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PCB, PCDD/F and PBDE levels and profiles in crustaceans from the coastal waters of Brittany and Normandy (France)

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Abstract

Polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) were analysed in the muscle of various edible marine crustaceans (spider crab, edible crab, velvet swimming crab and Norway lobster) from the Brittany and Normandy coasts (France). The highest concentrations were measured in species collected from Antifer (Seine Bay). PCB and PBDE patterns in crustacean muscles were similar and independent of the geographical area with the predominance of the high chlorinated PCBs (CB153, 138, 118 and 180), and of a few PBDE congeners (BDE47, BDE99, BDE100 and BDE28). Oppositely, dioxin contamination differed with site. The major component in crustaceans from the Seine Bay was 2378-TCDF, whereas specimens from cleaner areas had higher relative concentrations of OCDD. Finally, the comparison of the spider crab contaminant profiles to those measured in mussel and sea bass highlighted two different trends: decapod crustaceans possess relatively strong capacity to metabolise PCBs and PBDEs; however these species might be used as bioindicators for dioxin pollution monitoring in the marine coastal environment.

Keywords: PCBs; PCDD/Fs; PBDEs; Decapod crustaceans; Metabolisation; Food safety; France

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are widespread contaminants with important implications for environmental and human health. Because of their bioaccumulation capacities (Law et al., 2003; Voorspoels et al., 2003; Okumura et al., 2004), PCDD/Fs, PCBs and PBDEs reach very high levels in consumers, including humans. Dietary intake, especially the consumption of marine organisms, is considered to be the main way of human exposure to these compounds (Pompa et al., 2003; Domingo, 2004). The consumers, and thus the food agencies, are particularly concerned about the potential health effects associated with contaminated food. In order to minimize the risk associated with seafood consumption, regulations have been implemented to keep human exposure to contaminants within safe limits. Very recently, the European Commission has set new limits for foodstuff contamination by PCDD/Fs and DL-PCBs (dioxin-like PCBs) (Commission Regulation EC, 2006). In fish and fishery products, the maximum concentrations for dioxins were maintained at 4 pg WHO-PCDD/Fs-TEQ per gram of wet weight (3 pg g^{-1} w.w. for the action limit), whereas the limits for PCDD/Fs and DL-PCBs has been established at 8 pg WHO-PCDD/Fs-PCBs-TEQ per gram (w.w.).

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Decapod crustaceans like the spider crab (*Maja brachydactyla*), edible crab (*Cancer pagurus*), velvet swimming crab (*Necora puber*) and Norway lobster (*Nephrops norvegicus*) are macrobenthic, opportunistic feeders living in coastal water. Because of their relatively high trophic level, crustaceans tend to accumulate large amounts of lipophilic contaminants (Jimenez et al., 1998; Voorspoels et al., 2004). Crustaceans are a greatly appreciated food source in France, and their consumption represents about 10–15% of total fresh seafood consumption (OFIMER, 2003). Nevertheless, very little information is available on the levels of contamination in these edible species from the French coasts.

The main objectives of this study were first to obtain data on the concentrations of PCBs, PCDD/Fs and PBDEs in large crustaceans from the French coasts and to evaluate the potential sanitary risk for human consumption. The second objective was to compare contaminant fingerprints in crustaceans to those in mussel and sea bass tissues to assess their capacity of metabolisation. Sea bass are top predators that feed on supra-benthic species such as crustaceans (shrimps and mysidaceans) and small fish (e.g. gobies) (Loizeau et al., 2001), and they are able to metabolise organic contaminants (Opperhuizen and Sijm, 1990; Goerke and Weber, 2001; Stapleton et al., 2004a,b). Oppositely, mussels were selected as good bioindicators of aquatic contamination because of their ability to accumulate contaminants from detritic suspended particles and from phytoplankton and because of their limited capacities to biotransform them (Claisse, 1989). Moreover, mussels contribute to the crustacean diet, except *N. norvegicus*.

2. Experimental section

2.1. Sampling

Five stations were selected along the French coasts (Fig. 1) based on the crustacean fishing activity and the levels of contamination (Abarnou et al., 2002; Bodin et al., 2007). Antifer (station 1) is located near an oil terminal in the Seine Bay and is exposed to large contaminant discharges from the Seine River. The Seine watershed area (78,600 km^2) shelters approximately 18 million inhabitants and encompasses 40% of the French industrial activity as well as significant agricultural activity (Tessier, 2003). Granville (station 2) on the western side of the Cotentin Peninsula (Basse-Normandie), Roscoff (station 3) in Northern Brittany and Le Guilvinec (station 5) in Southern Brittany are mainly characterised by agricultural activities and summer tourism. Lastly, Le Conquet (Iroise Sea, station 4) is situated in Western Brittany where the coastal zone may be exposed to water exchanges flowing out the Rade of Brest, an urban area with about 250,000 inhabitants, a large naval base and various industrial activities.

Crustaceans were obtained from these areas on the basis of their availability; mussels and sea bass were only collected at Antifer and Le Conquet. To reduce the variability of the contamination data, the sampling exclusively focused on similarly sized individuals (higher than the minimum landing size for each edible species) (Table 1). Moreover, only male crustaceans and fish were kept for this study.

Crustacean muscle was carefully dissected from the inner body and pooled samples were made from three to six individual specimens for edible and spider crabs, 10 for velvet swimming crabs, and 20 for Norway lobsters. Sea bass samples were performed from the carefully filleted muscle tissue of 10 fishes. Mussels were soaked overnight in clean aerated seawater to eliminate solid particles from their gut and then were dissected and pooled together (35–40 individuals per sample). All samples were stored at −20 °C, and then freeze-dried and ground into a fine homogeneous powder. The water content (%) of the samples was obtained from their weights before and after freeze-drying (Table 1).

2.2. Chemical analysis

Eighteen individual PCB congeners were analysed, including the set of the seven indicators (M-PCBs) cur-

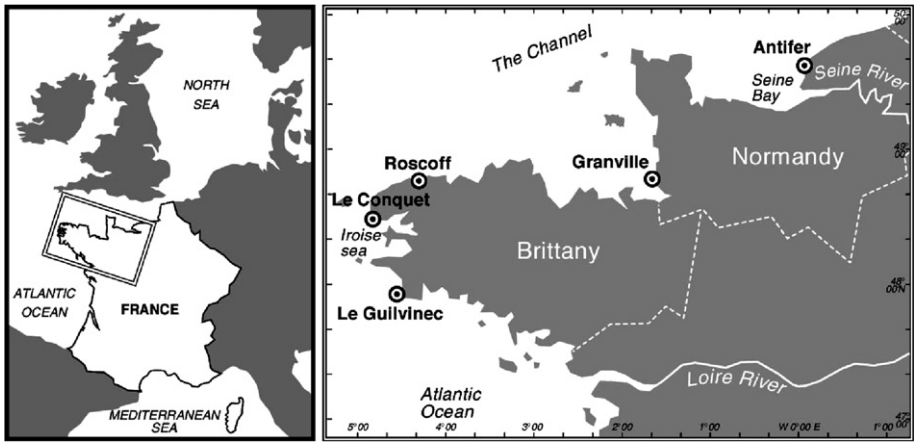

Fig. 1. Map of the sampling areas.

