JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Toxic Potency of Polychlorinated Dibenzo-*p*-dioxins, Polychlorinated Dibenzofurans, and Polychlorinated Biphenyls in Food Samples from Catalonia (Spain)

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A surveillance program on polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) in 29 foodstuff samples produced all over the four provinces in Catalonia (Spain) is presented. The study included the analyses of milk, egg, meat (beef, chicken, and pork), mussel, and olive oil samples. A previously developed method for the simultaneous analysis of the 2,3,7,8-substituted PCDDs/PCDFs and the dioxin-like PCBs, as well as the indicator PCBs, was employed. Total toxicity equivalent (TEQ) values were calculated using the toxicity equivalent factors (TEFs) proposed by the World Health Organization (WHO) for dioxin-like PCBs, PCDDs, and PCDFs. The $TEQ_{PCDD/F}$ levels were below the limits proposed in the draft of the EC regulation for food commercialization in the European countries. These limits are the following: 2 pg WHO-TEQ/g fat for pork, 3 pg WHO-TEQ/g fat for milk and chicken, 5 pg WHO-TEQ/g fat for egg and beef, and 3 pg WHO-TEQ/g whole product for fish. The contributions of PCDDs/Fs and dioxin-like PCBs in the total toxicity of the samples were calculated for each matrix. The results showed that the TEQ_{PCB} contribution varied from 27% in olive oil samples to 81% in mussel samples. These findings suggest that the regulation of TEQ contents in food should include not only the $TEQ_{PCDD/F}$, but also the TEQ_{PCB}.

KEYWORDS: Polychlorinated dibenzo-*p*-dioxins; polychlorinated dibenzofurans; polychlorinated biphenyls; food; total toxicity equivalent

INTRODUCTION

Polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) are resistant global pollutants. Among the 75 different PCDDs, 135 different PCDFs, and 209 possible PCBs, scientific interest has been typically centered on PCDDs/Fs with 2,3,7,8-chloro substitution (*1*) and on PCB congeners that are stereoisomers of 2,3,7,8-TCDD (*2*) because of their high toxicity. The dioxin-like PCB congeners are classified according to the number of chlorines in the *ortho*-position: non-*ortho*-Cl, mono-*ortho*-Cl, and di-*ortho*-Cl. The World Health Organization (WHO) has identified 12 PCBs as being similar in toxicity to the PCDDs/Fs. The list of these 12 PCBs includes 4 non-*ortho* (IUPAC nos. 77, 81, 126, and 169) and 8 mono-*ortho* congeners (IUPAC nos. 105, 114, 118, 123, 156, 157, 167, and 189) (*2*). In addition to these 12 congeners, Ahlborg et al. have identified two di-*ortho* congeners (IUPAC nos. 170 and 180) with toxic properties (*3*). Each of these 14 congeners has an assigned toxicity equivalent factor (TEF).

Because of their chemical stability and lipophility, PCBs, PCDDs, and PCDFs are compounds that accumulate in the food chain. In fact, food has been recognized widely as the main source of human intake for this kind of toxic chemicals (*4*). Knowledge about the adverse health effects of exposure to these toxicants has been enhanced by a number of dioxin contamination incidents involving food and feed (*5*−*8*). Since the Belgium dioxin episode in May 1999, in which a storage tank for animal fat was contaminated with PCBs, stringent regulations on dioxin levels in food have been enforced (*9*). In December 1999, the Department of Public Health (Departament de Sanitat i Seguretat Social) of the Catalonian government (Generalitat de Catalunya) deployed the first surveillance program on PCDDs and PCDFs in food (*10*). In December 2000, the second surveillance program was carried out, with the determination of not only PCDDs/Fs, but of PCBs also. The results of this program are presented in this study.

Comprehensive analytical procedures are necessary for determination of the dioxin-like PCBs. A number of countries have chosen to monitor PCBs as a set of seven indicator PCBs (IUPAC nos. 28, 52, 101, 118, 138, 153, and 180) to avoid the complexity involved in analyzing more congeners. Dioxin-like PCBs are not included in this list mainly because they occur at concentrations lower than the level of congeners mentioned above and are, therefore, very elaborate and complicated to analyze. In this study, a previously validated analytical method

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10.1021/jf011021v CCC: $22.00
Published on Web 01/23/2002

for simultaneous analysis of dioxin-like PCBs (IUPAC nos. 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189), PCDDs, and PCDFs (*11*) was used for the surveillance program in 29 food samples. This method was based on an automated cleanup system followed by an isotope-dilution high-resolution mass spectrometric analysis.

