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Occurrence of co-planar polybrominated/chlorinated biphenyls (PXBs), polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in breast milk of women from Spain

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ABSTRACT

In this study, for the first time, levels and accumulation profiles of eight currently available polybrominated/chlorinated biphenyl congeners (PXBs; XB-77, -105, -118, -126A, -126B, -126C, -156 and -169, named according to IUPAC nomenclature) in human breast milk collected form Spanish women in 2005 were reported. Concentrations and congener specific profiles of polychlorinated biphenyls (PCBs), including co-planar PCBs, (co-PCBs) and polybrominated diphenyl ethers (PBDEs) were also reported.

A concentration of 0.45 pg g^{-1} lipid weight was found for total PXBs, and arithmetic mean concentrations of 125, 25 and 5.5 ng g^{-1} lipid weight were determined for total PCBs, co-PCBs and total PBDEs respectively. Detectable levels of all congeners investigated, except CB-123 and XB-169 were found. Levels of PCBs were similar to those found in Spanish samples collected after 2000, and lower than those obtained before 2000. CB-138, -153 and -180 were the predominant PCB congeners. PBDE levels, dominated by BDE-47, -99, -100 and -209, were lower than PCB levels. PXB concentrations were the lowest, with XB-156 being the most abundant. The concentration levels of PCBs and PBDEs found in this study were in the same range as those from other European countries. Levels of PXBs were much lower than published values determined in Japan which were the only data found in the literature.

1. Introduction

Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are two families of Persistent Organic Pollutants (POPs) that have been extensively studied during recent years (de Wit, 2002; Polder et al., 2008). The origin of their presence in the environment as well as their main physico-chemical properties are well known and documented (Alcock et al., 2003; El-Shahawi et al., 2010). Similar to other POPs, they are characterised by high lipophylicity, chemical persistence and high bioaccumulation capacity through the food web with a high risk of causing adverse effects to human health and the environment (van den Berg et al., 2006). Despite the commercial use of these two families of compounds has been banned or restricted, PCBs since 1976 (Directive 1976/769/UE), technical mixtures (Directive Penta and Octa PBDE formulations (2003/11/EC) and Deca-bromo formulations (Court Proceeding 2008/c116/02), high levels of PCBs and PBDEs in human tissues and especially in breast milk have been reported recently (Meironyté et al., 1999; Akutsu et al., 2003; Sjödin et al., 2004).

On the contrary, to date information about polybrominated/chlorinated biphenyls (PXBs) is very scarce in the literature. PXBs are a new and emerging POP family with chlorine and bromine substitution on the biphenyl ring. The introduction of a second type of halogen into the polychlorinated moiety increases the number of possible congeners from 209 (in the case of PCBs) to 9180 (in the case of PXBs). Little is known about the sources of these compounds in the environment and knowledge about their behaviour is scarce. To date, only the formation of co-planar PXBs (co-PXBs) during the manufacturing process of Fe_3Cl has been reported (Nakano et al., 2007). The few studies involving these compounds suggest that their presence in the environment is probably due to incineration processes in the presence of brominated and chlorinated precursors such as brominated flame retardants (BFRs) and PCBs.

The presence of five co-PXB congeners in human samples (Ohta et al., 2007, 2008a), in some commercial food samples in Japan (Ohta et al., 2008b) and in fish from the Great Lakes in Canada (Alaee et al., 2008) has captured the attention of the scientific community. In all cases, the concentration levels of total

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co-PXBs (considering five congeners) were similar to those of total co-PCBs (12 congeners). These results indicate that these contaminants are bioaccumulative and persistent and that they have the potential of reaching high positions in the trophic food chain. As a result, information about their levels and behaviour in the environment were required in order to carry out a reliable risk assessment.

Breast milk is a source of lipophylic environmental contaminants which have been accumulated in the fatty tissues of the mother over time. As a result, lactation becomes an additional way of excreting xenobiotics, and thus a concern since infants may be exposed to high levels of these contaminants during a critical period of development. Traditionally, levels in human milk have been used as an indicator of overall human exposure (Malish and van Leeuwen, 2003). During the past several years there have been numerous studies on levels of POPs in breast milk, most of them conducted by the World Health Organization (WHO). It has been concluded that while PCB levels have been declining, thanks to efforts on restriction of production, use and emission of these contaminants. On the other hand concentrations of PBDEs have increased; as a result this has led to the prohibition or restriction of their use. All these findings have revealed a need for further investigation into the presence of these lipophylic contaminants in human samples, particularly in countries where data is limited, as is the case of Spain, and mainly for new contaminants, such as where PXBs have only recently been detected.

