PBDE Congener Pattern As An Indicator of Human PBDE Exposure Pathway in North America

Jianwen She[1], Arthur Holden[1], Margaret Sharp[1], Clark W Derry[2], Kim Hooper[1]

[1]Hazardous Materials Laboratory, Department of Toxic Substances Control
[2]Northwest Environment Watch, Seattle, WA, USA

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[1,2] have recently been confirmed by studies of PBDE body burdens of US residents from different regions [3]. However, what is the major exposure pathway of PBDE for human in North America remains a mystery. Obviously PBDE in diet will contribute to the body burden. However, we have found that the Σ PBDEs do not correlate with Σ PCBs in human milk sample[2,4]. This suggests some of the sources and pathways for PBDE exposures in humans differ significantly from sources and pathways for PCB exposures. This lack of correlation between PBDE and PCB levels in humans contrasts with the strong correlations between PBDEs and PCBs seen in eggs from California seabirds[5]. Such strong correlations may be limited to marine animals, where exposures to PBDEs and PCBs occur via the marine food chain. As we know that the food is the major pathway for exposures to PCBs for humans, and house/office dust may be a significant pathway for exposures to PBDEs, this paper tries to address this critical issue. We have analyzed more than 100 human milk samples for PBDEs, which provides us the opportunity to scrutinize the congener patterns from individual samples. Examining PBDE congener patterns in commercial Penta-BDE formulation, in human milk, in house dust, field blank and in laboratory method blank lead us to believe that the ratio of PBDE 99/47 could be an effective indicator for human PBDE exposure pathways.

Human milk sample analysis and PBDE data source

Recruitment of study participants, sample preparation, analysis and partial results from human milk samples could be found elsewhere[3]. PBDE data from laboratory blanks, field blanks and human milk samples were generated by the Hazardous Materials Laboratory. PBDE data from commercial Penta-BDE formulation, house dust are from the literature[6,7,8].

Results and Discussion

Ratio of BDE-99 to PBDE-47 in commercial Penta mixture. The majority (>97%) of Penta-BDE formulation is used in North America. The Penta-BDE formulation contains the three predominant congeners (BDE-47, -99, -100) which are found in human adipose tissue, and human milk. The Penta-BDE formulation contains almost equal amounts of BDE 47 and BDE 99 (about 40% each) and about 7% of BDE -100[6]. The ratio of BDE 99/BDE 47 in commercial Penta-BDE formulations should be close to 1.

Ratio of BDE-99 to PBDE-47 in house dust from two studies. The ratio of BDE-99/BDE 47 in dust from America houses [7,8] seems to be consistent with a ratio about 1 which is similar to the ratio found in commercial Penta-BDE formulation. The ratio ranges from 0.5 to 2. The authors of the original dust studies have examined the ratio and suggested that the possible debromination of other BDE congeners and different vapor pressure of BDE-47 and BDE-99 may cause the variation of the ratio of BDE-99/BDE-47 between samples. PentaBDE (48%) and decaBDE (41%) were the dominant mixtures measured in house dust found in America homes[8] while in UK study[7] the dominant BDE is deca-BDE (ppm) alone, while Penta-BDE exists in much low level (low to mid ppb). This is not surprising since most Penta-BDE formulation was used in North America (>97%). We did not find any significant deca-BDE (BDE 209) in human milk, the discussion in this paper will be limited to only Penta-BDE exposure.

Table 1: Ratio of BDE-99/BDE-47 in house dust from two America studies

NIST study																				
Ratio	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	Mean	Median	Ref.
99/47	1.8	0.93	1.6	0.70	0.76	1.5	1.5	1.8	0.49	1.2	1.6	1.2	1.5	1.2	1.3	0.95	1.3	1.2	1.3	6
EWG study																				
Ratio	FL	CA1	TX	CA2	CO	DC	MI	WA	OR	MT								Mean	Median	
99/47	1.8	0.77	0.60	1.2	0.76	0.38	1.3	0.77	1.4	1.5								1.0	0.98	5

Ratio of BDE-99 to BDE-47 in field blanks. Along with human milk samples, three field blank samples were collected. The mean and median ratios of BDE-99/BDE-47 are 0.61 and 0.57, respectively. The ratio is lower than the ratio in house dust but higher than that in human milk samples.

Ratio of BDE-99 to BDE-47 in laboratory blank. Since PBDEs are ubiquitous, they can be detected in laboratory blanks too. Ratios of BDE-99/BDE-47 from 22 blank samples are shown in Table 2. The mean and median ratios of BDE 99/BDE 47 are very close to each other with a value of about 0.6. The ratio is almost identical as in field blanks. However, it is much lower than the ratio in Penta-BDE formulation and house dust as shown in Table 1.