MATERIALS AND METHODS

Sampling. Food samples were collected from different locations throughout Catalonia (NE Spain) during November 2000. The 29 food samples analyzed were distributed as follows: whole milk, 5 samples; egg, 3 samples; steak of beef, 5 samples; steak of chicken, 5 samples; steak of pork, 5 samples; mussel, 4 samples; and olive oil, 2 samples. Samples were freeze-dried when received and stored in the refrigerator at 4 °C until their analytical treatment. Egg and mussel samples were pooled from different subsamples.

Chemicals. EPA Method 1613 standard solutions (CS-1 to CS-5, LCS, and ISS) and WP standard solutions (CS-1 to CS-7, LCS, and ISS) were purchased from Wellington Labs (Guelph, Ontario, Canada) for instrument calibration, quantification, and recovery of PCDDs/PCDFs and dioxin-like PCBs, respectively (see **Table 1**). Individual standard solutions (MBP-28, MBP-37, MBP-52, MBP-101, MBP-153, and MBP-180, Wellington Labs, Guelph, Ontario, Canada) were used to prepare mixture solutions for indicator PCB analyses. An internal standard at 1 ng/μL of concentration of each indicator PCB was prepared with nonane. Five calibration solutions were also prepared covering a range of concentrations between 10 and 500 pg. Solvents (acetone, dichloromethane, toluene, ethyl acetate, *n*-hexane, and cyclohexane) for organic trace analysis were purchased from Merck (Darmstadt, Germany).

Procedure. A previously tested method for the simultaneous analysis of PCBs, PCDDs, and PCDFs was used in this study (*11*). An extraction technique appropiate to the nature of each sample was used. The egg, meat, and mussel samples were liophilized, and the fat was extracted by Soxhlet for 24 h with toluene/cyclohexane (1:1). The lipid fraction contained in milk samples was removed by liquid−liquid extraction with diethyl ether and petroleum ether (*12*). Oil samples were directly dissolved in *n*-hexane. After gravimetric determination of the lipid content, samples were spiked with known amounts of ^{13}C-PCDDs, ^{13}C-PCDFs, and ^{13}C-PCBs. Then, fats were removed to allow analysis by a sulfuric acid treatment. The extracts were concentrated prior to the cleanup process. Purification was accomplished by an automated cleanup system based on the use of multilayer silica, basic alumina, and AX-21 carbon adsorbents. Prior to the automated cleanup process, the extracts had to be filtered so that particulate size would not exceed 100 μm. After loading the sample onto column 1 (multilayer silica), the following tasks were performed sequentially: (a) 130 mL of *n*-hexane at 10 mL/min were eluted from column 1 through column 2 (basic alumina) to waste; (b) 60 mL *n*-hexane/dichloromethane (98:2) at 10 mL/min were eluted from column 2; (c) 120 mL of *n*-hexane/dichloromethane (1:1) at 10 mL/min were eluted from column 2 through column 3 (AX-21 carbon) in the forward direction; (d) 75 mL of toluene at 5 mL/min were eluted through column 3 in the reverse direction. During this automated cleanup procedure, three solvent fractions were collected. The first (step b) and the second (step c) fractions contained the indicator and mono-*ortho* and di-*ortho* PCBs, and were collected as the same extract. The third fraction (step d) contained non-*ortho* PCBs, PCDDs, and PCDFs. The whole process was accomplished in approximately 1 h. Prior to HRGC/HRMS analysis, extracts were concentrated to incipient dryness prior to the addition of the recovery standards (ISS solutions).

Purified extracts were analyzed by HRGC/HRMS on an AutoSpec-Ultima mass spectrometer (Micromass, Manchester, UK) coupled with a GC 8000 series gas chromatograph (Carlo Erba Instruments, Milan, Italy). A DB-5 (J&W Scientific, Folsom, CA) fused-silica capillary column (60 m × 0.25 μm i.d., 0.25 mm film thickness) was used with helium as carrier gas at a linear velocity of 28 cm/s. The PCB analyses were based on the U.S. EPA Method 1668 (*13*). The temperature program was from 90 °C (held for 1 min) to 180 °C (held for 1 min) at 20 °C/min, and then from 180 °C to 300 °C (held for 10 min) at 3 °C/min, using the splitless injection mode. The HRGC/HRMS operating conditions were as follows: ion source and interface temperatures, 250 °C and 275 °C, respectively; ionization energy, 35 eV (electron ionization mode); and trap current, 300 mA. The resolving power was kept at ~10000 (10% valley definition) over the working mass range (m/z = 250 to m/z = 500). Verification of resolution in the working mass range was obtained by measuring perfluorokerosene reference