The main objective of this study was to report, for the first time, preliminary results on the concentration levels and accumulation profiles of co-PXB congeners in Spanish human breast milk. In addition, the co-PXB levels were compared with co-PCBs, *ortho*-PCB and PBDE levels. Finally, PCB and PBDE concentration levels were compared with previous studies carried out in other countries with breast milk samples collected after 2000.

2. Experimental

2.1. Standards and reagents

All reagents used for the analyses were of trace analysis grade. Acetone and toluene Pestipur grade were supplied from SDS (Peypin, France). *n*-Hexane, sulphuric acid (95–97%) and silica gel were supplied from Merck Co. (Darmstadt, Germany) and granular anhydrous sodium sulphate from J.T. Baker (Deventer, The Netherlands). Standards of native and $^{13}C_{12}$ labelled PCB and PBDE congeners were purchased from Wellington Laboratories (Ontario, Canada) and from Dr. Ehrenstorfer (Augsburg, Germany). Standards of native PXB congeners were purchased from Cambridge Isotope Laboratories (Andover, MA, USA).

2.2. PCB, PBDE and PXB congeners analysed

A total of twenty-four individual PCB congeners were analysed including the set of seven indicators, the most abundant PCBs in commercial mixtures and in environmental samples, and those PCBs that have been assigned a toxic equivalency factor by the WHO (CB-28, -52, -77, -81, -95, -101, -105, -114, -118, -123, -126, -132, -138, -149, -153, -156, -157, -167, -169, -170, -180, -183, -189 and -194). Fifteen BDE congeners were analysed including the most abundant in both technical mixtures, environmental matrices (BDE-17, -28, -47, -66, -85, -99, -100, -153, -154, -183 and -209) and those formed during the reductive debromination of BDE-209 (BDE-184, -191, -196 and -197). Finally, a total of eight commercially available Co-PXB congeners were also analysed (XB-77, -105, -118, -126A, -126B, -126C, -156 and -169).

2.3. Sampling collection

Breast milk samples were collected during 2005 from nine mothers living in Madrid and the surrounding area. All mothers were healthy, primiparous and over 15 years old. None of the donors reported any work related potential for exposure to POPs. Samples collected at different times of lactation were freeze-dried and stored at room temperature until analysis.

2.4. Analytical procedure

2.4.1. Sample preparation

Samples were prepared according to a previously described method (Bordajandi et al., 2004). Briefly, the extraction step involved a matrix solid-phase dispersion of the samples in anhydrous sodium sulphate and silica gel. Prior to the extraction with a mixture of acetone:*n*-hexane (1:1,V/V), the mixture was ground to a fine powder, loaded into a column and spiked with a mixture containing 12 $^{13}C_{12}$ labelled co-planar PCBs (Nos. 77, 81, 105, 123, 114, 118, 126, 156, 157, 167, 169 and 189). Further clean-up and lipid removal was achieved by using acid and basic impregnated silica gel multilayer columns using *n*-hexane as the elution solvent.

2.4.2. Instrumental analysis

2.4.2.1. Determination of ortho-PCBs using GC-ITD(MS/MS). The determination of *ortho*-PCB congeners was carried out by gas chromatography coupled to an ion trap mass spectrometry detector operated in its tandem mode (GC–ITD(MS/MS) on a Varian Gas Chromatograph CP-3800 (Varian, Palo Alto, CA, USA) coupled to an Ion Trap Mass Spectrometry Detector (Varian Saturn 2000), acquiring data in MS/MS mode. Samples were dissolved in a known concentration of the injection standard (CB- 70, -111, -138 and -170) and injected in a programmable temperature vapourizing injector (PTV) in splitless mode (4 μL). A VF-5MS (FactorFour™, Varian, Palo Alto, CA, USA) capillary column (50 m length, 0.25 mm i.d. and 0.25 μm film thickness) was employed. Oven program was as follows: from 100 °C (2 min) to 200 °C (3 min) at a rate of 30 °C min^{-1} and then to 230 °C (15 min) at a rate of 3 °C min^{-1} and finally to 270 °C (15 min) at a rate of 5 °C min^{-1}.

