Organohalogen Compounds, Volume 61, Pages 9-12 (2003)

POLYBROMINATED DIPHENYL ETHERS (PBDEs) AND SELECTED ORGANOCHLORINES IN HUMAN BREAST MILK SAMPLES FROM THE UNITED KINGDOM

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Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used as additive flame retardants in products such as paints, textiles and plastics to reduce fire risk[1]. They are lipophilic, have low vapour pressures and bioaccumulate through the foodchain[2]. PBDEs were first detected in the environment in Sweden, in 1981 by Andersson and Blomkvist[3]. Since then they have been found in many environmental matrices including human body fat stores[4].

PCBs and organochlorine pesticides have been widely studied and their toxicity and effects in humans are well known and documented[5]. In contrast, the health effects of PBDEs are relatively unknown. Since they are structurally similar to PCBs we can assume that they might be toxic to humans in the same way as PCBs. Over the last two decades there have been indications of increased human PBDE concentrations, although their levels are still generally lower than those of PCBs[6].

Being persistent chemicals, PBDEs, PCBs and OC pesticides accumulate in the human body. Because milk has a relatively high fat content, these lipophilic chemicals persist and accumulate in it. This study was undertaken to investigate the distribution of PBDEs in human breast milk from women in the UK, relate them to concentrations of PCBs and organochlorine pesticides in the same samples and compare any possible differences between an urban area and a more rural one.

Materials and methods:

Individual human milk samples were donated by volunteers, anonymously and without criteria, after ethical approval from the relevant local ethics committees had been obtained. A total of 52 samples were collected from the maternity units of hospitals in the Lancaster (NW England (n=25)) and London (Hammersmith, West Central London (n=27)) areas between late 2001 and January 2003. Samples were frozen immediately prior to analysis.

All solvents used were of HPLC or glass-distilled grade. Silica gel (Merck, 0.063-0.200 mm) was activated at 450^{o}C overnight for the acidified silica chromatography and extracted with DCM for

the silica-gel fractionation chromatography. Sodium sulphate was baked at 450^{o}C overnight and all sorbents were stored in sealed containers after activation. Extracts were stored in amber glassware and precautions were taken not to expose the samples to light. Standards were purchased from Promochem (Welwyn Garden City, UK) and QMx (Thaxted, UK).

The milk was centrifuged and about 0.5 g of milk fat was weighed into a flask, 5g of sodium sulphate was added. About 50 ml of hexane was added, the sample was boiled for 10 minutes and then allowed to cool. A sub-sample of the extract was taken for lipid determination and the remaining sample was spiked with recovery standards ($^{13}C_{12}$-labelled PCBs and dioxins) and evaporated to approximately 5 ml. The extract was then cleaned-up using acidified silica gel chromatography followed by gel permeation chromatography. $^{13}C_{12}$ labelled PCB internal standards in dodecane were added to the GPC fraction before they were evaporated to 25 µl for GC-MS analysis.

Gas chromatography for PBDE analysis was performed on a Finnigan Trace GC2000 series gas chromatograph equipped with a 30m DB-5MS 0.25 mm id capillary column (J&W Scientific) fitted with a retention gap (2 m long, 0.53 mm id). The quadrupole 'TRACE' mass spectrometer was set in selected ion recording mode, in CI- mode, using ammonia as the reagent gas. Gas chromatography for PCB and OC analysis was performed on a Fisons GC8000 series gas chromatograph equipped with a 50 m CPSil8 0.25 mm id capillary column (Chrompak), fitted with a retention gap as for PBDE analysis, above. The quadrupole 'MD800' mass spectrometer was set in selected ion recording mode, in EI+ mode.

