DIOXINS AND DIOXIN-LIKE PCBS IN MUSSELS AND FISHES FROM THE FRENCH COASTAL WATERS

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Introduction

PCBs, PCDDs and PCDFs are widespread contaminants of great environmental and health concerns because of their persistence, their capacity to bio-magnify in food chains and their toxicity. The main objective of this work was to obtain the first data on the dioxin contamination in the French coastal environment. For that purpose mussels or oysters were collected all around the French coast and analysed for PCDDs and PCDFs. Non-ortho, mono and di-ortho PCBs, or so-called dioxin-like PCBs, which have similar toxicity mechanisms as 2378-TCDD and possessing toxicity factors in equivalent to 2378-TCDD (TEF) (1), were also analysed as they have been recently recognised to contribute importantly to the Toxicity Equivalent Quantity. Besides this main objective, the project gives us the opportunity to get a rough estimation of the potential of dioxins and dioxin-like PCBs to bioaccumulate into food chain in view of their hydrophobic and toxic properties and thus their potential health effects to higher consumers.

Methods and Materials

Sampling strategy

The species collected were blue mussels (*Mytilus edulis* or *M. galloprovincialis*) or oysters (*Crassostrea gigas*) in marine coastal waters except of zebra mussel (*Dressenia polymorpha*) from the river Seine (sample D4). The sampling stations were chosen in order to cover the whole French coastline and the various orders of magnitude of contamination based on PCB results. Ten adult fishes were also sampled at four stations; for each station pooled samples of fish muscle and fish liver were analysed.

Contaminants analysis

Biological material was freeze dried before analysis. The extraction of an exactly weighted amount of dry material was carried out using a solvent mixture of toluene-cyclohexane in a hot Soxhlet extraction for twelve hours. After solvent evaporation the extract is weighed to obtain the fat content of the sample. A fat aliquot, typically 1-3 g, is diluted in hexane and sulfonated by sulfuric treated silica to destroy lipids. The extract is then pre-separated and thoroughly cleaned on three successive chromatographic columns: modified silica, alumina and activated charcoal–celite. Finally the clean extracts were 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

PCDDs and PCDFs in shellfish.

PCDD/F concentrations in mussels and oysters vary in a large range (figure 1). In most of the

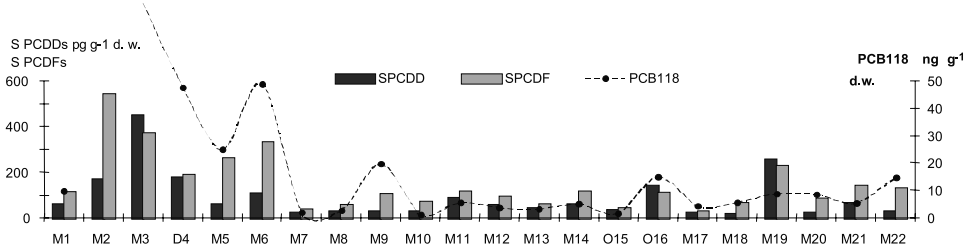

Figure 1. PCDDs, PCDFs and PCB118 in mussels and oysters from the french coasts.

samples the contamination by PCDFs is higher than that of PCDDs, by a factor of two on average. Data are also given for PCB118; this intense compound of the dioxin-like PCB group is also amongst the « indicator PCBs » commonly followed within the monitoring programmes. It has been shown that, in a same type of organisms, filter-feeders in that case, the PCB fingerprint remains approximately constant whatever the origin of the specimen; consequently any congener can be used to study the PCB contamination. PCDDs and PCDFs follow a similar geographical trend as PCBs. Estuarine samples are generally more contaminated, particularly from samples from the Bay of Seine.

Table 1. PCDDs and PCDFs in shellfishes (pg g^{-1} d.w.). Corrected mean and median are calculated after rejecting outliers

	Min	Max	Mean	Median	Corr. Mean	Corr. Med.
SumPCDDs	20.6	450	91±101	59	65±49	52
SumPCDFs	30.4	543	151±127	112	132±94	110

Concerning the TEQ (table 2 and figure 2), the contribution of the dioxin-like PCBs to the total TEQ is very important (60 to 80 %).