The identification and quantification, following the isotopic dilution technique, were based on the detection at the appropriate chromatographic retention time of the two most abundant ions of the product cluster and the maintenance of the theoretical ratio between them within an appropriate range for each native and ^{13}C-labelled PCB congener. The product cluster corresponded to the loss of two chlorine atoms for each PCB congener. The different parameters affecting MS/MS detection of PCBs have been published elsewhere (Gómara et al., 2006a).

2.4.2.2. Determination of PBDEs using GC-ECNI-MS. The fifteen PBDEs selected, including tri- to deca- substituted congeners (BDE -17, -28, -47, -66, -85, -99, -100, -153, -154, -183, -184, -191, -196, -197 and -209), were determined using a 6890 N gas chromatograph coupled to a 5975 quadrupole mass spectrometer (Agilent, Palo Alto, CA, USA) operated in electron capture negative ionisation mode (ECNI). Standards and samples were injected in hot splitless mode (300 °C, 1 μL; splitless time 2.0 min). A low bleed DB-5MS (15 m length, 0.2 mm i.d. and 0.2 μm film thickness) purchased from J&W Scientific (USA) was used for separation. The column temperature was programmed as follows: 110 °C (1.5 min) at 30 °C min^{-1} to 200 °C, then at 5 °C min^{-1} to 275 °C, then at 40 °C min^{-1} to 300 °C (10 min), and then at 10 °C min^{-1} to 310 °C (2 min). Helium was used as the carrier gas at a constant flow rate of 1.5 mL min^{-1}. The temperature of the transfer line was set at 310 °C and the source and quadrupole temperatures were fixed at 150 °C. The bromine ions (m/z = 79 and 81) were used as quantification ions, and the

two ions of the corresponding $[M-H_xBr_y]^-$ cluster, which are specific and characteristic of each BDE congener, were used as qualifier ions. $^{13}C_{12}$ labelled BDE-139 was used as injection standard. The different parameters affecting ECNI-MS detection of PBDEs has been reported elsewhere (Gómara et al., 2007a).

2.4.2.3. Determination of non-ortho-PCBs and PXBs. The quantification of non-*ortho*-PCBs and PXBs was performed by GC coupled to high resolution MS (GC-HRMS/EI(+)-SIM) on a GC 6890 Series GC (Agilent) coupled to an Autospec Ultima mass spectrometer (Micromass, Manchester, UK) at 10 000 resolving power (10% valley definition). Ionisation was carried out by EI at 37 eV. The injection temperature and transfer line were held at 280 °C and 260 °C, respectively. Samples were injected in splitless mode in a DB-5 fused-silica capillary column (60 m length, 0.25 mm i.d. and 0.25 μm film thickness) using helium as carrier gas. Oven program was as follows: from 120 °C (1.5 min) to 220 °C at a rate of 20 °C min^{-1} and then to 320 °C (15 min) at a rate of 2.5 °C min^{-1}. Isotopic dilution technique was used for identification and quantification of non-*ortho*-PCBs and PXBs; which were based on the detection, at the appropriate chromatographic retention time, of the two most abundant ions of the molecular cluster and the maintenance of the theoretical ratio between them within an appropriate range for each native and ^{13}C-labelled PCB congeners for non-*ortho*-PCBs, and ^{13}C-PCBs (mono-*ortho)* in the case of PXBs. Since most of the determinations of the eight individual co-PXBs in the nine samples of human milk provided concentration levels below the limits of quantification of the methodology used, it was decided to pool the samples and re-inject them as a single sample.

