Chemosphere 93 (2013) 526–531

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Polybrominated diphenyl ethers and polychlorinated biphenyls in cord blood from women in Poland

Agnieszka Hernik *, Katarzyna Góralczyk, Paweł Struciński, Katarzyna Czaja, Wojciech Korcz, Maria Minorczyk, Jan Krzysztof Ludwicki

Department of Toxicology and Risk Assessment, National Institute of Public Health – National Institute of Hygiene, Chocimska 24, 00-791 Warsaw, Poland

HIGHLIGHTS

- Selected PBDEs and PCBs have been analysed in cord blood from women resident in Warsaw.
- In over 90% of all samples PCB-153, PCB-138, PCB-180 and PBDE-47 were identified.
- The highest concentrations were found for PCB-153 and PCB-138 (43.4 and 11.8 ng g^{-1} fat).
- Human exposure to PBDEs and PCBs begins in the period of intrauterine life.

ARTICLE INFO

Article history:
Received 11 January 2013
Received in revised form 3 April 2013
Accepted 2 June 2013
Available online 12 July 2013

Keywords:
Polybrominated diphenyl ethers
Polychlorinated biphenyls
Cord blood
Human exposure
Poland

ABSTRACT

The purpose of this study was to assess human exposure in the prenatal period to selected PBDEs (BDE-47, BDE-99, BDE-153) and PCBs (CB-77, CB-101, CB-118, CB-126, CB-138, CB-153, CB-170, CB-180) basing on the analysis of these compounds in cord blood. The experimental material consisted of 89 cord blood samples taken from women resident in Warsaw and its vicinity. In over 90% of all tested samples the presence of congeners CB-153, CB-138, CB-180 and BDE-47 was identified. The least frequently found were CB-126 and BDE-153, which were present at relatively low concentration levels. Among all analysed PCBs, the highest average concentrations were found in the case of congeners CB-138 (11.8 ng/g of fat) and CB-153 (43.4 ng/g of fat), whereas the lowest was in the case of CB-170 (0.4 ng/g of fat) and CB-126 (0.1 ng/g of fat). In the case of PBDEs the greatest share in the total concentration was that of the congeners BDE-47 and BDE-99, whereas the smallest share was that of the higher brominated congener BDE-153. These results suggest that human exposure to the examined compounds begins already in the period of intrauterine life. The comparison of our own results with the findings of other authors indicates that the PCBs and PBDEs levels in cord blood of women living in Poland do not differ from the respective concentrations in cord blood of other female inhabitants of Europe.

1. Introduction

In recent years much attention has been devoted to persistent organochlorine pollutants which may disrupt human and animal endocrine system equilibrium via different mechanisms, known as endocrine disruptors (EDs). Among others these include persistent organochlorine pesticides (e.g.: DDT, lindane), as well as industrial products and pollutants, such as hexachlorobenzene (HCB) or polychlorinated biphenyls (PCBs) (Colborn et al., 1993). Despite the fact that in most countries their production is prohibited since some 30 years, the presence of these compounds is still found in a variety of samples taken from the environment, whereby the highest concentrations are noted in material of human origin. Among 209 PCBs congeners 12 so called dioxin like PCBs (DL – PCBs) are characterised by similar mechanism of toxicity to dioxins. Remaining congeners (non-dioxin like PCBs, NDL-PCBs) elicit different types of responses occurring via multiple toxicity pathways (European Food Safety Authority, 2012). Polybrominated diphenyl ethers (PBDEs) have also been classified as pertaining to the EDs category (Legler and Brouwer, 2003; McKinlay et al., 2008; Diamanti-Kandarakis et al., 2009). Since the nineteen-sixties they have been used as flame retardants in various commercial and household products (e.g.: computers, television sets, linings). They also serve as an additives i.a. in plastics, fabrics, polyurethane foams, paints and varnishes. When applied as flame retardants they enhance the users' safety, but unfortunately they are also able to migrate to various elements in the environment from the products, in which they have been used (Vos et al., 2003). Similarly as other persistent organic pollutants (POPs) category, they circulate

* Corresponding author. Tel.: +48 22 5421421; fax: +48 22 8497441.
E-mail address: ahernik@pzh.gov.pl (A. Hernik).

