LEVELS AND PATTERNS OF POLYCHLORINATED DIBENZO-*P*-DIOXINS, DIBENZOFURANS AND DIOXIN-LIKE POLYCHLORINATED BIPHENYLS IN POLISH FOODSTUFFS OF ANIMAL ORIGIN

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Introduction

In 2006 the European Union established maximum levels for the sum of polychlorinated dibenzo-*p*-dioxin (PCDDs), dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (dl-PCBs) in foodstuffs[1]. In parallel, the previously set maximum levels for PCDD/Fs in foodstuffs still apply for transitional period until at least the end of 2008. Correspondingly, action levels for dl-PCBs were established in 2006 as a complementary tool to the previously established action levels for PCDD/Fs[2]. Moreover, in 2006 the EU recommended the new Member States joining the European Community to monitor the background levels of PCDD/Fs and dl-PCBs in foodstuffs[3].

In Poland, concentration of PCDD/Fs and dl-PCBs in foodstuffs has never been determined on a regular basis and only limited data on PCDD/Fs and indicator PCBs were previously available. The first monitoring of the background levels was conducted in 2006 in foodstuffs of animal origin, which contributes to the majority of the human exposure to PCDD/Fs and dl-PCBs. The aim of the monitoring program was to generate fundamental data for subsequent trend analysis and to identify potentially contaminated groups of foodstuffs.

Materials and Methods

Foodstuffs were collected as aggregate samples and the method of sampling followed the requirements of official monitoring laid down in Commission Regulation 1883/2006[4]. Recommended categories of foodstuffs of animal origin were analysed: eggs, meat, milk, farmed and wild fish. All samples were collected at random, from farms, fishing ports, slaughterhouses, sorting facilities, processing and wholesale companies. Sampling was performed by authorized and qualified veterinary inspectors. Sampling covered all regions of Poland, including areas with heavy industrial impacts as well as purely agricultural lands.

All foodstuffs were analyzed according to the accredited method using high resolution gas chromatography coupled to high resolution mass spectrometry. Measured analytes were 17 PCDD/Fs and 12 dl-PCBs congeners. Samples were homogenized and freeze-dried. Fat was extracted by pressurized liquid extraction (ASE 300, Dionex), variety of extraction programs were used depending on a sample. Fat and moisture contents were determined gravimetrically. Samples were defatted on acidic silica columns and further purified and fractionated on Florisil and Carbopack C. PCDD/F, non-orto PCBs and mono-orto PCBs fractions were analysed by HRGC-HRMS (MAT 95XP, Thermo Scientific) on a DB-5MS (60m, J&W Scientific). The method used was previously comprehensively validated and all requirements given in Commission Regulation were fulfilled[4]. Expanded uncertainty was estimated at the level of interest and was established below 20% for WHO-TEQ sums. The analytical method was successfully tested by participation in international proficiency tests in foodstuffs of animal origin.

Results and Discussion

All results are presented as upperbound values[4]. For congener patterns determination, standardisation was performed on complete congener specific data, normalised to the sum of congeners (individual congener concentration divided by the sum of PCDD/Fs and the sum of dl-PCBs, respectively) to eliminate differences in concentration levels and other sample specific variations.

Table 1 summarises PCDD/F and dl-PCB concentrations in analysed assortments of foodstuffs. Concentrations in eggs, meat, milk and farmed fish samples never exceeded the maximum levels for both PCDD/Fs and the sum of PCDD/Fs and dl-PCBs. All the meat samples as well as the eggs and cow's milk samples contained both PCDD/F and dl-PCB levels fine below the action levels. The lowest levels of both PCDD/Fs and dl-PCBs were found in pork and poultry. The levels of both PCDD/Fs and dl-PCBs in goat's milk samples were elevated in comparison to those noted in cow's milk. The levels of PCDD/Fs and dl-PCBs in game were elevated in comparison to the levels in other meat samples; however maximum levels for game no longer exist within the EU legislation. In two salmon samples, the maximum level for PCDD/Fs was exceeded and the values in five samples were above the respective action level. None of the other Baltic fish species contained analytes in concentration above the maximum level for PCDD/Fs, but in one sample of herring and three samples of sprat the action level was exceeded. Similarly to PCDD/F, also the highest dl-PCB concentrations were measured in salmon samples. The dl-PCB concentrations in samples of herring and sprat, the most popularly consumed in Poland among fatty Baltic fishes, were below maximum levels. Two salmon samples were non-compliant with the EU maximum levels for the sum of PCDD/Fs and dl-PCBs and concentration in all eight samples were above the action level for dl-PCBs. None of the herring and sprat samples contained analytes in concentration above the maximum level for the sum of PCDD/F and dl-PCB, but in 2 herring and 8 sprat samples measured values exceeded the action level for dl-PCBs.