Table 1
Biological characteristics of the samples

Station	Species name	Common name	Abbreviation	*N*	Body weight (g)	Body size (cm)	Muscle fat content (% of d.w.)	Muscle water content (%)
Antifer	*Maja brachydactyla*	Spider crab	Maj 1	4	535 ± 205	11.5 ± 1.8	1.9	80
	Cancer pagurus	Edible crab	Canc 1	3	463 ± 284	13.8 ± 2.4	2.6	77
	Necora puber	Velvet swimming crab	Nec 1	10	84 ± 3	6.3 ± 0.6	2.5	77
	Mytilus edulis	Mussel	Myt 1	35	–	5.3 ± 0.4	8.9	82
	Dicentrarchus labrax	Sea bass	Dicen 1	10	608 ± 108	35 ± 2.1	5.3	75
Granville	*Maja brachydactyla*	Spider crab	Maj 2	3	1177 ± 185	15 ± 1.0	2.0	82
	Cancer pagurus	Edible crab	Canc 2	3	543 ± 31	14.9 ± 0.5	2.2	79
Roscoff	*Maja brachydactyla*	Spider crab	Maj 3	3	1090 ± 135	14.3 ± 0.6	2.3	78
Le Conquet	*Maja brachydactyla*	Spider crab	Maj 4	6	1642 ± 423	17.1 ± 1.5	2.3	78
	Cancer pagurus	Edible crab	Canc 4	5	921 ± 129	17 ± 0.9	1.9	78
	Mytilus edulis	Mussel	Myt 4	40	–	5.7 ± 0.3	5.8	85
	Dicentrarchus labrax	Sea bass	Dicen 4	10	678 ± 95	39 ± 1.2	4.6	76
Le Guilvinec	*Maja brachydactyla*	Spider crab	Maj 5	3	618 ± 109	12.8 ± 0.4	2.0	78
	Cancer pagurus	Edible crab	Canc 5	3	1001 ± 158	17.3 ± 0.3	1.3	78
	Nephrops norvegicus	Norway lobster	Nep 5	20	20 ± 7	3.0 ± 0.3	2.2	77

rently measured in pollution monitoring programs (PCBs 28, 52, 101, 118, 138, 153 and 180) and the 12 DL-PCBs (PCBs 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189). The concentrations of each of the seventeen 2378-substituted congeners of dioxins and furans were determined. The 2378-TCDD Toxicity Equivalent Quantity was estimated using the corresponding WHO-TEF factors of 2378 PCDD/Fs and DL-PCBs (Van den Berg et al., 1998). Finally, 13 PBDE congeners were analysed (PBDEs 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183 and 190).

All analyses were performed following the isotope dilution method (US EPA Method 1613, 1994). After addition of known amounts of a standard solution of 16 $^{13}C_{12}$-PCDD/Fs, 18 $^{13}C_{12}$-PCBs and 9 $^{13}C_{12}$-PBDEs, the samples were extracted with a solvent mixture of toluene-cyclohexane (50:50) for 12 h in a Soxhlet apparatus. The extracts were evaporated to dryness and weighed to obtain the extractible material used to estimate the lipid content (Table 1). The fatty co-extracted material was removed by sulphonation with sulphuric acid. For that purpose, the extract was taken up in 50 mL of hexane into a separatory funnel and partitioned 3 times against 50 mL of sulphuric acid, followed by once against deionised water. The aqueous layers were discarded and the extract was poured through a drying column of anhydrous sodium sulphate. A second purification step was performed on a multi-layer adsorption chromatography column successively packed from bottom to top with 1 g silica gel, 2 g basic silica gel, 1 g silica gel, 4 g acidic silica gel and 1 g silica gel. The column was pre-eluted with 30 mL of hexane, and the stopcock was closed when hexane reached the silica gel layer. The concentrated extract was then added to the column and PCDD/Fs, PCBs and PBDEs were eluted with hexane. The separation of PCBs, PBDEs and PCDD/Fs was performed on a Florisil column (60–100 mesh, activated at 600 °C for a minimum of 18 h, deactivated with 3% of water) (Malisch et al., 2000). The 6 g Florisil column was pre-eluted with 50 mL of heptane. The stopcock was closed when the heptane reached the Florisil layer and the concentrated extract was added. The co-extracted PCBs and PBDEs were eluted with 60 mL of heptane and PCDD/Fs were eluted with 60 mL of toluene. The first fraction (PBDEs and PCBs) was then fractionated on a Carbopack B column (mix of 2 g Carbopack B + 2 g Celite). PCBs were separated into three fractions of first di-ortho PCBs (elution with hexane), then mono-ortho PCBs (elution with hexane/toluene) and finally non-ortho PCBs. PBDEs were eluted in the two first fractions. After concentration and addition of syringe standards (3 $^{13}C_{12}$-PCBs and 2 $^{13}C_{12}$-PBDEs) to the respective fractions, PCBs and PBDEs were analysed by HRGC/HRMS (WATERS Autospec set at a resolution of 10,000; split/splitless injection of 1 or 1.5 μL, DB-5 column and/or HT8-PCB column from SGE). The PCDD/F fraction was concentrated to a final volume of 25 μL after addition of $^{13}C_{12}$-1234-TCDD and $^{13}C_{12}$-123789-HxCDD, and determination was performed by HRGC/HRMS (WATERS Autospec set at a

resolution of 10,000; split/splitless injection of 1.5 μL, DB-5MS column).

2.3. Quality control

All the performance criteria required for the analysis of dioxins were met (US EPA Method 1613, 1994). Analyte recovery ranged from 80% to 110%, except for OCDD and OCDF which were higher than 40%. The linearity was systematically checked and the response factors were estimated by running four standard solutions before any real sample series. The detection limits of the method ranged from 1 to 20 pg g^{-1} lipids for DL-PCBs, PCDD/Fs and PBDEs, and 1 pg g^{-1} lipids for M-PCBs. Several procedural blanks were analysed with the samples, showing very few or no interfering compounds. The accuracy of the protocol was assessed by analysing dioxins in a milk powder certified reference material (BCR-CRM607). The laboratory is accredited for the analysis of trace contaminants in food and feedstuff and has satisfactorily participated in several recent inter-laboratory comparison exercises on dioxins, DL-PCBs and PBDEs in food (2004 5th round and the 2005 study, Norwegian Institute of Public Health).