Table 1. Composition (pg/μL) of the Different Standard Solutions Used for Instrument Calibration, Quantification, and Recovery of PCDDs/PCDFs and Dioxin-Like PCBs

EPA 1613 solutions	CS1 to CS5	LCS	ISS
2378-TCDD	0.5–200	-	-
2378-TCDF	0.5–200	-	-
12378-PeCDD	2.5–1000	-	-
12378-PeCDF	2.5–1000	-	-
23478-PeCDF	2.5–1000	-	-
123478-HxCDD	2.5–1000	-	-
123678-HxCDD	2.5–1000	-	-
123789-HxCDD	2.5–1000	-	-
123478-HxCDF	2.5–1000	-	-
123678-HxCDF	2.5–1000	-	-
234678-HxCDF	2.5–1000	-	-
123789-HxCDF	2.5–1000	-	-
1234678-HpCDD	2.5–1000	-	-
1234678-HpCDF	2.5–1000	-	-
1234789-HpCDF	2.5–1000	-	-
OCDD	5.0–2000	-	-
OCDF	5.0–2000	-	-
^{13}C-2378-TCDD	100	100	-
^{13}C-2378-TCDF	100	100	-
^{13}C-12378-PeCDD	100	100	-
^{13}C-12378-PeCDF	100	100	-
^{13}C-23478-PeCDF	100	100	-
^{13}C-123478-HxCDD	100	100	-
^{13}C-123678-HxCDD	100	100	-
^{13}C-123478-HxCDF	100	100	-
^{13}C-123678-HxCDF	100	100	-
^{13}C-234678-HxCDF	100	100	-
^{13}C-123789-HxCDF	100	100	-
^{13}C-1234678-HpCDD	100	100	-
^{13}C-1234678-HpCDF	100	100	-
^{13}C-1234789-HpCDF	100	100	-
^{13}C-OCDD	200	200	-
^{13}C-1234-TCDD	100	-	200
^{13}C-123789-HxCDD	100	-	200
WP solutions	**CS1 to CS7**	**LCS**	**ISS**
PCB # 77	0.1–800	-	-
PCB # 81	0.1–800	-	-
PCB # 105	0.1–800	-	-
PCB # 114	0.1–800	-	-
PCB # 118	0.1–800	-	-
PCB # 123	0.1–800	-	-
PCB # 126	0.1–800	-	-
PCB # 156	0.1–800	-	-
PCB # 157	0.1–800	-	-
PCB # 167	0.1–800	-	-
PCB # 169	0.1–800	-	-
PCB # 189	0.1–800	-	-
^{13}C-PCB # 77	50	1000	-
^{13}C-PCB # 81	50	1000	-
^{13}C-PCB # 105	50	1000	-
^{13}C-PCB # 114	50	1000	-
^{13}C-PCB # 118	50	1000	-
^{13}C-PCB # 123	50	1000	-
^{13}C-PCB # 126	50	1000	-
^{13}C-PCB # 156	50	1000	-
^{13}C-PCB # 157	50	1000	-
^{13}C-PCB # 167	50	1000	-
^{13}C-PCB # 169	50	1000	-
^{13}C-PCB # 189	50	1000	-
^{13}C-PCB # 70	50	-	1000
^{13}C-PCB # 111	50	-	1000
^{13}C-PCB # 138	50	-	1000
^{13}C-PCB # 170	50	-	1000

Table 2. Mean PCDD and PCDF Levels (pg/g fat weight, or pg/g whole product for mussel) Corresponding to the Different Foods Studied

	milk ($n = 5$)[a]	egg ($n = 3$)	beef ($n = 5$)	chicken ($n = 5$)	pork ($n = 5$)	mussel ($n = 4$)	oil ($n = 2$)
2378-TCDF	0.30	0.16	0.07	0.28	0.07	4.08	0.04
12378-PeCDF	0.15	0.08	0.07	0.15	0.03	0.16	n.d.
23478-PeCDF	0.41	0.22	0.23	0.16	0.05	0.64	0.02
123478-HxCDF	0.22	0.17	0.86	0.38	0.07	0.21	n.d.
123678-HxCDF	0.21	0.12	0.55	0.17	0.03	0.07	0.03
234678-HxCDF	0.17	0.12	0.41	0.20	0.02	0.14	0.04
123789-HxCDF	0.19	0.04	0.14	0.04	0.01	0.01	0.03
1234678-HpCDF	0.55	0.38	5.99	1.58	0.27	0.32	0.06
1234789-HpCDF	0.10	n.d.	1.73	0.80	n.d.	0.04	n.d.
OCDF	1.11	0.49	3.18	2.49	0.24	0.47	0.19
2378-TCDD	n.d.[b]	0.05	0.08	0.22	0.09	0.03	n.d.
12378-PeCDD	0.19	0.11	0.25	0.24	0.04	0.08	0.02
123478-HxCDD	0.11	0.19	0.35	0.93	0.06	0.05	n.d.
123678-HxCDD	0.35	0.46	2.41	1.40	0.13	0.09	n.d.
123789-HxCDD	0.26	0.12	0.50	0.26	0.06	0.08	0.05
1234678-HpCDD	1.29	2.32	18.71	8.68	0.97	0.76	0.16
OCDD	2.36	8.00	46.60	43.53	5.70	4.06	1.01

