Marine Pollution Bulletin
Volume 54, Issue 6, June 2007, Pages 657-668
http://dx.doi.org/10.1016/j.marpolbul.2007.01.018

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

N. Bodin[a, b], A. Abarnou[a], D. Fraisse[c], S. Defour[c], V. Loizeau[a], A.-M. Le Guellec[a] and X. Philippon[a]

[a] IFREMER, Département Biogéochimie et Ecotoxicologie, Centre de Brest, BP70, 29280 Plouzané, France
[b] Université de Bordeaux 1, Laboratoire de Physico et Toxico-Chimie des Systèmes Naturels, CNRS, 351 Cours de la Libération, 33405 Talence, France
[c] CARSO, 321 avenue Jean Jaurès, 69362 Lyon Cedex 07, France

*: Corresponding author : n.bodin@lptc.u-bordeaux1.fr

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 of great concern for the environment and the human health. Because of their capacity for bioaccumulation (Law et al., 2003; Voorspoels et al., 2003; Okumura et al., 2004), PCDD/Fs, PCBs and PBDEs reach higher level consumers, including humans. Dietary intake, especially the consumption of marine organisms, is considered as one of the most important sources of these compounds for human beings (Pompa et al., 2003; Domingo, 2004). The consumers, and thus the food agencies, are particularly aware of the potential health effects associated with eating contaminated food. In order to prevent such hazards and to keep human exposure within safe limits, regulatory actions have been implemented: for instance, from 2001, the Council of the European Union fixed a Maximum Level for dioxins in fish and shellfish of 4 pg WHO-PCDD/F TEQ per gram. The next step is to include dioxin-like PCBs (DL-PCBs) in the estimation of this maximum safe TEQ level (Verstraete, 2002). However, in spite of the huge number of studies available on marker PCBs, information about DL-PCBs in food and more particularly in sea products is quite limited.

Decapod crustaceans like the spider crab (*Maja brachydactyla*), edible crab (*Cancer pagurus*), velvet swimming crab (*Necora puber*) and Norway lobster (*Nephrops norvegicus*) are macrobenthic species living in coastal waters and having an opportunistic diet behaviour. Because of their high trophic level, crustaceans tend to accumulate large amounts of lipophilic contaminants (Jimenez et al., 1998; Voorspoels et al., 2004). The French population greatly appreciates crustaceans; their consumption represents about 10-15% of that of fresh seafood (OFIMER, 2003). Nevertheless, very little information is available on the contamination of crustaceans from the French coast.

The main objectives of this study were first to obtain data for the concentration ranges of PCBs, PCDD/Fs and PBDEs in large crustaceans from the French coasts, and to evaluate the potential sanitary risk for human consumption. Then, contaminant fingerprints in crustaceans were compared to those measured in mussel and sea bass tissues in order to apprehend their metabolic capacities. Sea bass were chosen because they are able to metabolize organic contaminants (Opperhuizen and Sijm, 1990; Goerke and Weber, 2001; Stapleton et al., 2004b); they are at a higher trophic level, feeding on supra-benthic species such as crustaceans (shrimps and mysidaceans) and small fishes (e.g. gobies) (Loizeau et al., 2001). Oppositely, mussels were selected as good bioindicators of aquatic contamination due to 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 belong to the diet of the studied decapod crustaceans, except Nephrops norvegicus, and of the sea bass (Bernardéz et al., 2000).

2. Experimental section

2.1. Sampling

Five sampling stations, characterized by an important crustacean fishing activity and representing very different situations in term of organic chemical contamination (Abarnou et al., 2002; Bodin et al., accepted), were selected along the coasts of Brittany and Normandy (Fig 1). Antifer (station 1) is located near an oil terminal in the Seine Bay, and is largely exposed to large contaminant discharges from the Seine River. The Seine watershed area is about 78,600 km^2, regrouping approximately 30% of the French population. Moreover, 40% of the national industrial activity takes place in this watershed basin where agricultural activities are also significant (Tessier, 2003). Granville (station 2) on the western side of the Contentin Peninsula, Roscoff (station 3) in Northern Brittany and Le Guilvinec (station 5) in Southern Brittany are mainly characterized by agricultural activities and tourism in the summer period. Finally, Le Conquet is located in the Iroise Sea (station 4) in Western Brittany. The coastal waters near Le Conquet may be exposed to water exchanges flowing out the Rade of Brest, an urban area with about 250,000 inhabitants, and a large naval base also characterized by shipyard and various industrial activities.

The various crustacean species were obtained from these areas on the basis of their availability; mussels (*Mytilus edulis*) and sea bass (*Dicentrarchus labrax*) were only collected at Antifer and Le Conquet (Fig 1). For each species, only male adults of homogeneous size were kept in order to minimize the biological variability of the sampling. All these species are suitable for human consumption.

2.2. Sample preparation

The length, wet body weight and sex of the crustacean specimens were measured before dissection (Supplement information). For each species from each site, muscle was carefully dissected from the inner body to prepare a pooled sample made of 3 to 6 individual specimens for edible and spider crabs, 10 for velvet swimming crabs, and 20 for Norway lobsters. Sea bass were carefully filleted and muscle tissues from 10 fishes were pooled. Mussels were first left to soak overnight in clean aerated sea water to eliminate solid particles from their gut, and then dissected and pooled together (35 to 40 individuals per sample). All samples were kept at

–20°C, then freeze-dried and ground into a fine homogeneous powder. The water content of the samples is reported in supplement information to enable further comparison with published data expressed in wet weight.

2.3. Chemical analysis

Eighteen individual PCB congeners were analyzed, including the set of seven indicators (M-PCBs) currently measured in pollution monitoring programs (PCBs 28, 52, 101, 118, 138, 153 and 180) and the twelve dioxin like-PCBs (DL-PCBs) (PCBs 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189). PCB118 belongs to both sets of congeners. Concerning dioxins and furans, the concentrations of each of the seventeen 2378-substituted congeners were determined. The 2378-TCDD Toxicity Equivalent Quantity was estimated using the corresponding WHO-TEF factors of each 2378 PCDD/Fs and DL-PCBs (Van den Berg et al., 1998). Finally, thirteen PBDE congeners were also analyzed (PBDEs 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183 and 190). All analyses were performed by following the isotope dilution method (U.S. EPA Method 1613, 1994).

After addition of known amounts of a standard solution of sixteen $^{13}C_{12}$-PCDD/Fs, eighteen $^{13}C_{12}$-PCBs and nine $^{13}C_{12}$-PBDEs, the samples were extracted with a solvent mixture of toluene-cyclohexane (50:50) for 12 hours in a Soxhlet apparatus. The extracts were evaporated to dryness and weighed. The amount of extractible material estimated the lipid content (Supplement information). The fatty co-extracted material was removed by sulfonation with sulphuric acid: for that purpose, the extract was taken up in 50ml hexane into a separator funnel and partitioned three times against 50mL 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. Then, a second purification step was performed on a multi-layer adsorption chromatography column, successively packed from bottom to top with 1g silica gel, 2g basic silica gel, 1g silica gel, 4g acidic silica gel and 1g silica gel. The column was pre-eluted with 30mL of hexane and the stopcock was closed when hexane reached the silica gel layer. Then the concentrated extract was applied to the column and PCDD/Fs, PCBs and PBDEs eluted with hexane. Separation of PCB, PBDE and PCDD/Fs was performed on a Florisil column (60-100 mesh, activated at 600°C for a minimum of 18 hours, deactivated with 3% water) (Malisch et al., 2000). The 6 g Florisil column was pre-eluted with 50mL heptane. The stopcock was closed when the heptane reached the Florisil layer and the concentrated extract was applied. The co-extracted PCBs and PBDEs were eluted with 60mL heptane and PCDD/Fs were eluted with 60mL toluene.

