PCB AND PCB-DL CORRELATIONS IN MARINE ORGANISMS: A POSSIBLE APPROACH TO THE ESTIMATION OF THE TEQ?

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Introduction

High levels of PCBs and dioxins (PCDD/Fs) in the environment presents a risk of adverse effects to the wild life, to the functioning of ecosystems and to the health of consumers of high trophic level, including human beings. In environmental studies, PCBs in fish are currently measured either as technical mixture equivalent, typically in Aroclor equivalent in US or as congener specific concentrations based on a limited set of 7 Indicator-PCB congeners, as recommended in Europe (BCR-CE; ICES). In food control programmes, the high concern on dioxin-like PCBs (DL-PCBs) requires the measurement of the toxic non-ortho and mono-ortho substituted PCB congeners: the reference method for the analysis of dioxins and DL-PCBs relies on a complex clean up procedure of the extract and the final instrumental determination of the isolated compounds by high resolution gas chromatography - high resolution mass spectrometry and isotopic dilution. Bioanalysis has been proposed as an alternative to these time consuming and expensive HRGC-HRMS chemical analyses. However, the detailed examinations of the contaminant distribution in fish appear to offer another attractive way to estimate dioxin like compound concentrations in fish[1-3], thanks to correlations between their indicator-PCB and DL-PCBs content. Similarities in the composition of PCBs in fish and marine biota have also been observed reported. It has also been observed that the contribution DL-PCBs to the total TEQ in fish was much more important than that of PCDD/Fs, approximately 3-5 times higher. Here, our approach is to confirm these observations on a large database including results in different fish species and marine species from various geographic origins. The observed correlations between the measured TEQ and the concentrations of the main compounds will be discussed as possible relationships that could be used to estimate dioxin equivalent quantity from the concentrations of more easily measured components such as Ind-PCB.

Material and methods

The data base is a compilation of PCDD/F and PCB measurements in marine organisms from environmental studies on the coastal environment [(4-6)] and of results on various fish from the open sea. All results where obtained by HRGC-HRMS and isotopic dilution in three different laboratories accredited for food control. The data (222 samples) include measurements on bivalves molluscs (88 samples: mussels-75; oysters 6; scallops 8 from the French coastal waters, the Bay of Seine (Eastern Channel) is more particularly represented (30s/88s). A limited number of results on fish and crustaceans were also obtained in those investigations and added to the database. An important part of the data (78s/222s) comes from food control programmes on marketed fish conducted by the food control Directorate (DGAL) of the Ministry of Agriculture and Fishing. Very different fish species (35) are represented in this dataset, most of them from regional seas around France. A few results on imported fishery products (18s/78s) were also included in the base. Hence, the final spreadsheet is made of 222 observations described by their biological characteristics, by primary determinands 7 indicator-PCB congeners, 12 DL-PCBs, 17 (2378-substituted PCDD/F congeners and by additional calculated parameters (1998 WHO-TEQ[7]).

Results and discussion

Elementary statistics

Results are presented (tab.1) for CB118 that belongs to both groups of indicator PCBs and of DL-PCBs and thus is one main contributor to the DL-PCB-TEQ, for CB153 one major PCB congener in biota, for the sum of the seven indicator-PCB congeners. The data are also given for PCDD/F-TEQ, DL-PCB-TEQ and the total TEQ, as well as the relative contribution of DL-PCBs to the total Toxic Equivalent Quantities. In all these samples, dioxin levels (TEQWHO-PCDD/Fs) are well below 4 $pg.g^{-1}$ w. w., the maximum level for dioxins (PCDD/Fs) in fish and fishery products according to the European regulation[8]. The median PCDD/F-TEQs are in the range 0.1-0.35 $pg.g^{-1}$ w.w., one order of magnitude lower than the limit The total TEQ median concentrations vary in the range 0.2-1.2 $pg.g^{-1}$ w.w., generally well below 8 pg.g-1, the maximum level for dioxin and dioxin-like compounds, except in 25 samples in which this maximum regulatory level for total TEQ is exceeded. The levels follow the general order: mussels ~ fishes > crustaceans > cephalopods, regardless of the type of the species and the geographic origin. As already observed in fish the contribution of DL-PCBs to the total TEQ is important, averaging 70 and 77 % in mussels and fishes respectively; it might be lower in crustaceans and in cephalopods but the number of samples is too small in these two subgroups.

