 [nd–156]	63.7 [nd–206]	12.1 [nd–23.9]	54 [15–130]	30 [nd–110]	384 [nd–867]
	spring 2005 (11)	1.87 [nd–4.91]	12.8 [nd–31]	104 [33.7–216]	52 [9.9–82.7]	15.4 [1.4–29]	10.9 [0.42–73.9]	1.5 [nd–7.4]	20.9 [2.8–92]	56.8 [nd–378]
	autumn 2005 (9)	3.72 [nd–29.3]	0.57 [nd–2.1]	0.59 [nd–5.32]	25.9 [9.1–48]	147 [33–311]	32.8 [3.93–78]	17.7 [5.4–38]	12.5 [nd–29]	71.2 [5.1–157]

**Table 4**  
Mean muscle tissue concentration and range [minimum–maximum] (ng g<sup>-1</sup> dw) of HCB, pp'-DDE, aldrin, dieldrin, endrin, endrin aldehyde, fipronil and diuron, in trophic web components of the Vaccarès Lagoon, (Camargue, France) sampled in spring and autumn 2002 and 2005. (n) = count of individuals, (n<sup>+</sup>)= count of pools. nm = not measured; nd = not detected.

species	season of sampling	HCB	pp'-DDE	aldrin	dieldrin	endrin	endrin aldehyde	fipronil	diuron
cardium	spring 2002 (13)	40.4 [nd–444]	1.0 [nd–7.8]	4.4 [nd–14.2]	1.7 [nd–18.0]	1.6 [nd–7.3]	7.7 [nd–26.0]	3.3 [0.2–7.9]	157 [nd–506]
	autumn 2002 (6)	1.8 [nd–6.9]	5.4 [nd–17.2]	2.7 [nd–4.73]	4.85 [nd–21.1]	1.9 [nd–8.9]	12.0 [nd–50.1]	6.3 [nd–18.5]	37.9 [2.47–113]
	spring 2005	nm	nm	nm	nm	nm	nm	nm	nm
	autumn 2005	nm	nm	nm	nm	nm	nm	nm	nm
gammarids	spring 2002 (4*)	0.3 [nd–1.00]	4.6 [nd–15.8]	98.0 [21.2–198]	41.6 [4.0–111]	41.8 [nd–112]	191.3 [nd–765]	27.7 [nd–57.8]	277.2 [nd–1109]
	autumn 2002 (3*)	11.6 [nd–20.4]	31.6 [nd–92.1]	19.6 [nd–48.3]	nd	nd	nd	9.1 [nd–13.8]	168.4 [nd–460]
	spring 2005 (6)	21.5 [13.0–32.2]	6.0 [nd–13.2]	162.4 [11.1–357]	10.4 [nd–43.0]	19.1 [nd–69.1]	15.6 [nd–93.6]	nd	18.3 [nd–57.1]
	autumn 2005	nm	nm	nm	nm	nm	nm	nm	nm
brown shrimp	spring 2002 (19)	3.3 [nd–37.7]	4.5 [nd–38.9]	7.5 [nd–25.0]	10.0 [nd–48.2]	8.8 [nd–76.3]	21.4 [nd–95.3]	20.9 [nd–291]	77.9 [nd–10]
	autumn 2002 (7)	0.7 [nd–1.7]	1.1 [nd–4.2]	30.7 [0.6–71.9]	60.3 [nd–195.1]	nd	41.8 [nd–145]	10.7 [nd–39.3]	12.8 [1.42–21.7]
	spring 2005 (9)	3.1 [0.4–9.0]	4.4 [nd–20.2]	7.5 [nd–20.5]	11.2 [nd–23.2]	5.2 [nd–21.1]	9.0 [nd–30.7]	25.9 [nd–218]	149.9 [81.3–261]
	autumn 2005 (6)	19.9 [9.54–42.6]	4.78 [2.1–13.4]	0.21 [nd–1.25]	13.1 [nd–29.3]	12.2 [nd–22.9]	27.1 [nd–150]	7.4 [nd–22.4]	225 [15.1–443]
pink shrimp	spring 2002 (17)	4.6 [nd–12.6]	4.6 [nd–13.8]	23.4 [nd–113]	11.9 [nd–34.7]	21.2 [nd–115]	53.6 [nd–205]	20.8 [nd–94.5]	70.1 [nd–34]5
	autumn 2002 (3*)	1.3 [0.0–3.7]	0.9 [nd–2.8]	5.5 [2.9–7.3]	30.6 [4.5–80.9]	94.4 [0.5–282]	59.8 [8.7–143]	41.3 [nd–99.9]	32.8 [10.4–66.9]
	spring 2005 (9)	18.8 [4.0–30.9]	30.4 [nd–252]	134.3 [nd–534]	15.3 [2.6–31.0]	6.9 [nd–26.3]	14.5 [nd–39.2]	57.7 [nd–506]	20.4 [0.3–86.4]
	autumn 2005	nm	nm	nm	nm	nm	nm	nm	nm
stickelback	spring 2002 (19)	4.8 [nd–25.5]	15.8 [nd–76.6]	41.4 [nd–216]	28.9 [nd–183]	158.6 [nd–2676]	3.6 [nd–37.5]	23.2 [nd–229]	227.1 [nd–764]
	autumn 2002 (2*)	51.7 [1.0–103]	78.4 [2.9–154]	36.2 [14.7–57.7]	26.5 [19.7–33.2]	2.2 [nd–4.4]	8.9 [8.3–9.5]	25.9 [19.1–32.8]	225 [9.26–440]
	spring 2005	nm	nm	nm	nm	nm	nm	nm	nm
	autumn 2005	nm	nm	nm	nm	nm	nm	nm	nm
pipefish	spring 2002 (7)	6.7 [nd–41.4]	nd	39.5 [nd–275]	30.0 [nd–197]	10.8 [nd–73.6]	nd	8.2 [nd–43.4]	35.3 [nd–129]
	autumn 2002	nm	nm	nm	nm	nm	nm	nm	nm
	spring 2005 (6*)	6.9 [5.1–9.3]	19.3 [4.8–28.3]	13.1 [nd–33.4]	4.3 [1.4–10.4]	9.9 [nd–21.6]	14.6 [nd–35.2]	2.7 [nd–9.1]	7.2 [nd–22.9]