The first fraction (PBDEs and PCBs) was then fractionated on a Carbopack B column (mix of 2g Carbopack B + 2g 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, they were determined by HRGC/HRMS (WATERS Autospec set at a resolution of 10,000; split/splitless injection of 1 or 1.5µL, DB-5 column and/or HT8-PCB column from SGE). After addition of $^{13}C_{12}$-1234-TCDD and $^{13}C_{12}$-123789-HxCDD, the PCDD/F fraction was concentrated to a final volume of 25µL, and determination was performed by HRGC/HRMS (WATERS Autospec set at a resolution of 10,000; split/splitless injection of 1.5µL, DB-5ms column).

2.4. Quality control

All the performance criteria required for the analysis of dioxins (U.S. EPA Method 1613, 1994) were met. Analyte recovery ranged from 80-110%, except for OCDD and OCDF which were therefore higher than 40%. The linearity was checked systematically and the response factors were estimated by running four standard solutions before any real sample series, and repeated in the case of larger sample sets. The detection limits of the method ranged from 1 to 20 pg.g^{-1} lipids for DL-PCBs, PCDD/Fs and PBDEs, whereas they were 1 pg.g^{-1} lipids for M-PCBs. Several procedural blanks were analyzed with the samples, showing very few or no interfering compounds, except in the case of marker PCBs with no effects on the actual concentrations of the true samples. The accuracy of the protocol was assessed by analyzing 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 comparisons 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 reported on a dry weight (d.w.) basis (Tables 1 and 2).

Crustaceans from Antifer were the most contaminated samples for all contaminant families confirming 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 example, the Σ_{18}PCB concentrations in spider crabs M1 reached 30 ng.g^{-1}d.w, respectively about 6-, 12-, 15- and

20- fold higher than those measured in specimen from Le Conquet (M4), Le Guilvinec (M5), Roscoff (M3), and Granville (M2). 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 weak industrial activity like Granville and Roscoff, the PCB concentrations measured in spider crabs M5 were slightly higher than those in M2 and M3, suggesting an influence of the Loire River plume until the Western Brittany (Lazure and Jegou, 1998; Abarnou et al., 2002). All these differences in PCB contamination levels in spider crab muscles correlate well with those observed in spider crab hepatopancreas from the same areas (Bodin et al., accepted).

For each contaminant family and at each sampling area, similar concentration ranges were observed in the different crustacean species. Velvet swimming crabs and Norway lobsters presented the highest levels compared to spider and edible crabs, at Antifer and Le Guilvinec respectively. All individuals analyzed for this study were male adult crustaceans; the slight differences between species on each sampling area are probably due to a difference in their diet or in their way of life (habitat, migration, age) (Bodin et al., accepted).

Concerning the total TEQ, the maximum values were recorded in crustacean muscle collected at Antifer, and especially in velvet swimming crabs. They were 5- to 20-fold higher than those in species from the other sampling 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. These results confirm the major PCB inputs in Antifer are due to higher industrial activity in this region (Abarnou and Fraisse, 2002), and more likely due to the influence of the River Seine, which has been highly contaminated for a long time.

All TEQ values measured in crustacean muscles were under the maximum limit of 4 pg TEQ.g^{-1}w.w. set by the European Community for seafood intended for human consumption, whether considering only the PCDD/F TEQ or DL-PCB TEQ as the total TEQ values. Moreover, based on the Tolerable Monthly Intake set for 2378-PCDD/Fs and DL-PCBs at 2.33 pg TEQ.kg^{-1}b.w. per day (JECFA, 2002), and for the 7 indicator PCBs at 0.01 µg.kg^{-1}b.w. per day (AFSSA, 2003), it is possible to estimate the maximum amount of crustacean flesh that can be eaten before reaching the safety limit. Taking a mean body weight of 65 kg, this limit would be reached by consuming 10-40 g of crustacean muscle (Antifer), in an average daily consumption or one order of magnitude lower (110 g) for specimens from the other sampling stations.

Although no data were found in the literature on the contamination of the same studied

crustacean species, table 3 highlights the PCB, 2378-PCDD/F and PBDE concentrations reported in various similar organisms. As far as PCBs are concerned, the concentrations measured in the crustaceans from the Seine Bay are among the highest reported in the literature. 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 contaminated estuaries in Europe (Abarnou et al., 2000). In contrast, this study showed low PCDD/F and PBDE contamination in decapod crustaceans from the French coastal waters of Brittany and Normandy, compared to levels observed in organisms from different countries through the world.

3.2. Contaminant distribution in crustaceans

PCBs

PCB patterns observed in crustaceans were very similar, whatever their origin and their contamination levels (Fig. 2A). Among PCB congeners, the main compounds were CB153, CB118, CB180 and CB138. Together they accounted for 80-90% of the Σ_{18}PCBs, and the CB153 contributes 40-50% of this sum. Due to their high octanol-water coefficients, these major PCB congeners are accumulated by marine organisms, without being metabolized because of substitution positions, and are biomagnified along food webs (Kannan et al., 1995; Bright et al., 1995). Similar PCB profiles were observed in the spider crab hepatopancreas (Bodin et al., accepted), as well as in the flying crab *Lyocarcinus holsatus* (Voorspoels et al., 2004), and the shrimp *Crangon crangon* (Voorspoels et al., 2004; Kannan et al., 1995). However, the contribution of the congeners CB118 and CB138 to the Σ_{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. Moreover, CB118 was more present in spider crabs and Norway lobsters than in the two other crustaceans (respectively 20% and 10-15% of the Σ_{18}PCBs). These slight differences among the four crustacean species are probably due to differences in their diet, their habitat and their behavior.

The DL-PCBs, except for CB118, were presented at a much lower level: based on their concentrations they represented altogether less than 15% of the Σ_{18}PCBs. The DL-PCBs also showed a similar pattern in crustaceans whatever the sampling station and the species. Among them, the predominant congeners were CB105, CB156 and CB167 which contributed 35-40%, 20-25% and 15-20% to the sum of the DL-PCBs, without CB118.

As far 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 four congeners to the TEQ. For the mono-ortho PCBs, the main compounds were the CB118, CB156 and CB105, which together contributed 85-90% to the TEQ carried by this group.

PCDD/Fs

The PCDD/F distribution in crustaceans was characterized by very few congeners, namely OCDD, 2378-TCDF and 23478-PeCDF, which together account on average for 60-85% of the 17 toxic compounds (Fig. 2B). Except for 1234678-HpCDD which characterized 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% of the total 2378-PCDD/Fs.