[a] The number of samples analyzed in each case is given in parentheses. [b] n.d., Not detected.

peaks. The PCDD and PCDF analyses were based on the U.S. EPA Method 1613 (*14*). The temperature program was from 140 °C (held for 1 min) to 200 °C (held for 1 min) at 20 °C/min, and then from 200 °C to 300 °C (held for 20 min) at 3 °C/min, using the splitless injection mode. The HRGC/HRMS operating conditions were the same as those used for PCB analyses.

Quantification was carried out by the isotopic dilution method. Relative response factors (RRFs) for the individual isomers were obtained by analyzing standard solution mixtures (CS solutions). The recoveries of labeled standards were calculated using mixtures of labeled compounds (ISS solutions) added before the HRGC/HRMS analysis. The amounts of the recovery standards added to each sample were 500 pg of each compound (see composition in **Table 1**). Method blanks were analyzed and no contributions were detected. Values reported were not corrected by subtraction of the blank levels. TEQ values were calculated assuming that all values lower than the limit of detection (LOD) are equal to this LOD. The LOD was defined as background plus 3 SD (*15*).

RESULTS AND DISCUSSION

The efficiency of the automated cleanup system for the isotope-dilution HRMS analysis of PCBs, PCDDs, and PCDFs in foodstuff samples has been shown previously (*11*). The recoveries calculated for the spiked compounds, between 63 and 72% for PCBs and from 57 to 113% for PCDDs/Fs, were always in the range established in EPA methods as the minimum requirements of well accepted methods (*13*, *14*). RSDs obtained were also acceptable, with values below 20%. For PCDDs/Fs, the achieved detection limits using the procedure proposed in this work were as follows: 0.03−0.37 pg/g fat for milk samples, 0.01−0.17 pg/g fat for egg samples, 0.02−0.29 pg/g fat for meat samples, 0.02−0.07 pg/g fat for olive oil samples, and 0.01−0.20 pg/g for mussel samples. With respect to PCBs, the different LODs obtained were the following: 0.25−4.42 pg/g fat for milk samples, 0.18−5.02 pg/g fat for egg samples, 0.15−6.08 pg/g fat for meat samples, 0.27−5.10 pg/g fat for olive oil samples, and 0.11−9.17 pg/g whole product for mussel samples.

For the toxic potency assessment, the seven 2,3,7,8-substituted PCDDs, ten 2,3,7,8-substituted PCDFs, and twelve dioxin-like PCBs were normalized by multipliying their measured concentrations by the appropiate WHO-TEFs (*1*). The sum of these products yields $TEQ_{PCDD/F}$ and TEQ_{PCB}, which express these analyte concentrations as a single number, equivalent to that of a toxicity derived exclusively from 2,3,7,8-TCDD.

Table 3. Mean, Minimum, and Maximum PCDD and PCDF Levels (expressed in pg WHO-TEQ/g fat weight, or pg WHO-TEQ/g whole product for mussel) Corresponding to the Surveillance Programs Carried out in Catalonia, during 1999 and 2000

	surveillance program 2000[a]				surveillance program 1999[b]			
	n[c]	min	max	mean	n	min	max	mean
milk	5	0.57	1.14	0.81	19	0.11	1.08	0.43
egg	3	0.38	0.51	0.46	-	-	-	-
beef	5	0.28	3.91	1.19	-	-	-	-
chicken	5	0.36	2.52	0.96	12	0.40	33.63	3.65
pork	5	0.09	1.36	0.43	10	0.13	2.09	0.85
mussel	4	0.49	1.39	0.93	5	1.19	5.59	3.65
oil	2	0.11	0.13	0.12	15	0.12	0.38	0.21

[a] Present study. [b] Results from ref *10*. [c] *n*, number of samples analyzed.

