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RETROSPECTIVE TIME TREND STUDY OF BROMINATED FLAME RETARDANTS AND POLYCHLORINATED BIPHENYLS IN HUMAN SERUM FROM VARIOUS REGIONS OF THE UNITED STATES, 1985 - 2002

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Introduction

Brominated flame retardants (BFRs) are added to potentially flammable materials such as plastics and polyurethane foam uses include furniture, building materials, and electronic appliances.[1] Hence, BFRs among other flame retardants (FRs) serve an important function in modern society and save lives. Unfortunately, additive FRs such as polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) are not covalently bound to the polymer backbone and may migrate out of the product, potentially exposing humans and wildlife to these compounds. BFRs, such as PBDEs, have been reported in wildlife from most of the world, including Europe,[2] and in the United States.[3] The levels of PBDEs reported in North America generally are substantially higher than in Europe.[4]

We measured PBDEs (triBDEs to hexaBDEs) and 2,2',4,4',5,5'-hexaBB (BB-153) in archived human serum pools covering the years 1985 to 2002. We also determined the level of a stable and persistent PCB congener (2,2',4,4',5,5'-hexachlorobiphenyl; [CB-153]) in the same samples as a comparison to the levels for the BFRs.

Methods and Materials

Sampling: Samples were (1) archived serum pools (n=9) that have been used as quality assurance / quality control (QA/QC) materials at the Centers for Disease Control and Prevention (CDC) in Atlanta, GA; (2) serum pools collected in 2002 (n=4) (Interstate Blood Bank; Memphis, TN); and (3) a serum pool commercially available from Fisher Scientific (part# BP2657-100; lot# 026847) have been used in the current inventory. Specific information about the number of persons in each pool and collection location is given in Table 1.

Analysis: The method of analysis is published in the 2003 Organohalogen Compounds abstract collection in the "Analysis" section.[5] In brief, formic acid (4mL) and water (4mL) were added to serum samples (4mL) spiked with ^{13}C-labeled internal standards (six PBDE congeners, BB-153 and CB-153; 750pg/sample) using the automated Gilson 215 liquid handler (Middleton, WI). Extraction was performed in an automated procedure using the Zymark Rapid Trace® solid phase extraction (SPE) workstation (Hopkinton, MA). Cleanup was automated using the Rapid Trace® with custom-packed cleanup cartridge (Applied Separations; Allentown, PA) containing silica (0.1g): silica/sulfuric acid (2:1 by weight; 1g) packed in an SPE cartridge (3cc). The sample, dissolved in hexane, was added to the cleanup cartridge and

eluted with the same solvent. Contaminant load was determined by gas chromatography high-resolution mass spectrometry using a ThermoFinnigan MAT95 instrument (Bremen, Germany).

Results

Seven PBDE congeners (triBDE to hexaBDE), BB-153 and CB-153 were determined in 14 human serum pools covering the years 1985 to 2002 (Table 1). Concentration of 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) and the sum of PBDE congeners measured and the individual PCB and PBB congeners were plotted against collection year for the individual pools (Figure 1). Data on PBDEs and CB-153 from a Swedish retrospective time trend study using human milk (data expressed on a lipid weight basis) [6,7] also were plotted. The concentration of CB-153 in the two sets of data from the United States and Sweden [6,7] were similar, showing a constant decrease with time. BDE-47 and the sum of PBDE are both higher in the United States than in Sweden (Figure 1). Similar to the Swedish trend on PBDEs [6,7] an increase of BDE-47 and the sum of PBDEs with time is apparent in the US samples (Table 1 and Figure 1). BB-153 also was determined in the samples from the United States (Table 1 and Figure 1); the results indicate a decrease in concentration of this compound with time similar to that of CB-153.

Table 1. Concentration of individual polybrominated diphenyl ether (PBDE) congeners and 2,2',4,4',5,5'-hexabromobiphenyl (BB-153) and 2,2',4,4,',5,5'-hexachlorobiphenyl (CB-153). Year of collection for the individual pools are given.