Two typical patterns were observed depending upon the origin of the samples: the “Antifer pattern” and a “general pattern”. The first fingerprint characterized crustaceans from Antifer, irrespective of the species. In these more highly contaminated samples, the major components were 2378-TCDF (40-55% of the Σ2378-PCDD/Fs), OCDD (10-30%) and 23478-PeCDF (10-15%). Conversely, 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 characterized by the prevalence of OCDD (30-40% of the Σ2378-PCDD/Fs), 2378-TCDF (15-25%), 23478-PeCDF (5-10%) and 1234678-HpCDD. In crustaceans from Brittany and Basse-Normandie, the Σ2378-PCDDs were predominant with respect to Σ2378-PCDFs, and represented approximately 55-70% of the total 2378-PCDD/Fs, oppositely to samples from Antifer, where they only made up 20-40%.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 produced in high proportions in sewage sludge (Baker and Hites, 2000) and in combustion by-products of fuel oil mixtures (Hellou and Payne, 1993). As regards 2378-TCDF and 23478-PeCDF, they principally come from technical PCBs and combustion processes (Baker and Hites, 2000; Wakimoto et al., 1988). The prevalence of these compounds in samples from Antifer could indicate that urban waste incineration is a potential source of contamination, but also results of the high chronic PCB

contamination carried by the Seine River. These contaminants, associated with suspended matter carried by river discharges have settled down onto the superficial sediment, thus becoming a secondary source of contamination for benthic species and their predators.

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

PBDEs

Among PBDEs, a very similar pattern was observed in crustaceans from the five sampling stations (Fig. 2C), with the major compounds BDE47, BDE99, BDE100 and BDE28 making up approximately 85-95% of the Σ_{13}PBDEs. Other authors also reported quite similar PBDE patterns in *Pandalus borealis* (Law et al., 2003) and *Crangon crangon* (Voorspoels et al., 2003; Boon et al., 2002). However, the contribution of each congener to the Σ_{13}PBDEs was slightly different depending on the species. In edible crabs from our study, BDE47 represented only 40% of the Σ_{13}PBDEs, contrary to the other species where it accounted for approximately 60%. Moreover, in spider crabs and velvet swimming crabs, the contribution of BDE99 to the Σ_{13}PBDEs appeared to be lower than in edible crab and Norway lobster muscle (10-15% and 20-25%, respectively). These minor differences could result from differences in the crustacean diet, habitat and metabolization capacities.

These observations on the distribution of the three groups of contaminants in crustaceans pointed out differences between the contaminant families. PCB and PBDE congeners varied more or less together, and the global fingerprint remained more or less unchanged whatever the geographical situation and the contamination levels. In contrast, PCDD/Fs which originate as unwanted by-products of a large variety of processes, presented different types of distribution in crustaceans, probably related to the contamination levels and thus the proximity of emission sources.

3.3. Comparison of crustacean, mussel and sea bass contamination

PCBs:

Total PCB contamination levels were higher in sea bass than in mussel and spider crab tissues for the two sampling areas (Table 4). PCB concentrations in sea bass muscle from

Antifer were close to those measured in the sea bass from the Seine Estuary (Loizeau et al., 2001). As regards mussel contamination, PCB levels measured at Antifer and Le Conquet were in agreement with those of the monitoring program RNO (Claisse, 1989). At both stations, DL-PCBs represented approximately 15% of the Σ_{18}PCB congeners in mussels and sea bass, whereas they contributed 30% in the spider crabs. As regards TEQ values, the contribution of non-ortho PCBs to the DL-PCB TEQ was equal to 60-80% in the three species.

In the three species, the main compounds were CB153, CB101, CB118, CB138, and CB180, but they were distributed differently among the species tissues (Fig. 3A). In sea bass from the two sampling stations, the predominant congeners were present in the following decreasing order: CB153 (40% of Σ_{18}PCBs)> CB138 (15-20%)> CB118 (10-15%)> CB101 (10-15%)> CB180 (5-10%), which coincides with previously observed patterns in various fishes (Loizeau et al., 2001; Munschy et al., 2004). Similar patterns were observed in mussels collected at both Antifer and Le Conquet, except for the congener CB180. As described above, the main compounds found in spider crab muscle were: CB153 (40-50% of Σ_{18}PCBs)> CB118 (20%)> CB180 (12%)> CB138 (5-10%)> CB101 (2-5%). As regards DL-PCBs, a similar fingerprint was observed whatever the sampling station and the marine species, except for CB77 which accounted for only 0.5% of the sum of DL-PCBs in sea bass and 1.5 to 1.9% in mussels and spider crabs. The slight differences of PCB pattern between mussels, spider crabs and sea bass result from their diet, way of life and trophic level, and more likely depend on elimination and specific metabolization 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). Whereas CYP2B acts on the metabolization of *meta*- and *para*-unsubstituted congeners, like CB52 and CB101 which are present in much lower proportions in crustacean muscle compared to mussel and sea bass, only *ortho*- and *meta*-unsubstitued compounds, like CB77, CB105, CB118 and CB156, can be biotransfromed by CYP1A in fish. Another pattern difference concerns CB138, which was approximately 3 fold-lower in relative proportions in the 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 probably more bioavailable for water-column bivalves than for sediment dwellers like crustaceans (Thompson et al., 1999).

PCDD/Fs:

As regards 2378-PCDD/Fs, the highest concentrations at Antifer were measured in mussels, approximately 10 times higher than those observed in spider crabs and sea bass (Table 4). At Le Conquet, similar 2378-PCDD/Fs levels were recorded in mussels and spider crabs, about 5-fold higher than in sea bass muscle. Munschy et al. (2004) reported close levels in dab muscle from the Seine Estuary. As regards PCDD/F TEQ, the highest values were observed in mussels at both stations, about 2- to 5-fold higher than those measured in spider crabs and sea bass.

Concerning their distribution, a similar PCDD/F pattern was observed in mussels at both stations with the predominance of the 2378-PCDD compounds (60% of the Σ2378-PCDD/Fs) (Fig. 3B). The main congeners were OCDD (45% of the Σ2378-PCDD/Fs), 2378-TCDF (20-30%), 1234678-HpCDD (10-15%) and 23478-PeCDF (5%). The sea bass samples exhibited a similar profile whatever the sampling area, but which differed from that in mussels. In *Dicentrarchus labrax*, 2378-PCDFs (75% of the Σ2378-PCDD/Fs) were predominant compared to 2378-PCDDs; the main compounds were 2378-TCDF (40-45% of the Σ2378 PCDD/Fs), 23478-PeCDF (15-20%) and OCDD (10-15%). Similar results were obtained in dab from the English Channel (Munschy et al., 2004), and in mussels from French coastal waters (Abarnou and Fraisse, 2002). The relative distributions of 2378-PCDD/Fs in sea bass and mussel tissues may be explained by trophic level as well as the duration and extent of exposure and, importantly, by the metabolism. The uptake efficiency 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 fishes (Hektoen et al., 1994). With respect to PCDD/Fs in spider crabs, a similar fingerprint to that in mussels was observed in specimens from Le Conquet, whereas, at Antifer, *Maja brachydactyla* and *Dicentrarchus labrax* exhibited the same 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 in neither mussels nor sea bass. It can be explained by a higher bioavailability of sediment-associated contaminants to crustaceans, and especially 2378-PCDFs at Antifer which could result, as hypothesized above, from the high chronic PCB contamination carried by the Seine River.