Congener patterns of analytes normalized correspondingly to sums of PCDD/Fs and dl-PCBs were established in pg WHO-TEQ/g (Figure 1). PCDD/F profiles showed clear variations between assortments. The dominating PCDD/Fs among eggs, milk and meat samples were OCDD, followed by 1,2,3,4,6,7,8-HpCDD and 2,3,7,8-TCDF for eggs, but 2,3,4,7,8-PeCDF and 1,2,3,4,6,7,8-HpCDD for meat and milk. For fish species, 2,3,7,8-TCDF was the most abundant, followed by 2,3,4,7,8- and 1,2,3,7,8-PeCDF. When concentration in WHO-TEQs was considered, 2,3,4,7,8-PeCDF was the most important congener in all analysed assortments, followed by 1,2,3,7,8-PeCDD for Baltic fish and milk, and 2,3,7,8-TCDD for eggs and meat samples. Dl-PCB profiles were practically constant between all assortments, suggesting universal contamination sources for both terrestrial and aquatic matrices. Generally, the dominating dl-PCB congeners were PCB 118, followed by PCB 105 and PCB 156. Based on WHO-TEQs concentration, PCB 126 was the most abundant one with a share of more than 70% in the WHO-PCB-TEQ, followed by PCB 118, 156 and PCB 169.

Contribution of PCDD/F and dl-PCB fractions to the total WHO-TEQ is presented in Table 2. Contribution of PCDDs and PCDFs to WHO-PCDD/F-TEQ and that of non- and mono-*orto* dl-PCBs to WHO-PCB-TEQ are summarised in Table 3. Generally, PCDD/Fs prevailed over dl-PCBs in most kinds of foodstuffs, except for fish muscle. Among terrestrial foodstuffs, the highest contribution of PCDD/F (more than 70%) was noticed in egg samples. In general, considering contribution to WHO-PCDD/F-TEQ, PCDFs prevailed over PCDDs, except for eggs and muscle samples. In all foodstuffs, non-*orto*-PCB fraction prevailed against mono-*orto* one, with the highest contribution of the latter in fish. A share of dl-PCB in WHO-TEQ up to 60% was common for both farmed and Baltic fish, with the highest value for salmon. Consequently, the WHO-TEQ concentrations in foodstuffs were almost doubled with an addition of dl-PCBs in comparison to concentration of PCDD/Fs alone. The importance of inclusion of dl-PCBs in WHO-TEQ calculation was confirmed. Even though sampling covered all regions of Poland, the samples analysed did not show any apparent geographical trend.

The aim of this study was to obtain data on concentrations of PCDD/Fs and dl-PCBs in foodstuffs consumed in Poland and to verify whether they are in accordance with the EU Regulation[1] and Recommendation[2]. Generally, contamination of Polish foodstuffs of animal origin with PCDD/Fs and dl-PCBs is at similar levels as in other EU countries. Current contamination levels of terrestrial foodstuffs of animal origin in Poland are considerably below the respective maximum and action levels for both PCDD/Fs and sum of PCDD/Fs and dl-PCBs. Unfortunately, current contamination levels of marine foodstuffs originating from the Baltic Sea were frequently above the action levels and occasionally exceeded maximum levels.

References:

1. Commission Regulation 1881/2006 of 19 December 2006 *Official Journal of the EU* L 364/5.
2. Commission Recommendation 2006/88/EC of 6 February 2006 *Official Journal of the EU* L 42/26.
3. Commission Recommendation 2006/794/EC of 16 November 2006 *Official Journal of the EU* L 322/24.
4. Commission Regulation 1883/2006 of 19 December 2006 *Official Journal of the EU* L 364/32.

Figure 1: Normalised congener profiles of PCDD/Fs and dl-PCBs in analysed foodstuffs of animal origin (pg WHO-TEQ/g, WHO-TEF 1998)

