PCBS, PCDD/FS AND PBDES IN CRUSTACEANS FROM DIFFERENT FRENCH COASTAL SITES

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Introduction

There is very few information on the presence of persistent organo-halogenated contaminants in crustaceans from the French coast. A previous report[1] pointed out high levels of dioxins in seafood marketed in France, particularly in large crustaceans. However, these data were very limited and the dioxin concentrations were reported on a fat basis. In this paper new data on PCBs, PCDD/Fs and PBDEs in crustaceans will be discussed.

Our first objective was to obtain an estimation of the concentration ranges of those contaminants in large crustaceans from the French coast. For that purpose, three areas were selected : the first one in the Bay of Seine, the others along the Brittany coast. According to results obtained within the French marine pollution monitoring programme (RNO), these sites are assumed to represent very opposite situations : on the one hand the coasts of Brittany which are very little contaminated by such man-made contaminants of industrial origin, on the other hand the Bay of Seine where highest PCB levels are currently measured in mussels and other species living close to the Seine Estuary[2]. The second objective was to contribute to a better understanding of the factors acting on the distribution of these contaminants. Our approach is based on a detailed examination and comparison of the contaminant fingerprints in biological tissues according to either the origin of the samples, or the type of species in relation with their trophic position, feeding mode or metabolising capacities.

Material and Methods

Sampling strategy

Three main sites were studied (Fig 1). The species collected were edible crabs (*Cancer pagurus*) in Antifer, Granville and Le Guilvinec, spider crabs (*Maja brachydactyla*) in Granville, and prawns (*Nephrops norvegicus*) in Le Guilvinec. All crustaceans were obtained from local fishermen in February 2003. For each species, muscle sampled were carefully dissected from the inner body part to prepare a pooled sample from six individual specimens.

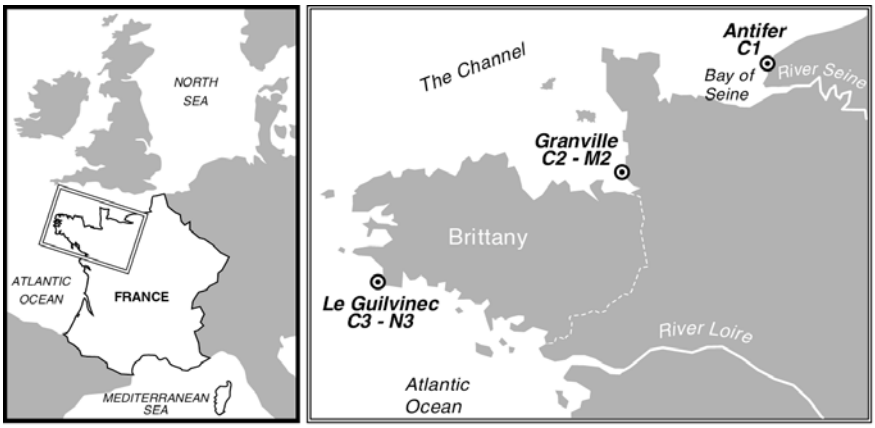

Figure 1 : Map of the sampling stations. M = *Maja brachydactyla*; C = *Cancer pagurus*; N = *Nephrops norvegicus*.

Analysis

Biological material was freeze dried before analysis. The analysis were carried out on dry material.

After a Soxtec extraction (hexane/acetone = 45 : 10, v/v), PCBs (52, 101, 105, 118, 128, 132, 138, 149, 153, 156, 170, 180, 187, 194) were analysed by GC-ECD on a Hewlett Packard 5880 chromatograph equipped with a CP Sil 19 CB capillary column.

PCDD/Fs, dioxin-like PCBs (DL-PCBs) and PBDEs (17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190) were extracted (Soxhlet extraction) with a solvent mixture of toluene-cyclohexane and analysed by HRGC-HRMS on a gas-chromatograph coupled to an Autopsec Ultima (Micromass, Manchester, UK) operated in the EI ionisation mode at 10000 resolution and SIM acquisition.

Results and discussion

Contaminant levels

PCBs, PCDD/Fs and DL-PCBs are much higher in crabs from Antifer compare to other sites which confirms a chronic pollution of the whole Bay of Seine mainly due to contaminant inputs by the Seine River[2] (Table 1). However, in each group of contaminants, differences between high and low contaminated sites are not so large. As an example, PCB concentrations differ by a factor of approximately 10 in crustaceans whereas the TEQ(PCCD/Fs) is only between 2 to 7 times higher for samples from the Bay of Seine than in those from Brittany. The contribution of PCBs to the total TEQ (PCDD/Fs and DL-PCBs) decreases from 60% close to the Seine Estuary to less than 50% in crabs from Brittany. TEQs in crustaceans from Granville and Le Guilvinec are lower than those measured in crabs collected in zones considered as very little contaminated areas in Italy (1.1 TEQ $pg.g^{-1}$ d.w.)[3].