2.5. Quality control and assurance

All analyses such as blanks, recoveries, and parallel analyses complied with analytical standards as recommended by the EU Commission in the directive for measuring dioxins in food (Commission Regulation 1883/2006/EC). Special attention was paid to blanks and BDE-209, due to high levels of this PBDE in Spanish household dust. A method blank in each set of analysis (three analyses and a blank) was carried out. To eliminate interferences in blanks, all the glassware, chemicals, solvents, and equipment used during extraction and clean-up procedures as well as the instrumentation used have been routinely checked. Satisfactory repeatability and intermediate precision were achieved when analysing standard solutions, with relative standard deviation (RSDs) generally below 13%, except for BDE 209 which was lower than 19%, for the three families of compounds determined(PXBs, PCBs and PBDEs). Recoveries of the labelled congeners in samples and in spiked blank samples were always higher than 85% with relative standard deviation (RSDs) generally below 13%, except for BDE 209 which was lower than 19%, for the three families of compounds determined(PXBs, PCBs and PBDEs). Recoveries of the labelled congeners in samples and in spiked blank samples were always higher than 85%. Our laboratory has participated in different international inter-laboratory studies and several international quality control studies for the analysis of PCBs and PBDEs in different food matrices, including human milk samples (Becher et al., 2007–2009). The results were consistent at all times with the consensus means given by the inter-laboratory organisation.

3. Results and discussion

3.1. PXB concentration levels and accumulation pattern

This study focused, for the first time, on the eight co-PXBs that are commercially available at present which included five non-*ortho* PXBs (XB-77, -126A, -126B, -126C and -169), and three mono-*ortho* PXBs (XB-105, -118 and -156). For the nomenclature and chemical names see Table 1. Preliminary results for PXBs in the pooled breast milk sample were presented in Table 2. The levels of total Co-PXBs (sum of the eight named congeners) was 0.45 pg g^{-1} lipid weight (l.w.), which was considerably lower than the co-PCB concentration (mean value of 25 ng g^{-1} l.w.) and PBDE concentration (mean value of 5.5 ng g^{-1} l.w.) (Table 2). All PXB congeners were detected, except XB-169. XB-156 exhibited the highest value (0.19 pg g^{-1} l.w.), followed by XB-126A (0.12 pg g^{-1} l.w.), XB-105 (0.051 pg g^{-1} l.w.), XB-77 (0.034 pg g^{-1} l.w.), XB-126B (0.030 pg g^{-1} l.w.), XB-118 (0.013 pg g^{-1} l.w.) and XB-126C (0.008 pg g^{-1} l.w.). The only other two studies in recent literature dealing with the five PXB congeners (XB-105, -118, -126A, -126B and -169) in human milk samples are from Japan (Ohta et al., 2007, 2008a). The pattern of these 5 PXBs congeners found in the human milk samples from Japan (XB 118 > XB 169 > XB 105 > XB126A > XB 126B) is different from those found in the present study (XB 126A > XB 105 > XB 126B > XB 118 > XB 169). The concentration levels found in human milk from Japanese women ranged between 12 and 349 pg g^{-1} lipid weight (the sum of five co-PXB congeners), these being considerably higher than those found in Spanish breast milk samples. It was also found that the concentration levels of the five co-PXBs were similar to those of the 12 dioxin-like co-PCBs which is not the case in this study where the levels of the eight co-PXBs were much lower than those of dioxin-like co-PCBs.

The low levels of PXBs found in Spanish breast milk samples suggest that exposure levels in the Madrid population were low.

3.2. PCB concentration levels and accumulation pattern

Arithmetic mean, standard deviation, median, maximum and minimum of PCB concentration levels found in the nine human milk samples investigated, expressed in ng g^{-1} lipid weight (l.w.), are shown in Table 2. Total PCB concentrations (sum of twenty-four congeners) ranged between 52 and 221 ng g^{-1} l.w. Mono-*ortho*-PCB values ranged between 3.5 and 71 ng g^{-1} l.w., and non-*ortho*-PCBs levels ranged between 0.44 and 1.0 ng g^{-1} l.w.

Taking into account the levels reported from 1988, a decreasing temporal trend in the total PCB concentrations in Spanish breast milk samples was observed until 2004, which, from this point forward remained fairly constant. Concentrations in 1988–1995 ranged between 880 and 5099 ng g^{-1} l.w. (Conde et al., 1993; Hernández et al., 1993; González et al., 1995; Ramos et al., 1997), the levels dropped to a mean value of 241 ng g^{-1} l.w. in 2001–2003, as reported by the WHO in their monitoring survey (Malisch and van Leeuwen, 2003). In 2002 the levels were 255 ng g^{-1} l.w. (Schumacher et al., 2007), and continued to drop to 111 ng g^{-1} l.w. in 2004 (Bordajandi et al., 2008). The mean value of the breast milk samples analysed in this study was 125 ng g^{-1} l.w.