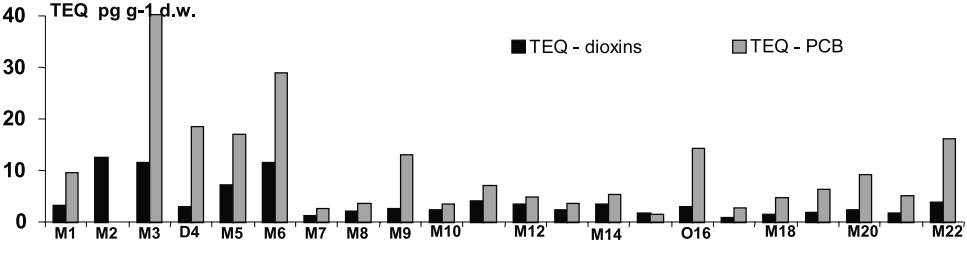

Figure 2. TEQ in mussels and oysters from the French coasts

These first results establish the current status of the contamination of the French coastal marine environment by dioxins and dioxin-like PCBs. They were not obtained in view of assessing the population exposure to dioxins due to seafood consumption. However the recently proposed tolerable

intake that includes both dioxins and dioxin like PCBs are easily reached.

A tolerable weekly intake (TWI) established at 14 pg TEQ /kg body weight would be reached by eating approximately 480 g mussels a week (adult, 60 kg b.w, ,median concentration TEQ 8.8 pg g^{-1} in mussel with a water content 80 % water).

Table 2. TEQ in shellfishes (pg g^{-1} d.w.)- Corrected mean and median after rejecting oultliers

	Min	Max	Mean	Media	Corr. Mean	Corr. Med.
TEQ PCDD/Fs	0.8	12.6	4.0±3.5	2.8		
TEQ PCBs	1.6	40.2	10.4±9.7	6.4	7.8±5.4	5.4
Total TEQ	3.4	54.7	13.9±12.4	8.8	13.9±12.4	

Contaminants distribution in bivalves

The distribution of dioxins and dioxins-like PCBs is very similar in most of the shellfish samples and characterised by the predominance of PCDFs over PCDDs. Within the dioxins, each group of chlorinated homologs is present in low and variable proportions, around 10-20 % each; in that of furans the TCDFs are the most abundant (80 %) and the contribution of other groups decreases with the number of chlorine atoms (approximately 15, 3, 2, and 1 % for PeCDF > HxCDFs > HpCDFs > OCDF respectively).

The dioxin fingerprint in low contaminated molluscs results from a combination of substances from various sources whose origins cannot be easily elucidated. However, the above features would give an indication of the predominance of the combustion processes on the origin of dioxins in the coastal environment. The contamination of coastal areas remains at low levels reasonably due to a mainly exposure to westerly oceanic winds except in the case of estuarine samples.

As far as the 2378-substituted compounds are concerned, the composition in bivalves as roughly the same. Based on their concentrations, the main compounds are OCDD, 1234678-HpCDD, 123678-HxCDD in the dioxin group, 2378-TCDF and 23478-PCDF in the group of furans, PCB congeners PCB118, 105, 156, 77, in the dioxin-like PCB group whereas, taking into account the TEFs, the main contributors to the TEQ are 12378-PCDD, 2378-TCDD, 23478-PCDF, 2378-TCDF and PCB 126, 118, 156 and 157.

Contaminants in fishes and bivalves : bioaccumulation or biotransformation ?

Besides this first assessment on the status of the dioxin contamination in the French coastal environment we were interested in the fate of those hazardous compounds in the marine foodwebs. For that purpose, dioxins and dioxin-like PCBs were also measured in a few fish samples, both in liver and in muscle. Contamination levels in fish are more or less in agreement with previously published data. Nevertheless such an inventory of dioxins in seafood requires a more appropriate sampling protocole.