	autumn 2005 (5*)	10.1 [3.34–19.2]	1.57 [0.5–3.05]	0.29 [nd–1.47]	4.86 [1.38–13.5]	4.37 [nd–10.7]	2.1 [nd–10.6]	14.4 [nd–41.7]	113 [1.35–540]
goby sp.	spring 2002 (17)	5.2 [nd–26.9]	8.8 [nd–64.3]	33.3 [nd–101]	20.2 [nd–96.9]	67.7 [nd–729]	71.4 [nd–564]	21.4 [nd–103]	103 [11.1–319]
	autumn 2002 (13)	4.9 [nd–26.4]	3.1 [nd–22.8]	30.4 [nd–134]	9.1 [nd–64.1]	16.2 [nd–196.5]	5.6 [nd–48.1]	7.4 [nd–34.4]	329 [2.87–1242]
	spring 2005	nm	nm	nm	nm	nm	nm	nm	nm
	autumn 2005	nm	nm	nm	nm	nm	nm	nm	nm
juv. mullet	spring 2002 (5)	0.3 [nd–1.2]	11.9 [nd–38.4]	120 [5.4–320]	27.4 [2.5–68.1]	7.1 [nd–16.0]	nd	9.0 [nd–19.8]	53.2 [nd–258]
	autumn 2002	nm	nm	nm	nm	nm	nm	nm	nm
	spring 2005 (6)	9.1 [0.0–47.2]	7.5 [nd–29.8]	148.5 [90.9–250]	10.7 [3.8–38.6]	26.7 [nd–94.1]	16.3 [nd–60.5]	0.2 [nd–0.7]	39.0 [nd–180.4]
	autumn 2005	nm	nm	nm	nm	nm	nm	nm	nm
sand smelt	spring 2002 (17)	6.5 [nd–33.1]	107.2 [nd–1140]	31.9 [nd–94.5]	7.4 [nd–31.1]	11.4 [nd–74.7]	69.8 [nd–298]	10.6 [nd–31.5]	371 [11.8–1933]
	autumn 2002 (6)	0.7 [nd–1.8]	6.2 [nd–14.5]	25.4 [nd–64.5]	36.0 [nd–118.9]	11.7 [nd–35.7]	85.0 [nd–324]	33.4 [nd–200.6]	41.5 [0.19–202]
	spring 2005 (14)	20.0 [nd–61.5]	17.6 [nd–63.2]	289 [nd–1396]	5.6 [nd–23.2]	22.1 [nd–57.1]	7.5 [nd–25.8]	0.6 [nd–6.3]	125 [nd–702]
	autumn 2005 (9)	15.3 [nd–28.6]	10.2 [nd–34.9]	21.8 [1.8–105]	11.2 [3.0–16.6]	13.9 [nd–45.5]	15.2 [nd–49.4]	5.8 [nd–34.2]	151 [7.63–465]
juvenile eel	spring 2002 (3)	3.8 [nd–11.3]	2.8 [nd–8.4]	186 [180–190]	nd	145 [nd–348]	61.6 [nd–185]	9.0 [nd–27.1]	nd
	autumn 2002	nm	nm	nm	nm	nm	nm	nm	nm
	spring 2005 (3)	nd	17.6 [4.3–30.3]	4.5 [nd–13.4]	12.9 [nd–38.8]	85.7 [65.9–95.7]	253 [81.1–406]	54.9 [nd–92.7]	3079 [1827–5259]
	autumn 2005 (3)	4.31 [nd–11.8]	21.2 [nd–48.2]	11.5 [nd–34.6]	14.5 [nd–37.1]	50.9 [nd–126.4]	144 [49.8–266]	77.0 [nd–189]	688 [548–861]
immature eel 1	spring 2002 (6)	0.7 [nd–3.3]	15.5 [nd–45.1]	257 [9.6–1200]	93.8 [nd–558]	199 [nd–1054]	195 [nd–1169]	175 [0.5–575]	12.2 [nd–35.6]
	autumn 2002 (6)	6.2 [nd–14.8]	13.1 [5.0–32.0]	14.7 [nd–35.5]	12.7 [nd–44.9]	4.6 [nd–19.5]	26.6 [nd–102]	15.0 [nd–42.0]	30.4 [nd–101]
	spring 2005 (4)	20.8 [15.7–26.9]	17.7 [8.2–30.2]	106 [nd–165]	9.0 [nd–26.7]	59.7 [47.1–67.7]	40.7 [9.9–109]	32.8 [9.9–68.2]	3073 [2590–4212]
	autumn 2005 (7)	0.58 [nd–2.88]	1.43 [nd–7.13]	nd	4.55 [nd–7.3]	15.3 [nd–45.8]	49.0 [nd–101]	57.9 [nd–137]	1453 [514–2884]
immature eel 2	spring 2002 (3)	8.1 [nd–14.8]	49.4 [10.9–99.5]	101.4 [8.4–240]	73.0 [1.0–216]	41.2 [nd–124]	506 [nd–1519]	76.9 [0.5–228]	210 [6.1–570]
	autumn 2002 (4)	2.6 [nd–7.4]	18.8 [6.2–35.7]	31.5 [2.32–66.5]	68.3 [15.7–216]	3.4 [nd–7.8]	189.8 [nd–705]	nd	108 [22.5–284]
	spring 2005 (11)	11.0 [nd–29.1]	23.1 [4.9–48.4]	120.4 [nd–292.8]	27.4 [nd–198]	62.4 [14.9–301]	36.1 [nd–217]	8.7 [nd–26.1]	1568 [1137–2146]
	autumn 2005 (9)	1.42 [nd–3.40]	1.16 [nd–6.36]	2.56 [nd–23.0]	2.52 [nd–8.6]	3.69 [nd–12.9]	15.8 [nd–82.8]	10.7 [nd–86]	960 [331–1962]

**Table 5**Concentration of some PCB congeners in components of the Vaccarès trophic web in spring and autumn 2002. Representative congeners and chlorination classes of PCB in ng g<sup>-1</sup> dw. nd = not detected.

