Unusual Pattern of Polybrominated Diphenyl Ethers (PBDEs) in US Breast Milk

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Introduction

Levels of polybrominated diphenylethers (PBDEs) among residents of North America are 10-70 times higher than those of individuals in Europe or Japan[1-6]. Our discovery of high levels of PBDEs in Californians[1-2] has been confirmed by recent studies showing high levels of PBDEs in US residents in different regions[3-5]. As a follow-up to these studies, our lab has analyzed 16 breast milk samples collected from residents of the Pacific Northwest, US by Northwest Environment Watch, a Washington state-based NGO, for 12 PBDE congeners including PBDE 209[6].

Materials and Methods

Breast milk samples (100 mL) were hand-expressed and collected from 16 healthy first-time mothers whose healthy infants were between 2-8 weeks of age. Samples were immediately frozen in foil-wrapped chemically clean sample jars, and the frozen samples were lyophilized until a stable weight was reached, around 72 hours and the moisture content determined. Approximately 3.5 grams of dried milk samples were spiked with ^{13}C-PBDE, PCB, and dioxin standards, and extracted on the ASE 200 with hexane:methylene chloride:methanol (5:2:1) for 11 minutes at 80^{o}C with extraction pressure of 1500 psi. Sample extracts were collected in tared 60 mL amber glass collection vials, and 2 mL aliquots extracts were placed in a tared aluminum weight boat for gravimetric fat determinations. The extracts were reduced to <1 mL using a Turbo Vap. Sample cleanup used a mixed silica gel column followed by GPC to remove residual fat.

The target analytes were identified and measured using a Finnigan Mat-95 high-resolution GC/MS equipped with a splitless injector and a 15-meter DB 5 ms column operating in electron impact ionization-selective ion monitoring mode with 10,000 resolution. Molecular ions were monitored to identify tri- to hexa-BDEs, and M-2Br ions identified hepta-, and deca-BDEs.

Exposure to UV light was minimized at every stage of sample handling. Sample collection jars and sample extracts were covered with aluminum foil, lab fluorescent lights were turned off, and

window-shades were drawn. All glassware were solvent rinsed with 1:1 hexane: methylene chloride, and covered with aluminum foil.

Results and Discussion

The analytical results for the milk samples from the 16 first-time mothers from the Pacific Northwest US are shown in Table 1. Total PBDE levels (lipid-based) ranged from 6-300 ppb (mean = 77 ppb; median = 48 ppb), results similar to our previous findings in breast adipose tissue from California women collected in 1996 - 1998 (n=23; mean = 86 ppb; median = 41 ppb)[1]. These data are also similar to PBDE levels (lipid-based) found in breast milk samples in a Texas study (n = 47; mean = 74 ppb; median = 34 ppb)[4], and slightly lower than levels reported in a study of US breast milk samples (n=20; mean = 159 ppb; median = 58 ppb)[5]. Although the adipose tissue study population of 1996 – 1998 is quite different (older, multiparous) from the 2003 breast milk studies, PBDE levels appear to be reasonably similar in different regions of the US over this 5-year period.

In our Pacific Northwest US study, PBDE 47 was the dominant congener in most (14 out of 16) of the samples (mean = 35 ppb; median = 31 ppb). PBDE 153 was the next highest congener (mean = 21 ppb; median = 5 ppb). PBDE 100 and 99 contributed equally to total PBDEs, with means of 9 and 7 ppb and medians of 5 and 5 ppb, respectively. Levels of all other PBDEs were lower than 1 ppb. Levels of both PBDE 183 and PBDE 209 were very low (< 0.4 ppb).

