PCDDs AND PCDFs IN THE MARINE FLATFISH DAB (Limanda limanda) FROM A CONTAMINATED ESTUARY IN FRANCE

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Introduction

This paper presents the results of a study of the contamination of the marine flatfish dab (Limanda limanda) from French coastal waters of the Eastern English Channel by polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Fish samples were collected at selected sampling sites located under the influence of the Seine river estuary, an area known to be contaminated by numerous persistent organic compounds. The level of contamination of fish in that area was compared to a less contaminated site, the Somme Bay. Concentration levels of PCDDs and PCDFs were determined by HRGC-HRMS in muscle and liver tissues of juvenile or adult fish of both sexes.

The results of this study provide original and scarce information on the environmental contamination levels of marine fish from French coastal waters by highly toxic, persistent and bioaccumulative contaminants. The results presented here are part of a project carried out to study the relationship between the chemical contamination and the occurrence of DNA lesions in dab. Results of the determination of genotoxic effects have been presented elsewhere [1]. Further assessments of the chemical contamination of dab by other persistent organic pollutants will also be made within this project.

Methods and Materials

Sampling sites

Fish samples were collected in September 2001 on board of the French Oceanographic Vessel "Gwen Drez" from different sites located in the French coastal waters of the Eastern English Channel. Six sites were selected for sampling (figure 1) : four sites (ES, An, EO, G) were located in the Seine Bay, a highly industrial and urban area, and two sites (BS1, BS2) located north in a less-contaminated zone (the Somme Bay). Dab were collected at each sampling site during this cruise except at the most remote location -site G.

Fish sampling and analysis

Fish were collected at depth of 7-40 meters using a trawl and sorted according to sex and length. Two age classes were studied : juvenile fish –less than 2 years (14-18 cm length)- and adult fish -between 2.5 and 4 years (22-26 cm length). Muscles and livers were collected and pooled for 15 individual fish from each age class and stored at –20°C until further analysis.

Analysis of muscle and liver samples were carried out according to NF-EN 1948 and NF EN 1528-2 methods. Briefly, samples were homogenized, freeze-dried, spiked with sixteen ^{13}C-labelled dioxins and furans, and extracted using Accelerated Solvent Extraction (ASE). Extracts were treated with concentrated sulfuric acid, and cleaned sequentially on activated charcoal, silica and alumina columns. Analysis were performed by HRGC-HRMS with a MAT 95 XL (Thermo Finnigan, Bremen,

Germany) operated in EI ionisation mode at a resolution of 10 000 in the selected ion monitoring mode (SIM), and equipped with a Hewlett-Packard (Palo Alto, CA, USA) 6890 Gas Chromatograph and a 60 m x 0.25 mm i.d. (0.25 µm film thickness) DB-5 MS column. Seven PCDDs and ten PCDFs were quantified for individual components by isotopic dilution.

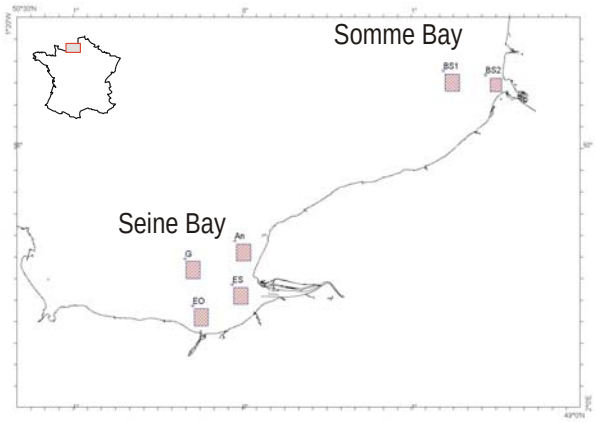

Figure 1 : Location of sampling sites

Results and Discussion

Concentration levels in muscle and liver and toxicity equivalency

Concentrations of individual PCDDs and PCDFs were determined in both muscle and liver tissues of dab. At all sampling sites, male and female of the same age class –juvenile or adult- were considered. The determination of the effect of age on the contamination level could not be assessed on that set of results. Furthermore, no significant differences were observed between the contamination levels determined in male and female individuals of the same age class at a specific site.

For both liver and muscle, the highest levels were recorded for samples collected at the ES site, located in an area under the influence of the Seine river estuary, a highly-contaminated industrial and urban site. These levels are four times higher than those recorded at the BS1 site (figure 2). Results from a study of the contamination of shellfish by PCDD/Fs have shown that the Seine Bay was the most contaminated area along the French coasts [2].

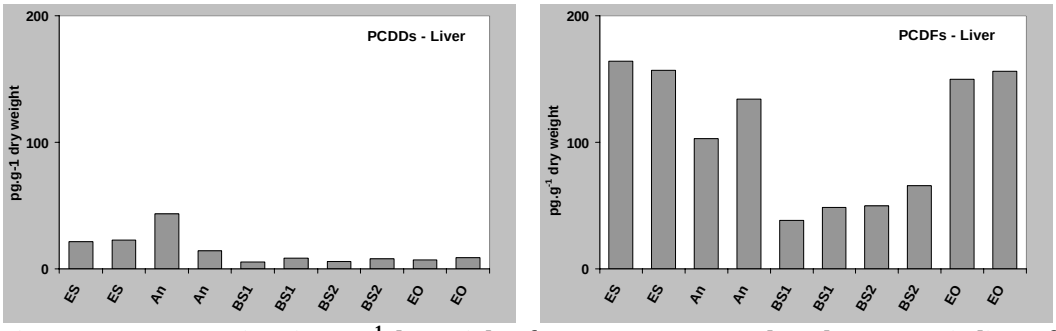

Figure 2 : Concentrations in pg.g^{-1} dry weight of PCDDs, PCDFs, and total PCDD/Fs in liver of dabs at different sampling locations in the Eastern Channel, France.