3. Results and discussion

3.1. Contamination levels in crustaceans

The concentrations of PCBs, PCDD/Fs and PBDEs are given in Tables 2 and 3; all data are reported on a dry weight (d.w.) basis.

Crustaceans from Antifer were the most contaminated which confirmed the chronic pollution of the Seine Bay mainly due to contaminant inputs by the Seine River (Abarnou et al., 2002; Johansson et al., 2004). For instance, the $\sum_{18}$PCB concentrations in *M. brachydactyla* (Maj 1) reached 30 ng g^{-1} d.w., respectively 6-, 12-, 15- and 20-fold higher than those measured in spider crabs from Le Conquet (Maj 4), Le Guilvinec (Maj 5), Roscoff (Maj 3), and Granville (Maj 2). Le Conquet was slightly more contaminated than the other sites of Brittany and Basse-Normandie, most likely due to the influence of the Rade of Brest discharges (Marchand et al., 1983). Moreover, although Le Guilvinec is characterised by a low industrial activity like Granville and Roscoff, the PCB concentrations measured in Maj 5 were slightly higher than those in Maj 2 and Maj 3. Different studies have pointed out an influence of the plume of the River Loire panache until the Western Brittany coasts (Lazure and Jegou, 1998), and high PCB levels have already been reported in the biota from the Loire Estuary (Abarnou et al., 2002). Moreover, the sampled area at Le Guilvinec is characterised by muddy clay bottoms, which may promote the trapping of contaminants in superficial sediments and further their availability for benthic organisms. These differences in PCB contamination levels in spider crab muscle correlate well with those observed in spider crab hepatopancreas from the same areas (Bodin et al., 2007). Similar geographical variations of PCDD/F and PBDE concentrations were observed; however the differences between Antifer and the other sites were less than for PCBs. For instance, Maj 1 were only 1.5–5 times more contaminated than specimens from Brittany and Basse-Normandie.

At Antifer, the highest levels of organohalogenated contaminants were recorded in velvet swimming crabs compared to spider and edible crabs. At Le Guilvinec, the most contaminated species was the Norway lobster. Since samples consisted of only male crustaceans of homogeneous size collected at the same period of the year in the same area, the slight differences of contaminant concentrations between species are probably due to the influence of other biological factors like diet, moulting, migratory behaviour, and metabolisation capacity.

By far, food is the major route of organic contaminant accumulation in organisms, and its contribution to biota contamination increases with trophic level. Decapod crustaceans have an omnivorous diet, consuming preferentially molluscs, small crustaceans and polychaetes (Bernárdez et al., 2000), but also algae, echinoderms and fish carcasses. Moreover, velvet swimming crabs, Norway lobsters and male edible crabs are non-migratory, unlike spider crabs which spend winter in deep bottoms (40–100 m), and migrate to shallow waters in summer for reproduction. *N. puber* and male specimens of *C. pagurus* are found all year long on intertidal rocky substrata in shallow waters, whereas *N. norvegicus* lives in burrows constructed in deeper superficial muddy sediment (90–120 m). Finally, moulting which contributes to the elimination of contaminants (Raessler et al., 2005) differs among crustacean species. Thus, the particular behaviours of the various crustacean species can bring out differences on the bioavailability, uptake and elimination of organohalogenated contaminants.

The maximum total TEQ values were recorded in crustacean muscle collected at Antifer, especially in velvet swimming crabs. Overall, the TEQ values of Antifer were 5–20-fold higher than those in species from the other sites. Moreover, the contribution of PCBs to the total TEQ decreased from 70% in crustaceans from Antifer to less than 55% at Granville, Roscoff, Le Conquet and Le Guilvinec. All TEQ values measured in crustacean muscles were under the maximum limits of 4 pg WHO-PCDD/Fs-TEQ g^{-1} w.w. and 8 pg WHO-PCDD/Fs-PCBs-TEQ g^{-1} w.w. set by the European Community for seafood intended for human consumption (Commission Regulation EC, 2006). Based on the Tolerable Monthly Intake set for 2378-PCDD/Fs and DL-PCBs (70 pg TEQ kg^{-1} b.w. per month; JECFA, 2002), and for the seven indicator PCBs (0.01 μg kg^{-1} b.w. per day; AFSSA, 2003), the maximum amount of crustacean flesh that can be eaten by an average adult (60 kg) before reaching the safety limits was estimated at 1–4 kg for specimen from Antifer, assuming average monthly consumption (i.e. around 40–150 g per day). This maximum amount was one order of magnitude higher

Table 2
PCB and 2378-PCDD/F concentrations (pg g^{-1} d.w.), and TEQ values (pg g^{-1} d.w.) in crustaceans, mussels and sea bass from French coastal sites