PBDEs:

Whatever the species, the organisms collected at Antifer were more contaminated than

those from Le Conquet (Table 4): levels of the Σ_{13}PBDE 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 studies exist on the PBDE contamination of marine organisms from French coasts. 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 and it constituted about 50-60% of the Σ_{13}PBDEs in mussels and spider crabs, whereas for sea bass, it reached 80% of the total level (Fig. 3C). In dab muscle from the Belgian North Sea and the Scheldt Estuary, BDE47 accounted for 75% of ΣPBDEs (Voorspoels et al., 2003). As regards PBDE patterns, mussels and spider crabs from the two sampling stations presented similar predominant congeners (BDE47, BDE99, BDE100 and BDE28), but they all contributed in slightly different proportions to the Σ_{13}PBDEs. For example, BDE99, BDE100 and BDE28 respectively made up 20-25%, 10% and 1-3% of the Σ_{13}PBDEs in mussels, which is in agreement with results of Johansson et al. (2004) and Christensen et al. (2002). As regards spider crabs, they represented about 10%, 4-8% and 6-7% of the Σ_{13}PBDEs, respectively. In sea bass, the PBDE fingerprints were quite different, the main compounds being the BDE47 (80% of the Σ_{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 predominant in *Mytilus edulis* from both Le Conquet and Antifer, were highly bioaccumulated this species. On the contrary, high bioaccumulation of BDE47 in the common carp *Cyprinus carpio* has been experimentally demonstrated, but not for congeners BDE99 and BDE153, which could be metabolized by debromination processes, resulting in the formation of BDE47 (Stapleton et al., 2004a, 2004b). As regards our results and data from the literature, the sea bass *Dicentrarchus labrax* seems to possess strong PBDE metabolic capacities. Comparing the spider crab PBDE pattern with those of mussels and sea bass revealed its intermediate biotransformation capacities.

To conclude, the comparison of contaminant patterns between species of different trophic levels and feeding behaviours allowed us to assess the metabolic capacities of decapod crustaceans. As regards PCBs, our results have highlighted higher biotransformation in the spider crab than in fish. Considering PCDD/Fs, crustaceans seem to possess very poor metabolic activities, which confirm their potential use as bioindicator species for dioxin marine pollution monitoring. Finally, the study highlighted intermediate biotransformation capacities of PBDE for the spider crab compared to mussel and sea bass.

Acknowledgements

This work was partially funded by the Regional Council of Brittany. We would like to thank the fishermen and professional organizations who kindly provided us with crustacean specimens. We also would like to express our gratitude to Pr. Guillou (IUEM, Plouzané), Dr. Latrouite (IFREMER, Plouzané) and Pr. Budzinski (LPTC, Bordeaux) for their advice and support during this work.

References

Abarnou, A., Burgeot, T., Chevreuil, M., Leboulenger, F., Loizeau, V., Madoulet-Jaouen, A., Minier, C., 2000. "Les contaminants organiques: quels risques pour le monde vivant ?" Fascicule Seine-Aval, 35 pp.

Abarnou, A., Fraisse, D., 2002. Dioxins and dioxin-like PCBs in mussels and fishes from the French coastal waters. Organohalogen. Compd. 56, 469-472.

Abarnou, A., Loizeau, V., Le Guellec, A-M., Jaouen-Madoulet, A., 2002. Contaminants in marine foodwebs. Revue Méd. Vét. 153, 425-432.

AFSSA, 2003. "Avis de l'Agence française de sécurité sanitaire des aliments sur l'existence éventuelle d'une corrélation significative entre les teneurs dans les différents congénères de PCB," Conseil Supérieur d'Hygiène Publique de France section Aliments et Nutrition.

Baker, J.I., Hites, R.A., 2000. Is combustion the major source of polychlorinated dibenzo-*p*-dioxins and dibenzofurans to the environment? A mass balance investigation. Environ. Sci. Technol. 34, 2879-2886.

Berge, J.A., Brevik, E.M., 1996. Uptake of metals and persistent organochlorines in crabs (*Cancer pagurus*) and flounder (*Platichthys flesus*) from contaminated sediments: Mesocosm and field experiments. Mar. Pollut. Bull. 33, 46-55.

Bernárdez, C., Freire, J., González-Gurriarán, E., 2000. Feeding of the spider crab *Maja squinado* in rocky subtidal areas of the Ría de Arousa (north-west Spain). J. Mar. Biol. Ass. U.K. 80, 95-102.

Bodin, N., Abarnou, A., Le Guellec, A-M., Loizeau, V., Philippon, X., accepted. Organochlorinated contaminants in decapod crustaceans from the coasts of Brittany and Normandy (France). Chemosphere.

Boon, J.P., Lewis, W.E., Tjoen-A-Choy, M.R., Allchin, C.R., Law, R.J., de Boer, J., Ten Hallers-Tjabbes, C.C., Zegers, B.N., 2002. Levels of polybrominated diphenyl ether (PBDE) flame retardants in animals representing different trophic levels of the North Sea food web. Environ. Sci. Technol. 36, 4025-4032.

Bragigand, V., 2005. Recherches écotoxicologiques sur les retardateurs de flamme bromés dans les écosystèmes estuariens (estuaires de Loire et de Seine). Faculté de Pharmacie, Nantes, France, 250 pp.

Bright, D.A., Dushenko, W.T., Grundy, S.L., Reimer, K.J., 1995. Effects of local and distant contaminant sources: polychlorinated biphenyls and other organochlorines in bottom-dwelling animals from an Arctic Estuary. Sci. Total Environ. 160-161, 265-283.

Brochu, C., Moore, S., Pelletier, E., 1995. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in sediments and biota of the Saguenay Fjord and the St Lawrence Estuary. Mar. Pollut. Bull. 30, 515-523.

Brown, J., John, F., 1992. Metabolic alterations of PCB residues in aquatic fauna: distributions of cytochrome P4501A- and P4502B-like activities. Mar. Environ. Res. 34, 261-266.

Burreau, S., Zebühr, Y., Broman, D., Ishaq, R., 2004. Biomagnification of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) studied in pike (*Esox lucius*), perch (*Perca fluviatilis*) and roach (*Rutilus rutilus*) from the Baltic Sea Chemosphere 55, 1043-1052.

Cai, Z., Ramanujam, V.M.S., Gross, M.L., 1994. Levels of polychlorodibenzo-*p*-dioxins and dibenzofurans in crab tissues from the Newark/Raritan Bay system. Environ. Sci. Technol. 28, 1528-1534.

Christensen, J.H., Glasius, M., Pecseli, M., Platz, J., Pritzl, G., 2002. Polybrominated diphenyl ethers (PBDEs) in marine fish and blue mussels from southern Greenland. Chemosphere 47, 631-638.

Claisse, D., 1989. Chemical contamination of French coasts: the results of ten years mussel watch. Mar. Pollut. Bull. 20, 523-528.

Domingo, J.L., 2004. Human exposure to polybrominated diphenyl ethers through the diet. J. Chromatogr. A 1054, 321-326.

Goerke, H., Weber, K., 2001. Species-specific elimination of polychlorinated biphenyls in estuarine animals and its impact on residue patterns. Mar. Environ. Res. 51, 131-149.

Gustafsson, K., Björk, M., Burreau, S., Gilek, M., 2004. Bioaccumulation kinetics of brominated flame retardants (Polybrominated diphenyl ethers) in blue mussels (*Mytilus edulis*). Environ. Toxicol. Chem. 18, 1218-1224.

Hagen, M.E., Colodey, A.G., Knapp, W.D., Samis, S.C., 1997. Environmental response to decreased dioxin and furan loadings from British Columbia coastal pulp mills. Chemosphere 34, 1221-1229.