Concentrations levels for total PCDDs and PCDFs in liver are between 43.5 pg.g^{-1} dry weight (d.w.) at BS1 site and 185.9 pg.g^{-1} d.w. at ES site, whereas the concentrations in muscle tissues are in the 4.3 pg.g^{-1} (BS1) d.w. to 16.9 pg.g^{-1} (ES) range at these sites. For most of the samples, concentrations of PCDFs exhibits higher levels than PCDDs. For liver samples, PCDFs contribute from 70 % to 96 % of the total PCDD/Fs. In the muscle tissue samples, concentration of many individual compounds are below the detection limit of the method.

At all sites and for all type of samples, the contamination levels of total PCDD/Fs determined in liver are at least ten times higher than those in muscle tissue. The higher accumulation of hydrophobic contaminants like dioxins and furans in high proportions in fish liver has been previously demonstrated, in relation to the highest content of lipids in liver [3].

Concentration ranges of PCDDs and PCDFs are presented on a dry weight basis in table 1 for liver and muscle samples and after conversion to 2,3,7,8-TCDD toxicity equivalents (TEQs), by using Toxic Equivalency Factors (TEFs) consensus values for fish [4]. In relation to the highest concentration levels of the compounds, concentrations of TEQs are greater in liver, ranging from 6.5 pg.g^{-1} d.w. (or 3.3 pg.g^{-1} w.w.) to 26.9 pg.g^{-1} d.w (12.9 pg.g^{-1} w.w.). These values are in the range of those found in shellfish from the French coastal zones, and would be much higher if the contribution of dioxin-like PCBs would be included [2].

		PCDDs pg.g^{-1} d.w.	PCDFs pg.g^{-1} d.w.	PCDD/Fs TEQ pg.g^{-1} d.w.
MUSCLE	Min	< L.D.	1.4	0.07
	Max	12.6	7.8	1.03
LIVER	Min	5.3	38.2	6.5
	Max	43.5	164.3	26.9

Table 1 : PCDDs and PCDFs concentration ranges in liver tissues of dab collected in the Eastern English Channel. Results are expressed on a dry weight basis in pg.g^{-1} and after conversion to 2,3,7,8-TCDD toxicity equivalents with TEF consensus values for fish. Congeners below the detection limit of the method were counted as equal to zero.

Distribution profiles

The congener distribution of PCDDs and PCDFs show the same pattern for all samples for both liver and muscle over the different sites, and independently of sex and age. The distribution patterns are dominated by tetra- and pentachlorodibenzofurans for PCDFs and by octa- hexa- and pentachlorodibenzo-p-dioxins for PCDDs (figure 3) and are similar to those reported in other studies for marine or fresh water fish [5]. Among PCDFs, the most prevalent congener is the 2,3,7,8-substituted isomer in both liver and muscle, followed by the 2,3,4,7,8-substituted pentafuran, whereas the 2,3,7,8-TCDD isomer is always less than or near the limit of detection. The most prevalent dioxin congener in liver and muscle is OCDD. This compound has been identified as the most prevalent dioxin in sediments in relation to atmospheric particles from combustion processes [6, 7]. The distribution pattern observed in fish is the result of both exposition to contaminants from various sources and to the ability of organisms to metabolize the compounds. Our results suggest that fish from the Seine Bay and from the Somme Bay are exposed to the same type of sources. In the coastal marine environment, the sources of contamination by PCDD/Fs are from combustion processes through atmospheric deposition and sewage sludge, urban and industrial sources through river discharges.

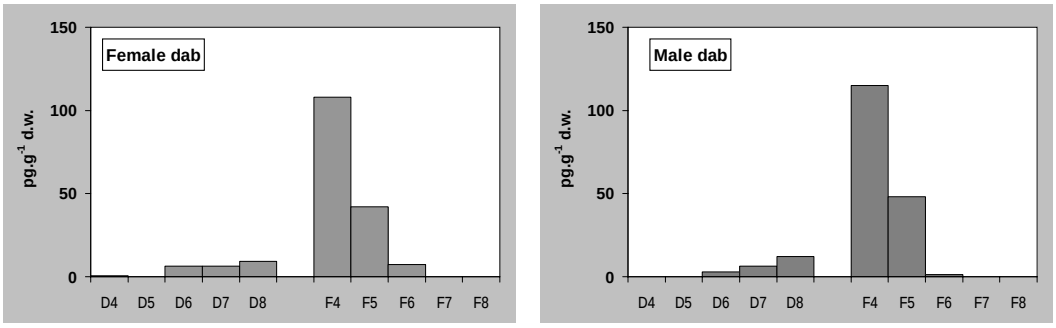

Figure 3 : Distribution profiles of PCDDs and PCDFs in liver of juvenile dabs at ES sampling site. D4, D5, D6, D7, D8 are for tetra-, penta-, hexa-, hepta- and octachloro-dibenzo-p-dioxins respectively. F4, F5, F6, F7, F8 are for tetra-, penta-, hexa-, hepta- and octachloro-dibenzofurans respectively.

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