Table 1
Chemical name, IUPAC number and *ortho* substitution pattern of the eight PXBs analysed in this study.

Chemical name	IUPAC number	*Ortho* substitution pattern
3,4-DiBr-3′,4′-DiCB	XB-77	Non-*ortho*
4′-MoBr-2,3,3′,4-TeCB	XB-105	Mono-*ortho*
4-MoBr-2,3′,4,5-TeCB	XB-118	Mono-*ortho*
4′-MoBr-2,3′,4,5-TeCB	XB-126A	Non-*ortho*
3′,4′,5′-TriBr-3,4-DiCB	XB-126B	Non-*ortho*
3,4,-DiBr-3′,4′,5TriCB	XB-126C	Non-*ortho*
4-MoBr-2,3,3′,4,5-PeCB	XB-156	Mono-*ortho*
4-MoBr-3,3,4,5,5-PeCB	XB-169	Non-*ortho*

Table 2
Arithmetic mean, standard deviation (SD), median and range of PXBs, PCBs and PBDEs found in Spanish breast milk samples collected in 2005.

Congener	Mean	SD	Median	Min	Max
PXBs (pg g^{-1} l.w.)					
XB-118	0.013[a]				
XB-105	0.051[a]				
XB-126A	0.12[a]				
XB-77	0.034[a]				
XB-169	<LOQ[a]				
XB-126B	0.030[a]				
XB-156	0.19[a]				
XB-126C	0.008[a]				
Total PXB	**0.45**[a]				
PCBs (ng g^{-1} l.w.)					
CB-28	0.89	1.1	0.51	0.15	3.0
CB-52	1.6	0.63	1.6	0.70	2.4
CB-95	2.2	1.3	1.8	0.90	4.5
CB-101	1.8	1.9	1.1	0.58	5.5
CB-149	0.76	0.90	0.43	0.24	2.6
CB-123	<LOQ	–	<LOQ	–	–
CB-118	6.2	8.7	2.2	1.8	24
CB-114	9.9	14	2.4	0.35	32
CB-153	39	21	33	20	65
CB-132	5.3	5.0	5.0	<LOQ	13
CB-105	4.2	7.7	0.79	<LOQ	20
CB-138	16	11	12	5.5	32
CB-183	2.1	1.7	1.6	0.44	4.5
CB-167	1.4	1.8	0.68	<LOQ	4.8
CB-156	1.2	1.3	0.99	<LOQ	3.5
CB-157	0.44	0.83	0.015	<LOQ	2.1
CB-180	22	8.2	20	15	36
CB-170	6.2	4.4	4.6	2.8	15
CB-189	0.42	0.31	0.37	0.14	0.96
CB-194	1.7	1.1	1.5	0.42	3.6
CB-77	0.32	0.078	0.32	0.22	0.40
CB-81	0.17	0.022	0.17	0.12	0.21
CB-126	0.052	0.048	0.034	0.023	0.15
CB-169	0.096	0.091	0.058	0.047	0.28
Mono-*ortho*-PCBs	**24**	**27**	**14**	**3.5**	**71**
Non-ortho-PCBs	**0.63**	**0.21**	**0.60**	**0.44**	**1.0**
Total PCBs	**125**	**67**	**103**	**52**	**221**
PBDEs (ng g^{-1} l.w.)					
BDE-17	<LOQ	–	<LOQ	–	–
BDE-28	0.032	0.037	0.010	<LOQ	0.097
BDE-47	0.53	0.27	0.54	0.15	0.97
BDE-66	<LOQ	–	<LOQ	<LOQ	0.017
BDE-100	0.55	0.23	0.58	0.19	0.81
BDE-99	0.52	0.13	0.51	0.32	0.69
BDE-85	0.14	0.11	0.15	<LOQ	0.26
BDE-154	0.061	0.098	0.017	<LOQ	0.26
BDE-153	0.24	0.22	0.16	0.040	0.63
BDE-184	<LOQ	–	<LOQ	–	–
BDE-183	0.42	0.23	0.38	0.16	0.85
BDE-191	<LOQ	–	<LOQ	–	–
BDE-197	0.42	0.41	0.34	<LOQ	1.2
BDE-196	0.11	0.10	0.11	<LOQ	0.26
BDE-209	2.5	1.9	2.7	0.20	5.7
Tri- to hexa-BDEs	**2.1**	**0.67**	**2.0**	**1.3**	**2.9**
Hepta- to deca-BDEs	**3.4**	**2.6**	**3.4**	**0.39**	**8.01**
Total PBDEs	**5.5**	**3.1**	**5.3**	**2.1**	**11**