ng g <sup>-1</sup> dw			PCB 52	PCB 101	PCB 138	PCB 153	∑di-CB	∑tri-CB	∑tetra-CB	∑penta + hexa-CB	∑hepta-CB	∑octa-CB	
Spring 2002	cardium	(11 pools)	421 ± 136 [nd-1566]	3.0 ± 2.5 [nd-28]	2.3 ± 1.9 [nd-21]	51.9 ± 48.6 [nd-537]	273 ± 132 [nd-1548]	988 ± 376 [nd-3145]	2764 ± 1194 [364-13913]	990 ± 628 [14-6958]	147 ± 196 [nd-1082]	35.3 ± 28.9 [nd-321]	
	brown shrimp	(12 pools)	310 ± 124 [nd-1439]	9.8 ± 4.9 [nd-58]	52.4 ± 50.1 [nd-604]	67.4 ± 28.7 [nd-334]	45.1 ± 22.2 [nd-262]	138 ± 34 [17-345]	350 ± 119 [13-1297]	217 ± 97 [13-1233]	139 ± 79 [6-987]	4.1 ± 2.5 [nd-29]	
	pink shrimp	(12 pools)	271 ± 90 [nd-869]	39.8 ± 15.8 [nd-142]	6.1 ± 2.0 [nd-17]	57.2 ± 25.6 [1-332]	153 ± 107 [nd-1312]	584 ± 134 [160-1654]	961 ± 310 [112-3496]	639 ± 233 [46-2922]	351 ± 252 [22-3117]	127 ± 116 [nd-1408]	
	juvenile eel	(2)	5396 ± 4174 [1222-9570]	21.8 ± 21.8 [nd-65]	40.4 ± 40.4 [nd-121]	nd	318 ± 225 [nd-753]	639 ± 555 [83-1750]	3799 ± 2928 [500-9639]	4309 ± 1398 [1570-6161]	392 ± 111 [203-589]	nd	
	pipefish	(4)	nd	17.8 ± 7.1 [nd-35]	19.4 ± 19.4 [nd-78]	16.4 ± 12.8 [nd-54]	13.6 ± 4.7 [nd-22]	576 ± 105 [341-814]	66 ± 28 [16-139]	153 ± 76 [10-359]	72.7 ± 25.4 [20-142]	19.4 ± 19.4 [nd-78]	
	stickleback	(11)	95.9 ± 40.7 [nd-379]	31.5 ± 18.6 [nd-207]	1.3 ± 1.3 [nd-14]	17.0 ± 12.2 [nd-136]	65.2 ± 22.2 [nd-189]	302.7 ± 82.9 [22-1003]	200 ± 92 [12-1058]	225 ± 60 [8-570]	72.3 ± 36.3 [nd-417]	1.35 ± 1.25 [nd-14]	
	sand smelt	(8)	455 ± 376 [nd-3090]	23.3 ± 13.6 [nd-147]	35.9 ± 30.3 [nd-337]	121.0 ± 57.2 [nd-636]	218 ± 140 [nd-1418]	1065 ± 327 [83-3648]	1952 ± 950 [213-10921]	1386 ± 524 [64-6144]	295 ± 117 [nd-1266]	48.1 ± 36 [nd-411]	
	goby sp.	(11)	66.8 ± 39.3 [nd-441]	10.3 ± 7.5 [nd-80]	13.0 ± 11.7 [nd-130]	46.9 ± 17.2 [nd-164]	28.7 ± 18.0 [nd-201]	121 ± 58 [nd-643]	288 ± 123 [1-1349]	495 ± 275 [5-3062]	203 ± 117 [nd-1285]	nd	
	immature eel 1	(6)	250 ± 162 [13-1047]	10.0 ± 3.3 [nd-19]	nd	164 ± 143 [nd-877]	26.3 ± 13.9 [nd-95]	154 ± 61 [6-363]	314 ± 158 [29-1072]	954 ± 384 [81-2410]	20.4 ± 12.5 [nd-80]	nd	
	immature eel 2	(3)	643 ± 466 [8-1552]	294 ± 194 [12-664]	60.0 ± 31.0 [nd-104]	6.4 ± 3.8 [nd-13]	127 ± 68 [nd-232]	203 ± 50 [117-290]	991 ± 493 [35-1678]	9521 ± 1430 [941-1441]	244 ± 130 [29-479]	nd	
	Autumn 2002	cardium	(6 pools)	51.0 ± 12.0 [12-100]	0.7 ± 0.7 [nd-4]	nd	nd	nd	40.8 ± 6.8 [9-55]	90 ± 17 [31-148]	281 ± 120 [101-1120]	15.7 ± 13.7 [nd-84]	11.6 ± 7.4 [nd-47]
		gammarids	(3 pools)	77.2 ± 29.0 [24-123]	10.5 ± 8.2 [nd-27]	6.8 ± 6.8 [nd-20]	1.8 ± 1.8 [nd-5]	nd	213 ± 109 [13-389]	113 ± 38 [37-151]	851 ± 169 [171-1223]	nd	68.6 ± 45.5 [10-158]
brown shrimp		(3 pools)	63.9 ± 18.7 [44-101]	22.7 ± 10.1 [12-43]	nd	10.8 ± 7.3 [2-25]	15.9 ± 8.7 [nd-30]	19.3 ± 9.6 [1-34]	56 ± 20 [32-95]	751 ± 141 [1301-157]	17.6 ± 12.0 [2-41]	1.3 ± 1.3 [nd-4]	
pink shrimp		(3 pools)	179 ± 146 [18-471]	16.6 ± 15.0 [nd-46]	nd	2.2 ± 1.5 [nd-5]	nd	3.4 ± 2.4 [nd-8]	65 ± 54 [10-173]	351 ± 113 [181-50]	5.6 ± 3.3 [nd-11]	nd	
sand smelt		(6)	43.5 ± 27.2 [8-178]	3.4 ± 1.9 [nd-12]	9.2 ± 5.8 [1-38]	8.1 ± 6.1 [nd-39]	2.6 ± 1.9 [nd-12]	28.7 ± 4.7 [15-47]	78 ± 28 [21-213]	621 ± 124 [19-172]	7.2 ± 5.4 [nd-34]	1.1 ± 0.3 [nd-2]	
goby sp.		(8)	117 ± 85 [nd-707]	6.8 ± 4.1 [nd-28]	6.5 ± 3.7 [nd-31]	14.0 ± 7.5 [nd-48]	42.7 ± 30.7 [nd-255]	188 ± 66 [18-538]	154 ± 98 [16-828]	1741 ± 1110 [10-937]	8.7 ± 7.0 [nd-56]	0.85 ± 0.75 [nd-6]	
immature eel 1		(6)	309 ± 161 [20-892]	10.9 ± 8.3 [nd-52]	31.4 ± 27.1 [nd-167]	33.6 ± 26.0 [nd-161]	11.1 ± 7.1 [nd-38]	32.4 ± 8.5 [8-66]	365 ± 182 [33-1059]	1721 ± 198 [19-630]	30.3 ± 24.5 [nd-151]	0.6 ± 0.5 [nd-3]	
immature eel 2		(4)	289 ± 203 [24-883]	9.4 ± 3.9 [4-21]	9.0 ± 4.6 [3-23]	nd	11.3 ± 6.7 [nd-30]	18.5 ± 6.7 [6-37]	375 ± 246 [38-1102]	59 ± 22 [32-125]	8.2 ± 4.8 [nd-18]	nd	
common sole		(4)	540 ± 460 [68-1920]	0.3 ± 0.3 [nd-1]	0.4 ± 0.4 [nd-2]	nd	0.2 ± 0.2 [nd-1]	43.8 ± 15.2 [7-79]	1486 ± 1355 [85-5550]	228 ± 225 [0-902]	6.9 ± 4.1 [nd-16]	30.5 ± 21.1 [nd-93]	
bream		(6)	28.3 ± 4.6 [13-40]	4.9 ± 2.3 [2-16]	1.8 ± 1.0 [nd-6]	2.1 ± 1.5 [nd-9]	3.9 ± 2.5 [nd-14]	22.7 ± 5.7 [11-47]	50 ± 12 [20-101]	36 ± 13 [11-88]	1.9 ± 1.5 [nd-9]	10.2 ± 4.2 [nd-23]	