PCDD and PCDF Levels. In **Table 2** are presented the arithmetic means of the concentrations of each PCDD and PCDF congener found in a number of samples for each of seven matrixes investigated. The concentrations are reported on a lipid-adjusted basis, with the exception of the mussel samples, for which levels are reported on a whole product basis. The highest levels were found to be those of beef (1.19 pg WHO-TEQ/g fat), followed by chicken (0.96 pg WHO-TEQ/g fat) > mussel (0.93 pg WHO-TEQ/g whole product) > milk (0.81 pg WHO-TEQ/g fat) > egg (0.46 pg WHO-TEQ/g fat) > pork (0.43 pg WHO-TEQ/g fat) > olive oil (0.12 pg WHO-TEQ/g fat). All the calculated TEQs were far from the limits proposed in the draft of the EC Regulation for food commercialization in the European countries (*9*): 2 pg WHO-TEQ/g fat for pork, 3 pg WHO-TEQ/g fat for milk and chicken, 5 pg WHO-TEQ/g fat for egg and beef, and 3 pg WHO-TEQ/g whole product for fish.

When $TEQ_{PCDD/F}$ results were compared with those obtained in the 1999 surveillance program (*10*), a decline was observed for chicken and mussel levels, whereas milk, pork, and olive oil concentrations remained virtually unchanged (**Table 3**).

A number of studies have reported PCDD and PCDF levels from different food samples. As regards milk samples, Ramos et al. (*16*), in a determination of the background levels of milk samples in Spain, found a range of contamination between 1.3 and 2.5 pg TEQ/g fat. These levels were higher than those found in this study. The results of Liem and Theelen (*17*), who reported concentrations between 0.2 and 4.3 pg TEQ/g fat in various

Table 4. Mean Dioxin-Like PCB Levels (pg/g fat weight, or pg/g whole product for mussel) and Indicator PCB Levels (ng/g fat weight, or ng/g whole product for mussel) Corresponding to the Different Foods Studied (the number of samples analyzed in each case is given in parentheses)

	milk ($n = 5$)	egg ($n = 3$)	beef ($n = 5$)	chicken ($n = 5$)	pork ($n = 5$)	mussel ($n = 4$)	oil ($n = 2$)
			Dioxin-like PCBs				
PCB # 81	1.07	1.03	0.25	0.98	0.26	9.56	0.21
PCB # 77	2.67	8.98	2.16	9.56	3.92	160.77	1.81
PCB # 126	10.02	3.77	3.41	2.22	0.46	37.25	0.34
PCB # 169	1.29	0.80	0.87	0.57	0.45	6.09	0.10
PCB # 105	174.79	177.32	70.66	124.78	36.77	962.51	18.85
PCB # 114	14.52	13.44	7.59	8.97	5.07	19.12	0.90
PCB # 118[a]	729.47	652.83	413.48	411.37	184.93	2711.36	43.12
PCB # 123	8.21	9.51	4.15	6.77	2.89	179.94	0.92
PCB # 156	83.74	100.41	55.76	65.18	51.29	458.85	5.54
PCB # 157	18.67	16.57	9.82	11.82	10.32	118.70	1.04
PCB # 167	158.00	134.11	80.06	109.03	84.67	1169.91	10.25
PCB # 189	7.28	10.20	11.26	7.85	5.61	111.28	0.71
PCB # 170	273.87	338.65	349.00	237.65	198.26	229.64	11.16
PCB # 180[a]	555.13	711.59	870.53	526.57	408.92	1287.94	19.67
WHO-TEQ_{PCB}	1.20	0.58	0.48	0.36	0.14	4.55	0.05
			Indicator PCBs				
PCB # 28	0.06	0.27	0.06	0.29	0.13	0.63	0.02
PCB # 52	0.07	0.06	0.12	0.20	0.19	0.94	0.03
PCB # 101	0.10	0.08	0.14	0.26	0.21	4.85	0.06
PCB # 153	1.21	1.72	1.31	1.03	0.90	22.51	0.04
PCB # 138	0.94	1.28	0.87	0.81	0.74	9.49	0.06
Σ indicator PCBs	3.67	4.75	3.79	3.53	2.77	42.41	0.26

[a] PCBs #118 and 180 are both dioxin-like and indicator PCBs.