[a] Pool of the nine investigated samples.

A comparison of PCB levels in human breast milk from the 80s to the year 2000, along with comparison with other surveys conducted on samples collected since 2000 to present were presented in Table 3. The number of PCB congeners included in the total PCB calculation is different in each study, but in all of them, except data reported from Germany (Raab et al., 2008), the seven PCB indicators which normally contribute to more than 60% of the total were included. The mean total PCB concentrations found in this study are similar to those obtained in USA and Canada (She et al., 2007), Norway (Polder et al., 2008), Poland (Jaraczewska et al., 2006) and Japan (Nakamura et al., 2008); higher than those found in Turkey (Çok et al., 2009), and lower than those found in the UK (Kalantzi et al., 2004), Russia (Polder et al., 2008), Germany (Raab et al., 2008), Italy (Ingelido et al., 2007), and China (Zhao et al., 2007), and much lower than those found in Iran (Dahmardeh Behrooz et al., 2009).

As shown in Fig. 1, PCB accumulation pattern found in breast milk samples analysed in this study was dominated by CB-138, -153 and -180, each contributing to more than 12% of the total PCB concentration. Similar accumulation patterns of the major PCBs have been found in breast milk samples reported in the literature collected after 2000 in Spain (Bordajandi et al., 2008; Fernández et al., 2008), Russia (Polder et al., 2008), Italy (Ingelido et al., 2007), UK (Kalantzi et al., 2004), USA and Canada (She et al., 2007), China (Zhao et al., 2007) and Japan (Nakamura et al., 2008). The mono-*ortho*-PCB congeners contribute approximately 19% to the total PCB content, with CB-105, -114 and -118 being the most abundant congeners, each one having a contribution of greater than 4% each. In regard to the four non-*ortho* substituted congeners, CB-77 and -81 are predominant in all samples except in one where CB-169 is the second most abundant. The non-*ortho*-PCB patterns found by other authors in other surveys were different. CB- 126 and -169 were the most predominant in human breast milk samples from Germany (Raab et al., 2008), while CB-77 and -126 were the most predominant in human milk samples from Turkey (Çok et al., 2009). González et al. (1995) and Ramos et al. (1997) studied the relative abundance of these congeners throughout the breast-feeding period and observed a different profile depending on the week of breast-feeding. While CB-77 was predominant between weeks 8 and 11, CB-126 was the most dominant in week 12. This fact could explain the differences observed in the present study, since the samples were collected at different times during the lactation period.

3.3. PBDE levels and accumulation patterns

Arithmetic mean, standard deviation, median, maximum and minimum of PBDE congener concentration levels found in the nine human milk samples investigated, expressed in ng g^{-1} lipid weight, are shown in Table 2. The total PBDE (sum of fifteen BDE congeners) values ranged between 2.1 and 11 ng g^{-1} l.w., tri- to hexa-BDEs ranged between 1.3 and 2.9 ng g^{-1} l.w., and hepta- to deca-BDEs ranged between 0.39 and 8.0 ng g^{-1} l.w. The contribution of the higher brominated congeners (hepta- to deca-BDEs) to the total PBDE amount was around 60%, indicating the importance of determining the concentration of highly brominated PBDEs, mainly BDE-183 and BDE-209. These two BDE congeners have a high contribution to the total PBDEs in the EU countries, where the Deca-PBDE formulation have been mainly used (BSEF; De Poortere, 2000). In fact, BDE-183 and -209, as well as BDE-47, -99, -100 and -153, were detected in all the samples analysed.