Table 1 Elementary statistics on the PCB, DL-PCB and TEQ concentrations ($pg.g^{-1}$ wet weight)

		Nb data	Mean	Min.	Max	Median	Cent. 10	Cent. 90
Bivalves	**CB118**	88	3366	31	24627	812	182	12136
	CB153	29	12630	99	79346	962	151	49050
	S7 Ind. PCBs	29	31977	255	200795	2420	391	119082
	PCB-TEQ	88	1,87	0,01	9,82	0,79	0,17	6,57
	PCDD/Fs-TEQ	88	0,56	0,01	2,54	0,35	0,12	1,47
	Total-TEQ	88	2,42	0,03	12,36	1,19	0,30	8,25
	PCB-TEQ/Total-TEQ	88	0,68	0,26	0,87	0,70	0,53	0,83
Fishes	**CB118**	105	5158	9	73094	1051	69	21254
	CB153	93	13376	23	178965	2612	235	36429
	S7 Ind. PCBs	93	33955	88	536978	8053	643	91233
	PCB-TEQ	105	2,67	0,01	23,36	0,91	0,06	8,65
	PCDD/Fs-TEQ	105	0,57	0,00	3,26	0,27	0,03	1,45
	Total-TEQ	105	3,24	0,01	25,44	1,25	0,09	10,20
	PCB-TEQ/Total-TEQ	105	0,76	0,18	0,99	0,77	0,60	0,90
Crustaceans	**CB118**	20	1081	10	3364	237	50	3037
	CB153	19	2022	32	5692	510	110	5443
	S7 Ind. PCBs	19	7637	97	24660	2477	299	19503
	PCB-TEQ	20	1,07	0,01	3,65	0,28	0,07	3,35
	PCDD/Fs-TEQ	20	0,44	0,01	1,06	0,27	0,06	1,00
	Total-TEQ	20	1,51	0,03	4,71	0,58	0,12	4,30
	PCB-TEQ/Total-TEQ	20	0,58	0,35	0,78	0,55	0,46	0,78
Cephalopods	**CB118**	7	353	17	1311	128	22	933
	CB153	7	1423	230	3730	870	326	3106
	S7 Ind. PCBs	7	3320	497	9406	1803	610	7459
	PCB-TEQ	7	0,31	0,01	1,11	0,13	0,01	0,80
	PCDD/Fs-TEQ	7	0,19	0,04	0,51	0,10	0,04	0,47
	Total-TEQ	7	0,50	0,05	1,62	0,21	0,05	1,27
	PCB-TEQ/Total-TEQ	7	0,48	0,18	0,69	0,58	0,19	0,69

PCB composition in marine organisms

PCB composition in fishery products is very similar. PC analysis (not shown) on the data has demonstrated that in those samples PCBs vary altogether whichever the species or the geographical origin of the samples. The general pattern of indicator PCBs is dominated by CB153 (fig.1) and may present little changes between species, like for example the relative distribution of congeners CB101 and 118 which differs between molluscs and crustaceans. DL-PCB concentrations also vary simultaneously.