Table 1: Summary results of 16 Northwest US breast milk samples (PBDEs in pg/g, lipid)

PBDE Congeners	Min	Max	Mean	Median	SD	CV
Moisture%	85.6	88.8	87.0	86.7	0.965	1.11
Fat%	2.78	5.06	4.19	4.50	0.69	16.6
PBDE-32	5.04	459	94.5	23.0	151	160
PBDE28/33	257	6970	2630	1570	2310	87.7
PBDE-71	38.5	1020	313	160	305	97.6
BDE-47	2630	87500	35200	31400	28400	80.8
PBDE-66	29.2	693	203	104	221	109
PBDE-100	549	38200	9070	4860	10400	115
PBDE-99	810	18800	7310	5360	5860	80
PBDE-85	3.79	2450	774	551	787	102
PBDE-154	25.4	2980	782	639	813	104
PBDE-153	992	169000	21400	4970	44900	210
PBDE-183	6.08	1550	347	211	388	112
PBDE-209	48.2	1460	376	250	402	107
∑Tri-PBDE	266	7110	2740	1720	2400	87.7
∑Tetra-PBDE	2720	88100	35200	28800	28800	81.8
∑Penta-PBDE	1360	54700	17200	11900	15600	90.9
∑Hexa-PBDE	1060	172000	21900	4000	45600	208
∑Hepta-PBDE	6.08	1550	347	211	388	112
∑PBDE	6340	309000	77500	48500	79600	103

The homologue profile for the 16 Northwest US breast milk samples, using means of tri-, tetra-, penta-, hexa-, hepta-, and deca-BDEs, was shown in Figure 1.

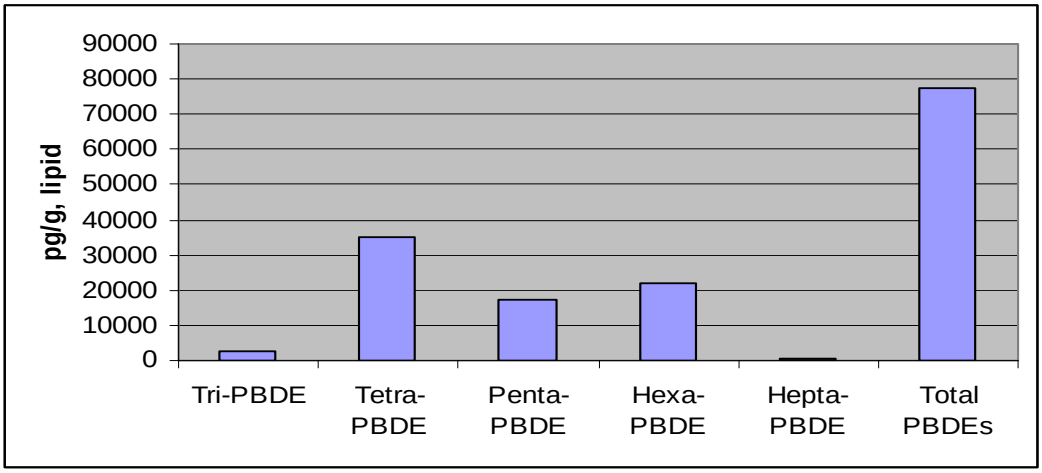

Figure 1: Homologue profile of PBDEs in Northwest US breast milk (n = 16, mean)

As seen in Figure 1, tetra-BDEs (mostly PBDE 47) were the most abundant homologues in the breast milk samples. Hexa-BDEs (mostly PBDE 153) were the second-most abundant homologue group, surpassing the penta-BDEs (PBDE 99 and 100).

The congener profile of the 12 PBDEs analyzed in the Northwest US samples is shown in Figure 2. Using mean values, PBDE 153 contributed more than PBDE 99 or 100 to the total PBDEs. Using median values, these differences, and those above, disappeared.