**Table 6**Concentration of PCB congeners in components of the Vaccarès trophic web in spring and autumn 2005. Representative congeners and chlorination classes of PCB in ng g<sup>-1</sup> dw. nd = not detected.

			PCB52	PCB101	PCB138	PCB153	∑di-CB	∑tri-CB	∑tetrac-CB	∑penta + hexa-CB	∑hepta-CB	∑octachloro	
Spring 2005	OSM	(5)	16.3 ± 4.7 [7–34]	1.7 ± 1.3 [nd–7]	1.1 ± 0.7 [nd–3]	4.1 ± 1.8 [1–11]	1.2 ± 1.2 [nd–6]	28.8 ± 9.2 [11–53]	686 ± 148 [127–984]	26 ± 8 [11–55]	3.2 ± 0.8 [2–6]	nd	
	<i>Zostera</i> sp.	(6 pools)	113.6 ± 40.0 [33–270]	19.8 ± 5.8 [nd–44]	15.0 ± 5.0 [nd–34]	8.2 ± 2.6 [nd–19]	100.8 ± 92.9 [nd–564]	354 ± 293 [nd–1813]	163 ± 46 [52–312]	463 ± 131 [57–969]	29.6 ± 8.3 [5–65]	1.0 ± 0.5 [nd–3]	
	copepods	(8 pools)	252.1 ± 167.3 [12–1374]	5.6 ± 5.1 [nd–41]	5.4 ± 5.4 [nd–43]	6.2 ± 5.3 [nd–43]	nd	4.6 ± 4.6 [nd–37]	315 ± 164 [74–1403]	37 ± 27 [1–225]	12.4 ± 4.4 [nd–38]	5.9 ± 3.0 [nd–19]	
	sphaeroma	(6 pools)	28.5 ± 10.5 [10–79]	8.1 ± 3.2 [nd–22]	11.0 ± 4.6 [nd–31]	3.2 ± 1.1 [nd–8]	25.4 ± 25.4 [nd–153]	78.9 ± 78.9 [nd–473]	70 ± 30 [28–212]	146 ± 47 [4–320]	8.4 ± 2.6 [nd–17]	1.7 ± 1.5 [nd–9]	
	gammarids	(6 pools)	68.0 ± 8.3 [32–89]	35.3 ± 8.6 [13–59]	15.9 ± 10.5 [nd–67]	3.4 ± 1.1 [nd–7]	110.8 ± 24.8 [53–214]	161.7 ± 40.5 [75–340]	264 ± 26 [209–351]	926 ± 131 [590–1369]	25.4 ± 3.8 [16–36]	8.5 ± 1.3 [3–12]	
	brown shrimp	(9)	103.5 ± 20.5 [27–241]	11.9 ± 4.2 [3–39]	6.3 ± 2.1 [nd–16]	13.4 ± 5.1 [2–45]	3.4 ± 1.6 [nd–12]	19.2 ± 4.7 [2–49]	654 ± 147 [120–1218]	89 ± 27 [23–211]	5.7 ± 1.3 [1–14]	0.25 ± 0.15 [nd–2]	
	pink shrimp	(9)	174 ± 94 [48–926]	16.7 ± 5.7 [4–60]	16.2 ± 3.2 [nd–32]	13.8 ± 5.6 [3–58]	93.7 ± 15.2 [5–146]	194.6 ± 61.7 [18–642]	423 ± 99 [159–1189]	1359 ± 228 [71–2019]	46.2 ± 14.4 [9–158]	23.2 ± 4.6 [nd–39]	
	juvenile eel	(5)	210 ± 47 [92–348]	45.3 ± 13.3 [17–94]	41.0 ± 12.6 [16–84]	27.5 ± 17.3 [5–96]	16.9 ± 11.4 [nd–57]	26.1 ± 24.9 [nd–125]	700 ± 128 [144–535]	700 ± 128 [301–1028]	700 ± 128 [16–171]	13.2 ± 10.7 [nd–56]	
	pipefish	(6)	436.7 ± 94.5 [145–744]	50.7 ± 9.7 [32–94]	19.0 ± 10.2 [nd–63]	10.9 ± 2.6 [5–19]	139.3 ± 40.3 [52–312]	459 ± 61 [305–723]	584 ± 105 [289–951]	345 ± 61 [153–569]	41.4 ± 3.9 [32–59]	42.8 ± 11.3 [14–86]	
	juvenile mullet	(6)	281.1 ± 230.9 [7–1432]	43.7 ± 33.0 [nd–207]	17.3 ± 12.2 [nd–77]	78.2 ± 56.9 [3–362]	5.0 ± 5.0 [nd–30]	56.7 ± 37.4 [nd–234]	415 ± 280 [36–1802]	541 ± 243 [74–1679]	122.3 ± 25.1 [8–178]	33.6 ± 27.3 [nd–169]	
	sand smelt	(14)	93.5 ± 17.5 [20–233]	46.6 ± 15.7 [5–239]	36.0 ± 14.5 [nd–218]	114.4 ± 39.0 [10–567]	74.3 ± 30.3 [nd–335]	131.9 ± 27.4 [nd–368]	382 ± 68 [122–980]	1594 ± 518 [236–7478]	52.2 ± 16.3 [16–256]	22.6 ± 8.0 [nd–86]	
	immature eel 1	(3)	44.2 ± 7.0 [31–54]	26.0 ± 4.5 [17–31]	14.6 ± 2.2 [11–19]	37.3 ± 14.6 [21–66]	5.9 ± 3.0 [nd–10]	179.9 ± 67.5 [94–313]	103 ± 26 [59–147]	365 ± 46 [272–417]	20.9 ± 2.3 [18–25]	1.1 ± 0.6 [nd–2]	