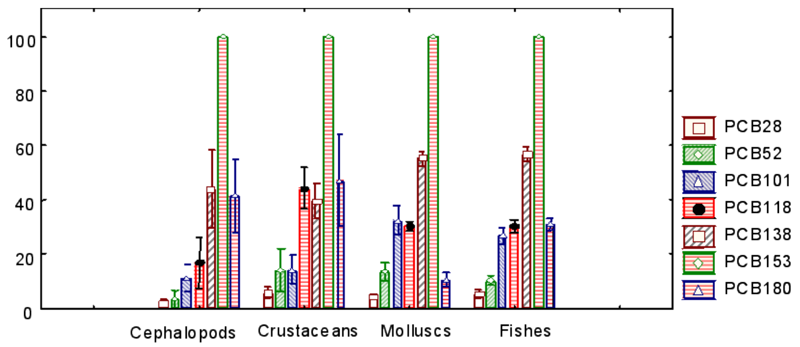


Figure 1: PCB distribution in fishery products. (mean concentration relative to CB153(100*[CBx]/[CB153]

However, their very low levels in most samples and their partial bio-transformation which is species dependent explain a greater variability of DL-PCB fingerprints in fishery product, compared to Indicator PCBs. On the basis of their relative contribution to the sum of DL-PCB concentrations their importance follows the order CB118 (60%) > CB105 (15%) > CB105, CB156 (5%) > all others <2%) whereas, when considering the TEQ, the order changes to CB126 (70% of the DL-PCB-TEQ) >>CB118 (12%) > CB156 (6%) > CB157 (2%) > CB169 (1%) all others (< 0.5 %). Due to its higher TEF, CB126, a non-ortho substituted congener present at very low levels and only measured by HRGC-HRMS contributes very importantly to the TEQ. Conversely, CB 118 that belongs to both groups is the second contributor to the TEQ, and the sum of. CB 118, 156 and 105, which are commonly analyzed by simple and cheap techniques (GC-ECD), represents about 85 % of the DL-PCB concentrations and only 20-25 % of the DL-PCB – TEQ. The main point about the PCB distribution in marine organisms is that because of their similar and approximately constant PCB composition in fishery products, the PCB contamination in a sample can be described by any congener, and notably by the major ones (CB153), or by the sum of concentrations with an indication of which ones have been selected, or by any linear combination of congener concentration.

PCB - TEQ correlations

For this same reasons, the DL-PCB-TEQ in marine organisms, a sum of individual concentrations, weighed by their respective TEF, is very well correlated to the concentrations of individual indicator PCBs or to their sum: examples are presented Sum7 Ind.-PCB (fig 2) or given in the table 2). All data have been log-transformed before calculating the correlation because of the skewed distributions of the concentrations. All TEQs have been calculated using 1998-WHO-TEFs[7], the same approach using the more recent 2005-WHO-TEFs[9] would lead to lower TEQs and hence different coefficients of the regression equations but would not change the conclusions

