



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 from 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.

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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 lipophilicity, 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 Fe₃Cl 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 (Alae 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 lipophilic 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 lipophilic 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 $^{13}\text{C}_{12}$ 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 using 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 $^{13}\text{C}_{12}$ 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

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