Hektoen, H., Berge, J.A., Ingebrigtsen, K., Knutzen, J., Oehme, M., 1994. Elimination of polychlorinated dibenzofurans and dibenzo-*p*-dioxins from blue mussel (*Mytilus edulis*) and tissue distribution of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). Chemosphere 29, 1491-1499.

Hellou, J., Payne, J.F., 1993. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in cod (*Gadus morhua*) from the Northwest Atlantic. Mar. Environ. Res. 36, 117-128.

JECFA, 2002. Polychlorinated dibenzodioxins, polychlorinated dibenzofurans, and coplanar polychlorinated biphenyls. In Safety Evaluation of Certain Food Additives and Contaminants. Report of the 57th Meeting of the Joint FAO/WHO Expert Commitee on Food Additives and Contaminants; Canady, R., Crump, K., Feeley, M., Freijer, J., Kogevinas, M., Malisch, R., Verger, P., Wilson, J., Zeilmaker, M., Eds.; World Health Organisation, Geneva, 48, 451-664.

Jimenez, B., Hernandez, L.M., Gonzalez, M.J., Eljarrat, E., Rivera, J., Fossi, M.C., 1998. Congener specific analysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in crabs and sediments from the Venice and Orbetello lagoons, Italy. Environ. Sci. Technol. 32, 3853-3861.

Johansson, I., Moisan, K., Guiot, N., Truquet, I., Munschy, C., Tronczynski, Y., 2004. Levels and trends of organohalogen compounds in mussels from the Seine estuary in 1981-2003. Organohalogen. Compd. 66, 1868-1876.

Kannan, N., Reusch, T.B.H., Schulz-Bull, D.E., Petrick, G., Duinker, J.C., 1995. Chlorobiphenyls: Model compounds for metabolism in food chain organisms and their potential use as ecotoxicological stress indicators by application of the metabolic slope concept. Environ. Sci. Technol. 29, 1851-1859.

Karl, H., Ruoff, U., Bluthgen, A., 2002. Levels of dioxins in fish and fishery products on the German market. Chemosphere 49, 765-773.

Knutzen, J., Bjerkeng, B., Naes, K., Schlabach, M., 2003. Polychlorinated dibenzofurans/dibenzo-*p*-dioxins (PCDF/PCDDs) and other dioxin-like substances in marine organisms from the Greenland fjords, S. Norway, 1975-2001: present contamination levels, trends and species specific accumulation of PCDF/PCDD congeners. Chemosphere 52, 745-760.

Law, R.J., Alaee, M., Allchin, C.R., Boon, J.P., Lebeuf, M., Lepom, P., Stern, G.A., 2003. Levels and trends of polybrominated diphenyl ethers and other brominated flame retardants in wildlife. Environ. Int. 29, 757-770.

Lazure, P., Jegou, A-M., 1998. 3D modelling of seasonal evolution of Loire and Gironde plumes on Biscay Bay continental shelf. Oceanol. Acta 21, 165-177.

Loizeau, V., Abarnou, A., Menesguen, A., 2001. A steady-state model of PCB bioaccumulation in the sea bass (*Dicentrarchus labrax*) food web from the Seine Estuary (France). Estuaries 24, 1074-1087.

Malisch, R., Bruns-Weller, E., Knoll, A., Fürst, P., Mayer, R., Wiesmüller, T., 2000. Results of an "emergency quality control study" as confirmation of a PCDD/PCDF-contamination of milk and butter samples. Chemosphere 40, 1033-1040.

Marchand, M., Caprais, J.C., Cosson-Mannevy, M.A., Morinière, P., 1983. Apports et distribution des résidus organochlorés à haut poids moléculaire dans la rade de Brest (milieu marin semi-fermé). Oceanol. Acta 6, 269-282.

Menone, M.L., Bortolus, A., Botto, F., Aizpun de Moreno, J.E., Moreno, V.J., Iribarne, O., Metcalfe, T.L., Metcalfe, C.D., 2000. Organochlorine contaminants in a coastal lagoon in Argentine: Analysis of sediment, crabs, and cordgrass from two different habitats. Estuaries 23, 583-592.

Munschy, C., Moisan, K., Tronczynski, Y., 2004. Levels and patterns of PCBs and PCDD/Fs in different tissues of the marine flatfish dab (*Limanda limanda*) from the English Channel, France. Organohalogen. Compd. 66, 1695-1703.

Oehme, M., Bartonova, A., Knutzen, J., 1990. Estimation of polychlorinated dibenzofuran and dibenzo-*p*-dioxin contamination of a coastal region using isomer profiles in crabs. Environ. Sci. Technol. 24, 1836-1841.

OFIMER, 2003. Division Observatoire Economique Entreprise "Consommation des produits de la pêche et de l'aquaculture. Bilan annuel 2003," Office National Interprofessionnel des Produits de la Mer et de l'Aquaculture.

Okumura, Y., Yamashita, Y., Kohno, Y., 2004. Bioaccumulation of PCDD/Fs and Co-PCBs in lower-trophic-level organisms in Sendai Bay, Japan. Water Air Soil Pollut. 159, 291-312.

Opperhuizen, A., Sijm, D.T.H.M., 1990. Bioaccumulation and biotransformation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in fish. Environ. Toxicol. Chem. 9, 175-186.

Pompa, G., Caloni, F., Caloni, F., Pompa, G., Fracchiolla, M.L., 2003. Dioxin and PCB contamination of fish and shellfish: assessment of human exposure. Review of the international situation. Vet. Res. Communications 27, 159-167.

Rappe, C., Bergqvist, P.-A., Kjeller, L., Belton, T., Ruppel, B., Lockwood, K., Kahn, P.C., 1991. Levels and patterns of PCDD and PCDF contamination in fish, crabs, and lobsters from Newark Bay and the New York Bight. Chemosphere 22, 239-266.

Sakurai, T., Kim, J-G., Suzuki, N., Matsuo, T., Li, D-Q., Yao, Y., Masunaga, S., Nakanishi, J., 2000. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in sediment, soil, fish, shellfish and crab samples from Tokyo Bay area, Japan. Chemosphere 40, 627-640.

Stapleton, H.M., Letcher, R.J., Baker, J.E., 2004b. Debromination of polybrominated diphenyl ether congeners BDE 99 and BDE 183 in the intestinal tract of the common carp (*Cyprinus carpio*). Environ. Sci. Technol. 38, 1054-1061.

Stapleton, H. M., Letcher, R. J., Li, J., Baker, J. E., 2004a. Dietary accumulation and metabolism of polybrominated diphenyl ethers by juvenile carp (*Cyprinus carpio*). Environ. Toxicol. Chem. 23, 1939-1946.

Tessier, L., 2003. Transport et caractérisation des matières en suspension dans le bassin versant de la Seine: identification de signatures naturelles anthropiques. Ecole Nationale des Ponts et Chaussée, Paris, France, 344 pp.

Thompson, S., Budzinski, H., Garrigues, P., Narbonne, J.F., 1999. Comparison of PCB and DDT distribution between water-column and sediment-dwelling bivalves in Arcachon Bay, France. Mar. Pollut. Bull. 38, 655-662.

U.S. EPA Method 1613, 1994. Tetra- through octa-chlorinated dioxins and furans by isotopic dilution HRGC-HRMS. Office of Science and Technology, U.S. EPA; U.S. Government Printing Office: Washington, DC.