dairy products, are in reasonably good agreement with the results reported here. They also reported levels in egg samples, with values between 0.2 and 2.0 pg TEQ/g fat, and in beef samples, with concentrations ranging from 0.3 to 7.2 pg TEQ/g fat. In both cases, our results were between these ranges. Regarding chicken samples, the results obtained in this study were similar to those found in different countries: 1.4−2.3 pg TEQ/g fat in Germany (*18*), 2.6 pg TEQ/g fat in Canada (*19*), 1.7 pg TEQ/g fat in The Netherlands (*20*), and 1.3 pg TEQ/g fat in the U.S. (*21*). As regards pork samples, Malish et al. (*22*) determined a range of contamination between 0.05 and 2.29 pg TEQ/g fat in German samples. Lower levels were found by Liem and Theelen (*17*), ranging from 0.2 to 0.6 pg TEQ/g fat. Finally, Liem and Theelen (*17*) reported levels for oils between 0.02 and 0.03 pg TEQ/g fat, and Vieth et al. (*23*) found 0.02 pg TEQ/g fat in oil samples from Germany. Thus, we can conclude that the levels of PCDD/F contamination found in the foods from Catalonia (Spain) are essentially similar to those reported for food samples from other countries.

It is also important to compare the findings of our work with those of a similar study developed in Catalonia by Domingo et al. (*24*). They reported PCDD and PCDF levels in different food samples, such as milk and dairy products (1.49 pg TEQ/g fat), eggs (1.22 pg TEQ/g fat), meat (1.39 pg TEQ/g fat), and fats and oils (0.56 pg TEQ/g fat). Our results were always in the same order, but they were slightly lower than those reported in the above-mentioned study.

PCB Levels. In **Table 4** are presented the arithmetic means of the concentrations of each PCB congener found in a number of samples for each of seven matrixes investigated. The concentrations are reported on a lipid-adjusted basis, with the exception of the mussel samples, for which levels are reported on a whole product basis. The highest indicator PCB levels were found to be those of mussel (42.41 ng/g whole product), followed by egg (4.75 ng/g fat) > beef (3.79 ng/g fat) > milk (3.67 ng/g fat) > chicken (3.53 ng/g fat) > pork (2.77 ng/g fat) > olive oil (0.26 ng/g fat). Thus, the rank of contamination established for PCDD/F deviated considerably, and no correlation between the two families of toxic compounds could be established. Not much information has been published concerning indicator PCB levels in food samples. Thereby, it was not possible to compare the concentrations reported with those of food samples from other countries. However, our results could be considered as low levels when comparing with the tolerance level set at 200 ng/g fat in the Belgium contamination episode (*25*). Thus, a background level around 3−4 ng/g fat is established for indicator PCBs in foodstuff samples of Catalonia (Spain).

As regards dioxin-like PCBs, it should be pointed out that the concentrations of di-*ortho* PCBs were higher than those of the mono-*ortho* PCBs, with the lowest values corresponding to the non-*ortho* PCBs. The PCB # 180 was the predominant di-*ortho* congener, and the PCB # 118, followed by PCB # 105 and 167, prevailed among the mono-*ortho* PCBs. In the case of non-*ortho* PCBs, PCBs # 77 and # 126 were the congeners that exhibited the highest values. The 14 dioxin-like PCBs were normalized by multiplying their measured concentrations by the appropiate WHO-TEFs (*3*). The sum of these products yields TEQ_{PCB}. The highest values of TEQ_{PCB} were those of mussel (4.55 pg WHO-TEQ/g whole product), followed by milk (1.20 pg WHO-TEQ/g fat) > egg (0.58 pg WHO-TEQ/g fat) > beef (0.48 pg WHO-TEQ/g fat) > chicken (0.36 pg WHO-TEQ/g fat) > pork (0.14 pg WHO-TEQ/g fat) > olive oil (0.05 pg WHO-TEQ/g fat), which matched reasonably well with the rank of contamination found for the indicator PCBs. With the exception of the mussel samples, all the calculated TEQs were below the limits proposed in the draft of the EC Regulation (*9*): 2 pg WHO-TEQ/g fat for pork, 3 pg WHO-TEQ/g fat for milk and chicken, 5 pg WHO-TEQ/g fat for egg and beef, and 3 pg WHO-TEQ/g whole product for fish.