	immature eel 2	(10)	89.1 ± 13.5 [48–167]	73.9 ± 15.3 [32–188]	28.9 ± 4.1 [10–47]	63.9 ± 20.1 [11–200]	44.3 ± 25.6 [2–271]	318.5 ± 51.6 [76–510]	260 ± 42 [92–431]	666 ± 67 [383–1028]	41.8 ± 6.3 [18–91]	3.1 ± 0.9 [nd–9]	
	Autumn 2005	brown shrimp	(5)	62.4 ± 5.7 [46–77]	17.5 ± 6.8 [7–44]	16.8 ± 1.6 [13–23]	21.8 ± 8.6 [8–54]	106.9 ± 14.8 [69–160]	126.2 ± 23.2 [83–215]	291 ± 47 [181–442]	1181 ± 213 [675–1762]	30.4 ± 4.8 [18–48]	19.8 ± 2.0 [15–26]
		juvenile eel	(3)	187.7 ± 35.2 [121–241]	28.6 ± 19.2 [nd–65]	6.3 ± 4.4 [nd–15]	9.6 ± 5.4 [nd–19]	14.1 ± 14.1 [nd–42]	10.8 ± 5.7 [nd–19]	214 ± 50 [121–295]	84 ± 47 [0–162]	5.5 ± 1.4 [3–7]	nd
		pipefish	(5)	123.7 ± 74.4 [20–418]	7.2 ± 0.5 [6–8]	7.3 ± 3.3 [nd–18]	13.1 ± 1.0 [11–16]	38.9 ± 23.4 [nd–100]	56.0 ± 26.6 [9–123]	212 ± 66 [78–461]	452 ± 247 [33–1078]	14.3 ± 4.1 [2–25]	6.5 ± 4.0 [nd–19]
		sand smelt	(9)	184.5 ± 76.2 [15–709]	33.3 ± 17.8 [2–173]	20.7 ± 5.2 [nd–46]	59.8 ± 39.7 [1–376]	72.5 ± 18.2 [nd–132]	124.3 ± 37.7 [2–362]	427 ± 80 [109–809]	1547 ± 348 [18–3022]	55.0 ± 22.0 [12–222]	26.6 ± 7.3 [nd–68]
immature eel 1		(5)	175.4 ± 53.8 [35–352]	13.6 ± 5.3 [nd–32]	4.3 ± 2.2 [nd–12]	9.9 ± 4.1 [1–20]	4.0 ± 4.0 [nd–20]	43.8 ± 26.4 [nd–139]	215 ± 49 [124–394]	117 ± 39 [7–244]	7.6 ± 2.4 [3–17]	nd	
immature eel 2		(9)	252.0 ± 128.6 [32–1258]	12.7 ± 2.5 [2–22]	9.2 ± 3.7 [nd–32]	7.8 ± 1.4 [1–16]	2.8 ± 1.5 [nd–10]	43.9 ± 24.6 [nd–229]	338 ± 139 [47–1409]	114 ± 34 [24–355]	10.4 ± 2.7 [4–30]	nd	
yellow eel		(2)	109.9 [70–150]	6.0 [4–8]	8.1 [3–13]	18.2 [9–28]	1.7 [nd–3]	3.1 [nd–6]	147 [115–180]	97 [53–140]	50.8 [47–55]	0.9 [0.5–1.5]	

In 2002, the seasonal variations were substantial. Indeed, in spring, the total content of PCB ranged from  $1871 \pm 916 \text{ ng g}^{-1}\text{dw}$  in consumers I to  $1420 \pm 345 \text{ ng g}^{-1}\text{dw}$  in consumers II-2. In autumn  $\sum\text{PCB}$  (i.e. sum of measured PCB) were between 2.3 and 5 times lower (from  $p < 0.0001$  to  $p = 0.019$ ), furthermore the concentration increased with the TL. In spring 2005, producers and consumers I showed a concentration similar ( $638 \pm 198$  and  $605 \pm 174 \text{ ng g}^{-1}\text{dw}$ , respectively), but lower than 3 years earlier ( $p = 0.034$ ) in consumers I, and inferior than in consumers II ( $>1000 \text{ ng g}^{-1}\text{dw}$ ). Organisms analyzed in autumn 2005 showed a decreasing  $\sum\text{PCB}$  value with their TL. The consumers II were less contaminated than in spring, but from 2 to 6 times more than 3 years earlier. In top predators, as fish-eating birds, Berny et al. (2002) showed that such PCB were the major contaminants. Indeed, in the little egret eggs, PCB concentrations ranked from 0.14 to  $12.1 \mu\text{g Kg}^{-1}\text{ww}$  (wet weight).