The concentrations of PBDEs in crustaceans show a similar geographical variation except in prawns (N3 = 342 $p.g^{-1}$ d.w.). In those species the higher levels are probably due to their habitat, trophic mode and origin; they live and feed on sandy-mud bottom where superficial sediment could be enriched by settling particles of terrestrial origin.

Table 1 : PCBs, PCDD/Fs and PBDEs in crabs, spider crabs and prawns ($pg.g^{-1}$ d.w.).

	C1	C2	M2	C3	N3
PCBs	41250	4420	2300	3240	4700
Sum PCDDs	9.8	7.2	2.9	2.1	11.9
Sum PCDFs	30.7	11.7	4.9	2.9	10.2
TEQ (PCDD/Fs)	1.61	0.72	0.30	0.25	0.82
TEQ (DL-PCBs)	2.51	0.57	0.39	0.25	0.75
PBDEs	156	105	52	33	342

Contaminant distribution

Very similar contaminants distributions are observed in crustaceans. In figures 2, 3 and 4, the contaminant distributions in crustaceans are compared to that in mussels. These filter-feeder organisms accumulate contaminants from detritic suspended particles and from phytoplankton, and possess a very limited capacity to biotransform contaminants. On the opposite, crustacean are situated at higher trophic levels, feed on various organisms and are able to biotransfrom contaminants.

For crustaceans, the main PCB congeners are the more chlorinated compounds : their relative abundance is as follow CB153 (25-40%) > CB138 (15-20%) > CB180 and CB187 (7-9%) (Fig. 2). These more hydrophobic compounds are associated to fine particles of superficial sediment, enter the food chain and resist to biotransformation. On the contrary, the characteristic PCB fingerprint in bivalve molluscs shows the prevalence of the least chlorinated congeners and consequently the more soluble (CB52, CB101, CB118) and the less persistent ones. Moreover, several component ratios point out differences between the PCB distribution in bivalves and in crustaceans. The CB138/CB153 ratio decreases from 0.8 in mussels to around 0.6 in crustaceans and unlike mussels, crabs present CB149/CB118 and CB132/CB105 ratios lower than 1. These differences can be

explained by specific metabolisation capacities, crustaceans being able to partially biotransform PCBs.

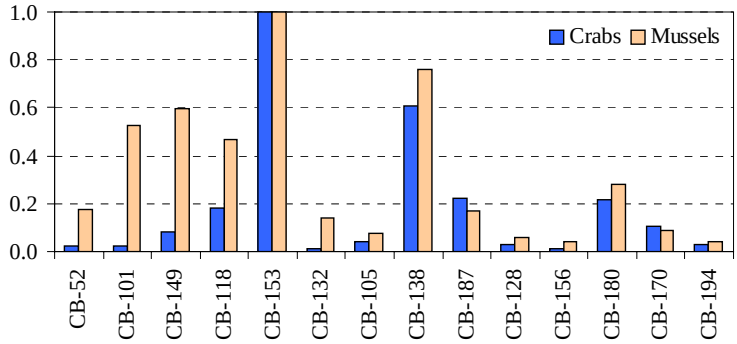

Figure 2 : PCB profiles in crabs and mussels collected in Antifer (standardization compared to the CB153).

The distribution of dioxins in all crustacean species is characterized by the prevalence of the PCDF (45-75%) compared to the PCDD. The main compounds are the OCDD (28-46%) of PCDDs, and TCDF (46-70%) of PCDFs (Fig. 3). These fingerprints are very similar to those observed in mussels and also look like to typical pattern of combustion processes[4].

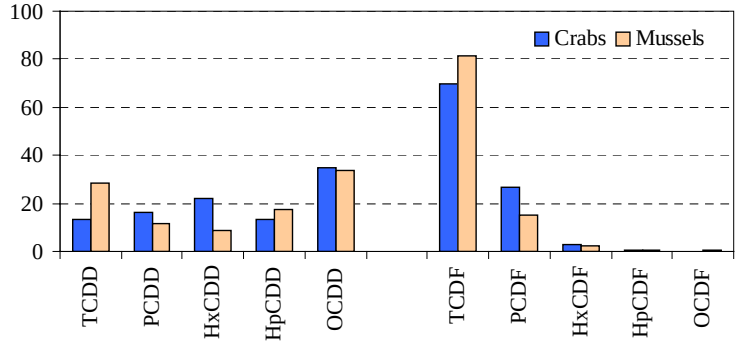

Figure 3 : PCDD/F profiles in crabs and mussels collected in Antifer (standardization compared to ΣPCDDs and ΣPCDFs).