Collection Year	N	BDE28	BDE47	CB153	BDE100	BDE99	BB153	BDE154	BDE85	BDE153
		ng/g lipid weight								
1985 [a]	~200	<0.1	<1	120	<0.5	<2	7.6	<0.5	<0.5	<0.5
1987 [a]	~200	<0.1	<1	100	<0.5	<2	6.4	<0.5	<0.5	0.73
1988 [a]	~200	<0.1	1.3	82	<0.5	<2	8.0	<0.5	<0.5	0.37
1988 [a]	~200	<0.1	<1	76	<0.5	<2	7.1	<0.5	<0.5	<0.5
1988 [a]	~200	<0.1	7.9	105	1.0	2.6	11	<0.5	<0.5	1.3
1989 [a]	~200	<0.1	14	85	2.3	4.3	11	<0.5	<0.5	1.6
1989 [a]	~200	<0.1	5.8	95	0.89	1.7	9.2	<0.5	<0.5	1.0
1990 [a]	~200	<0.1	5.9	39	0.96	2.1	3.8	<0.5	<0.5	0.71
1992 [a]	~200	<0.1	7.7	71	1.1	2.9	10	<0.5	<0.5	0.85
2002 [b]	9	<0.1	31	21	5.8	15	3.5	1.1	1.2	9.9
2002 [c]	5	0.88	45	35	11	22	5.9	1.7	1.4	13
2002 [d]	15	0.55	27	21	5.9	9.6	1.4	0.96	0.81	6.6
2002 [e]	15	0.90	33	21	6.4	10	1.7	0.84	0.76	6.3
2002 [f]	[g]	0.84	33	55	7.9	10	5.1	1.0	0.77	8.4

[a] Serum pool from South-Eastern U.S.; [b] Louisville, KY; [c] Miami, FL; [d] Mixed pool from Memphis, TN, Miami, FL and Philadelphia, PA; [e] Louisville, KY and Philadelphia, PA; [f] Serum pool from Fisher Scientific made from North American serum; [g] Information not provided.

Abbreviations: BDE28, 2,2',4-tertabromo diphenyl ether; BDE47, 2,2',4,4'-teraBDE; BDE85, 2,2',3,4,4'-pentaBDE; BDE99, 2,2',4,4',5-pentaBDE; BDE100, 2,2',4,4',5,6'-pentaBDE; BDE153, 2,2',4,4'5,5'-hexaBDE; BDE154, 2,2',4,4',5,6'-hexaBDE.

Discussion

Levels of triBDEs to hexaBDEs are well known to be increasing with time in Europe, as documented by studies in Sweden,[7] Germany,[8] and Norway.[9] More recently, however, an indication of a decrease in concentration has been noted in the Swedish trend.[6] Our results showed a similar increase with time for the United States. The number of samples analyzed does not permit assessment of whether current levels are increasing, decreasing, or remaining steady. Samples from 1990 to 2000 are needed to better describe the US trend (Figure 1). However, the average of BDE-47 in 2002 is 4.4 times higher than the measurement made in 1992, indicating a doubling in concentration in about 5 years for this period.

The reason for the apparently higher, concentrations of PBDEs in the United Sates is unknown, although elevated general population levels for North America in relation to Europe have been published.[10,11] It can thus be stated that a large proportion of the market demand for the commercial pentaBDE product is within North America. This product contains mainly tetraBDEs to hexaBDEs. In 2001, the world demand for pentaBDE was 7,500 metric tons of which 95% of the demand was within North America.[12] The proportion of pentaBDE product exported as consumer products is unknown.
The routes of exposure to humans are likely to be similar to those of other persistent or semi-persistent organohalogen compounds, such as polychlorinated biphenyls (PCBs), for which dietary exposure plays a major role. For example, the estimated dietary intake of total PBDEs is 44 ng/day in Canada based on a food basket survey including approximately 40 different foods.[13] However, for chemicals that are still being used, other direct exposures such as inhalation of particulate matter containing BFRs and/or dermal contact can not be excluded.

One brominated biphenyl, BB-153, also was determined in these same samples. BB-153 was the main constituent of commercially produced hexabromobiphenyl. This product has not been commercially produced in the United States since the mid-1970s following an accident in Michigan in which cattle feed was contaminated with this product. No current production of this product is known. The concentration of BB-153 seems to be decreasing in serum from US general population samples (Figure 1). This decrease is similar to that for CB-153, which has not been commercially used since the mid-1970s.

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