	Antifer					Granville		Roscoff	Le Conquet				Le Guilvinec		
	Maj 1	Canc 1	Nec 1	Myt 1	Dicen 1	Maj 2	Canc 2	Maj 3	Maj 4	Canc 4	Myt 4	Dicen 4	Maj 5	Canc 5	Nep5
CB28	235	211	844	2429	3505	48	66	51	91	44	122	230	91	16	59
CB52	71	129	63	20,456	30,176	41	44	24	114	20	280	1383	39	15	75
CB77	175	86	359	1326	695	12	19	12	27	17	28	50	21	7	13
CB81	2.8	1.7	4.5	27.3	22.6	0.4	0.6	0.4	0.6	0.7	1.3	2.3	0.6	0.2	0.4
CB101	396	433	177	80,534	108,669	55	138	33	254	94	880	5983	74	50	159
CB105	1173	511	3073	11,532	17,099	62	92	74	181	126	438	2543	112	40	133
CB114	41	16	96	400	824	2.8	2.9	3.0	6.9	6,7	10.6	102.7	3.8	1.6	3.7
CB118	6264	2760	16,494	58,597	92,037	289	349	277	967	579	1145	7810	389	143	496
CB123	41	26	107	504	909	1.2	2.1	2.1	6.0	6.6	7.9	102.2	4.2	0.8	3.5
CB126	34	20	52	252	251	3.2	4.9	3.2	4.5	4.1	10.5	41.4	3.7	2.1	4.8
CB138	1840	2748	12,513	123,984	116,597	135	491	159	401	657	2567	13,231	328	240	998
CB153	13,946	7621	26,810	213,266	251,209	622	971	677	1903	1586	4339	26,000	1020	459	1976
CB156	736	249	1822	3771	6976	27	33	45	140	71	152	1245	50	13	73
CB157	199	96	498	1616	2444	11	14	14	34	20	46	323	18	7	25
CB167	493	254	1189	5046	6818	25	35	30	86	55	122	735	39	16	64
CB169	3.7	1.9	5.9	21.4	13.8	0.5	0.8	0.6	0.6	0.4	1.7	3.0	0.5	0.3	1.0
CB180	3487	2012	6833	14,686	45,956	180	248	285	583	398	304	7231	295	121	541
CB189	73	37	197	466	869	3.7	4.9	6.0	15.1	5.8	14.8	129.7	6.2	2.1	11.2
$\sum_7$PCBs	26,239	15,914	63,734	513,952	648,149	1369	2306	1505	4313	3378	9638	61,867	2236	1045	4303
$\sum_8$PCBs	29,138	17,176	70,942	538,448	684,203	1514	2511	1689	4798	3686	10,456	67,015	2489	1134	4625
TEQ DL-PCBs	4.71	2.51	8.54	35.55	41.62	0.39	0.57	0.39	0.67	0.54	1.34	6.08	0.42	0.25	0.47
2378D	0.06	0.03	0.18	0.47	nd	0.01	0.02	0.02	0.02	0.01	0.05	0.03	0.02	0.02	0.03
12378D	0.37	0.30	0.45	0.76	0.18	0.10	0.19	0.11	0.13	0.07	0.21	0.07	0.16	0.10	0.21
123478D	0.13	0.09	0.23	0.40	nd	0.03	0.07	0.04	0.06	0.05	0.11	0.01	0.07	0.03	0.11
123678D	0.26	0.30	0.83	1.73	0.44	0.09	0.49	0.11	0.15	0.11	0.31	0.04	0.19	0.11	0.39
123789D	0.13	0.16	0.30	0.68	1.05	0.04	0.15	0.05	0.09	0.05	0.20	0.01	0.10	0.04	0.15
1234678D	0.42	0.43	1.49	10.29	0.73	0.22	0.58	0.17	0.37	0.31	2.17	0.08	0.45	0.20	0.86
OCDD	1.90	3.40	3.79	56.03	1.01	1.32	2.05	1.01	3.33	1.55	6.42	0.30	1.24	0.68	1.84
2378F	6.82	4.88	17.44	37.45	5.62	0.65	1.50	0.70	2.00	1.28	2.72	0.83	0.80	0.49	0.57
12378F	0.03	0.27	1.40	1.72	0.34	nd	0.20	0.01	0.01	0.15	0.37	0.11	0.11	0.05	0.25
2347SF	1.77	1.38	4.11	8.26	2.19	0.19	0.51	0.30	0.58	0.45	0.87	0.36	0.37	0.13	0.52
123478F	0.13	0.11	0.55	0.78	0.21	0.02	0.08	0.03	0.07	0.08	0.12	0.03	0.10	0.01	0.16
123678F	0.02	0.05	0.28	0.41	0.21	nd	0.06	nd	nd	0.05	0.15	0.03	0.06	0.02	0.09
234678F	0.16	0.11	0.36	0.73	0.10	0.02	0.10	0.05	0.07	0.06	0.17	0.02	0.09	0.02	0.11
123789F	nd	nd	0.01	0.02	nd	nd	nd	nd	nd	nd	0.00	0.00	nd	nd	nd
1234678F	0.21	0.09	0.47	1.15	0.48	0.09	0.23	0.05	0.09	0.10	0.45	0.05	0.18	0.06	0.15
1234789F	0.02	0.05	0.04	0.13	nd	nd	nd	nd	nd	nd	0.03	0.01	0.01	0.01	0.01
OCDF	0.45	0.05	0.49	1.46	0.34	0.24	0.47	0.13	0.03	0.24	0.31	0.05	0.10	0.16	0.12
$\sum$2378-PCDD/Fs	12.9	11.7	32.4	122.5	12.9	3.0	6.7	2.8	7.0	4.5	14.7	2.0	4.1	2.1	5.6
TEQ PCDD/Fs	2.08	1.61	4.77	9.78	2.06	0.30	0.72	0.38	0.69	0.48	1.12	0.38	0.52	0.25	0.68
Total TEQ	6.79	4.12	13.32	45.33	43.68	0.68	1.29	0.77	1.36	1.02	2.45	6.46	0.94	0.50	1.15

Table 3
PBDE concentrations (pg g^{-1} d.w.) in crustaceans, mussels and sea bass from French coastal sites

	Antifer					Granville		Roscoff	Le Conquet			Le Guilvinec		
	Maj 1	Canc 1	Nec 1	Myt 1	Dicen 1	Maj 2	Canc 2	Maj 3	Maj 4	Canc 4	Myt 4	Dicen 4	Maj 5	Canc 5	Nep 5
BDE-17	0.3	2.4	0.4	7.2	26.1	0.2	0.7	0.2	0.2	0.2	0.8	1.4	1.8	0.1	0.2
BDE-28	8.1	7.6	12.8	14.1	300.1	2.5	2.6	1.8	4.3	1.1	4.5	39.9	8.2	0.9	6.7
BDE-47	96.5	83.2	106.3	224.9	8736.1	29.1	55.4	21.8	41.9	18.9	154.2	1189.5	70.7	16.8	108.9
BDE-66	0.3	0.3	0.2	0.2	1.0	0.2	0.3	0.3	0.1	0.1	0.1	0.1	0.0	0.1	0.3
BDE-71	3.8	1.6	2.7	8.0	23.2	0.8	1.0	1.0	1.9	0.1	7.4	3.1	1.0	0.3	0.2
BDE-85	1.1	0.4	2.2	3.6	13.9	0.1	0.4	0.5	0.3	0.1	2.5	8.2	0.6	0.1	0.9
BDE-99	17.6	31.5	21.3	77.9	59.4	11.3	23.1	7.4	5.8	9.2	84.4	13.6	25.5	8.2	38.6
BDE-100	9.1	16.4	18.7	38.2	1377.2	4.4	9.6	2.7	5.3	3.7	39.2	234.7	9.0	3.2	13.7
BDE-138	1.6	0.9	0.2	0.5	1.3	0.2	0.2	0.2	0.2	0.2	1.5	0.1	nd	0.1	1.0
BDE-153	69	3.9	3.0	4.2	42.8	0.8	3.5	0.5	0.6	1.8	7.8	4.4	nd	1.4	1.1
BDE-154	4.2	4.4	3.7	2.3	418.1	0.6	2.6	0.9	0.7	1.1	13.9	33.8	nd	1.1	0.9
BDE-183	7.2	1.3	3.7	2.8	3.8	1.2	4.1	1.1	1.3	1.5	4.5	0.8	3.5	0.8	7.8
BDE-190	6.7	2.1	0.5	1.0	1.1	0.4	1.5	0.2	0.2	0.2	0.1	0.1	0.2	0.3	0.7
$\sum_{13}$PBDEs	164	156	176	385	11,004	52	105	39	63	38	321	1530	121	33	181

(12–30 kg per month) for crustaceans from Brittany and Basse-Normandie.