Results and discussion

PBDE congeners 47, 100, 99 and 153 were found in all milk samples. PBDEs 28, 35, 71, 17 and 32 were also usually found (in the respective order of abundance). Total PBDE concentrations ranged from 0.3 to 68.6 ng/g lipid, with a geometric mean of 6.6 ng/g lipid. PBDE 47 was always found at the highest concentration, followed by 153, 99 and 100. PBDE 47 concentrations ranged from 0.1 to 36.5 ng/g lipid, with a geometric mean of 3 ng/g lipid, accounting for 45% of the total PBDE concentration. Other studies also support the dominance of PBDE 47 in PBDE congener profiles in human milk[7] and human blood plasma[8]. Geometric mean concentrations and % of the total PBDE concentration for the other major congeners were: PBDE 153, 1.4 ng/g lipid (21%), PBDE 99, 0.9 ng/g (13%), PBDE 100, 0.6 ng/g (9%) and PBDE 154, 0.5 ng/g (8%). A summary of the PBDE data can be seen in Table 1.

Comparing PBDE data from other studies on humans[4,9,10,11,12], it is observed that the concentrations measured in this study were higher than those of Swedish, German, Finnish, Canadian and Japanese mothers. This is probably related to the fact that the UK has had very strict fire regulations since 1988 and as a result has used larger quantities of the penta-product for flame retarding soft furnishing for indoor applications. However, in comparison with some recent US data of 150-200 ng/g fat[13], the results presented in this study are much lower. To our knowledge this is the first report of PBDEs in UK human breast milk.

Total PCB concentrations ranged from 2.6 to 530 ng/g lipid, with a geometric mean of 120 ng/g lipid. The major congeners were 153, 138, 180, 118, 174, 187 and 99 (in respective order of abundance). PCB 153 contributed an average of 25% of the total PCB concentration, PCB 138 contributed 20% and PCB 180 contributed 12%. This is in agreement with previous studies[14]. The major OC pesticides occurred in the sequence (and concentration range) as follows: p,p' DDE (geometric mean= 110 ng/g lipid, range=1.7–1590 ng/g lipid) > ΣHCHs (geometric mean=14 ng/g lipid, range=0.2-1540 ng/g lipid) > p,p' DDT (geometric mean=4.9 ng/g lipid, range=0.1-760 ng/g lipid) > HCB (geometric mean=14 ng/g lipid, range=0.3-180 ng/g lipid). A summary of the PCB and OC pesticide data can be seen in Table 2. Norén *et al*.[4], found total PCB concentrations of 324 ng/g lipid and p,p' DDE concentrations of 129 ng/g lipid in human breast milk from Swedish women collected in 1997, which is higher than the levels reported in this study.

Some individuals were extreme outliers in the data. For PBDEs those individuals numbered three, for ΣDDXs they were two, one of which was also an outlier for HCB whilst the other an outlier for ΣHCHs. Highest concentrations of all three classes of compounds were found in samples collected from London and lowest concentrations were generally associated with individuals located in the less urban Lancaster area. Further work is ongoing to look at the relationships between the patters of congeners and their relationship to location, age of mothers and lifestyle factors.

Acknowledgements
The authors would like to thank Lancaster University for providing the funding, the Neonatal staff at the Royal Lancaster Infirmary and Gillian Weaver at the Hammersmith Hospital Milk Bank for the provision of breast milk samples.

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Table 1 - Summary of the main PBDE congener concentrations observed in milk samples (in ng/g lipid)

PBDE congener	minimum	maximum	geometric mean
47	0.1	36.5	3
99	0.1	12.5	0.9
100	0.1	7	0.6
153	0.2	5	1.4
154	0.1	2.5	0.5
ΣPBDE	0.3	68.6	6.6

Table 2 - Summary of the main PCB congener and OC pesticide concentrations observed in milk samples (in ng/g lipid)

	minimum	maximum	geometric mean
pcb28	0.03	10	1.9
pcb74	0.06	40	4.8
pcb99	0.1	21	4.2
pcb118	0.2	43	7.5
pcb138	0.5	100	24
pcb153	0.6	135	30
pcb156	0.1	13	3.5
pcb170	0.1	49	6.9
pcb180	0.2	120	15
pcb187	0.03	39	4.5
pcb194	0.03	27	2.5
ΣPCB	2.6	530	120
p,p' DDE	1.7	1590	110
p,p' DDT	0.1	760	4.9
HCB	0.3	180	14
β HCH	0.1	1540	16