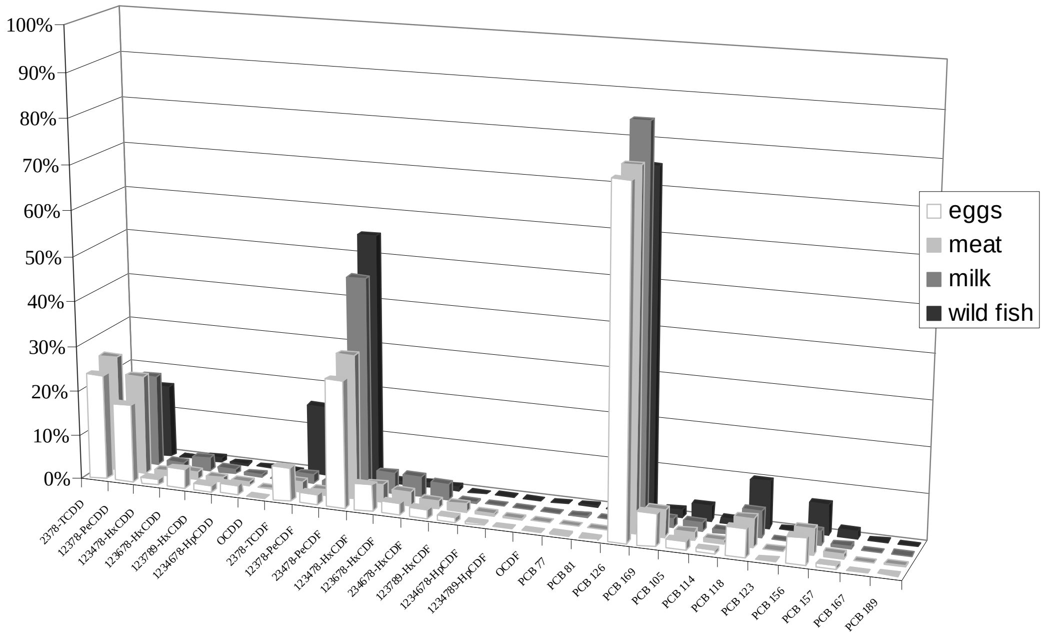

Table 1: Summary of the monitoring of foodstuffs of animal origin in Poland (2006)

Foodstuffs	PCDD/Fs	dl-PCBs	Σ	Maximum levels		Action levels	
				PCDD/Fs	Σ	PCDD/Fs	dl-PCBs
			[pg WHO-TEQ/g of fat]				
Eggs (Σ)	0.56±0.22	0.22±0.19	0.78±0.30				
Chicken (n=17)	0.59±0.24	0.25±0.22	0.84±0.33	3.0	6.0	2.0	2.0
Others (n=7)	0.50±0.16	0.15±0.04	0.65±0.19				
Milk (Σ)	0.84±0.58	0.56±0.33	1.40±0.89				
Cow milk (n=10)	0.65±0.35	0.42±0.18	1.07±0.51	3.0	6.0	2.0	2.0
Goats milk (n=3)	1.47±0.83	1.01±0.32	2.48±1.14				
Muscle (Σ)	0.69±0.47	0.52±0.49	1.21±0.92				
Game (n=3)	1.21±0.17	1.18±0.73	2.40±0.90	-	-	-	-
Beef (n=6)	0.90±0.64	0.68±0.59	1.58±1.20	3.0	4.5	1.5	1.0
Mutton (n=3)	0.95±0.21	0.56±0.12	1.51±0.34				
Pork (n=6)	0.24±0.07	0.15±0.04	0.38±0.10	1.0	1.5	0.6	0.5
Poultry (n=6)	0.55±0.20	0.36±0.20	0.92±0.35	2.0	4.0	1.5	1.5
			[pg WHO-TEQ/g of f.w.]				
Baltic fish (Σ)	2.69±0.90	3.60±1.68	6.29±2.53				
Herring (n=11)	2.15±0.62	2.29±0.75	4.45±1.35	4.0	8.0	3.0	3.0
Salmon (n=8)	3.42±1.16	5.76±1.53	9.18±2.66				
Sprat (n=11)	2.66±0.51	3.28±0.58	5.95±1.01				
Farmed fish (n=10)	0.29±0.20	0.40±0.21	0.68±0.24	4.0	8.0	3.0	3.0

Table 2: Contributions of PCDD/Fs and dl-PCBs to total WHO-TEQ in analysed foodstuffs

Foodstuffs	PCDD/Fs [%]	dl-PCBs [%]
Eggs	74	26
Milk	58	42
Muscle	60	40
Baltic fish	44	56
Farmed fish	45	55
Σ	57	43

Table 3: Contributions of PCDDs and PCDFs to WHO-PCDD/F-TEQ and mono- and non-*orto* dl-PCBs to WHO-PCB-TEQ in analysed foodstuffs

Foodstuffs	PCDDs [%]	PCDFs [%]	non-*orto* dl-PCBs [%]	mono-*orto* dl-PCBs [%]
Eggs	50	50	84	16
Milk	37	63	88	12
Muscle	53	47	84	16
Baltic fish	18	74	77	23
Farmed fish	37	63	77	23
Σ	41	59	82	18