Although no data were found in the literature on the contamination of the same studied crustaceans, Table 4 highlights the PCB, 2378-PCDD/F and PBDE concentrations reported in various similar organisms. As far as PCBs are concerned, the concentrations measured in crustaceans from the Seine Bay are among the highest ever reported. This result is in agreement with high contamination levels found in biota of the Seine Estuary, which is considered to be one of the most PCB contaminated estuaries in Europe (Abarnou et al., 2000). In contrast, the PCDD/F and PBDE contamination in decapod crustaceans from the French coastal waters of Brittany and Normandy were low compared to measurements in similar organisms worldwide (Table 4).

3.2. Contaminant distribution in crustaceans

3.2.1. Polychlorinated biphenyls

PCB patterns observed in crustacean muscles were very similar regardless of the origin and levels of the contamination (Fig. 2a). Among PCB congeners, the main compounds were CB153, CB118, CB180 and CB138. Together they accounted for 80–90% of the $\sum_{18}$PCBs. Among theses congeners, CB153 was the most common contributing 40–50% to $\sum_{18}$PCBs. Due to their high octanol–water coefficients and their structure (substitution positions), these major PCB congeners are accumulated by marine organisms, without being metabolised, and thus are biomagnified along food webs (Bright et al., 1995; Kannan et al., 1995). Similar PCB profiles were observed in the spider crab hepatopancreas (Bodin et al., 2007), as well as in the flying crab *Lyocarcinus holsatus* (Voorspoels et al., 2004), and the shrimp *Crangon crangon* (Kannan et al., 1995; Voorspoels et al., 2004). However, the contribution of the congeners CB118 and CB138 to the $\sum_{18}$PCBs appeared to differ slightly among the four examined crustaceans. In spider crabs, CB138 represented only 5–15% of the sum of PCBs, whereas its contribution reached 15–20% in edible crabs, velvet swimming crabs and Norway lobsters. The CB138, which is highly hydrophobic and very abundant in formerly used technical mixtures, is associated with suspended particles and characterises the river influence (Marchand et al., 2000). The higher contribution of this congener in male adult specimens of *N. norvegicus*, *N. puber* and *C. pagurus* reflected their sedentary behaviour (Latrouite and Le Foll, 1989) and suggested that they are more representative of the area PCB contamination than the adult male spider crabs.

The dioxin-like PCBs were found at a much lower levels in crustacean muscle: based on their concentrations, they represented altogether 20–35% of the $\sum_{18}$PCBs. The DL-PCBs also showed a similar pattern in crustaceans whatever the geographical origin and the species. The predominant DL-PCB congeners were CB118, CB105 and

Table 4
Data from literature on crustacean contamination by PCBs, PCDD/Fs and PBDEs

Species	Tissues	Location	Contaminants	Levels	References
Brown shrimp (*Crangon* sp.)	Whole body	Sendai Bay (Japan)	DL-PCBs (pg g^{-1} w.w.) DL-PCB TEQ (pg g^{-1} w.w.)	308 0.4	Okumura et al. (2004)
Flying crab (*Licarcinus holsatus*)	Whole body	Scheldt Estuary (Europe)	CB153 (ng g^{-1} w.w.)	5.4–68	Voorspoels et al. (2004)
Estuarine crab (*Chasmagnathus granulata*)	Muscle	Argentina	CB153(ng g^{-1} lipid)	40–52	Menone et al. (2000)
Brown shrimp (*Crangon crangon*)	Whole body	Southern Baltic Sea		80	Kannan et al. (1995)
Brown shrimp (*Crangon crangon*)	Whole body	Sendai Bay (Japan)	2378-PCDD/Fs (pg g^{-1} w.w.) 2378-PCDD/F TEQ (pg g^{-1} w.w.)	6.6 1.1	Okumura et al. (2004)
Edible crab (*Cancer pagurus*)	Muscle	Grenland fjords (Norway)		3.5	Knutzen et al. (2003)
		Southern Norway	2378-PCDD/F (pg g^{-1} w.w.)	15–34	Oehme et al. (1990)
Brown shrimp (*Crangon crangon*)	Whole body	North Sea	2378-PCDD/F TEQ (pg g^{-1} w.w.)	0.66–1.1	Karl et al. (2002)
Shrimp (*Pandalus borealis*)	Whole body	Norway Greenland		0.25 0.12	Karl et al. (2002)
Rock crab (*Charybdis japonjca*)	Muscle	Tokyo Bay (Japan)	2378-PCDD/Fs(pg g^{-1} w.w.) 2378-PCDD/F TEQ (pg g^{-1} w.w.)	12 2.6	Sakurai et al. (2000)
Green crab (*Carcinus aestnarii*)	Whole body	Venice/Orbettello Lagoons (Italy)	2378-PCDD/Fs (pg g^{-1} w.w.) 2378-PCDD/F TEQ (pg g^{-1} w.w.)	9–152 1.1–5.2	Jimenez et al. (1998)
Lobster (*Hommarus americans*)	muscle	Casco Bay (USA)		0.8	Wade et al. (1997)
Dungeness Crab (*Cancer magister*)	muscle	British Columbia (Canada)		<8	Hagen et al. (1997)
Snow Crab (*Chianoecetes opilio*)	Whole body	St Lawrence Estuary (Canada)	2378-PCDD/Fs (pg g^{-1} w.w.)	50–70 31–61	Brochu et al. (1995)
Blue crab (*Callinectes sapidus*)	muscle	Netwark/Raritan Bay (New Jersey)	2378-PCDD/Fs (ng g^{-1} w.w.)	55–60	Cai et al. (1994)
Brown shrimp (*Crangon crangon*)	Whole body	Scheldt Estuary (Europe)	PBDEs[a] (ng g^{-1} w.w.)	0.2–8.3 0.02–0.08	Voorspoels et al. (2003)
Flying crab (*Liocarcinus holsatus*)	Whole body	Scheldt Estuary (Europe) Belgian North Sea (Europe)		1.2–30 0.4–1.4	Voorspoels et al. (2003)
Shrimp (*Pandalus borealis*)	Muscle	St Lawrence Estuary (Canada)	BDE47 (ng g^{-1} w.w.)	0.17	Law et al. (2003)
Shrimp	Whole body	North Sea (Europe)	BDE47 (ng g^{-1} lipid)	35–39	Boon et al. (2002)
Hermit crab (*Pagurus bernhardus*)	Abdomen			8–118	

[a] Sum of 6 PBDE congeners: 28, 47, 99, 100, 153, 154 (in ng g^{-1} w.w.).