0045-6535/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2013.06.045

in the environment and may be transmitted across large distances. There is still relatively limited information, however, concerning their toxicity or carcinogenicity for humans. Yet, there are justified grounds to regard this category of compounds as the successor of PCBs in terms of environmental pollution and their remote impact on human health. Both in terms of their structure and impact PBDEs appear to be similar to polychlorinated biphenyls (Fitzgerald et al., 2012).

The presence of PBDEs, similarly as PCBs, is confirmed in all elements of the environment. It was evidenced in samples originated from Poland that organohalogen contaminants were present in sediments, water and sludge (Falandysz et al., 2006; Grabowska, 2010), soils (Falandysz et al., 2001), ambient air (Falandysz et al., 1999) and bioindicators of environmental contaminations such as pine needles (Falandysz et al., 2012) and game animals (Falandysz and Kannan, 1992; Szymczyk-Kobrzyńska and Zalewski, 2003; Zasadowski et al., 2003; Niewiadowska et al., 2010; Tomza-Marciniak et al., 2011). Their presence has been reported in fish catched in Polish fishing grounds in the Baltic Sea (Falandysz et al., 2002; Szlinder-Richert et al., 2009; Piskorska-Pliszczyńska et al., 2012; Waszak et al., 2012) and noted in adipose tissue of livestock, cow milk, eggs and butter (Niewiadowska et al., 2010; Roszko et al., 2013; Witczak et al., 2013). Food of animal origin is considered as a main source of human exposure to PCBs (IPCS, 2003; European Food Safety Authority, 2012). Consequently they are also in human specimens: adipose tissue, blood, semen, as well as women's milk (Tanabe et al., 1993; Covaci et al., 2002a; Guvenius et al., 2003; Jaraczewska et al., 2006; Szyrwińska and Lulek, 2007; Raab et al., 2008; Shen et al., 2008; Herbstman et al., 2010; Hernik et al., 2011; Gomara et al., 2012; Liu et al., 2012). Not all the sources of human exposure to PBDEs have come to be fully known. In the general population a number of potential ways of exposure to this category of compounds may be indicated. These include: direct contact with products containing PBDEs, intake with food – mainly animal fat, meat, fish and dairy products. A significant source of exposure consists also of household dust (Bocio et al., 2003; Domingo, 2004; Kiviranta et al., 2004; Darnerud et al., 2006; European Food Safety Authority, 2011; Törnkvist et al., 2011; Frederiksen et al., 2012; Góralczyk et al., 2012).

The greatest exposure to these compounds, however, exists in infants fed with their mothers' milk (Schecter et al., 2005). This is a consequence both of the intake of PBDEs contained in milk and of exposure during the prenatal period, which was confirmed by study indicating that these compounds are able to penetrate through the placenta to the foetus (Covaci et al., 2002b; Herbstman et al., 2008; Meijer et al., 2008a,b; Roze et al., 2009; Schecter et al., 2005).

The least knowledge concerns *in utero* exposure, which is supposed to be especially high, because it occurs at a time of extraordinary mobilisation of fat reserves in the organism of the mother for the purpose of feeding the foetus as it grows, which is accompanied by the concurrent release of these compounds from tissue deposits (Saxena et al., 1981; Asante et al., 2011).