Unfortunately, the present database of dioxin-like PCBs is far less complete than those for the PCDDs and PCDFs. Moreover, most of the data published referred to only non-*ortho* PCBs, and the other dioxin-like PCBs (mono-*ortho* and di-*ortho*)

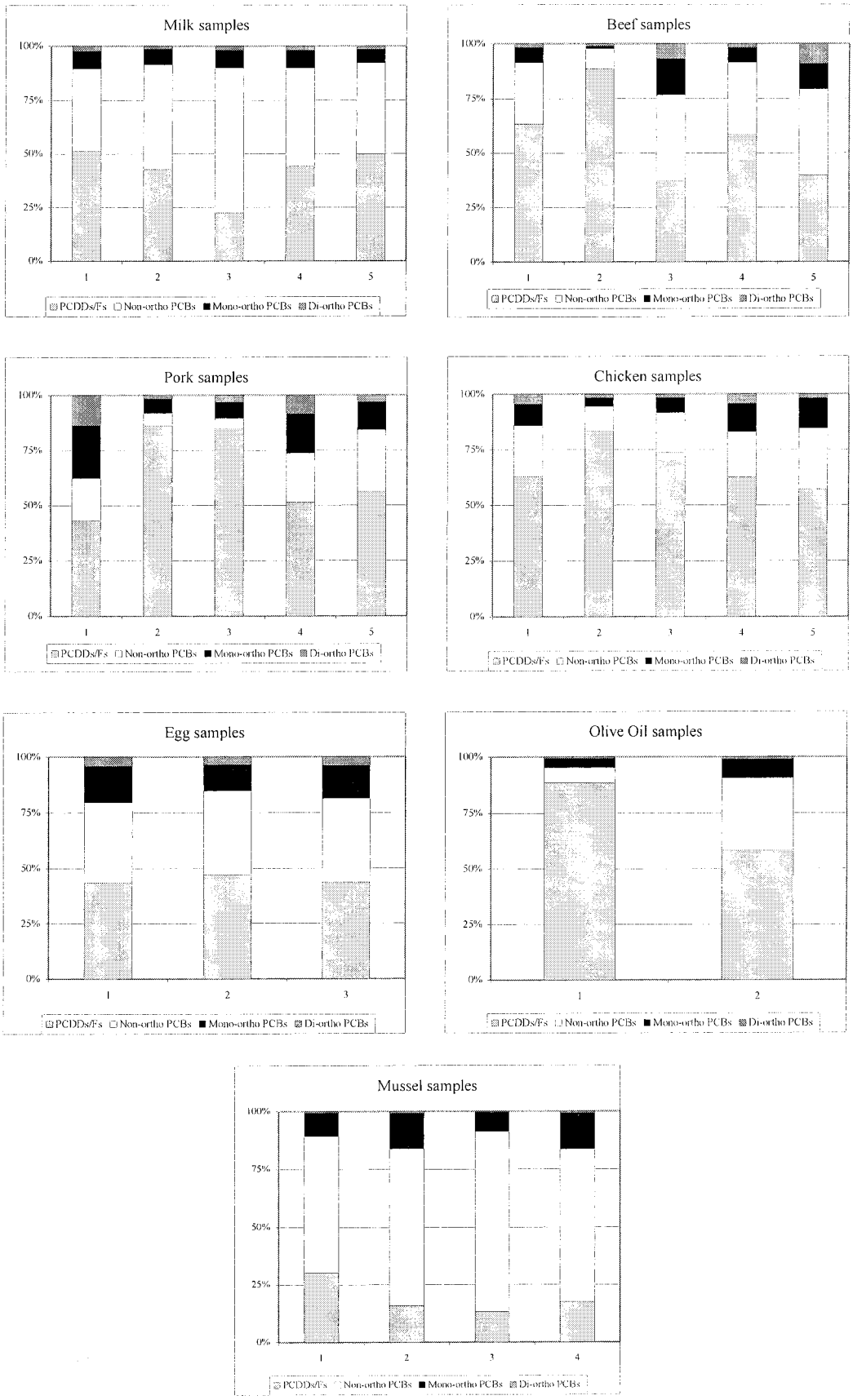

Figure 1. Percentage contribution to the Total TEQ from non-*ortho*, mono-*ortho,* and di-*ortho* PCBs, and PCDDs/Fs.

were not taken in account. Liem and Theelen (*17*) reported non-*ortho* PCB levels in different food samples: 0.5−1.8 pg TEQ/g fat in dairy products, 0.9−2.4 pg TEQ/g fat in beef samples, 0.2 pg TEQ/g fat in pork samples, and 0.9−1.8 pg TEQ/g fat in egg samples. In our study, the TEQs derived from non-*ortho* PCBs were 1.02 pg WHO-TEQ/g fat in milk samples, 0.35 pg WHO-TEQ/g fat in beef samples, 0.06 pg WHO-TEQ/g fat in pork samples, and 0.39 pg WHO-TEQ/g fat in egg samples.