The total indicator PCB concentrations (sum of concentrations of PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, PCB 180 on dw basis) ranged from  $120 \pm 47 \text{ ng g}^{-1}$  in producers sampled in spring 2005 to  $682 \pm 221 \text{ ng g}^{-1}$  in consumers sampled in spring 2002. Comparable levels were reported by Storelli et al. (2007) in eels (*A. anguilla*) from the Lesina Lagoon, (Adriatic Sea, Italy)  $284.0 \pm 20.2 \text{ ng g wet weight}$  (i.e.  $1136 \pm 81 \text{ ng g}^{-1}\text{dw}$ ), whereas eels from Flanders were more contaminated about  $600 \text{ ng g}^{-1}\text{wet weight}$  (i.e.  $>2000 \text{ ng g}^{-1}\text{dw}$ ) (Maes et al., 2008). In a previous paper devoted to the contamination of eels from Camargue in 2003, we quoted higher levels of PCB, notably indicator congeners, as PCB 153 and PCB 138 who reached levels  $>100 \text{ ng g}^{-1}\text{dw}$  (Oliveira Ribeiro et al., 2008).

The temporal profile of the indicator PCBs followed those of  $\sum\text{PCB}$ . Indicator PCBs represented on average about 40% of the total concentration of analyzed PCB but from 0% in spring 2002 in some cockles, juvenile eels, stickleback and pipefish to 100% in several young eels. The dioxin-like PCB (sum of concentrations of PCB 77, 81; 126; 169; 105; 114; 118; 123; 156; 157; 167; 180; 189) represented from 6 to 19%, in 2002, and from 10 to 36% of measured congeners, in 2005. In 2002, 40% of tested individuals were not contaminated vs 13% in 2005. Among dioxin-like PCB, the PCB 126 and 169 are the more hazardous congeners (Van den Berg et al., 1998; Vezina et al., 2004), but in the present study the PCB 77 and 105 were the dominant dioxin-like PCB. As in our previous paper (Oliveira Ribeiro et al., 2008), the TEQ (Toxic Equivalents) of dioxin-like PCB were calculated using the WHO-TEFs for fish. The recent revised amount admissible WHO-TEQ in fish filets is  $8 \text{ pg g}^{-1}\text{wet weight}$ . Table 7 shows that such a limit was largely exceeded in spring 2005 in all the trophic guilds. That suggests that the majority of the species were unsuitable for human consumption. However, in autumn 2005, TEQ clearly decreased showing uncontrollable fluctuations and pointing up difficulties to validate such indicator in risk assessment. Indeed comparison of experimental data with regulatory limits does not prove realistic ( $8 \text{ pg vs } >10^4 \text{ pg}$ ).

### 3.3. Relation with trophic positions

It has been demonstrated for a long time that PCB and persistent OCPs tend to biomagnify in aquatic food chains (Hunt and Bischoff, 1960; Risebrough et al., 1968) and more recently reviews of this topic have been published (Zaranko et al., 1997; Binelli and Proveni, 2003; Burreau et al., 2004, 2006). The biomagnification potential of any compound is regarded on the basis of the  $\log K_{ow}$ . A  $\log K_{ow}$  ranking from 5 to 8 should confer an excellent aptitude to biomagnify, however our analysis shows, that diuron and HCH, for example ( $\log K_{ow}$  2.67 and 4.26 respectively) can experience a significant biomagnification along trophic chains (Table 7). In looking forward to an efficient mechanistic food web model as

**Table 7**

Arithmetic mean  $\pm$  standard deviation and extreme values of TEQ calculated on the basis of PCB content in trophic guilds from the Vaccarès Lagoon in experimental seasons between 2001 and 2005. Values between the brackets: number of samples, replicates or pools of individuals.

	TEQ $\text{pg g}^{-1}\text{wet weight}$	Minimum	Maximum
autumn 2001			
consumers I (9)	$60.2 \pm 39.8$	nd	371.2
consumers II-2 (7)	$19.9 \pm 5.0$	4.6	44.7
consumers II-3 (8)	$8.0 \pm 3.0$	2.0	27.7
spring 2002			
consumers I (12)	$32.9 \pm 13.4$	nd	135.6
consumers II-1 (48)	$40.8 \pm 9.5$	nd	340.4
consumers II-2 (21)	$9.5 \pm 3.3$	nd	65.1
consumers II-3(3)	$39.4 \pm 7.6$	29.1	54.2
autumn 2002			
consumers I (6)	nd		
consumers II-1 (11)	$1.6 \pm 0.7$	nd	8.2
consumers II-2 (11)	$7.9 \pm 6.2$	nd	69.8
consumers II-3 (21)	$1.6 \pm 0.7$	nd	14.1
autumn 2003			
consumers II-3 (27)	$354 \pm 69$	13.0	1574
spring 2005			
SOM (6)	$0.5 \pm 0.2$	nd	1.5
producers (11)	$1127 \pm 411$	0.2	5681
consumers I (9)	$587 \pm 301$	0.02	2167
consumers II-1 (28)	$3366 \pm 1045$	2.8	18903
consumers II-2 (15)	$1724 \pm 575$	5.2	7506
consumers II-3 (19)	$4496 \pm 687$	1564	13635
autumn 2005			
consumers I (3)	$341 \pm 181$	16	641
consumers II-1 (13)	$352 \pm 127$	0.03	1567
consumers II-2 (7)	$31.5 \pm 14.3$	0.18	97
consumers II-3 (14)	$197 \pm 85$	0.082	1158

developed by Nfon and Cousins (2006, 2007) for a Baltic food web, taking into account the uptake of pollutants by respiration from the water column and sediment pore water, or the feeding and growth rate plus the lipid content of organism according to the length of trophic web, we relied on a basic correlation analysis and biomagnification factor (BMF) calculations according to Strandberg et al. (1998) (Table 7).