CB156, which together contributed 60–70%, 15–20% and 5–10% to the sum of the DL-PCBs.

As far as potential toxicity is concerned, the non-ortho PCBs made up about 70–90% of the DL-PCB TEQ, much more than the mono-ortho congeners. With regards to the non-ortho PCBs, CB126 was the prevalent congener, accounting for more than 95% of the whole contribution of these congeners to the TEQ, whereas CB118, CB156 and CB105 were the predominant mono-ortho PCBs (85–90% of the mono-ortho PCB contribution to DL-PCB TEQ).

3.2.2. 2378-Polychlorinated dibenzo-p-dioxins and dibenzofurans

The PCDD/F distribution in crustaceans was characterised by very few congeners, namely OCDD, 2378-TCDF and 23478-PeCDF, which together account on average for approximately 60–85% of the 17 toxic compounds (Fig. 2b). Except for 1234678-HpCDD which characterised samples with low contamination levels, the other congeners were not significantly present in our samples. For instance, 2378-TCDD, the reference compound of the dioxin group, is a very minor component with a contribution of less than 1% to the total 2378-PCDD/Fs.

Two typical patterns were observed depending upon the sample origin: the ''Antifer pattern'' and a ''general pattern''. The first fingerprint characterised crustaceans from Antifer, irrespective of the species. In these more contaminated samples, the major components were 2378-TCDF (40–55% of the $\sum$2378-PCDD/Fs), OCDD (10–30%) and 23478-PeCDF (10–15%). The second PCCD/F pattern was observed in Basse-Normandie and Brittany and could reflect the distribution in crustaceans from areas not directly exposed to contaminant inputs. This distribution was mainly characterised by the prevalence of OCDD (30–40% of the $\sum$2378-PCDD/Fs), 2378-TCDF (15–

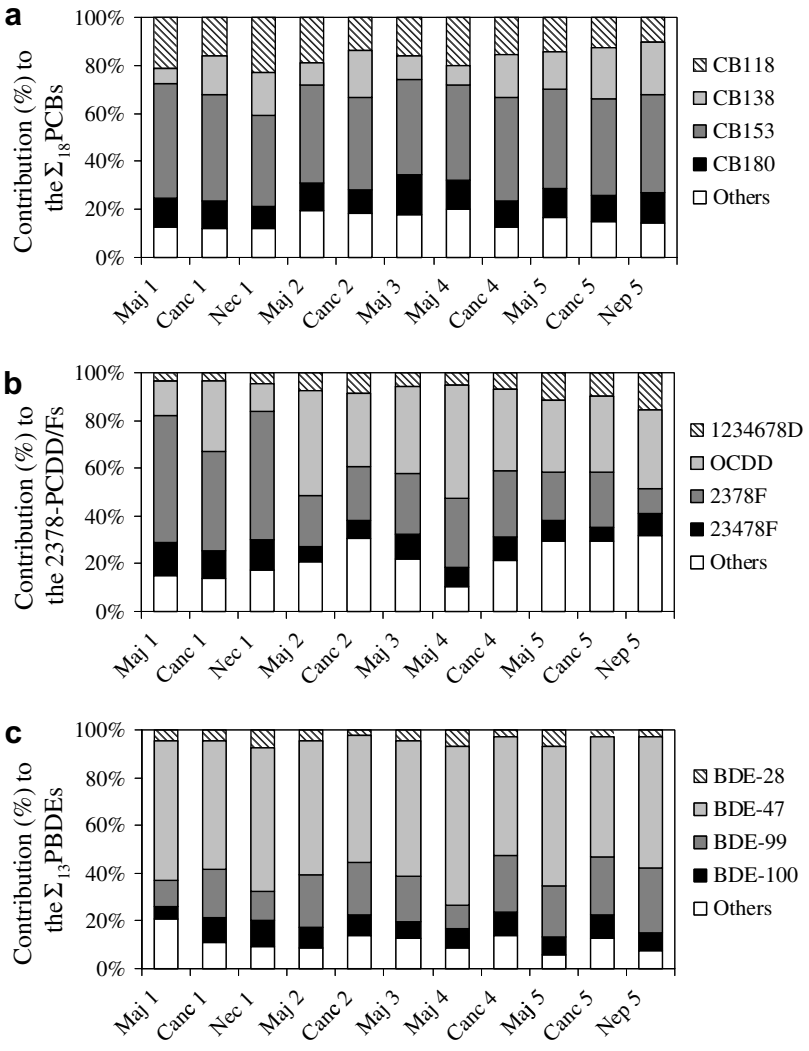

Fig. 2. PCB (a), PCDD/F (b) and PBDE (c) patterns in crustaceans from Antifer (Maj 1, Canc 1, Nec 1), Granville (Maj 2, Canc 2), Roscoff (Maj 3), Le Conquet (Maj 4, Canc 4) and Le Guilvinec (Maj 5, Canc 5, Nep 5).

25%), 23478-PeCDF (5–10%) and 1234678-HpCDD. In crustaceans from Brittany and Basse-Normandie, the 2378-PCDDs were predominant (55–70% of the total 2378-PCDD/Fs), whereas they only made up 20–40% in samples from Antifer. The congener patterns found in these crustaceans were quite similar to that found in the green crab from the Venice Lagoon (Jimenez et al., 1998) and, in the blue crab and the lobster from Newark Bay and the New York Bight (Rappe et al., 1991). The interpretation of the dioxin fingerprint in crustaceans from this study is very difficult because of the very low levels encountered and because of the various potential sources of contamination. However, it is known that the OCDD isomer is present in high proportions in sewage sludge (Baker and Hites, 2000) and is produced in combustion by-products of fuel oil mixtures (Hellou and Payne, 1993). With regards to 2378-TCDF and 23478-PeCDF, they principally come from technical PCBs and combustion processes (Wakimoto et al., 1988; Baker and Hites, 2000). The prevalence of these compounds in samples from Antifer could indicate that urban waste incineration is a potential source of contamination. Moreover, this pattern could result from the long time exposure of the Seine Bay to commercial PCB mixtures. Associated with suspended matter carried by the Seine River discharges, PCBs as well as co-produced tetra- and penta-chlorinated dibenzofurans can settle onto the superficial sediment and become a secondary source of contamination for benthic species and their predators.

