PBDEs Are Higher Than PCBs In Thirty Percent Breast Milk Samples From The Pacific Northwest

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Introduction

Levels of polybrominated diphenylethers (PBDEs) in residents of North America are 10 - 40 times higher than those of individuals in Europe or Japan. High levels of PBDEs in Californians[1] have recently been confirmed by studies of PBDE body burdens of US residents from different regions[2] . As a follow-up to these studies, our lab has analyzed 12 PBDE congeners, including PBDE 209, as well as 80 PCB congeners, in 40 breast milk samples collected from residents living in the Pacific Northwest. Samples were collected by Northwest Environment Watch, a non-governmental organization in the state of Washington.

Materials and Methods

Recruitment of Study Participants: Participants were recruited by Northwest Environment Watch from Montana, Oregon, Washington, and British Columbia during the period April-November, 2003 by placing classified ads in local newspapers. All 40 study participants resided in the Pacific Northwest, with 10 each from greater metropolitan regions of Seattle, WA, Portland, OR, Vancouver, BC, or Missoula, MT. All participants were healthy, first-time breastfeeding mothers, with singleton infants between the ages of 2-8 weeks. Participants hand-expressed two milk samples (~100 mL each) into two chemically clean, 120 mL foil-wrapped glass jars.

Sample Preparation. Samples were prepared for analysis in four steps: lyophilization, extraction and fat determination, mixed silica gel column cleanup, and GPC column cleanup. The milk sample was lyophilized to a stable dry weight. Breast milk lyophilizates were extracted by accelerated solvent extraction using the ASE 200 (Dionex). A homogenized portion of milk lyophilizate (~3.5 g) was weighed, combined with bulking agent (sand) to make a homogeneous mixture. The mixtures were spiked with internal standards of PBDEs and PCBs consisting of 3 $^{13}C_{12}$ – PBDE congeners ($^{13}C_{12}$ – BDE-77, -153, and –209) and 6 $^{13}C_{12}$ –PCB congeners ($^{13}C_{12}$ –PCB 28, 52, 101, 153, 180, and 209). Sample extracts(< 1.0ml) were loaded onto silica gel columns and the column were eluted with 100 mL hexane/methylene chloride (1:1). Column concentrates were passed over an Envirogel™ GPC column (Waters). After the solvent was removed by under a stream of ultra-pure nitrogen, the recovery standards for PBDEs ($^{13}C_{12}$ - PBDE 99) and for PCBs ($^{13}C_{12}$ – 128 and 178) were added into samples.

HRGC/HRMS analysis. PBDEs and PCBs were analyzed using a Finnigan MAT 95 high-resolution mass spectrometer (HRGC/HRMS) connected to a Hewlett-Packard 6890 gas chromatograph, with a split/splitless injector and a 60 meter (0.25 mm ID, 0.25 µm film-thickness) DB-5 column. HRMS operated in electron impact (EI) mode at 9,000 resolution for PCBs and 6,000 for PBDEs. BDE-154, -153, and -209 were monitored by molecular ions minus two bromines (M – 2 Br). Other PBDEs and PCB's were monitored by molecular ion clusters. Precautions were taken at every step of the analytical protocol to minimize exposure to UV light.

Results and Discussion

High levels of PBDEs found in human milk. Analytical results for milk samples from the 40 first-time mothers from the Pacific Northwest are shown in Table 1. Five of the 12 congeners analyzed (BDE 32, 71, 66, 85, and 154) contributed <1% each to total PBDEs (Σ PBDEs). Σ PBDEs were calculated by summing values for the 12 PBDE congeners analyzed, and ranged from 6-321 ppb (lipid-weight) (mean = 96 ppb lw; median = 50 ppb lw).