The objective of the present work was to assess human exposure in the prenatal period to selected most commonly analysed in human specimens representatives of polybrominated diphenyl ethers (PBDE-47 (2,2′,4,4′-tetrabromodiphenyl ether), PBDE-99 (2,2′,4,4′,5-pentabromodiphenyl ether), PBDE-153 (2,2′,4,4′,5,5′-hexabromodiphenyl ether) and polychlorinated biphenyls, dioxin-like PCBs (PCB-77 (3,3′,4,4′-tetrachlorobiphenyl), PCB-118 (2,3′,4,4′,5-pentachlorobiphenyl), PCB-126 (3,3′,4,4′,5-pentachlorobiphenyl) and non dioxin-like PCBs (PCB-101 (2,2′,4,5,5′-pentachlorobiphenyl), PCB-138 (2,2′,3,4,4′,5′-hexachlorobiphenyl), PCB-153 (2,2′,4,4′,5,5′-hexachlorobiphenyl), PCB-180 (2,2′,3,4,4′,5,5′-heptachlorobiphenyl), PCB-170 (2,2′,3,3′,4,4′,5-heptachlorobiphenyl). It was also attempted to determine the possible link between the concentrations of the examined substances in cord blood and the age and body mass index (BMI) of the donors, as an additional factor that may contribute to the release of these compounds from the body deposits. In the latter case, the study on the possible relationship could be a contribution to the general debate on the role of the diet and other factors in the exposure to the examined compounds.

2. Materials and methods

2.1. Material and samples collection

The research material consisted of 89 samples of cord blood from women living in Warsaw and its vicinity. Consent to fill out the questionnaire was given by 84 donors.

After having obtained permission from the Bioethical Committee the samples were taken at one of the maternity hospitals in Warsaw over the years 2002–2005. Information was obtained from the donors concerning their age, body weight, height, number of childbirths, the kind of diet followed, and their general health condition. Until the time of testing the samples were stored in the temperature of −20 °C.

2.2. Chemicals

For the purposes of the method validation and internal quality control the following standards were used: PBDE-47, PBDE-99, PBDE-153 solutions in nonane (Cambridge Isotope Laboratories), PCBs mix (PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153, PCB-180), solution in isooctane (LGC Promochem), PCB-77, purity 99.5% (dr Ehrenstorfer), PCB-126, purity 99.0% (dr Ehrenstorfer), PCB-170, purity 99.0% (dr Ehrenstorfer). The following solvents and reagents were applied: *n*-hexane, for residues analysis (Merck), anhydrous sodium sulphate, for residues analysis (Merck), dichloromethane (DCM) pro analysis (Merck), ethanol 96%, isopropanol, (Chempur), BioBeads S-X3 (Bio-Rad Laboratories, Inc.), water cleaned by the reverse osmosis method.

2.3. Extraction and clean-up

A modified version of the extraction method described by Päpke et al. (2004), was applied. The cord blood sample was diluted in water and after addition of ethanol it was extracted twice with *n*-hexane, followed by two consecutive extractions with a mixture of *n*-hexane and isopropanol in the proportion of 3:2. The combined extracts were rinsed with water and dried with sodium sulphate. After evaporation of the solvent the fat content was determined gravimetrically. The dry residue was dissolved in hexane/dichloromethane mixed in proportion of 1:1 (v/v) and refined using gel permeation chromatography. BioBeads S-X3 were used as packing of the column. Each column contained 6 g of packing. In order to determine the elution volume of the examined compounds the elution profile of the column used was examined. Elution was conducted using a mixture of dichloromethane and *n*-hexane (1:1, v/v). The fraction containing the analysed compounds was collected from 17 to 28 mL.

2.4. Gas chromatography

Quantitative determination was carried out using the gas chromatography with an electron captor detector. The following working conditions of the chromatograph were applied: column HP-5 (0.32 mm i.d. × 30 m, 0.25 μm film thickness), oven temperature: 70 °C (1.7 min), 30 °C min^{-1} – 190 °C, 3 °C min^{-1} – 240 °C, 30 °C min^{-1} – 280 °C; injector temperature: 260 °C; injection volume: 5 μL; detector temperature: 300 °C; carrier gas: helium.