Van den Berg, M., Birnbaum, L., Bosveld, B.T.C., Brunström, B., Cook, P., 1998. Toxic equivalents factors (TEF) for PCBs, PCDDs, PCDFs for humans and wildlife. Environ. Health Perspect. 106, 775-792.

Van der Oost, R., Beyer, J., Vermeulen, N.P.E., 2003. Fish bioaccumulation and biomarkers in environmental risk assessment: a review. Environ. Toxicol. Pharmacol. 13, 57-149.

Verstraete, F., 2002. Development and implementation of an EC strategy on dioxins, furans and dioxin-like PCBs in food and feed. Environ. Sci. Pollut. Res. 9, 297-299.

Voorspoels, S., Covaci, A., Maervoet, J., De Meester, I., Schepens, P., 2004. Levels and profiles of PCBs and OCPs in marine benthic species from the Belgian North Sea and the Western Scheldt Estuary. Mar. Pollut. Bull. 49, 393-404.

Voorspoels, S., Covaci, A., Schepens, P., 2003. Polybrominated diphenyls ethers in marine species from the Belgian North Sea and the Western Scheldt Estuary: levels, profiles and distribution. Environ. Sci. Technol. 37, 4348-4357.

Wade, T.L., Jackson, T.J., Gardinali, P.R., Chambers, L., 1997. PCDD/PCDF sediment concentration distribution: Casco Bay, Maine, USA. Chemosphere 34, 1359-1367.

Wakimoto, T., Kannan, N., Ono, M., Tatsukawa, R., Masuda, Y., 1988. Isomer-specific determination of polychlorinated dibenzofurans in Japanese and American polychlorinated biphenyls. Chemosphere 17, 743-750.

Table and figure list

Table 1. PCB and 2378-PCDD/F concentrations ($pg.g^{-1}$d.w.), and TEQ values ($pg.g^{-1}$d.w.) in crustacean muscles from French coastal sites.

	Antifer			Granville		Roscoff	Le Conquet		Le Guilvinec		
	M1	C1	Np1	M2	C2	M3	M4	C4	M5	C5	Nn5
CB28	235	211	844	48	66	51	91	44	91	16	59
CB52	71	129	63	41	44	24	114	20	39	15	75
CB77	175	86	359	12	19	12	27	17	21	7	13
CB81	2.8	1.7	4.5	0.4	0.6	0.4	0.6	0.7	0.6	0.2	0.4
CB101	396	433	177	55	138	33	254	94	74	50	159
CB105	1173	511	3073	62	92	74	181	126	112	40	133
CB114	41	16	96	2.8	2.9	3.0	6.9	6.7	3.8	1.6	3.7
CB118	6264	2760	16494	289	349	277	967	579	389	143	496
CB123	41	26	107	1.2	2.1	2.1	6.0	6.6	4.2	0.8	3.5
CB126	34	20	52	3.2	4.9	3.2	4.5	4.1	3.7	2.1	4.8
CB138	1840	2748	12513	135	491	159	401	657	328	240	998
CB153	13946	7621	26810	622	971	677	1903	1586	1020	459	1976
CB156	736	249	1822	27	33	45	140	71	50	13	73
CB157	199	96	498	11	14	14	34	20	18	7	25
CB167	493	254	1189	25	35	30	86	55	39	16	64
CB169	3.7	1.9	5.9	0.5	0.8	0.6	0.6	0.4	0.5	0.3	1.0
CB180	3487	2012	6833	180	248	285	583	398	295	121	541
CB189	73	37	197	3.7	4.9	6.0	15.1	5.8	6.2	2.1	11.2
Σ_7 PCBs	26239	15914	63734	1369	2306	1505	4313	3378	2236	1045	4303
Σ_{18} PCBs	29138	17176	70942	1514	2511	1689	4798	3686	2489	1134	4625
TEQ DL-PCBs	4.71	2.51	8.54	0.39	0.57	0.39	0.67	0.54	0.42	0.25	0.47
2378D	0.06	0.03	0.18	0.01	0.02	0.02	0.02	0.01	0.02	0.02	0.03
12378D	0.37	0.30	0.45	0.10	0.19	0.11	0.13	0.07	0.16	0.10	0.21
123478D	0.13	0.09	0.23	0.03	0.07	0.04	0.06	0.05	0.07	0.03	0.11
123678D	0.26	0.30	0.83	0.09	0.49	0.11	0.15	0.11	0.19	0.11	0.39
123789D	0.13	0.16	0.30	0.04	0.15	0.05	0.09	0.05	0.10	0.04	0.15
1234678D	0.42	0.43	1.49	0.22	0.58	0.17	0.37	0.31	0.45	0.20	0.86
OCDD	1.90	3.40	3.79	1.32	2.05	1.01	3.33	1.55	1.24	0.68	1.84
2378F	6.82	4.88	17.44	0.65	1.50	0.70	2.00	1.28	0.80	0.49	0.57
12378F	0.03	0.27	1.40	nd	0.20	0.01	0.01	0.15	0.11	0.05	0.25
23478F	1.77	1.38	4.11	0.19	0.51	0.30	0.58	0.45	0.37	0.13	0.52
123478F	0.13	0.11	0.55	0.02	0.08	0.03	0.07	0.08	0.10	0.01	0.16
123678F	0.02	0.05	0.28	nd	0.06	nd	nd	0.05	0.06	0.02	0.09
234678F	0.16	0.11	0.36	0.02	0.10	0.05	0.07	0.06	0.09	0.02	0.11
123789F	nd	nd	0.01	nd	nd	nd	nd	nd	nd	nd	nd
1234678F	0.21	0.09	0.47	0.09	0.23	0.05	0.09	0.10	0.18	0.06	0.15
1234789F	0.02	0.05	0.04	nd	nd	nd	nd	nd	0.01	0.01	0.01
OCDF	0.45	0.05	0.49	0.24	0.47	0.13	0.03	0.24	0.10	0.16	0.12
Σ 2378-PCDD/Fs	12.9	11.7	32.4	3.0	6.7	2.8	7.0	4.5	4.1	2.1	5.6
TEQ PCDD/Fs	2.08	1.61	4.77	0.30	0.72	0.38	0.69	0.48	0.52	0.25	0.68
Total TEQ	6.79	4.12	13.32	0.68	1.29	0.77	1.36	1.02	0.94	0.50	1.15

Table 2. PBDE concentrations ($pg.g^{-1}$d.w.) in crustacean muscles from French coastal sites.