Table 2: PBDE levels (ng/g lw) in individual Pacific Northwest breast milk samples (n = 40)

	Fat%	BDE-47	BDE-153	BDE-100	BDE-99	BDE-154	BDE-209	BDE-183	∑PBDEs
Min	1.43	2.63	0.841	0.495	0.789	0.025	0.048	0.006	6.34
Max	6.12	201	169	76.5	49.2	3.94	4.26	1.55	321
Mean	3.99	50.1	16.3	11.7	10.3	0.81	0.80	0.26	95.6
Median	4.06	27.8	4.79	5.25	5.36	0.40	0.43	0.20	50.4
SD	1.01	52.1	30.9	14.7	11.4	0.87	0.97	0.26	93.6

BDE-47 was the dominant congener in most (37/40) of the samples (range = 3-201 ppb lw; mean = 50 ppb lw; median = 28 ppb lw). BDE-153 was the next highest congener (range = 1-169 ppb lw; mean = 16 ppb lw; median = 5 ppb lw). BDE-99 and -100 contributed equally to Σ PBDEs (means = 10, 12 ppb lw; medians = 5, 5 ppb lw, respectively). Mean and median of BDE-28 are 4 and 2 respectively. All other PBDEs were < 1 ppb lw. Levels of BDE-183 and BDE-209 were low (both mean and median <1 ppb lw).

PCB levels in breast milk samples. The 10 major PCB congeners and total PCBs (∑ PCBs) from 80 congeners analyzed are shown in Table 2. The 10 congeners contribute about 60% of ∑ PCB levels (mean 180 ng/g lw, median 128 ng/g, lw). Compared with other studies, Σ PCB levels in NEW study is lower. However, date of study may also play a role. For example, the NEW study has the lowest Σ PCBs, but it is one of the most recent studies, which may reflect a general decrease of the level of PCBs.

Table 2: PCB levels (ng/g lw) in individual Pacific Northwest breast milk samples (n = 40)

HML #	PCB-153	PCB-138	PCB-180	PCB-118	PCB-170	PCB-99	PCB-74	PCB-156	PCB-187	PCB-66	∑ PCBs
MIN	5.54	2.31	3.29	2.17	0.977	1.49	0.66	1.79	1.03	0.765	49.0
MAX	370	338	75.2	125	62.7	33.8	106	12.7	26.4	14.4	1454
MEAN	29.9	21.9	12.6	11.8	8.35	7.43	7.36	5.76	4.92	4.32	180
MEDIAN	19.8	11.4	9.46	6.69	4.32	5.41	2.24	5.33	3.77	3.76	128
SD	56.5	52.2	11.9	19.8	11.3	6.17	17.1	2.61	4.25	2.86	222
CV	189	238	94.1	168	135	83.0	232	45.2	86.3	66.2	123

ΣPBDEs > ΣPCBs in some samples. Although the ranges of PCB and PBDE levels were comparable (49 – 415 ng/g lw vs, 6 -321 ng/g lw, respectively, excluding one sample with extremely high PCB, 1454 ng/g lw) in the population, there were significant differences in the PCB/PBDE ratios among individual women. Σ PBDEs and Σ PCBs were calculated for each study participant by summing values for 12 PBDEs (Table 1) and 82 PCBs, respectively, and are displayed for each participant in Figure 1. Among 13 of the 40 study participants, Σ PBDEs > Σ PCBs.

Table 2: PCB levels (ng/g lw) in individual Pacific Northwest breast milk samples (n = 40)

HML #	PCB-153	PCB-138	PCB-180	PCB-118	PCB-170	PCB-99	PCB-74	PCB-156	PCB-187	PCB-66	∑ PCBs
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MEAN	29.9	21.9	12.6	11.8	8.35	7.43	7.36	5.76	4.92	4.32	180
MEDIAN	19.8	11.4	9.46	6.69	4.32	5.41	2.24	5.33	3.77	3.76	128
SD	56.5	52.2	11.9	19.8	11.3	6.17	17.1	2.61	4.25	2.86	222
CV	189	238	94.1	168	135	83.0	232	45.2	86.3	66.2	123