However this limited set of results demonstrates that the dioxin composition in fish differs from that observed in bivalves molluscs. More over, a very similar pattern is observed both in liver and in muscle from the same specimen. Remarkably the contamination pattern in fish from coastal contaminated waters is the same as the one in the cod liver oil. This sample bought at a chemist's is currently used as a workable fish oil in the lab and comes from open sea in the Northern Atlantic. The observation of an identical contamination pattern in our fishes and in cod liver oil would suggest that the biological factors act on the distribution of the compounds markedly.

To get insight the fate of these contaminants in the marine foodweb, their distribution in mussel were compared with that in fish: bivalves molluscs feed on suspended matter and detritus are not able

to metabolise xenobiotics whereas, on the opposite, fishes (Flounder, *Platichtys flesus*, in our given example) are higher predators, eat small crustaceans, bivalves, various smaller fish species and are able to biotransform contaminants. An apparent bioaccumulation factor defined for any contaminant as the concentration ratio in fish (ABF= Conc. in fish/ Conc. in mussel) was calculated that is largely affected by the biological factors acting on bioaccumulation, mainly feeding rate, diet composition and growth. By normalising the concentrations to a common substance, the fate of the various compounds can be compared independently on the way they enter the food chain. Thus the bioaccumulation factor of any contaminant *X* becomes the ratio of normalised concentrations or Metabolisation Index:

M.I. = (*X* fish/PCB153 fish) / (*X* mussel/PCB153 mussel).

These ratios were calculated for dioxins, for dioxin-like PCBs, and for indicator PCBs and PAHs. For the various compounds, the M.I .vary differently depending on their belonging to different structurally related groups (figure 3). It appears that compared to the well known persistent and bioaccumulated PCBs and to PAHs which, on the opposite, are readily biotransformed in the foodweb, dioxins, (PCDDs and PCDFs), behave rather like PAHs being partially biotransformed in such an over-simplified food chain (mussel - fish).

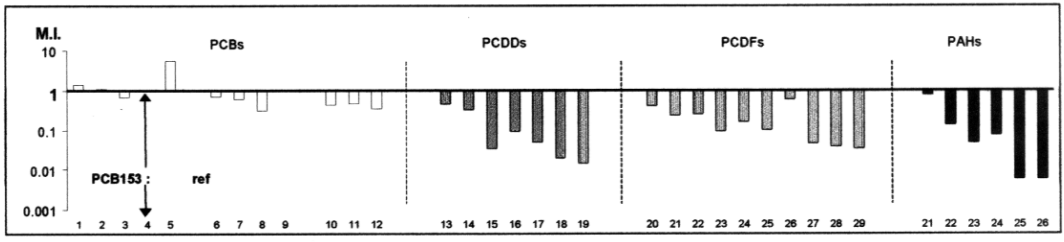

Figure 3. Metabolization Index for PCBs, PCDDs/Fs and PAHs.(unitless on a log scale). (numbers denote compounds, 1-12 correspond respectively to PCBs (52, 101, 138, 153, 180, 105, 118, 123, 156, 77, 126, 169); 13-19 to PCDDs (2378-TCDD, 12378-PCDD, 123478-Hx CDD, 123678-HxCDD,234678-HxCDF, 123789-HxCDD, 1234678-HpCDD, OCDD); 20 to 30 to PCDFs (2378-TCDF, 12378-PCDF, 23478-PCDF, 123478-HxCDF, 123678-HxCDF, 234678-HxCDF, 1234678-HpCDF, 1234789-HpCDF, OCDF), .30 to 35 to PAHs (anthracene, pyrene, benzanthracene, chrysene, benzo(k) fluoranthene, benzo(a) pyrene).

In view of their hazardous effects it is of great concern to investigate more precisely the transfer of dioxins in the marine food chain, particularly to know if bioaccumulation and biotransformation processes necessarily imply an increase of the TEQ and also, to evaluate at which levels in the trophic chains these change might occur.

Acknowledgments

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