	Antifer			Granville		Roscoff	Le Conquet		Le Guilvinec		
	M1	C1	Np1	M2	C2	M3	M4	C4	M5	C5	Nn5
BDE-17	0.3	2.4	0.4	0.2	0.7	0.2	0.2	0.2	1.8	0.1	0.2
BDE-28	8.1	7.6	12.8	2.5	2.6	1.8	4.3	1.1	8.2	0.9	6.7
BDE-47	96.5	83.2	106.3	29.1	55.4	21.8	41.9	18.9	70.7	16.8	108.9
BDE-66	0.3	0.3	0.2	0.2	0.3	0.3	0.1	0.1	0.0	0.1	0.3
BDE-71	3.8	1.6	2.7	0.8	1.0	1.0	1.9	0.1	1.0	0.3	0.2
BDE-85	1.1	0.4	2.2	0.1	0.4	0.5	0.3	0.1	0.6	0.1	0.9
BDE-99	17.6	31.5	21.3	11.3	23.1	7.4	5.8	9.2	25.5	8.2	38.6
BDE-100	9.1	16.4	18.7	4.4	9.6	2.7	5.3	3.7	9.0	3.2	13.7
BDE-138	1.6	0.9	0.2	0.2	0.2	0.2	0.2	0.2	nd	0.1	1.0
BDE-153	6.9	3.9	3.0	0.8	3.5	0.5	0.6	1.8	nd	1.4	1.1
BDE-154	4.2	4.4	3.7	0.6	2.6	0.9	0.7	1.1	nd	1.1	0.9
BDE-183	7.2	1.3	3.7	1.2	4.1	1.1	1.3	1.5	3.5	0.8	7.8
BDE-190	6.7	2.1	0.5	0.4	1.5	0.2	0.2	0.2	0.2	0.3	0.7
Σ_{13}PBDEs	163.5	155.9	175.7	51.9	105.0	38.7	62.7	38.3	120.6	33.4	180.9

Table 3. 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.)	308	Okumura et al., 2004
			DL-PCB TEQ (pg.g^{-1}w.w.)	0.4	
Flying crab (Liocarcinus 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 sp.*)	whole body	Sendai Bay (Japan)	2378-PCDD/Fs (pg.g^{-1}w.w.)	6.6	Okumura et al., 2004
			2378-PCDD/F TEQ (pg.g^{-1}w.w.)	1.1	
Edible crab (*Cancer pagurus*)	muscle	Grenland fjords (Norway)		3.5	Knutzen et al., 2003
		Southern Norway	2378-PCDD/Fs (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		0.25	Karl et al., 2002
		Greenland		0.12	
Rock crab (*Charybdis japonica*)	muscle	Tokyo Bay (Japan)	2378-PCDD/Fs (pg.g^{-1}w.w.)	12	Sakurai et al., 2000
			2378-PCDD/F TEQ (pg.g^{-1}w.w.)	2.6	
Green crab (*Carcinus aestuarii*)	whole body	Venice/Orbettello Lagoons (Italy)	2378-PCDD/Fs (pg.g^{-1}w.w.)	9-152	Jimenez et al., 1998
			2378-PCDD/F TEQ (pg.g^{-1}w.w.)	1.1-5.2	
Lobster (*Hommarus americanus*)	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 (*Chionoecetes opilio*)	whole body	St Lawrence Estuary (Canada)	2378-PCDD/Fs (pg.g^{-1}w.w.)	50-70	Brochu et al., 1995
		Saguenay Fjord (Canada)		31-61	
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	Voorspoels et al., 2003
		Belgian North Sea (Europe)		0.02-0.08	
Flying crab (*Liocarcinus holsatus*)	whole body	Scheldt Estuary (Europe)		1.2-30	Voorspoels et al., 2003
		Belgian North Sea (Europe)		0.4-1.4	
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 congeners: BDE28, 47, 99, 100, 153, 154

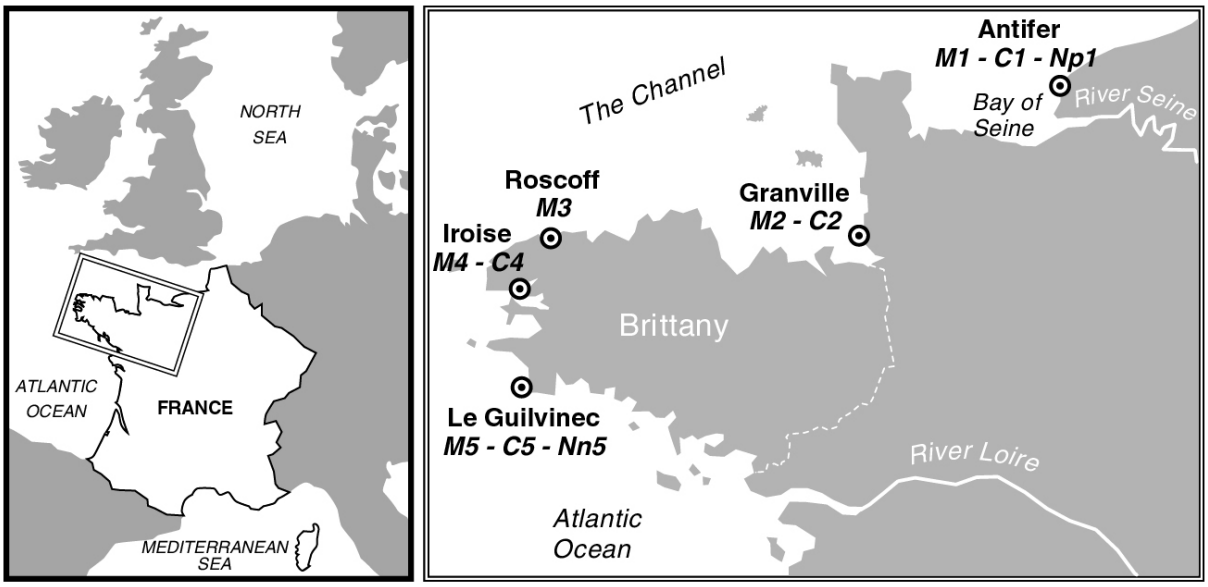

Fig. 1. Map of the sampling areas. M = *Maja brachydactyla*; C = *Cancer pagurus*; Np = *Necora puber*; Nn = *Nephrops norvegicus*.