Considering all the experiments carried out during second half of the experimental decade (2001–2005), Pearson coefficients ascertained that two pesticides families were significantly biomagnified, i.e. lindane ( $\gamma$ -HCH plus isomers), and endosulfan (plus an isomer and a metabolite) (Fig. 4). Indeed, concentrations showed significant correlations with TL calculated on the basis of  $\delta^{15}\text{N}$  signature. To a lesser extent fipronil and diuron exhibited similar correlations. At last, total measured PCB,  $\sum$ dioxin-like,  $\sum$ indicator, and the more chlorinated PCB were also positively correlated with TL presuming a biomagnification process. Nevertheless, it is to be noticed that the progression of values levelled in the secondary consumers of type 2 (Fig. 4) because of the relative weakness of the impregnation in the 2 dominant species of this guild, sand smelts weighting  $1.7 \pm 0.3\text{g}$  and juvenile eels 2 (weight  $90 \pm 17\text{g}$ ), i.e.  $\sum\text{PCB}$  concentrations were  $906 \pm 131$  and  $925 \pm 455 \text{ ng g}^{-1}\text{dw}$ , respectively (see details Table 5). Such a reduction could be explained with the mobility (habitat) of fish and the nature of their preys, at their stages of maturity.

Many authors consider that, at lower TL, the contamination profile depends on the bioconcentration (water-biota transfer) related to the hydrosolubility of compounds and the lipid nature of organisms and, at the higher TL, the determining factors are lipophilicity and persistence of compounds, as well as metabolic activity and level of food transfer (Kidd et al., 1995; Borga et al., 2001; Fisk et al., 2001;

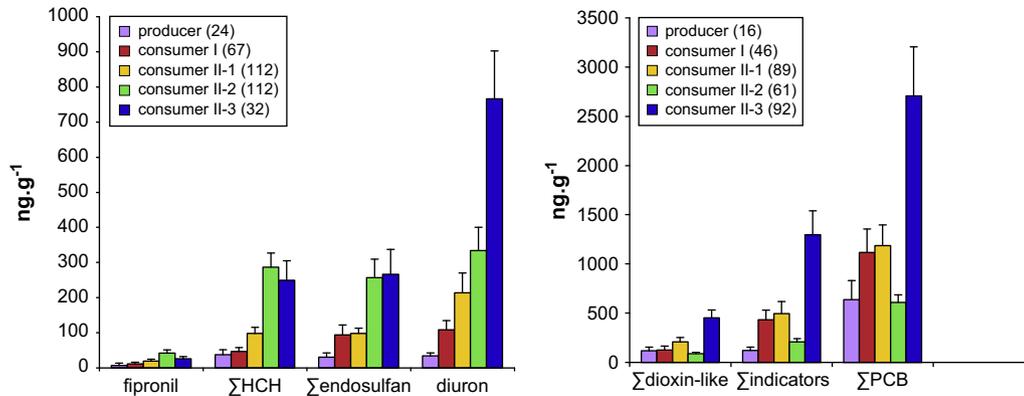


Fig. 4. Global contamination profiles (on a dry weight basis) of the 5 trophic compartments of the Vaccarès Lagoon community sampled between 2001 and 2005.

Ruus et al., 2002). Generally, the influential factors for bioavailability are the pollutant exposure (chronic inputs or persistence), the physicochemical characters of the compounds and the metabolic capacities of organism. In the present paper, the trophic transfer of organochlorines was characterized by their bioaccumulation profile in the trophic guilds and by a correlation analysis. Fisk et al. (2001), inter alia, considered that, in the case of compounds with a log  $K_{ow} > 4-5$  only, a high level of food transfer in the higher TL leads to a biomagnification process. However, here, the global analysis of results obtained from several study campaigns showed that compounds slightly lipophilic, like diuron (log  $K_{ow} = 2.67$ ) or endosulfan (log  $K_{ow} = 3.50$ ) and endosulfan sulphate (log  $K_{ow} = 3.64$ ) were concentrated along the food chain. The biomagnification of these low lipophilic molecules, easily degradable and continuously released into the ecosystem (via the Rhone River), could be related to a retention at the lowest levels of the trophic web (SOM,

phytoplankton). Therefore, their bioavailability for a direct bioconcentration (a passive transfer of contaminants from medium through teguments) should decrease and their potential trophic transfer should increase in the consumers. The PCB concentration in tissues of aquatic organisms translates the steady state between the absorption and elimination rates; the least-chlorinated compounds (di-, tri-, tetra-CB, log  $K_{ow} = 5.05, 5.69, 6.34$ , respectively) being more easily eliminated or metabolized than PCBs of a higher level of chlorination (penta-, hexa-, hepta-, octa-CB: log  $K_{ow} = 6.98, 7.52, 8.91, 9.64$ , respectively) (Goerke et al., 2004). On the other hand, Stapleton et al. (2001) estimated that species exposed to benthic and pelagic sources of contamination (i.e. sedimentary and atmospheric sources), accumulated more PCB contaminating the aquatic environment. Thus, the high levels of PCBs found in cockles sampled in 2002 (Table 5) were probably in relation with their specific ecological niches. By studying the bioconcentration and the re-deposition of

Table 8

Significant relations between trophic level and OC contamination from 2001 to 2005 in the Vaccarès Lagoon. Biomagnification factors of organochlorines in biota from zooplankton to eels as a function of their trophic guilds (sub-compartment).  $R$  = Pearson coefficient ( $p$ -value),  $n$  = number of contaminated samples.