Table 2: Ratio of BDE-99/BDE-47 in milk method blank samples (22 samples from two studies)

NEW study													
Blank	1	2	3	4	5	6	7	8	9	10	11	Mean	Median
99/47	0.81	0.48	0.69	0.64	0.44	0.97	0.39	0.70	0.44	0.88	0.88	0.66	0.69
CA Study													
Blank	1	2	3	4	5	6	7	8	9	10	11	Mean	Median
99/47	0.94	0.72	0.55	0.94	0.55	0.72	0.53	0.53	0.27	0.55	0.82	0.64	0.55

Ratio of BDE-99 to BDE-47 in human milk from three studies. It is Penta-BDE (not Deca-BDE) that was found to be increasing in concentration in breast milk in North America. Although it is commonly assumed that food represents the most significant intake route for these bioaccumulative BDEs, their presence at significant levels in house dust suggests more direct exposure routes might also be important in the home. However, efforts to correlate PBDE levels in breast milk with PBDE levels in house dust did not succeed, partially due to the small number of the sample were taken in the study[7]. We suggest using the ratio of BDE-99/BDE-47 to assess the direct PBDE exposure. We know that PBDE-47 is more bioaccumulative than PBDE-99. If the major source of PBDE in the human body is from the diet (such as from fish, milk or eggs), we would expect that more and more BDE -47 would be built up and less and less BDE -99 would remain. However, if human get PBDE directly from dust, we will expect a lower ratio of BDE-47/BDE-99 (or higher BDE-99/BDE-47), since direct exposure does not involve multiple selective biomagnification process. The ratios of BDE-99/BDE -47 in human body (milk) will reflect the direct exposure source(s) if it is the major pathway. Table 3 shows us the ratio of BDE-99/BDE-47 in three milk studies from North America. On the average the ratio of BDE99/BDE 47 in milk samples from three different milk studies is between 0.2 to 0.3, which is much lower than the ratio in house dust, field blank and laboratory blank samples. However four individual samples from three studies had ratios of BDE99/BDE 47 around 0.6. This means that in all breast milk samples, level of BDE 99 is at most half as BDE-47. Checking the total PBDE level for those higher ratios (BDE99/BDE47>0.5) revealed that most of those samples have also high total PBDE levels. The following number pairs are ratio of BDE-99/BDE-47 and their corresponding total PBDE level in human milk (ng/g, lw): 0.67, 31.8 ng/g lw (NEW); 0.54, 377 ng/g lw(Texas); 0.57, 386 ng/g lw (Texas); 0.53, 1078 ng/g lw (EWG). Except for the first pair, all other three samples represent the one of the highest level reported in the corresponding studies. It may be reasonable to suggest that a high ratio of BDE 99/BDE 47 in human milk samples indicated additional direct exposure possibility, while a low ratio could mean the exposure is mainly from diet. Data from our current work with California milk samples seems to support this idea, too.

Table 3: Ratio of BDE-99/BDE-47 in human milk samples from three human milk studies from North America

Max	Mean	Median	SD	CV	Ref
0.67	0.23	0.20	0.11	48	4
0.53	0.20	0.18	0.10	49	10
0.57	0.31	0.28	0.11	35	11

Conclusions

1) Ratio of BDE-99/BDE-47 in house dust samples, laboratory blank samples, field blank samples are much high than that in human milk samples, which suggests that diet may still be the major exposure pathways for PBDEs in most human milk samples.

2) For some human milk samples, the ratio of BDE-99/BDE-47 is as high as 0.5. This high ratio may indicate those women may have direct PBDE exposure from dust or air in addition to the exposure through diet.

3) Higher ratio of BDE-99/BDE-47 could be used as an assessment of direct dust exposure. Combined with Questionnaire data, major exposure pathways may be be identified.

*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

1. She J, Petreas M, Winkler J, Visita P, McKinney M, Kopec D. 2002. Polybrominated diphenyl ethers (PBDEs) in the San Francisco Bay area: measurements in harbor seal blubber and human breast adipose tissue. Chemosphere 46:697-707.

2. Myrto Petreas, Jianwen She, F. Reber Brown, Jennifer Winkler, Gayle Windham, Even Rogers, Guomao Zhao, Rajiv Bhatia, and M. Judith Charles " High Body Burden of 2,2',4,4'-Tetrabromodiphenyl Ether (BDE 47) in California Women, Environmental Health Perspectives, 111 (9), 1175 – 1179, 2003

3. Hites R.A., Polybrominated Diphenyl Ethers in the Environment and in People: A Meta-Analysis of Concentrations, Environ Sci Technol. 2004 Feb 15;38(4):945-56.

4. Jianwen She, Arthur Holden, Margaret Sharp, Clark Williams-Derry, and Kim Hooper, PBDEs Greater Than PCBs in 30% of Breast Milk Samples from the Pacific Northwest, Dioxin2005, submitted.

5. She J, Holden A, Tanner M, Adelsbach T, Schwarzbach S, Thompson CS, Mahaffy M, Petreas M, Simmons BP, Hooper, K. High PBDE levels in Piscivorous seabird eggs from the San Francisco Bay and Washington state. Organohalogen Cmpds, 61, 33 -36, 2003

6. Mehran Alaee, Pedro Arias, Andreas Sjödin, Åke Bergman, An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release, Environmental International 29 (2003), 683 -689.

7. Environmental Working Group, http://www.ewg.org/reports/inthedust/part2.php

8. Heather M., Stapleton, Nathan G. Dodder, John H. Offenberg, Michele M. Schantz, and Stephen A. Wise, Polybrominated Diphenyl Ethers in House Dust and Clothes Dryer Lint, Environ. Sci. & Technol.

9. David Santillo, Iryna Labunska, Helen Davidson, Paul Johnston, Mark Strutt and Oliver Knowles, http://www.greenpeace.org.uk/MultimediaFiles/Live/FullReport/5679.pdf

10. Sharp R, Lunder S. 2003. Mother's Milk. www.ewg.org/reports_content/mothersmilk

/pdf/MothersMilk_final.pdf

11. Schecter A, Pavuk M, Papke O, Ryan JJ, Birnbaum L, Rosen R. 2003. Polybrominated diphenyl ethers (PBDEs) in US mothers' milk. Environ Health Perspect 111:1723-9.