With regard to the contribution of each congener to the PCDD/F TEQ, a similar pattern was observed whatever the area and the crustacean species. The main compounds were the 23478-PeCDF, 2378-TCDF and 12378-PeCDD, these three congeners contributing 80–95% to the PCDD/F TEQ. Similar observations were made in edible crab from Norway (Knutzen et al., 2003).

3.2.3. Polybrominated diphenyl ethers

Among PBDEs, a very similar pattern was observed in crustaceans from the five sampling sites (Fig. 2c), with the major compounds BDE47, BDE99, BDE100 and

BDE28 making up 85–95% of the $\sum_{13}$PBDEs. Other authors also reported quite similar PBDE fingerprints in *Pandalus borealis* (Law et al., 2003) and *C. crangon* (Boon et al., 2002; Voorspoels et al., 2003). However, the contribution of each congener to the $\sum_{13}$PBDEs was slightly different depending on the species. In edible crabs from our study, BDE47 represented only 40% of the $\sum_{13}$PBDEs, contrary to the other species where it accounted for 60%. Moreover, in spider crabs and velvet swimming crabs, the contribution of BDE99 to the $\sum_{13}$PBDEs appeared to be lower than in edible crab and Norway lobster muscle (10–15% and 20–25%, respectively).

These observations on the contaminant distribution in crustaceans highlight differences between the contaminant families. PCB and PBDE congeners varied more or less together, and the global fingerprint remained more or less unchanged regardless of the geographical situation and the contamination levels. In contrast, PCDD/Fs which originate as unwanted by-products of a large variety of processes were distributed differently in crustaceans. This variation is probably related to the contamination levels and thus the proximity of emission sources.

3.3. Comparison of crustacean, mussel and sea bass contamination

3.3.1. Polychlorinated biphenyls

The PCB contamination levels were higher in sea bass than in mussel and spider crab tissues for the two areas sampled (Table 2). PCB concentrations in sea bass muscle from Antifer were similar to those measured in the sea bass from the Seine Estuary (Loizeau et al., 2001). With regard to mussel contamination, PCB levels measured at Antifer and Le Conquet were in agreement with those reported within the monitoring program RNO (Claisse, 1989). At both sites, DL-PCBs represented approximately 15% of the $\sum_{18}$PCB congeners in mussels and sea bass, whereas they contributed 30% in the spider crabs. With regards to TEQ values, the contribution of non-ortho PCBs to the DL-PCB TEQ was equal to 60–80% in the three species.

The main PCBs found in the analysed edible organisms were CB153, CB101, CB118, CB138, and CB180, but they were distributed differently among the three species (Fig. 3a). In sea bass, the predominant congeners were present in the following decreasing order: CB153 (40% of $\sum_{18}$PCBs) > CB138 (15–20%) > CB118 (10–15%) > CB101 (10–15%) > CB180 (5–10%), which agrees with previously observed patterns in various fishes (Loizeau et al., 2001; Munschy et al., 2004). Similar fingerprints were observed in mussels collected either at Antifer and or at Le Conquet, except for the congener CB180. As described above, the main compounds found in spider crab muscle were: CB153 (40–50% of $\sum_{18}$PCBs) > CB118 (20%) > CB180 (12%) > CB138 (5–10%) > CB101 (2–5%). With regards to DL-PCB congeners, a similar fingerprint was observed across all areas and species, except for CB77 which accounted for only 0.5% of the sum of DL-PCBs in sea bass and 1.5–1.9% in mussels and spider crabs. The slight differences of PCB pattern between mussel, spider crab and sea bass are potentially influenced by differences in diet, behaviour and trophic level, but most likely depend on elimination and specific metabolisation capacities. The P-450 gene superfamily occurs in a very large number of living organisms where it plays a fundamental role in the oxidative biotransformation of endogenous and xenobiotic compounds. Different authors have pointed out the presence of cytochrome P-450 2B in crustacean tissues (Brown and John, 1992; Goerke and Weber, 2001), and cytochrome P-450 1A in fishes (Brown and John, 1992; Van der Oost et al., 2003). CYP2B acts on the metabolisation of meta- and para-unsubstituted congeners, like CB52 and CB101 which are present in much lower proportions in crustacean compared to mussel and sea bass. Only ortho- and meta-unsubstituted compounds, like CB77, CB105, CB118 and CB156, can be biotransformed by CYP1A in fish. Another pattern difference between the three species concerns CB138, which was approximately 3-fold lower in relative proportions in spider crab than in mussel and sea bass. As this higher chlorinated congener is non-degradable and specifically bound to the smaller fraction of the sediment, it is more bioavailable for water-column bivalves than for sediment dwellers like crustaceans (Thompson et al., 1999).

3.3.2. 2378-Polychlorinated dibenzo-p-dioxins and dibenzofurans

With regards to 2378-PCDD/Fs, the highest concentrations at Antifer were measured in mussels, approximately 10 times more than those observed in spider crabs and sea bass (Table 2). At Le Conquet, 2378-PCDD/Fs levels were similar in mussels and spider crabs and about 5 times higher than in sea bass muscle. Munschy et al. (2004) reported similar levels in dab muscle from the Seine Estuary. The highest PCDD/F TEQ values were observed in mussels and were about 2- to 5-fold higher than those measured in spider crabs and sea bass.

The PCDD/F pattern observed in mussels was similar at both stations and dominated by the 2378-PCDD compounds (60% of the $\sum$2378-PCDD/Fs) (Fig. 3b). The main congeners were OCDD (45% of the $\sum$2378-PCDD/Fs), 2378-TCDF (20–30%), 1234678-HpCDD (10–15%) and 23478-PeCDF (5%). The sea bass samples differed from mussels and exhibited a similar profile regardless of site. In *Dicentrarchus labrax*, 2378-PCDFs (75% of the $\sum$2378-PCDD/Fs) were predominant compared to 2378-PCDDs; the major compounds were 2378-TCDF (40–45% of the $\sum$2378 PCDD/Fs), 23478-PeCDF (15–20%) and OCDD (10–15%). Similar fingerprints were obtained in dab from the English Channel (Munschy et al., 2004), and patterns observed in mussels agreed well with previous observations in bivalves from the French coast (Abarnou and Fraisse, 2002). The relative distributions of 2378-PCDD/Fs in sea bass and mussel tissues may be explained by the trophic level, the duration and the extent of