As in the case of PCBs, it is necessary to take some precautions when comparing PBDE concentrations with values reported in the literature given the different criteria followed to obtain the PBDE levels, influencing the final results. Table 3 showed the results obtained in human breast samples from various countries collected since 2000, including the number of congeners analysed in each study. Most papers report on tri- to hexa-BDE congeners, so it was not possible to take into account the contribution of high brominated PBDE congeners.

The mean of 5.5 (SD = 3.1) ng g^{-1} l.w. of total PBDEs found in this study was similar to those previously found in human breast milk samples collected in Madrid (Spain) in 2003–2004 (Gómara et al., 2007b; Bordajandi et al., 2008) and were in the same range as those recently reported by other European and Asian countries (Kalantzi et al., 2004; Jaraczewska et al., 2006; Eslami et al., 2006; Chao et al., 2007; Ingelido et al., 2007; Polder et al., 2008;

Table 3
Arithmetic mean and range of PCB and PBDE levels (in ng g^{-1} lipid weight) found in human milk samples from various countries.

Country	No. of samples	Year of sampling	Total PCBs No. of congeners	Total PCBs mean (range)	co-PCBs mean (range)	Total PBDEs No. of congeners	Total PBDEs mean (range)	References
Spain (Madrid)	9	2005	24	125 (52–221)	25 (3.9–72)	15	5.5 (2.1–11)	This study
UK (London and Lancaster)	54	2001–2003	15	200 (26–530)		6	8.9 (3.1–69)	Kalantzi et al. (2004)
Russia (Murmansk)	10	2000–2002	16	346 (188–696)		8	1.2 (0.81–1.9)	Polder et al. (2008)
Poland (Wielkopolska region)	22	2004	16	153 (63–413)		6	2.5 (0.8–8.4)	Jaraczewska et al. (2006)
Norway (Tromso and Oslo)	29	2000–2002	20	172 (76–256)	34 (NP)	7	3.8 (1.7–9.7)	Polder et al., 2008
Germany (Bavaria)	42	2005		230 (60–600)	21.2 (6.84–53)	5	1.9 (0.57–6.5)	Raab et al. (2008)
Italy (Rome)	10	2000–2001	16	240*		11	4.1	Ingelido et al. (2007)
USA (Texas)	47	2001				13	74 (6.2–713)	Schecter et al. (2003)
USA and Canada	40	2000–2002	12	147 (49–315)		12	96 (6.3–321)	She et al. (2007)
Iran (Nour city)	53	2006	7	1820 (ND-12430)				Dahmardeh Behrooz et al. (2009)
Turkey (Istanbul)	13	2007	7	19 (5.4–64)	6.8 (1.5–14)			Çok et al. (2009)
China (Nanjing)	9	2004				14	7.7 (2.7–15)	Sudaryanto et al. (2008)
China (Pingqiao)	16	2003–2005	23	206 (69–677)				Zhao et al., 2007
Taiwan (central)	20	2000–2001				12	3.9 (SD = 1.7)	Chao et al., 2007
Japan (13 regions)	105	2004				6	2.5	Eslami et al., 2006
Japan (Tohoku region)	49	2001–2003	28	118 (31–272)	15 (3.4–39)			Nakamura et al., 2008

Pooled samples; ND = non detected; SD = standard deviation.

