POLYBROMINATED DIPHENYL ETHERS (PBDEs), POLYCHLORINATED BIPHENYLS (PCBs) AND ORGANOCHLORINE PESTICIDES IN HUMAN MILK IN POLAND

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Abstract
28 breast milk samples from Warsaw citizen and women from neiberhood were analyzed for polybrominated diphenyl ethers (BDE-47, BDE-99, BDE-153), polychlorinated biphenyls (PCB-77, PCB-101, PCB-118, PCB-126, PCB-138, PCB-153, PCB170, PCB-180) and organochlorinated pesticides (HCB, β-HCH, γ-HCH, p,p'-DDE, p,p'-DDD, p,p'-DDT). For extraction and clean-up procedure was used method described by O. Kalantzi et al. [1] with minor modification. The profile of PBDE congeners in milk was dominated by BDE 47 than BDE 99 and 153. There was no correlation between concentrations of PBDEs and maternal characteristics (age, BMI). PCB congeners profile observed in the investigated milk samples are similar to those previously reported from Europe with congeners 153, 180 and 138 as the most abundant compounds. p,p'-DDT and its metabolites, together with HCB and HCH were found in all milk samples. The analysis of the results showed individual differences in the excretion of this compounds, and the levels in milk are strongly correlated to the fat content of the milk.

Introduction
Anthropogenic halogenated compounds, including some of the persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and organochlorinated pesticides (OCPs) have been identified as contaminants with a global distribution and are present in wildlife species in both aquatic and terrestrial ecosystems. Environmental concentrations of PBDEs have increased exponentially opposite to the PCBs and OCPs levels. Both groups, chlorinated and brominated compounds, are lipophilic and accumulate in the human body. The elimination of such compounds and their metabolites from body fat is very low. This compounds are transferred to milk. The levels in milk are strongly correlated to the fat content of milk. The persistent organohalogenated compounds monitoring in human body is important to estimate the exposure to this compound and possible related health risks.

Materials and Methods
The study material were 28 samples of human breast milk measured for the content of HCB, β-HCH, γ-HCH, p,p'-DDE, p,p'-DDD, p,p'-DDT, PCB-77, PCB-101, PCB-118, PCB-126, PCB-138, PCB-153, PCB170, PCB-180, BDE-47, BDE-99, BDE-153 and PBB-153. Samples were collected in the maternity clinic in Warsaw. The donors completed detailed survey regarding (among others) their age, body weight, number of deliveries, diet and health conditions. The samples were kept frozen at -20º C until analysis. The extraction and clean-up procedure was used with minor modification of methods described by O. Kalantzi et al. After defrosting milk samples were centrifuged at 3000 rpm for 17 min, than separated the milk-fat layer from the aqueous phase. The mixture of milk fat, sodium sulfate and hexane was boiled for 10 min and allowed to cool before lipid determination. The extracts were clean up using concentrated sulfuric acid. Evaporated to 2 ml mixtures were applied to gel permeation chromatography column packed with Biobeads SX 3 and eluted with hexane/dichloromethane (1:1, v:v). The purified extracts were analyzed by GC/ECD and GC/MS. The column of GC/ECD was a fused silica capillary column HP-5 (0,32 mm i.d. × 30 m, 0,25 μm). The injector temperature was kept at 260ºC, and the injection volume 5.0 μl. The initial column temperature was 70ºC for 1,7 min. The temperature was thereafter increased by 30 °C min-1 to 190 °C, 3 °C min-1 to 240 °C and 30 °C min-1 to 280 °C. For GC/MS (Varian 4000) samples were injected in the splitless mode (5 μl) on the DB-5MS capillary column (30 m x 0,32 mm i.d., 0,25 μm film thickness). The column temperature program was as follows: 70 °C

(1 min), 30 °C min-1 – 170 °C, 8 °C min-1 – 300 °C (15 min). Helium was used as carrier gas at a constant flow rate of 1 ml/min. Transfer line and trap temperatures were set at 260 °C and 200 °C, respectively. The mass spectrometer was operated in the MS/MS mode for PBDEs.

Results and Discussion

The characteristics of participated in the present study women (n = 28) are summarized in the Table 1.

Table 1. General characteristics of women participating in this study.