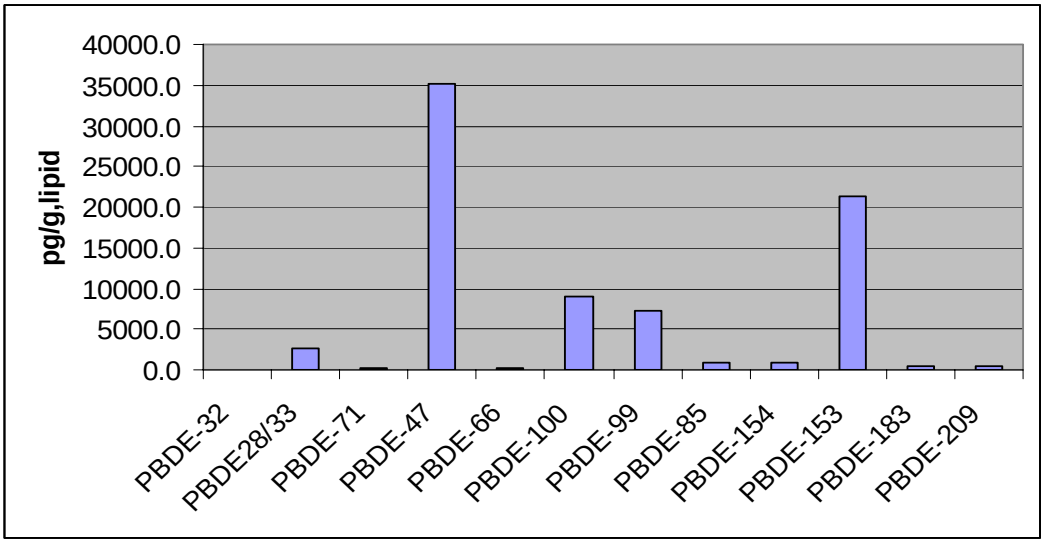

Figure 2: Congener pattern of 12 PBDE congeners analyzed in Northwest US breast milk samples (n = 16, mean).

In 2 of the 16 Northwest US samples, PBDE 153 levels were 2X greater than levels of PBDE 47 (Table 2), a pattern also found in 3 of the 20 samples from the US study, whose samples were also collected from healthy first-time mothers with healthy infants 2-8 weeks of age[5]. A similar pattern of PBDE 153 > PBDE47 was found in 1 of the 47 samples collected in the Texas study from mothers of different parities with infants of different ages (N=47) [4].

We did not see this pattern in our earlier study of breast adipose tissue samples from California women[1]. However, the adipose tissue study population was quite different from both the US and Northwest US sampled populations, as adipose tissue was collected from older (28 -62 yrs) women with different and multiple parities. A similar pattern of BDE-153 > BDE-47 was reported in 47 serum samples collected from members of the European Parliament, although the EU PBDE levels were much (20-fold) lower[7].

Table 2: Unusual PBDE congener patterns in six breast milk samples from Northwest US, Texas, and US studies[4,5,6] (pg/g lipid)

PBDEs	Northwest US 1	Northwest US 2	US 1[5]	US 2[5]	US 3[5]	Texas[4]
Moisture%	86.80	87.30	NA	NA	NA	NA
Fat%	4.51	4.03	NA	NA	NA	3.5
PBDE-32	22	34	NA	NA	NA	NA
PBDE28/33	5780	2489	3380	3140	360	700
PBDE-71	75	105	30	20	10	NA
PBDE-47	76200	29600	30800	22200	5560	6900
PBDE-66	71	99	310	240	60	ND
PBDE-100	38200	15400	4250	4860	1890	4600
PBDE-99	14300	4110	5750	4550	1360	1300
PBDE-85	2190	22	450	470	80	120
PBDE-154	2980	709	310	300	90	190
PBDE-153	169000	89300	31600	40500	17500	8500
PBDE-183	251	120	80	80	70	60
PBDE-209	207	131	ND	ND	300	NA

In the two breast milk studies (Northwest US and US) with comparable study populations (first-time mothers with infants 2-8 weeks of age), five of the 36 participants (about 14%) shared the unusual PBDE 153>PBDE 47 pattern. This unusual pattern may arise from a different source(s) of PBDE exposure, e.g. commercial octa-BDE, with significant 153-BDE and the major peak of 183-BDE, which forms 153 by losing an ortho-Br. In summary, PBDE 153 was the dominant congener for 14% of the breast milk samples. In all samples, PBDE 183 and PBDE 209 contributed less than 1% to the total PBDEs.

*The opinions given by the authors are not necessarily those of the DTSC or the California Environmental Protection Agency (Cal-EPA). Mention of any products or organization does not constitute an endorsement by DTSC or Cal-EPA.

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