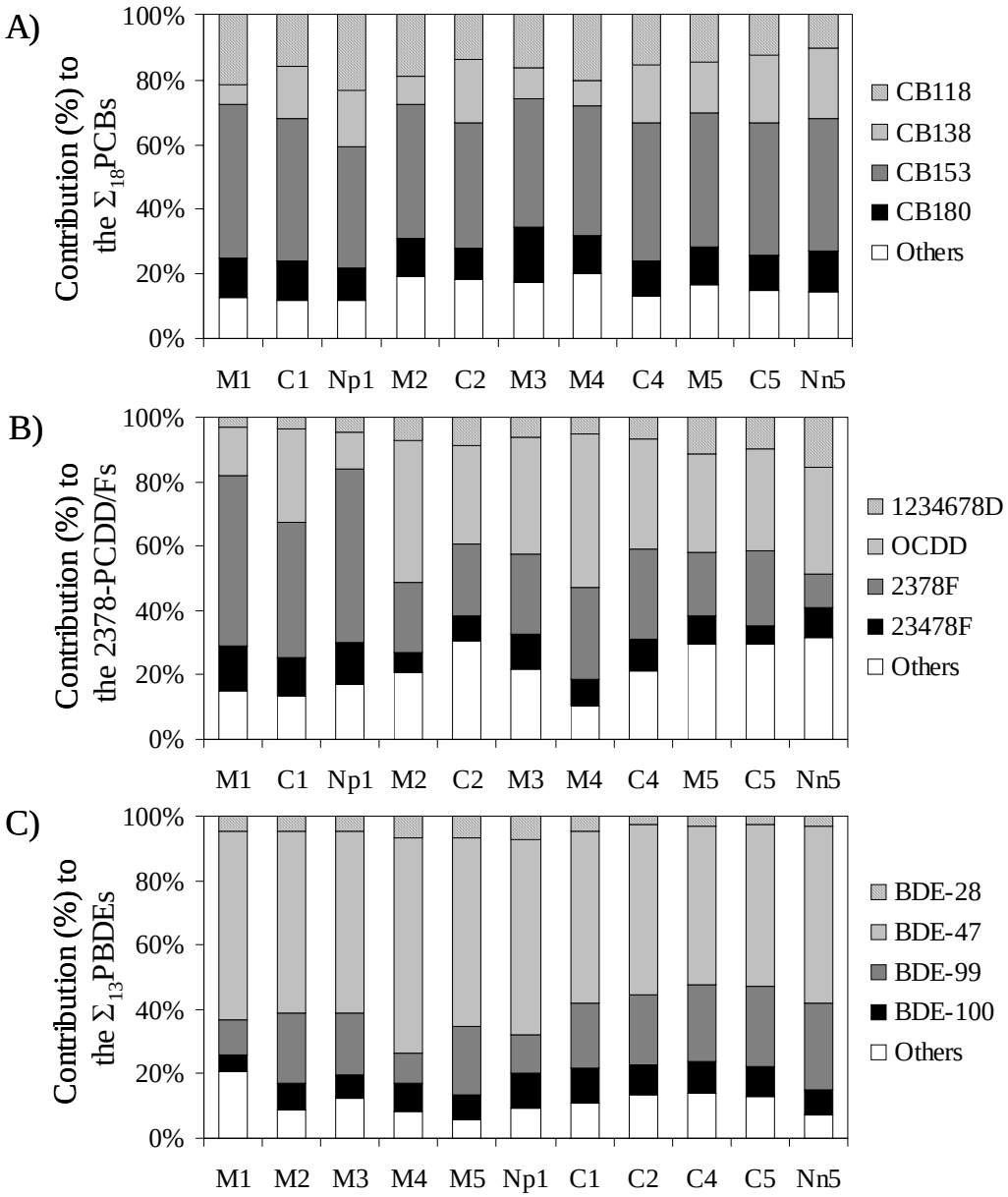

Fig. 2. PCB (A), PCDD/F (B) and PBDE (C) patterns in the muscle of crustaceans from Antifer (M1, C1, Np1), Granville (M2, C2), Roscoff (M3), Le Conquet (M4, C4) and Le Guilvinec (M5, C5, Nn5).

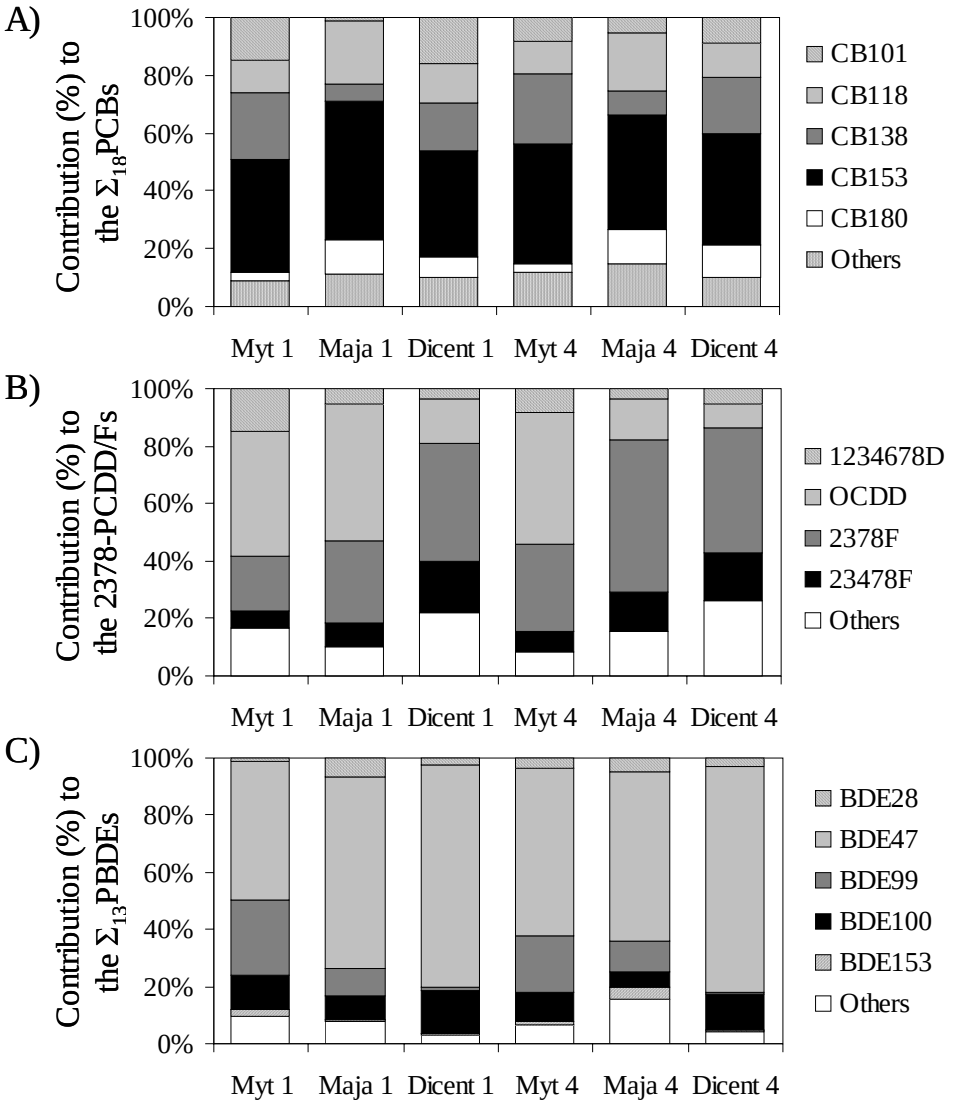

Fig. 3. PCB (A), PCDD/F (B) and PBDE (C) patterns in mussels, spider crabs and sea bass from Antifer (Myt 1, Maja 1, Dicentr 1), and Le Conquet (Myt 4, Maja 4, Dicentr 4).

Supplement Information

Table S1. Biological characteristics of the sampled crustaceans.

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	M1	4	535 ± 205	11.5 ± 1.8	1.9	80
	Cancer pagurus	edible crab	C1	3	463 ± 284	13.8 ± 2.4	2.6	77
	Necora puber	velvet swimming crab	Np1	10	84 ± 3	6.3 ± 0.6	2.5	77
Granville	*Maja brachydactyla*	spider crab	M2	3	1177 ± 185	15 ± 1.0	2.0	82
	Cancer pagurus	edible crab	C2	3	543 ± 31	14.9 ± 0.5	2.2	79
Roscoff	*Maja brachydactyla*	spider crab	M3	3	1090 ± 135	14.3 ± 0.6	2.3	78
Le Conquet	*Maja brachydactyla*	spider crab	M4	6	1642 ± 423	17.1 ± 1.5	2.3	78
	Cancer pagurus	edible crab	C4	5	921 ± 129	17 ± 0.9	1.9	78
Le Guilvinec	*Maja brachydactyla*	spider crab	M5	3	618 ± 109	12.8 ± 0.4	2.0	78
	Cancer pagurus	edible crab	C5	3	1001 ± 158	17.3 ± 0.3	1.3	78
	Nephrops norvegicus	norway lobster	Nn5	20	20 ± 7	3.0 ± 0.3	2.2	77