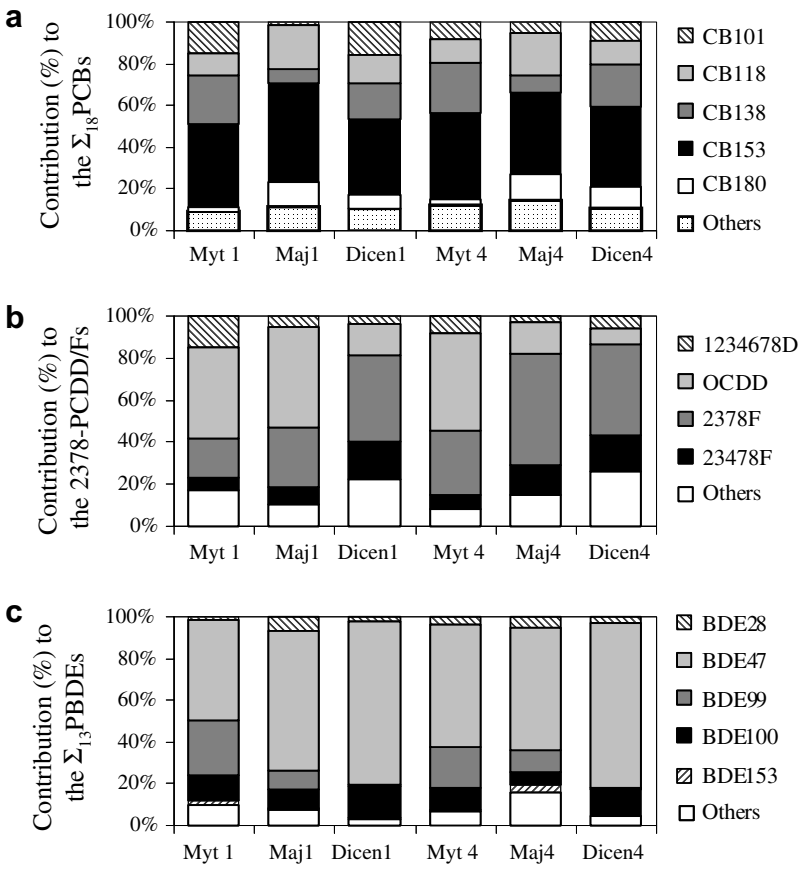

Fig. 3. PCB (a), PCDD/F (b) and PBDE (c) patterns in mussels, spider crabs and sea bass from Antifer (Myt 1, Maj 1, Dicen 1), and Le Conquet (Myt 4, Maj 4, Dicen 4).

exposure and, very importantly, by the metabolisation ability of the organisms. The uptake of PCDDs in flounder was reported to be less efficient than for PCDFs (Berge and Brevik, 1996). Moreover, capacities to biotransform PCDD/Fs through the activation of the CYP1A have been reported in fish (Hektoen et al., 1994). Spider crabs displayed a PCDD/F fingerprint similar to that in mussel specimens from Le Conquet, whereas at Antifer both *M. brachydactyla* and *D. labrax* exhibited a fingerprint with the predominance of 2378-PCDFs compared to 2378-PCDDs. The inversion of PCDD/F profiles in spider crab tissues between Antifer and Le Conquet was observed neither in mussels nor in sea bass. This inversion can be explained by a higher bioavailability of sediment-associated contaminants to crustaceans, especially 2378-PCDFs at Antifer, which could result from the high chronic PCB contamination carried by the Seine River, as hypothesized above.

3.3.3. Polybrominated diphenyl ethers

All organisms from Antifer were more contaminated than those from Le Conquet (Table 3): the $\sum_{13}$PBDE levels were about 50-, 6- and 10-fold higher respectively in mussels, spider crabs and sea bass from Antifer. The highest PBDE concentrations were reported in sea bass at both stations. Very few results have been published so far on PBDEs in marine organisms from the French coasts. For instance, BDE47 levels in mussels from the Seine Estuary were 420–820 pg g^{-1} d.w. (Bragigand, 2005), which is very close to those measured in this study.

BDE47 was the predominant congener in all samples. It constituted 50–60% of the $\sum_{13}$PBDEs in mussels and spider crabs, but reached 80% in sea bass (Fig. 3c). In dab muscle from the Belgian North Sea and the Scheldt estuary, BDE47 accounted for 75% of $\sum$PBDEs (Voorspoels et al., 2003). With regards to PBDE patterns, mussels and spider crabs from both sites presented the same predominant congeners (BDE47, BDE99, BDE100 and BDE28), but they all contributed in slightly different proportions to the $\sum_{13}$PBDEs. For example, BDE99, BDE100 and BDE28 respectively made up 20–25%, 10% and 1–3% of the $\sum_{13}$PBDEs in mussels, which is in agreement with results of Johansson et al. (2004) and Christensen et al. (2002). Spider crabs represented about 10%, 4–8% and 6–7% of the $\sum_{13}$PBDEs, respectively. In sea bass, the PBDE fingerprints were quite different, the main compounds being the BDE47 (80% of the $\sum_{13}$PBDEs) > BDE100 (15%) > BDE154 (2–4%) > BDE28 (2%) > BDE99 (0.5–1%). Similar patterns were observed in pike and roach from the Baltic Sea (Burreau et al., 2004), as well as in the shorthorn sculpin from Greenland (Christensen et al., 2002). Another interesting trend was observed when

comparing the ratio between BDE47 and BDE99 in the different biological samples. In mussels, the BDE47:BDE99 ratio was 70:30 for specimens from both Le Conquet and Antifer. In spider crabs and sea bass, the ratios were respectively 85:15 and 99:1. Conversely, the BDE47:BDE100 ratios were similar among all studied species. A laboratory experiment on blue mussels (Gustafsson et al., 2004) found that BDE47 and BDE99, which were common in *Mytilus edulis*, are highly bioaccumulated in this species. In the common carp *Cyprinus carpio*, the high accumulation of BDE47 has been experimentally demonstrated, but not for congeners BDE99 and BDE153, which are metabolised by debromination processes, leading to the formation of BDE47 (Stapleton et al., 2004a,b). According to our results and the published data, sea bass seems to possess a strong capacity to metabolise PBDEs. The comparison of the spider crab PBDE pattern with those of mussels and sea bass revealed its intermediate biotransformation capacities.

To conclude, the comparison of the contaminant patterns between species of different trophic levels and feeding behaviours allowed us to assess the metabolic capacities of decapod crustaceans. With regards to PCBs, our results have highlighted a higher biotransformation in spider crab than in fish for the selected congeners. Oppositely, crustaceans have a limited capacity to metabolise PCDD/Fs which argues for their use as bioindicator species for dioxin pollution monitoring in coastal waters. Finally, the study highlighted intermediate biotransformation of PBDE by the spider crab compared to mussel and sea bass.

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