Thus, our results were slightly lower than those reported by Liem and Theelen. Haraguchi et al. (*26*) reported the TEQs derived from all the dioxin-like PCBs in different meat samples from Japan, and they found levels between 0.5 and 5.0 pg TEQ/g. The results reported here for meat lie near the lower limit of this range.

TEQ Contribution of PCDDs/Fs and PCBs. The total WHO-TEQ ($TEQ_{PCDD/F} + TEQ_{PCB}$) values were calculated for the 29 food samples. The data obtained were the following: 2.01 pg/g fat for milk samples, 1.04 pg/g fat for egg samples, 1.67 pg/g fat for beef samples, 1.32 pg/g fat for chicken samples, 0.58 pg/g fat for pork samples, 5.47 pg/g whole product for mussel samples, and 0.17 pg/g fat for olive oil samples. Thus, with the exception of the mussel samples, all the values were below the limits proposed in the draft of the EC Regulation (*9*).

An investigation into relative abundances between PCDDs/Fs and dioxin-like PCBs in food samples, on the basis of TEQs, was carried out. **Figure 1** shows the percentage contribution to the total TEQ from non-*ortho*, mono-*ortho*, and di-*ortho* PCBs, and PCDDs/Fs. As it can be seen, the contribution of each family of compounds varies with the matrix. In milk samples, a similar contribution was found for PCDDs/Fs (42%) and dioxin-like PCBs (58%). Similar behavior was observed for egg samples, with 45% of PCDD/F contribution and 55% of dioxin-like PCB contribution. For meat samples, the PCDD/F contribution is slightly higher than those of PCBs: 58, 64, and 68% for beef, pork, and chicken samples, respectively. Regarding oil samples, 73% of the TEQ value is attributed to PCDDs/Fs. Finally, a different trend was detected in mussel samples, where 81% of the TEQ values is due to the dioxin-like PCB toxicity.

Moreover, in all the cases the largest contribution to TEQ_{PCB} came from the non-*ortho* PCBs, followed by the mono-*ortho* PCBs; with the contribution of di-*ortho* PCBs being almost negligible. This situation was clear in the mussel samples studied with a percentage contribution of 68% for the non-*ortho* PCBs, of 12% for the mono-*ortho* PCBs, and less than 1% for the di-*ortho* PCBs.

Recent studies have also demonstrated that PCB toxicity contribution was important in food samples. Liem et al. (*27*) found that the dietary intake of PCDDs and PCDFs by the general population of industrialized countries is 1−3 pg I-TEQ per kg body weight per day. However, if the contribution of dioxin-like PCBs is considered also, the daily TEQ intake can be a factor of 2 to 3 higher. Hori et al. (*28*) remarked that dioxin-like PCBs make a larger contribution than PCDDs/Fs to the total dietary risk. In addition, the toxic contribution is remarkable in the food group of fish and shellfish, whereas it is minor in other food groups. They also indicated that the mono-*ortho* PCB contribution to the total dietary risk is around 20%. The PCB importance in the toxic contribution in fish samples was also studied by Robinson et al. (*29*). They found that TEQ_{PCB} contributed around 60−80% in white and oily fish samples. Moreover, the results obtained in a "pilot study" on mono-*ortho* PCBs in the International Intercalibration on Dioxin in Food 2000 showed similar results. There was a considerable contribution (15−20%) from the mono-*ortho* PCBs to the total TEQ in the samples analyzed, and in the fish, chicken, and butter samples the greatest contribution to the dioxin-like activity (53−67%) was derived from the PCBs (results unpublished). Our findings were in accordance with these recent studies.

CONCLUSIONS

A simple and fast method, based on an automated cleanup system, for simultaneous analysis of PCBs, PCDDs, and PCDFs has been used for the surveillance program in food samples produced in Catalonia (Spain) during 2000. All the calculated $TEQ_{PCDD/F}$ values were below the limits proposed in the draft of the EC Regulation (*9*). However, when the TEQ_{PCB} is taken into account, the mussel samples exceeded the limit set at 3 pg WHO-TEQ/g whole product.

An assessment of the relative contribution of PCDDs/Fs and dioxin-like PCBs in the different food samples was carried out. The contribution of dioxin-like PCBs varied from 27% in olive oil samples to 81% in mussel samples. Thus, the TEQ_{PCB} calculation should be included for TEQ regulations.

ACKNOWLEDGMENT

The authors thank J. Sauló, M. G. Martrat, and M. A. Adrados for their contributions to this work.

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Received for review July 31, 2001. Revised manuscript received October 29, 2001. Accepted October 30, 2001. The Departament de Sanitat de la Generalitat de Catalunya funded this work (contract 2001).

JF011021V