The relative distribution of the toxic congeners are more or less the same in crustaceans (Fig. 4). The main compounds (on concentration basis) are OCDD and 2378-TCDF, their relative ratio become inverted in crabs from Antifer compared with other samples. This is probably due to chronic and large contaminant inputs by the Seine River. In organisms from South Brittany (C3, N3), levels are much lower but 2378-TCDF is less present in prawns than in crabs which is probably due to their way of life.

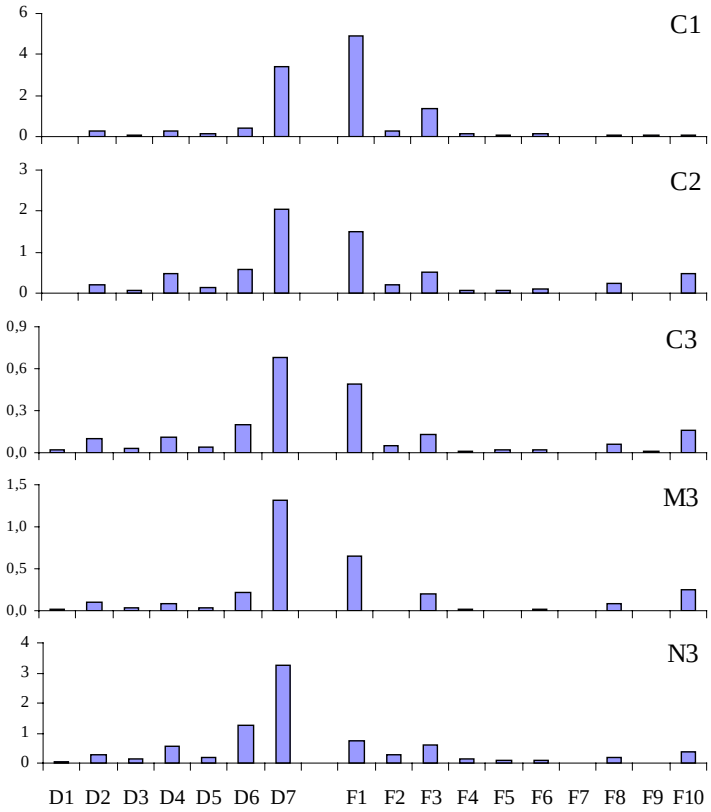

Figure 4 : Distribution of the 2,3,7,8-substituted PCCD/Fs.

In the group of PBDEs, BDE47 is the main congener, representing 50 % of the sum, and the major compounds are BDE47> BDE99> BDE100> BDE28> BDE154> BDE153 (Fig. 5). Comparable results are observed in mussels. A particular attention must be drawn to the congeners CB99 and CB153 which can theoretically be metabolised in CB47 by processes of debromination[5,6]. In dab muscle from the Belgian North Sea and the Scheldt Estuary[5], BDE47 accounts for 75% of ΣPBDEs and the main ones are BDE47> BDE100> BDE99> BDE153> BDE154> BDE28. These profile differences would be due to different capacities of PBDE biotransformation of these species.

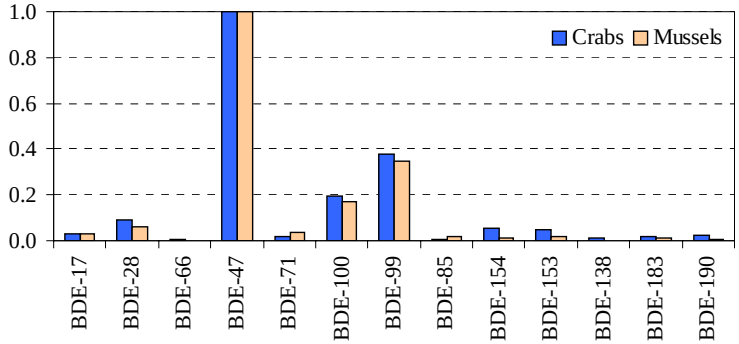

Figure 5 : PBDE profiles in crabs and mussels collected in Antifer (standardization compared to the BDE47).

Acknowledgments

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