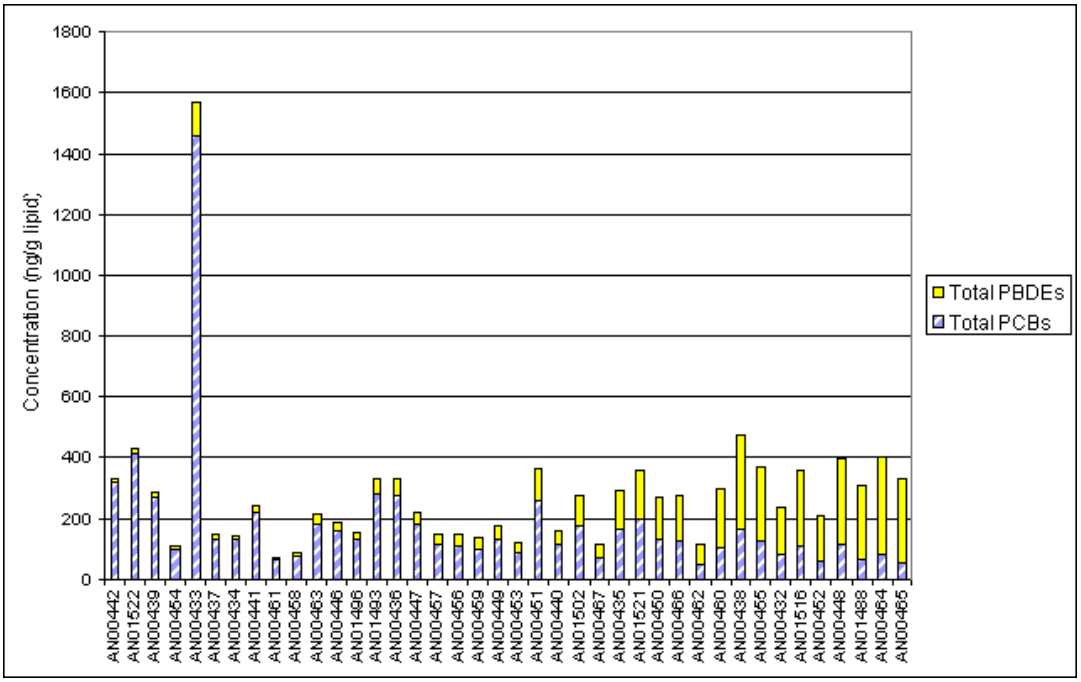

Figure 1. Σ PBDEs and Σ PCBs in Pacific Northwest breast milk samples (n = 40, ng/g lw).

A major concern with the lower brominated PBDEs is the exponential increase in their levels in humans, wildlife, and the environment. Over the past 20 years, rising levels of PBDEs have been found by almost every study that has examined time-trends, especially studies in North America. Levels of the lower brominated PBDEs in harbor seals from the San Francisco Bay appear to have increased 100-fold over a ten-year period ending in 1998. Increases have also been reported for fish from the Columbia River, the Great Lakes, and San Francisco Bay.

Previously, in most biological samples, levels of Σ PBDEs < Σ PCBs. However, as a consequence of the increasing PBDE levels, this may be changing: in this breast milk study, samples from 13 of 40 participants had levels of Σ PBDEs > Σ PCBs (right side of Figure 1). For these 13 participants, the ratio of Σ PBDEs / Σ PCBs averages about 2.

Comparisons between the levels of the dominant PCB and PBDE congeners reveals a similar trend. In breast milk samples from ~65% (25/40 mothers) of the mothers, levels of BDE-47 > PCB 153. For these 25 participants, the ratio of Σ PBDEs / Σ PCBs averages about 3. Clearly, the lower brominated PBDEs are surpassing PCBs as a major environmental concern in North America.

Σ PBDEs do not correlate with ΣPCBs. Using data from breast milk samples from individual mothers, Σ PBDEs do not correlate with Σ PCBs. In fact, 16/40 participants have Σ PBDEs << Σ PCBs, and 10/40 have Σ PBDEs >> Σ PCBs (Figure 1). This suggests some of the sources and pathways for PBDEs exposures in humans differ significantly from sources and pathways for PCB exposures. Food is the major pathway for exposures to PCBs, and house/office dust may be a significant pathway for exposures to PBDEs. This lack of correlation between PBDE and PCB levels in humans contrasts with the strong correlations between PBDEs and PCBs (r^2 = 0.64) seen in eggs from California seabirds[3]. Such strong correlations may be limited to marine animals, where exposures to PBDEs and PCBs occur via the marine food chain.

Conclusions

1. ~30% mothers (13/40) had Σ PBDEs > Σ PCBs in their breast milk samples, making PBDEs the major persistent organic pollutant (POP) in these breast milk samples.

2. The mean level of BDE-47, the most abundant PBDE congener, is higher than the mean level of the most

abundant PCB congener, PCB-153.

3. PBDE and PCB levels did not correlate, suggesting different sources and pathways of exposures.

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

References

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