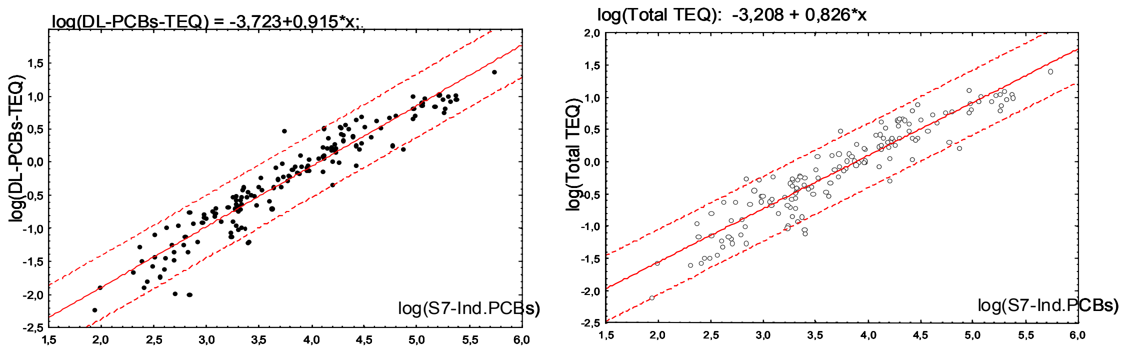


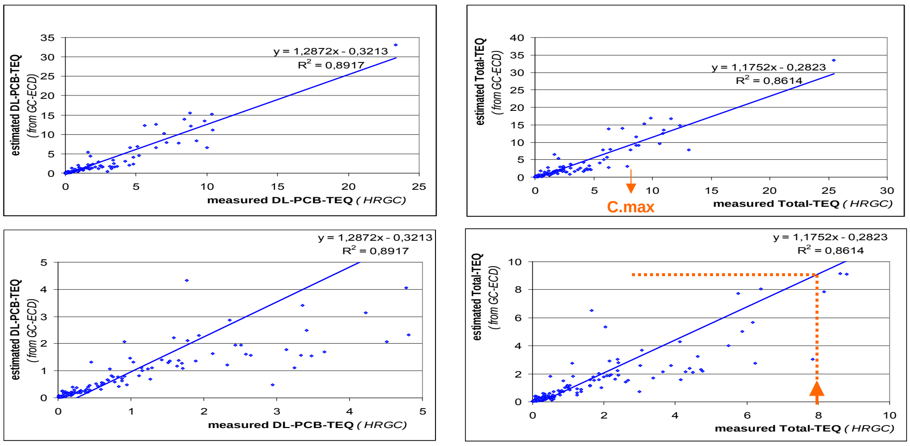
Figure2: DL-PCBs and total TEQ correlations with the sum of indicator PCBs.

Table2: Correlations between measured TEQs and PCB concentrations.

y=ax +b	x	a	b	r2
log(PCCD/Fs-TEQ)	log(PCB153)	0,6374	-2,816	0,6429
	log(PCB118)	0,6	-2,338	0,6674
	log(S7 Ind-PCBs)	0,6418	-3,091	0,6446
	log(S3 DL-PCBs)	0,6238	-2,498	0,6864
log(DL-PCBs-TEQ)	log(PCB153)	0,9041	-3,314	0,8948
	log(PCB118)	0,8642	-2,688	0,9144
	log(S7 Ind-PCBs)	0,9152	-3,723	0,9094
	log(S3 DL-PCBs)	0,8969	-2,914	0,9372
log(Total-TEQ)	log(PCB153)	0,8183	-2,847	0,8714
	log(PCB118)	0,7799	-2,275	0,8886
	log(S7 Ind-PCBs)	0,826	-3,308	0,8808
	log(S3 DL-PCBs)	0,8094	-2,479	0,9109

Obviously best correlations are obtained between DL-PCBs-TEQ and PCB concentrations because all PCB congeners have the same common origin and vary more or less all together. The correlations between total TEQs and the indicator PCBs are still good, due to the major importance of the contribution of DL PCBs to the total TEQ and probably to a longer persistence of PCBs compared to that of PCDD/Fs. The contribution of PCBs to the TEQs is by far (about 75% in fishes, table1); more important as far as fishes are concerned and moreover increases in the case of lower contaminated samples, as it is the case in this database that includes mostly low contaminated marine fishes collected far from terrestrial sources. Further investigations on the validation of these correlations and possibly, their generalisation correlations will be directed towards more contaminated samples including freshwater fishes (Babut et al., in prep.). Dioxins(PCDD/Fs) generally present very low contamination levels in marine organisms and have various anthropogenic origins, hence their concentrations are also quite well correlated but at a lesser extent with PCBs, which come exclusively from urban and industrial sources. For these reasons a practical approach is proposed to estimate the TEQs from measurements of indicator PCB congeners which are more easily obtained by conventional techniques. Examples are given for DL PCB-TEQs and Total TEQs estimated from the sum of the 7 indicator PCBs. Accordingly, TEQs are generally slighty overestimated compared to the TEQs obtained by the reference method using HRGC (fig3). By the way, for food control on marine organisms, it appears safe to estimate the total TEQ from PCB measurements obtained by common GC ECD technique; however the confirmation of the results is required when the estimated Total TEQs reach and exceed 8 pg.g^{-1} w.w, which remains below the regulatory maximum (extended fig 3) . This approach is to be validated on a larger data set, including more contaminated samples It appears as a promising alternative allowing an efficient control of fishery products, more results obtained more rapidly than by the official method could be achieved at a limited expense.

Figure3: Comparison between estimated and measured TEQs in marine organisms



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