	$R$ Correlation ( $p$ -value)	$n$	Biomagnification factor (BMF)			
			producer vs. consumer I.	consumer I vs consumer II-1	consumer II-1 vs consumer II-2	consumer II-2 vs consumer II-3
$\gamma$ -HCH	0.28 (<0.0001)	266	1.03	1.37	4.06	0.32
$\delta$ -HCH	0.44 (<0.0001)	257	3.23	1.66	0.74	0.66
$\Sigma$ HCH	0.42 (<0.0001)	327	2.13	1.56	1.23	0.49
$\alpha$ endosulfan	0.30 (<0.0001)	229	2.24	1.05	0.69	0.82
$\beta$ endosulfan	0.15 (0.027)	222	2.66	0.85	0.56	0.74
endosulfan sulphate	0.42 (<0.0001)	201	14.97	0.59	1.54	0.94
$\Sigma$ endosulfan	0.35 (<0.0001)	338	5.00	0.73	1.06	0.86
fiipronil	0.25 (0.0002)	221	5.31	0.68	1.14	0.48
diuron	0.13 (0.022)	302	2.00	1.61	1.30	2.00
CB28	0.23 (0.0012)	202	14.7	0.12	0.48	3.35
CB44	0.16 (0.024)	212	7.49	1.14	0.38	0.93
CB77/123	0.33 (<0.0001)	224	0.51	1.25	0.45	4.01
CB101	0.31 (<0.0001)	242	2.65	0.51	0.57	3.58
CB105	0.17 (0.012)	229	1.33	0.79	0.11	3.95
CB110	0.20 (0.012)	155	2.52	2.41	0.24	2.61
CB138	0.31 (<0.0001)	190	0.41	3.10	0.25	12.2
CB144	0.22 (0.0009)	222	3.46	1.03	0.62	1.30
CB151	0.18 (0.007)	225	2.97	1.60	0.42	0.87
CB153	0.23 (0.0002)	241	3.90	1.42	0.26	6.16
CB180	0.29 (<0.0001)	202	1.38	0.90	0.13	5.27
CB194	0.35 (<0.0001)	146	14.1	1.14	0.32	5.59
$\Sigma$ pentaCB	0.27 (<0.0001)	303	1.32	0.85	0.28	3.06
$\Sigma$ hexaCB	0.24 (<0.0001)	299	1.67	1.25	0.43	2.35
$\Sigma$ hepta-CB	0.24 (0.0003)	229	3.36	0.56	0.12	5.00
$\Sigma$ octa-CB	0.35 (<0.0001)	172	27.1	1.09	0.45	2.49
$\Sigma$ PCB measured	0.24 (<0.0001)	322	2.74	0.57	0.33	1.86
$\Sigma$ dioxin-like PCB	0.20 (0.0004)	300	1.15	0.83	0.28	2.32
$\Sigma$ indicator PCB	0.26 (<0.0001)	316	4.02	0.63	0.22	2.96

PCB in *Dreissena polymorpha*, Cho et al. (2004) showed the impact of filters feeders on the PCB dynamics. Indeed, filter bivalves would have the capacity by several ways to increase the retention time of PCBs: by means of bioconcentration, by purification of suspended particles, by their release in water in dissolved form or by their re-deposition in sediments, as many mechanisms which contribute to make them available for benthic food webs through the detritivorous. The part of the feeding as source of contamination in fishes is not easy to evaluate. Some authors think that the trophic transfer of contaminants in fish is secondary or even negligible in comparison to the direct absorption through the gills (Leblanc, 1995; Randall et al., 1998). The use of the isotopic ratio of nitrogen to define the TL in order to analyze a food transfer of pollutants, would subsequently be only efficient at the higher TL (Fisk et al., 2001; Ruus et al., 2002; Burreau et al., 2004).

In addition, a biomagnification factor (BMF) was calculated. Usually, BMF is >1 when the pollutant biomagnifies, on the contrary, BMF < 1 means that elimination exceeds bioaccumulation. However in field studies, this theory must be adapted to characteristics of the biotope and the biota. In Table 8, BMF is reported for compounds for which concentration showed a significant correlation with  $\delta^{15}\text{N}$ . The BMF values ranked from 0.11, in consumers II-2 for PCB105, to 27 in consumers I for  $\Sigma$ octa-CB. Such range of values was in accordance to other studies carried out in quite different ecosystems (Maruya and Lee, 1998). In invertebrates (consumers I) BMF (0.41–27) were generally higher than in the smallest fish (consumers II-1 and II-2) (0.12–3.48). BMF were <1 in consumers II-3 (top-consumers) for all pesticides biomagnified except diuron (=2), but BMF were >1 for PCB except CB44 (=0.93) and CB151 (=0.87). Consumers II-2 showed very low BMF of PCB (0.11–0.62) related to consumers II-1, in accordance to the low contamination level already described in this trophic sub-compartment (Fig. 4). In contrast to Antunes et al. (2007), we did not find correlations of BMF with  $\log K_{ow}$ , since endosulfan sulphate, PCB28, PCB138 and PCB194 were the only to exhibit BMF higher to 10 and a  $\log K_{ow}$  very different. However, this assertion may be contended, because in consumer I, the octa-CB homologues ( $\log K_{ow} = 8.91$ ) showed the highest BMF value, probably, due to their high hydrophobic nature.  $\Sigma$ PCB (total measured, indicators or dioxin-like) showed BMF < 1 in secondary consumers II-1 and II-2, illustrating a high susceptibility to biotransformation, in contradiction with Fisk et al. (2001), who estimated that BMF of  $\Sigma$ POP vary considerably from those of individual compartment of chemicals. A BMF value > 1 for diuron was found in the four trophic sub-compartments, showing that the uptake exceeds elimination. The high BMF of endosulfan sulphate in consumers I, compared to the mother molecules  $\alpha$  and  $\beta$ -endosulfan, indicated that invertebrates were not able to complete the metabolization. As Hoekstra et al. (2003) announced it, fish are able of metabolizing HCH isomers, consequently BMF of  $\gamma$ - and  $\delta$ -HCH were <1 in the top-consumer fishes, as in primary consumers, however the secondary consumers 1 did not seem able to have the same aptitude (BMF = 3.48 and 1.75, respectively).

#### 4. Conclusion

The occurrence of a bioconcentration process of organochlorine pollutants was presumed in a coastal wetland, the Vaccarès Lagoon in the Biosphere Reserve of Camargue (France) due to the permanent and uncontrolled agricultural wastewater inflow in this coastal wetland. Chemicals are both coming from drainage ditch and from irrigation systems collecting water from the Rhone River. It is, particularly significant with persistent pesticides like lindane and endosulfan, banned since several years, diuron, herbicide still used in the Rhone basin, and PCBs of which a pervasive and worrying pollution of the Rhone river – notably of its estuarine area – has been shown up in these last years. However, its assessment

has proven uneasy despite the fact that various trophic guilds are concerned, the contamination level displayed strong fluctuations with time. The careful integration of the 10-years-results from researches carried out in this water body, has enabled us to demonstrate that persistent pollutants, like lindane and endosulfan (plus isomers and/or metabolites) and PCBs, are biomagnified along the food chain and contaminate seriously top predators like European eels, whose pathology prevalence is increasing and its population decline has reached such a level that it jeopardizes its future in the whole Rhone delta.

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