Medical parameters	Mean ± SD	Range
Age (years)	29,86 ± 3,56	23 - 40
Weight before pregnancy (kg)	59,25 ± 9,44	45 - 89
Pre-pregnant body mass index (kg/m^2)	21,39 ± 3,18	17 - 32

SD – standard deviation

As shown in Table 1, women in the study population were of age 23 – 40 years and the pre-pregnant body mass index (BMI) was between 17 and 32. Mean lipid value for milk samples was 1,37 %. Lipid percentage in milk was relatively low due to sample collection during the first lactation days.

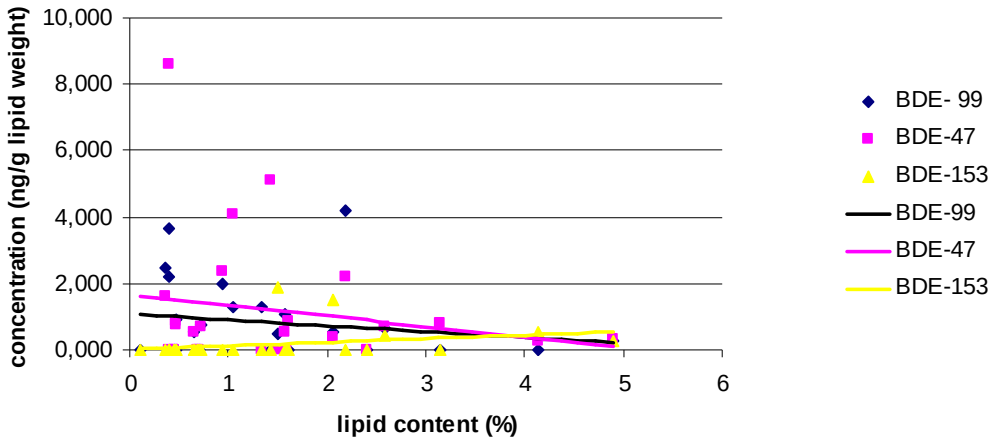
Analytical results are shown in the Table 2. The method limits of quantification (LOQ) for PCBs, OCPs and PBDEs ranged between 0,6 - 2,0 ng/g lipid weight. The recoveries ranged were from 54 % to 95 %.

Table 2. PCBs, OCPs and PBDEs concentrations expressed in ng/g lipid weight.

Compound	% > LOQ	Mean	GM	Range
HCB	100	10,6	7,1	2,0 - 66,8
b-HCH	100	31,9	17,8	5,9 - 202,9
g-HCH	96	23,8	9,1	< LOQ- 200,0
p,p'-DDE	100	2146,9	1374,2	241,5 - 12803,1
p,p'-DDD	100	124,4	27,0	2,8 - 1883,3
p,p'-DDT	100	383,2	192,4	< LOQ- 3055,5
PCB 77	79	33,6	12,1	< LOQ- 411,3
PCB 101	32	16,9	13,5	< LOQ- 251,9
PCB 118	46	1,9	2,9	< LOQ- 15,2
PCB 126	18	4,5	4,8	LOQ- 107,8
PCB 138	86	23,6	17,1	< LOQ- 173,4
PCB 153	90	39,8	24,4	< LOQ- 200,0
PCB 170	57	4,6	6,3	< LOQ- 26,6
PCB 180	96	26,1	18,4	< LOQ- 163,9
BDE 99	57	0,8	1,1	< LOQ- 4,2
BDE47	64	1,1	1,1	< LOQ- 8,6
BDE 153	22	0,2	0,7	< LOQ- 1,9

The PBDEs levels in milk were correlated to the fat content of milk – are shown in the Figure 1.

Figure 1. Relationship between PBDEs levels and fat content in the breast milk.



The OCPs mean levels in milk samples in the present study were lower in comparison to levels in previous Polish study from 1992-1993 years [2]. There was no correlation between concentrations of PBDEs and maternal characteristics (age, BMI). The levels of PCBs and PBDEs found in this study are generally at the same level in comparison to levels in Polish breast milk published by K. Jaraczewska in 2006 [3]. The dominated congener of PBDEs was, similar like in milk from other European countries, BDE-47 followed by BDE 99 and 153.

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