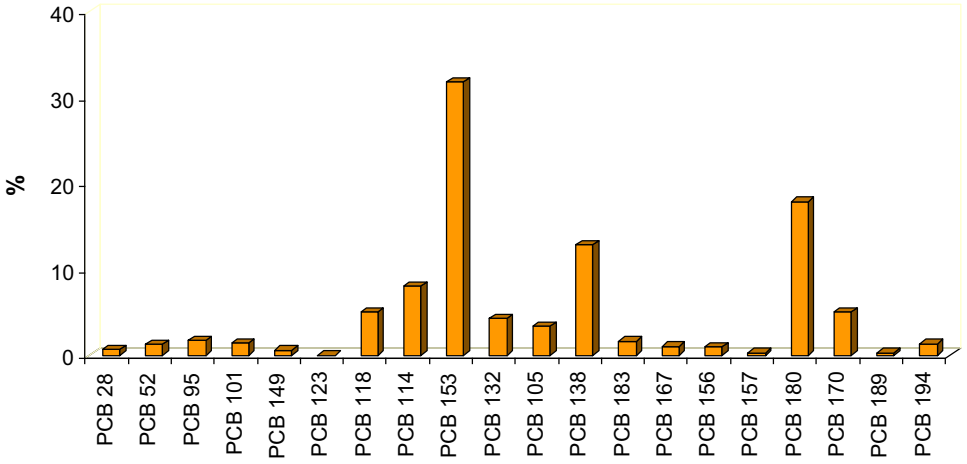

Fig. 1. Contribution (in percentages) of each PCB congener to the total PCBs.

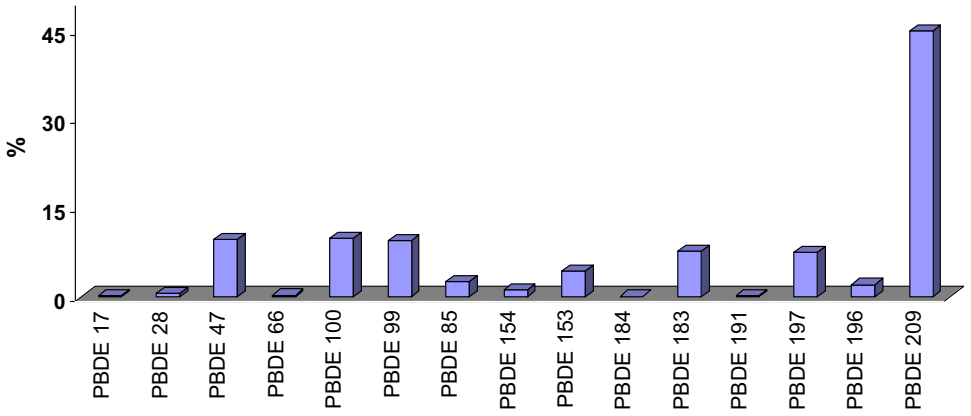

Fig. 2. Contribution (in percentages) of each PBDE congener to the total PBDEs.

Raab et al., 2008; Sudaryanto et al., 2008), and much lower than those found in USA and Canada (Schecter et al., 2003; She et al., 2007).

PBDE congener profiles (in percentages) in this study are shown in Fig. 2. BDE-209 was the most predominant (accounting around 45% to total PBDEs), followed by BDE-47, -99 and -100 (around 10% each of them). The high contribution of BDE-209 to the total PBDEs has been already reported in previous studies conducted in the Madrid population (Gómara et al., 2007b); and it is not very surprising since this congener was the most predominant one in Spanish food (Gómara et al., 2006b), in Spanish household dust (Fabrellas et al., 2005) and in sediment samples from several hot spots in the Spanish coast (Eljarrat et al., 2005). It is difficult to compare PBDE profiles reported in this study with previous ones in the literature since different PBDE congeners were included in each study. BDE-47 is normally the most abundant congener in breast milk samples, with some exceptions that have been reported recently. In studies where BDE-209 was included, its contribution to the total PBDEs was quite high in Asian and European countries where the Deca-PBDE technical products have been frequently used (Chao et al., 2007; Polder et al., 2008; Sudaryanto et al., 2008). By contrast, in countries such USA and Canada, where until recently Penta-PBDE commercial mixture has been used extensively the contribution of BDE-209 to the total PBDEs was much less significant (Schecter et al., 2003; She et al., 2007).

4. Conclusions

This study presented for the first time data on PXBs in Spanish breast milk. The levels of PXBs found were lower than those of PBDEs and much lower than those of PCBs. Although PXB levels are low, the fact that they have been detected in breast milk samples indicated that they have entered into the trophic food chain, and therefore further research is needed to assess their distribution and accumulation within the human population.

Although the number of samples presented in this study was limited, the presence of PXBs, the negligible decrease of PCB levels since 2000, along with the important levels of PBDEs, mainly the BDE 209, in breast milk samples studied, showed the necessity for a large scale monitoring study in different countries, including Spain.

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